KINETIC STUDIES OF SOME PHOTOCHEMICAL REACTIONS OF QUINONES

A Thesis

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by

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ABSTRACT

The photochemical reactions of toluquinone with cyclohexane, iso-propyl and methyl alcohols have been studied using carbon tetrachloride as a solvent. The reactions have been carried out at 365 mµ and 25.0°C in the atmosphere of nitrogen or under vacuum and the quantum efficiencies for the formation of hydroquinone have been determined. The measurements were made over a wide range of reductant concentrations and light intensities.

The results have been interpretted in terms of reaction mechanisms and the ratios of certain rate constants have been determined. Pure samples of cyclohexane and iso-propyl alcohol gave quantum efficiencies of about 0.5 and 1 respectively. In solutions in carbon tetrachloride there is evidence for reduction in quantum efficiency by the cage effect. The excited state of toluquinone reacts about as effectively with cyclohexane as it does with iso-propyl alcohol. It is slightly less reactive towards methyl alcohol. The results of the present work are compared with earlier observations on similar reactions.

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A.R.

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1. INTRODUCTION

A great deal of work has been done on the photolysis of quinones from both the qualitative and quantitative points of view. The qualitative work was merely aimed at the identification of the main reaction products. The quantitative studies were concerned with the determination of the quantum efficiency for the loss of quinone using various quinones, and the effect of change of wavelength of irradiation on the quantum efficiency. Some quantitative studies have been made of the kinetics of photochemical reactions of benzoquinone with ethyl and propyl alcohols (1).

In the present work similar studies of the reactions of toluquinone are described. The aim of investigations of this type is to establish the mechanism of the reaction and to determine rate constants for individual steps in the mechanism.

In the first chapter of this thesis the mechanism of oxidation-reduction reactions will be surveyed and it will be shown that photochemical reactions of this type probably occur by free radical mechanisms. Previous quantitative work on photochemical reactions of quinones will be summarized.

1.1. Mechanism of Oxidation-Reduction Reactions

In this section a review of the mechanism of oxidation-reduction reactions will be presented. At each stage especial consideration will be given to evidence for the occurrence of a mechanism in reactions of quinones. Also, where experimental evidence has not been found, the circumstances in which a mechanism might be applicable to reactions of quinones will be discussed.

In this thesis the reactions of special concern are of the type :

$$Q + AH_2 \longrightarrow QH_2 + A$$

Q Quinone.

AH_2 Alcohol.

QH_2 Hydroquinone.

A Aldehyde or ketone depending on whether the alcohol is primary or secondary.

There are numerous ways by which the oxidation of compounds takes place, but consideration will be given to the oxidation of compounds containing hydrogen.

The reactions may be classified as :

1.1.1. Reactions involving unit change in oxidation state.

Under these circumstances the oxidation will be brought about by either

(i) loss of hydrogen atom, H or

(ii) loss of electron, $\bar{e}$

In the systems of interest both the products are free radicals and they will react further to produce the final stable products. The final result here may be a double change in oxidation state produced in two steps.

1.1.2. Reactions involving a double change in oxidation state, occurring in one step.

Here the oxidation may take place by one of the following processes :

(i) loss of two hydrogen atoms, 2H in a single process

(ii) loss of a hydride ion, $\bar{H}$

(iii) loss of two electrons, 2 $\bar{e}$

1.1.3. Reactions involving a double change in oxidation state, occurring via ester formation.

These processes will be explained with examples.

1.1.1. Reactions involving unit change in oxidation state

Numerous examples of reactions of this type are known. Thus Walling (2) found that photochemically induced chlorination of methane includes the following step :

$$CH_4 + Cl \longrightarrow CH_3 + HCl$$

In combustion the reaction,

$$CH_4 + O_2 \longrightarrow CH_3 + HO_2$$

is followed by,

$$HO_2 + CH_4 \longrightarrow H_2O_2 + CH_3$$

In inorganic chemistry there are oxidations taking place by electron transfer,

$$Ce^{++++} + Fe^{++} \longrightarrow Ce^{+++} + Fe^{+++}$$

Quinones often react through the semiquinone route, which involves a unit change in oxidation state. It is however sometimes difficult to determine whether the step involves hydrogen atom or electron transfer. Bridge and Porter (3,4) and Wells (5,6) showed that the primary process in the reaction of certain excited quinones with alcohol is hydrogen atom abstraction and not electron abstraction. This conclusion has been discussed by Wells (6), and the detailed treatment is given in section 1.3.

The course of reaction can be depicted as :

$$Q + h\nu \longrightarrow Q^*$$

$$Q^* + AH_2 \xrightarrow{k_2} QH + AH$$

The disproportionation of radicals,

QH and AH may take place as :

$$QH + QH \xrightarrow{k_8} QH_2 + Q$$

$$AH + AH \xrightarrow{k_9} AH_2 + A$$

The Radical, AH may be a strong enough reducing agent to react with unexcited quinone

$$Q + AH \xrightarrow{k_{11}} QH + A$$

The radical, QH may react with alcohol molecule as:

$$QH + AH_2 \xrightarrow{k_{12}} QH_2 + AH$$

In the presence of oxygen the radicals generated by photochemical reaction can pick up oxygen, and the production of acid has been explained by Bolland and Cooper (7) on the basis of the following reaction steps :

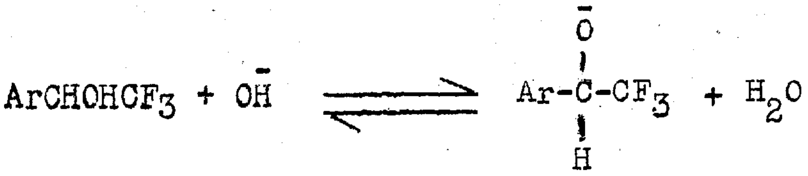
$$AH + O_2 \xrightarrow{k_{13}} AHO_2$$

$$QH + O_2 \xrightarrow{k_{14}} Q + HO_2$$

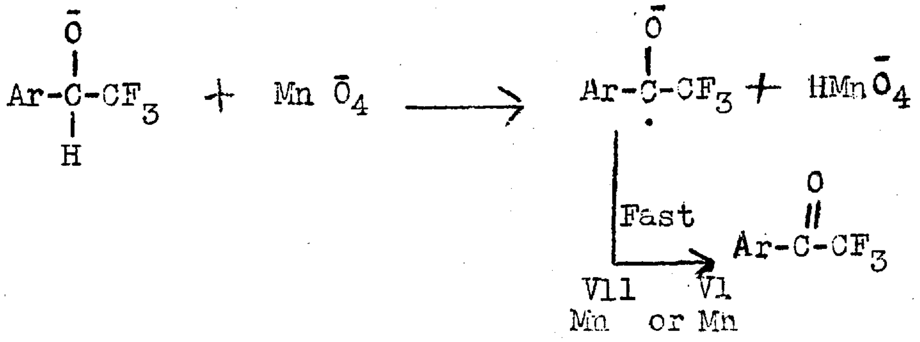
$$AHO_2 + AHO_2 \xrightarrow{k_{15}} 2\ \text{acid} + H_2O_2$$

In general it is reasonable to assume that free radicals are formed during the photochemical reactions of quinones with alcohols.

Stewart and Linden (8) investigated the oxidation of fluorinated alcohols, $ArCHOHCF_3$, $(CF_3)_2CHOH$, and CF_3CH_2OH by permanganate in neutral and basic solutions and suggested a mechanism in which hydrogen atom is abstracted from the alkoxide by permanganate:



$$ArCHOHCF_3 + \bar{O}H \rightleftharpoons Ar-\underset{H}{\overset{\bar{O}}{C}}-CF_3 + H_2O$$



This hydrogen atom abstraction mechanism for permanganate-alcohol reaction has been supported by Candlin and Halpern (9), who studied the permanganate oxidation of formate ion complexed to cobalt (III), and the mechanism of reaction was found to be a hydrogen atom abstraction. The reaction rate was similar to the normal formate-permanganate reaction. Therefore, the latter also occurs by hydrogen atom abstraction as shown below:

$$\bar{O}_2CH + Mn\bar{O}_4 \xrightarrow{Slow} C\bar{O}_2\cdot + HMn\bar{O}_4$$

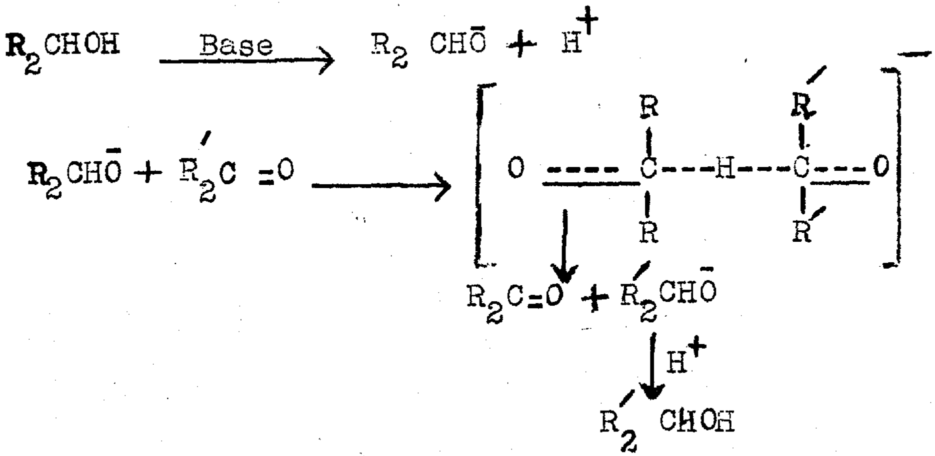
$$C\bar{O}_2\cdot + Mn\bar{O}_4 \xrightarrow{Fast} CO_2 + Mn\bar{\bar{O}}_4$$

The similarities between ordinary permanganate-formate reaction and the permanganate alkoxide reaction, suggest that hydrogen atom abstraction is the correct mechanism for the alcohol-permanganate reaction.

1.1.2. Reactions involving a double change in Oxidation, occurring in one step

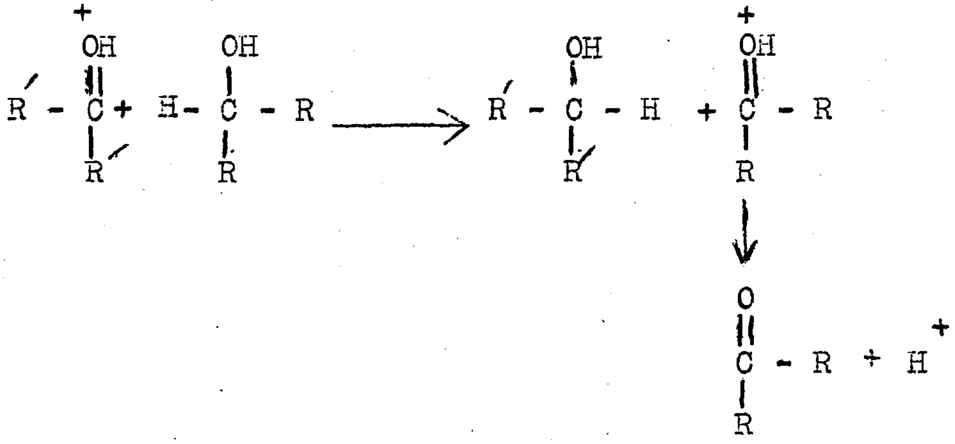
A reaction involving either two hydrogen atoms or two electrons for the formation of hydroquinone from quinone in one step, has not been found.

Doering and Aschner (10) and Sprinzak (11) examined the base-catalysed carbinol-carbonyl equilibrium, and suggested a mechanism, in which hydride ion is transferred from alkoxide ion to carbonyl compound.

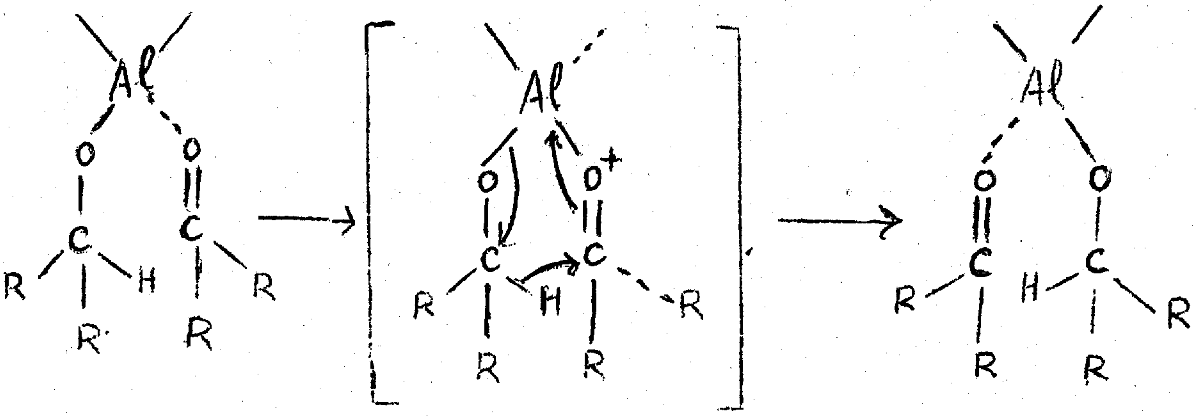


Deno, Saines and Spangler (12) found that the carbinol-carbonyl equilibrium was also catalysed by strong acid, and the mechanism presented was similar to the process described already for base-catalysed equilibrium, in which hydride ion is transferred from alcohol to protonated carnonyl instead of from alkoxide to carbonyl compound.

$$R'_2C = O + H^+ \xrightarrow{Acid} R'_2C = \overset{+}{O}H$$



Woodward, Wendler and Brutschy (13) showed that when Lewis-acid catalysts such as aluminium alkoxides, were used to interconvert alcohols and ketones (Meerwein-Pondorff-Oppenauer equilibrium), a cyclic mechanism was probably operative. These reactions are considered hydride transfers, because the metal atom will polarize the carbonyl group and will assist hydride addition to carbon.



Linstead and Co-workers (14, 15) suggested a hydride ion abstraction mechanism for the formation of hydroquinone from quinone. They studied the thermal hydrogen transfer between 1:4- dihydronaphthalene and various quinones in phenetole solvent. The reaction proceeds as :-

$$\text{Quinone} + 1{:}4\text{- dihydronaphthalene} \longrightarrow \text{hydroquinone} + \text{naphthalene}$$

Jackman and Thompson (16) studied the dehydrogenation of a series of substituted 1:2-dihydronaphthalenes by tetrachloro- 1:2- benzoquinone, using 1:2- dichlorobenzene as solvent.

Their observations were rationalized by a heterolytic mechanism involving a rate determining transfer of a hydrogen atom with a pair of bonding electrons from the hydrocarbon to the quinone, followed by a rapid proton transfer from $R.\overset{+}{H}$ to the hydroquinone anion :

$$Q + RH_2 \xrightarrow{\text{Slow}} Q\bar{H} + R.\overset{+}{H} \xrightarrow{\text{Fast}} QH_2 + R$$

1.1.3. Reactions involving a double change in Oxidation state, occurring via ester formation

The formation of an ester as the intermediate in the oxidation of organic compounds, is applicable to reactions of the type :

Alcohol + chromate, bromate and persulphate.

In this reaction alcohol acts as a base and forms an ester with the acid species.

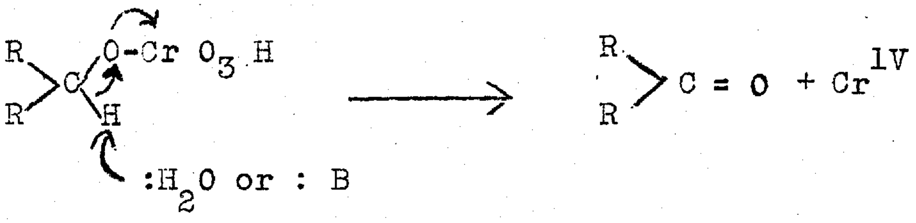
Westheimer and Co-workers (17,18) studied the oxidation of iso-propyl alcohol by chromic acid and the rate of reaction was found to be function of concentration of alcohol, acid chromate ion, and hydrogen ion :

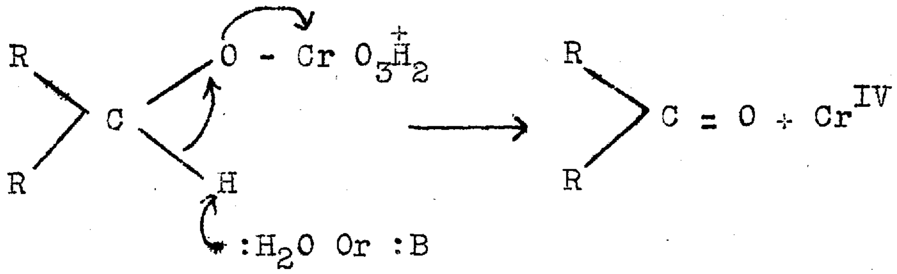
$$\text{Rate} = k_a \left[R_2CHOH\right]\left[H\ Cr\ \bar{O}_4\right]\left[\overset{+}{H}\right] + k_b \left[R_2CHOH\right]\left[HCr\bar{O}_4\right]\left[\overset{+}{H}\right]^2$$

Added manganous ion was found to reduce the rate of reduction of chromium (VI). The following mechanism was suggested in which chromate ester decomposes by proton loss to any available base and the chromium (I V) ion is eliminated :

$$R_2CHOH + H\ Cr\ \bar{O}_4 + \overset{+}{H} \longrightarrow R_2CHOCrO_3H + H_2O$$

$$R_2CHOH + H\ Cr\bar{O}_4 + 2\overset{+}{H} \longrightarrow R_2CHOCrO_3\overset{+}{H}_2 + H_2O$$





followed by

$$Cr^{IV} + Cr^{VI} \xrightarrow{Fast} 2\ Cr^{V}$$

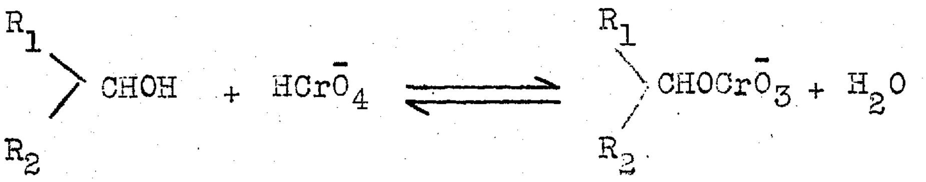
$$2\ Cr^{V} + 2R_2\ CHOH \xrightarrow{Fast} 2\ Cr^{111} + \ 2\ R_2C = O + 4\overset{+}{H}$$

or by

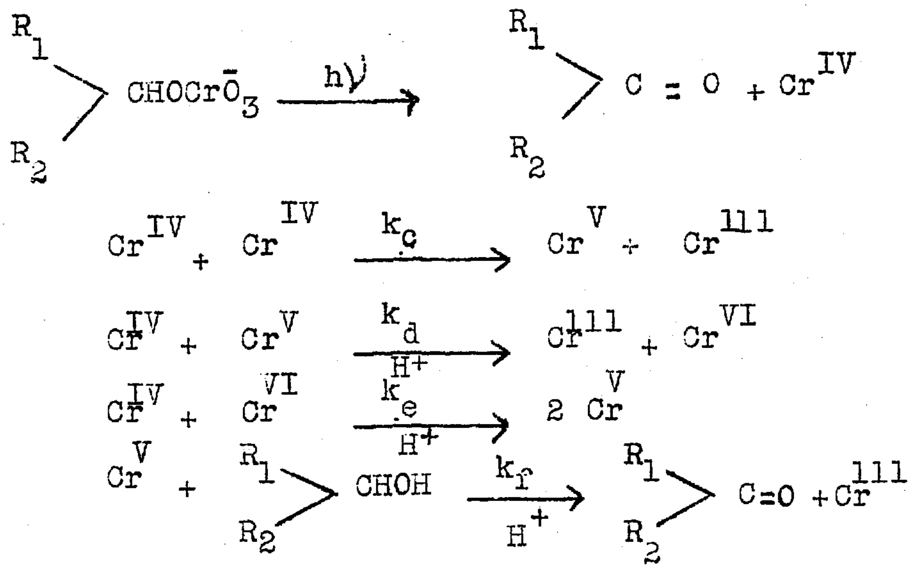
$$Cr^{IV} + Mn^{11} \xrightarrow{Fast} Cr^{111} + Mn^{111}$$
$$Cr^{IV} + Mn^{111} \xrightarrow{Fast} Cr^{111} + Mn\ O_2$$

This ester mechanism for alcohol-chromic acid reaction has been supported by Roček and Co-workers (19).

Kläning (20) studied the photoinduced oxidation of alcohols by acid chromate ion in aqueons solution. The data which included the effect of Mn^{11}, Ce^{111} and oxygen were accounted for by the following mechanism :



$$\begin{matrix}R_1\\R_2\end{matrix}\!\!>CHOH + HC\bar{r}O_4 \rightleftharpoons \begin{matrix}R_1\\R_2\end{matrix}\!\!>CHOC\bar{r}O_3 + H_2O \qquad (a)$$



$$\begin{matrix} R_1 \\ R_2 \end{matrix} > CHOCr\bar{O}_3 \xrightarrow{h\nu} \begin{matrix} R_1 \\ R_2 \end{matrix} > C = O + Cr^{IV} \qquad (b)$$

$$Cr^{IV} + Cr^{IV} \xrightarrow{k_c} Cr^{V} + Cr^{111} \qquad (c)$$

$$Cr^{IV} + Cr^{V} \xrightarrow[H^+]{k_d} Cr^{111} + Cr^{VI} \qquad (d)$$

$$Cr^{IV} + Cr^{VI} \xrightarrow[H^+]{k_e} 2\ Cr^{V} \qquad (e)$$

$$Cr^{V} + \begin{matrix} R_1 \\ R_2 \end{matrix} > CHOH \xrightarrow[H^+]{k_f} \begin{matrix} R_1 \\ R_2 \end{matrix} > C=O + Cr^{111} \qquad (f)$$

From the quantum yield measurements $k_c/(k_e)^2$ and $k_e k_f/k_d$ were calculated. $k_c/(k_e)^2$ was small (6.10^{-11} moles^3 litre^{-3} sec.$^{-1}$) The values for $k_e\ k_f/k_d$ for the various alcohols are given in table 1.1.

TABLE 1.1

Alcohol	$k_e\ k_f/k_d$ litre^2 mole^{-2} sec.$^{-1}$
Methyl	0.62
Ethyl	5.8
n-Propyl	6.1
iso-Propyl	1.3
sec-Butyl	1.9

Mn^{11} and Ce^{111} were found to diminish the quantum yield for the reduction of Cr^{VI} to one third of its upper limiting value by the catalysis of disproportionation of Cr^{IV}. Oxygen also diminished the quantum yield by oxidation of the chromium intermediates to Cr^{VI}.

Levitt and Levitt (21) investigated the persulphate oxidation of 2-propanol and 2-butanol. They found that the first order rate constant (k) was retarded by the addition of organic compounds, which were themselves oxidized at a relatively slow rate by ~~pa~~persulphate under the same conditions. The mechanism appeared to involve an equilibrium of the type :

$$R_2CHOH + S_2O_8^{=} \rightleftharpoons \text{Ester} \longrightarrow R_2C{=}O + 2\,H\,S\bar{O}_4$$

The results indicated that one alcohol could displace another from its ester. When 2-butanol was added to 2-propanol solution, the value of k decreased from 0.84 to 0.29 $hr.^{-1}$; on the other hand, 2-propanol was not able to displace 2-butanol since k increased only slightly from 0.22 to 0.26 $hr.^{-1}$, when 2-propanol was added to 2-butanol solution. The ester interchange could be represented as :

$$R'OH + R\text{-ester} \rightleftharpoons R\,OH + R'\text{-ester}$$

The probable structures for the ester could be :

$RO\text{-}SO_2\text{-}O\text{-}O\text{-}S\bar{O}_3$ (an alkyl peroxy disulphate) or

$RO - O - S\bar{O}_3$ (an alkyl peroxymonosulphate).
The latter might be formed by the displacement of
$S\overset{=}{O}_4$ from $S_2\overset{=}{O}_8$ by the alcohol molecule.

The reaction of quinone with alcohol does not proceed by this mechanism, because quinone is not sufficiently acidic to form an ester.

1.2. Photochemical Reactions of Quinones

In the previous section evidence is presented which shows that the photochemical reactions of quinones proceed by hydrogen atom transfer. On this basis, the following reactions may be included in the mechanism of photochemical reactions of quinones, though in any one system not all of them will be met.

$$Q + h\nu \longrightarrow Q_S^*$$

$$Q_S^* \xrightarrow{k_{ST}} Q_T^* \quad \text{internal conversion}$$

$$\left.\begin{array}{l} Q_S^* \xrightarrow{k_{1S}} Q \qquad \text{''} \qquad \text{''} \\ Q_T^* \xrightarrow{k_{1T}} Q \qquad \text{''} \qquad \text{''} \end{array}\right\} Q^* \xrightarrow{k_1} Q$$

$$\left.\begin{array}{l} Q_S^* + AH_2 \xrightarrow{k_{2S}} QH + AH \\ Q_T^* + AH_2 \xrightarrow{k_{2T}} QH + AH \end{array}\right\} Q^* + AH_2 \xrightarrow{k_2} QH + AH$$

$$\left.\begin{array}{l} Q^*_S + AH_2 \xrightarrow{k_{3S}} Q+AH_2 \\ Q^*_T + AH_2 \xrightarrow{k_{3T}} Q+AH_2 \end{array}\right\} \quad Q^* + AH_2 \xrightarrow{k_3} Q+AH_2$$

$$\left.\begin{array}{l} Q^*_S + Q \xrightarrow{k_{4S}} Q+Q \\ Q^*_T + Q \xrightarrow{k_{4T}} Q+Q \end{array}\right\} \quad Q^* + Q \xrightarrow{k_4} Q + Q$$

$$Q^*_S + Q \xrightarrow{k_{4ST}} Q^*_T + Q$$

$$\left.\begin{array}{l} Q^*_S + QH_2 \xrightarrow{k_{5S}} Q+QH_2 \\ Q^*_T + QH_2 \xrightarrow{k_{5T}} Q+QH_2 \end{array}\right\} \quad Q^* + QH_2 \xrightarrow{k_5} Q+QH_2$$

$$\left.\begin{array}{l} Q^*_S + S \xrightarrow{k_{6S}} \text{Products e.g. } QH+P \\ Q^*_T + S \xrightarrow{k_{6T}} \text{Products} \end{array}\right\} \quad Q^* + S \xrightarrow{k_6} \text{Products}$$

$$\left.\begin{array}{l} Q^*_S + I \xrightarrow{k_{7S}} Q + I \\ Q^*_T + I \xrightarrow{k_{7T}} Q + I \end{array}\right\} \quad Q^* + I \xrightarrow{k_7} Q + I$$

$$QH+QH \xrightarrow{k_8} Q+QH_2$$

$$AH+AH \xrightarrow{k_9} A + AH_2$$

when $\phi > 0.5$

$$Q^* + AH_2 \xrightarrow{k_{10}} QH_2 + A$$

$$Q + AH \xrightarrow{k_{11}} QH + A$$

$QH + AH_2 \xrightarrow{k_{12}} QH_2 + AH$ may be included.

where

Q^*_S	Excited quinone in singlet state.
Q^*_T	Excited quinone in triplet state.
Q^*	Excited quinone, state unidentified.
AH	Free radical from oxidation of alcohol.

e.g. CH_2OH from methyl alcohol.

S Solvent.

P Unidentified product.

I Unidentified inhibitor.

These symbols for species and rate constants have been used throughout this thesis.

The emphasis on this survey will be on describing work that has provided information concerning the values of the rate constants in the above mechanism.

Table 1.2 gives a brief summary of early qualitative work on the photochemical reactions of quinones.

TABLE 1.2

Quinone	Reducing Agent	**Reaction Products**	Reference
Benzo-	Water	QH_2 + Complex Product	Ciamician and Silber (22)
"	Water	$QH_2 + C_{12}H_8O_5$	Hartley and Leonard (23)
"	Water	$QH_2 + C_{12}H_8O_5$	Hartley and Little (24)
"	Water	QH_2 + QOH	Poupé (25)
"	Me OH	QH_2 + Formaldehyde	Gibbs (26)
"	Me OH (25%	QH_2 + Formaldehyde	Poupé (25)
"	Et OH	QH_2 + Acetaldehyde + Complex Product	Ciamician and Silber (22)

Table 1.2 Contd.

Quinone	Reducing Agent	Reaction Products	Reference
Benzo-	iso-PrOH	QH_2+ Acetone + Complex Product	Ciamician & Silber (22)
Thymo-	EtOH	QH_2+ Acetaldehyde	" "
Chloranil	EtOH	QH_2	Klinger (27)
Anthra-	EtOH	QH_2+ Acetaldehyde	Meyer and Eckert (28)
"	iso-PrOH	QH_2 + Acetone	" "
Phenanthra-	EtOH	QH_2 + Acetaldehyde	" "
"	iso-PrOH	QH_2 + Acetone	" "

In the above table QH_2 is the relevant hydroquinone derivative. In addition to the two major products, complex side products are sometimes formed. These usually absorb visible light.

The early quantitative work on the reactions of quinones with alcohols in the absence of oxygen is summarized in table 1.3. More recent figures for quantum efficiency in 100% alcohol (Scrutton) and strong alcohol solutions (Atkinson and Di) are also included.

TABLE 1.3

Quinone	Alcohol	Solvent	Wavelength mμ	ϕ for loss of Quinone	Reference
Benzo-	-	Water	365	$0.9^{\dagger}$	Leighton & Forbes (29)
"	-	Water	436	$0.16^{\dagger}$	" "
"	EtOH(8.5M)	Water	253.7 - 436	0.5	" "
"	EtOH(8.5M)	"	546	0.23	" "
"	EtOH(17M)$^{\neq}$	-	253.7 - 436	0.5	" "
"	EtOH(17M)$^{\neq}$	-	546	0.23	" "
Temperature coefficient, $\triangle K_{10}$ (20°-30°C), approximately unity.					
Benzo-	EtOH(5M)	Water	436	1.0	Berthoud & Porret (30)
"	iso-PrOH(5M)	Water	436	1.0	" "
Temperature coefficient, $\triangle K_{10}$ (15°-25°C), approximately unity, and no dark reaction detected.					
Benzo-	EtOH (5.27-0.185M)	CCl_4	436	0.78^{*}	Atkinson and Di (1)
"	n-PrOH (0.212M)	CCl_4	436	0.77^{*}	" "
"	iso-PrOH (0.209M)	CCl_4	436	0.78^{*}	" "
Duro-	iso-PrOH	-	365	0.12	Scrutton (31)
Benzo-	"	-	365	0.93^{*}	"
Tolu-	"	-	365	0.97^{*}	"
Chloranil	"	-	365	0.49	"
Naphtho-	"	-	365	0.53	"
Duro-	tert-BuOH	-	365	0.13^{*}	"
Benzo-	"	-	365	0.83^{*}	"

Table 1.3 Contd.

Quinone	Alcohol	Solvent	Wa~~m~~velength mμ	Ø for loss of Quinone	Reference
Tolu-	tert-BuOH	-	365	0.84*	Scrutton (31)
Chloranil	"	-	365	0.41*	"

† Induction period in the beginning.

* Quantum efficiency for hydroquinone formation.

‡ Thermal reaction, 10% loss of quinone per hour, allowed for.

Some correlations between oxidation-reduction potential of quinone and threshold region, quantum efficiency and mole-cular weight have been proposed and the relevant data aregiven in table 1.4. .

TABLE 1.4

After Leighton and Dresia (32)

Quinone	Alcohol	Oxid.-Red. Potential	Approximate Threshold Region in mμ	MeanØ in Const.Region	Molecular Weight
Thymo-	Et OH	0.5875	400-435	0.309	164
Tolu-	"	0.6454	400-435	0.403	122
Benzo-	"	0.6990	435-500	0.505	108
Monochloro-	"	0.7125	Circa 500	0.354	142.5
Dichloro-	"	0.7220	Circa 500	0.256	177
Tetrachloro-	"	-	577	0.095	246

Results of Linstead and co-workers (14,15) for the thermal hydrogen transfer between 1:4- dihydronaphthalene and quinones in phenetole solution are given in table 1.5. There is indication of a linear relation between the rates of reaction of quinones and their oxidation-reduction potentials .

TABLE 1.5

After Linstead and Co-workers (14,15)

Quinone	Oxid.Red. Potential	$10^4\ k^{101^\circ}$ gm.mol.$^{-1}$ l.sec.$^{-1}$	Molecular Weight
Benzo-	0.711	1.32	108
Tolu-	0.656	0.428	122
Thymo-	0.589	0.087	164
1:4-Naphtho-	0.493	0.032	158

Scrutton (31) did not find any correlation between oxidation-reduction potential of quinone and the quantum efficiency of reaction, molecular weight of the quinone and the quantum efficiency.

The maximum quantum efficiency is determined by the mechanism. If the reactive species is the singlet state :

(i) the maximum quantum efficiency of 1 will be obtained by the processes 2S, 8 and 11,

(ii) the maximum quantum efficiency of 0.5 will be the result of processes 2S, 8 and 9,

(iii) the maximum quantum efficiency can be more than 1 if the processes involved are 2S, 11, 12, (8 or 9).

If on the other hand triplet state is reactive, the maximum quantum efficiency will be given as :

$$\phi_{\text{max.}} = \frac{k_{ST}}{k_{1S} + k_{ST}} \times 1 \text{ or } 0.5 \text{ or unlimited}$$

in the circumstances stated above.

In all the circumstances lower values of quantum efficiency are obtained if quenching processes of the type 3S or 3T are alternatives to reaction.

There is no relationship between the molecular weight and the rate of reactions of the type 1S or 3S or 3T. The values of quantum efficiency in the above tables cannot be interpretted on any single assumption. They require much more detailed explanation than is provided by simply attempting to relate them to molecular weight.

Therefore, the work in this field should be aimed at establishing which of the processes listed on pages(14,15)are significant in any particular system, and deriving the rate constants for these processes.

Studies of reaction rate at constant light intensity may lead to values of ratios of rate constants. Determination of absolute rate constants for single reactions requires rate measurements on systems not in a steady state. This can be done by flash photolysis.

Three major approaches have been used in the detailed study of the photochemical reactions of quinones :

(a) Measurement of rate in solution at a range of concentration and light intensity [Atkinson and Di (1) and Scrutton (31)].

(b) Measurements similar to (a) but in the presence of a third substance that reacts efficiently with the free radical intermediates, i.e., oxygen. This method has been used by Wells (5,6).

(c) Measurements by flash photolysis [Bridge and Porter (3,4)].

Atkinson and Di (1) made a thorough investigation of the photochemical oxidation of ethyl and propyl alcohols by benzoquinone in carbon tetrachloride solution, at 25°C, and at both 365 mμ and 436 mμ.

The solutions were irradiated under nitrogen, using a wide range of alcohol concentrations and light intensities. The reduction of the quinone was usually less than 5%, and no dark reaction was found. With ethyl alcohol the major products of the reaction were hydroquinone and acetaldehyde in equivalent amounts. The maximum quantum efficiencies at high concentrations of ethyl alcohol, n-propyl alcohol and isopropyl alcohol were 0.78, 0.77 and 0.78 respectively. These figures are intermediate between those of Berthoud and Porret and of Leighton and Forbes, because the solvent used was different. The quantum efficiencies were determined for the formation of hydroquinone rather than for the loss of quinone. In agreement with the previous workers, a side product was detected, which was thought to be present in small quantities.

In agreement with previous workers it was found that at high ethyl alcohol concentrations (5.27 to 0.185M) the quantum efficiencies were independent of quinone concentrations in the range 10^{-2} to 10^{-3} M, and the variation of light intensity from 10^{-8} to 0.07×10^{-8} einst. sec.$^{-1}$ It was also found that the quantum efficiency was independent of ethyl alcohol concentration in the range 5.27 to 0.185M. When ethyl alcohol concentration was below 10^{-1} M, the quantum efficiency decreased with the decrease in alcohol concentration, and in the range 10^{-1} to 10^{-3} M alcohol a marked dependence of quantum efficiency on light intensity was found. These variations in quantum efficiency at lower alcohol concentrations were quantitatively accounted for by the following mechanism :

$$\begin{array}{lcll}
Q + h\nu & \xrightarrow{\qquad} & Q^* & (0) \\
Q^* & \xrightarrow{k_1} & Q & (1) \\
Q^* + AH_2 & \xrightarrow{k_2} & QH + AH & (2) \\
QH + QH & \xrightarrow{k_8} & Q + QH_2 & (8) \\
AH + AH & \xrightarrow{k_9} & A + AH_2 & (9) \\
QH + AH_2 & \xrightarrow{k_{12}} & QH_2 + AH & (12)
\end{array}$$

This scheme gives the maximum value of quantum efficiency as unity, whereas the observed value for the three alcohols is about 0.78. It was thought that only 78% of the excited quinone molecules were capable of reacting with alcohol though, allowance for the side reactions might make the figures to be somewhat higher.

By applying the stationary state treatment to the above scheme, taking the rate of reaction (0) as $\alpha[I]$, where $[I]$ is the concentration of light absorption in einst. $l.^{-1}$ $sec.^{-1}$, the following expression for the quantum efficiency was deduced:

$$\phi = \frac{d[QH_2]}{[I]\,dt} = \frac{\alpha X}{2} - \frac{Y[AH_2]^2}{[I]} + \frac{Y[AH_2]^2}{[I]}\left[1 + \frac{[I]\alpha X}{Y[AH_2]^2}\right]^{1/2} \quad \ldots 1.1$$

$$\text{where} \quad X = \frac{k_2[AH_2]}{k_2[AH_2] + k_1} \quad \ldots 1.2$$

$$\text{and} \quad Y = \frac{k_{12}^2}{4k_8} \quad \ldots 1.3$$

When $[AH_2]$ is high, the equation 1.1 reduces to

$\phi = \alpha X$

When $[AH_2]$ is low, $\dfrac{1}{\phi} = \dfrac{2}{\alpha} + \dfrac{2k_1}{k_2}\dfrac{1}{[AH_2]}$ ...1.4

Values for the ratio $\dfrac{k_1}{k_2}$ and $\dfrac{k^2_{12}}{k_8}$ for the three alcohols are shown in table 1.6.

TABLE 1.6

Alcohol	k_1/k_2 mole $l.^{-1}$ x 10^3	k^2_{12}/k_8 $l.mole^{-1}$ $sec.^{-1}$ x 10^5
Ethyl	0.38	7.4
n-Propyl	0.52	8.5
iso-Propyl	0.49	7.8

The ratio $^{k}2/k_1$ provides a comparison of the ease of removal of hydrogen atoms by molecules from the alcohols. The ratio $k^2{}_{12}/k_8$ is a measure of the reactivity of the semiquinone free radical towards the alcohol, and thus the ratio provides a means of comparing the ease of removal of hydrogen atoms by free radicals from alcohols. These ratios have been compared in tables 1.7 and 1.9.

TABLE 1.7

Comparison of Relative Rates of Hydrogen Transfer from Alcohols to Free Radicals

Alcohol	Trotman-Dickenson (33) Methyl (in gas phase)	Merz & waters (34) $S\bar{O}_4$ (in aqueous soln)	Farmer & McDowell (35) Peracetyl (in gas phase)	Atkinson and Di (1) Semi-quinone (in CCl_4)
Methyl	0.30	0.35	0.06	
Ethyl	1.00	1.00	1.00	1.00
n-Propyl		0.98	1.50	1.07
iso-Propyl	1.55	1.44	2.52	1.03

Table 1.7 shows that there is no agreement between each set of results. However, the general trend is that the reactivity increases along the series

$\mathrm{Me\ OH} < \mathrm{Et\ OH} \simeq n\text{-}\mathrm{Pr\ OH} < iso\text{-}\mathrm{Pr\ OH}$

If it is assumed that it is the α-hydrogen atom that is removed by the free radicals, the ease of removal of hydrogen atom will be in the order

primary H $<$ secondary H $<$ tertiary H.

Scrutton (31) reviewed the photochemical reactions of five quinones, duroquinone, chloranil, benzoquinone, toluquinone and naphthoquinone in pure alcohols, alcohol solutions in carbon tetrachloride and in other solvents. The reactions were generally carried out at 365 mμ and 25.0°C in the atmosphere of nitrogen. The reactions were followed either by analysis of hydroquinone produced, or by observation of rate of loss of quinone. The quinones were found to fall into two categories, those with maximum quantum efficiencies less than 0.5 (duroquinone and chloranil), and those with maximum quantum efficiencies in the range 0.8 to 1 (benzoquinone, toluquinone and naphthoquinone). In the reactions of duroquinone and chloranil the photolysis was inhibited by the hydroquinone formed, and the reaction mechanism presented was :

$$Q + h\nu \longrightarrow Q^* \qquad (0)$$

$$Q^* + AH_2 \xrightarrow{k_2} QH + AH \qquad (1)$$

$$Q^* + QH_2 \xrightarrow{k_5} Q + QH_2 \qquad (5)$$

$$QH + QH \xrightarrow{k_8} Q + QH_2 \qquad (8)$$

$$AH + AH \xrightarrow{k_9} A + AH_2 \qquad (9)$$

This scheme gives the maximum quantum efficiency of 0.5 before inhibition starts. Apart from inhibition (quenching of excited quinone by hydroquinone) ,self-quenching by quinone was **found** in the chloranil-ethyl alcohol system

$$Q^* + Q \xrightarrow{k_4} Q + Q \qquad (4)$$

The maximum quantum efficiency was found to be close to 0.5 with chloranil, but it was only 0.12 with duroquinone. This was explained by assuming that duroquinone reacted only in the triplet state, and the initial reaction steps were :

$$Q^*_S \xrightarrow{k_{1S}} Q \qquad (IS)$$

$$Q^*_S \xrightarrow{k_{ST}} Q^*_T \qquad (ST)$$

$$Q^*_T \xrightarrow{k_{1T}} Q \qquad (IT)$$

The ratios of rate constants k_5/k_2 and k_4/k_2 for 100% alcohol are given in table 1.8.

TABLE 1.8

Quinone	Alcohol	k_5/k_2	k_4/k_2
Duro-	EtOH	2.8×10^5	
Duro-	iso-PrOH	1.55×10^5	
Chloranil	EtOH	1.1×10^5	1.1×10^4
Chloranil	iso-PrOH	1.6×10^4	

Naphthoquinone was not fully investigated, and so the mechanism applicable to benzoquinone and toluquinone was presented. The quantum efficiency greater than 0.5 was explained by the reaction

$$QH + AH_2 \xrightarrow{k_{12}} QH_2 + AH \qquad (12)$$

In the reactions of benzoquinone and toluquinone with iso-propyl alcohol, no side product was observed, and the maximum quantum efficiencies were with benzoquinone (0.93) and with toluquinone (0.97) . Reactions in which a side product was formed gave lower quantum efficiencies.

The fall in quantum efficiency at very low alcohol concentration was explained by the loss of energy due to internal conversion

$$\overset{*}{Q} \xrightarrow{k_1} Q \qquad (1)$$

No inhibition by the hydroquinone product (reaction 5) was observed with either benzoquinone or toluquinone.

Duroquinone, benzoquinone, toluquinone and chloranil were found to react with tert-butyl alcohol. The quantum efficiencies of these reactions were similar to the corresponding reactions of these quinones with other alcohols. Hence tert-butyl alcohol was not found to be an inert solvent. Cyclohexane and carbon tetrachloride also gave photochemical reactions with quinones, and no completely inert solvent was found.

1.3. Photolysis of Quinone Solutions containing Oxygen

Bolland and Cooper (7) studied the autoxidation of ethyl alcohol photosensitized by anthraquinone-2:6- sulphonate and explained the production of acid by the following mechanism :

$$Q + h\nu \longrightarrow \overset{*}{Q} \qquad (0)$$

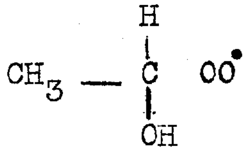
$$Q^{*} + AH_2 \xrightarrow{k_2} QH + AH \tag{2}$$

$$AH + O_2 \xrightarrow{k_{13}} AH\,O_2 \tag{13}$$

$$QH + O_2 \xrightarrow{k_{14}} Q + HO_2 \tag{14}$$

$$AHO_2 + AHO_2 \xrightarrow{k_{15}} 2\ \text{acid} + H_2O_2 \tag{15}$$

where AHO_2 represents the radical



$$CH_3 - \overset{\displaystyle H}{\underset{\displaystyle OH}{C}}\ OO^{\bullet}$$

and the acid formed is acetic acid.

Wells (5,6,36) studied the reactions of alcohols with photo-excited sodium anthraquinone - 2 - sulphonate in aqueous solution, and determined the relative reactivities of alcohols to hydrogen transfer by measuring the rate of oxygen uptake of the system under varying conditions. The aims of his kinetic investigations were :

(i) to find out the point of initial attack of the photoexcited sensitizer on the alcohol,

(ii) to distinguish whether the process of attack is transfer of a hydrogen atom or the transfer of an electron,

(iii) to measure the reactivity of the reductant to the excited sensitizer to know the effect of structure on the reactivity. In addition to the chemical deactivation processes, (0) (2), (13) and (14) given in the mechanism of Bolland and Cooper (7), he included the following sequence of reactions, as the possible physical modes of deactivation in his scheme :

$$Q^{*} + AH_2 \xrightarrow{k_3} Q + AH_2 \qquad (3)$$

$$Q^{*} + H_2O \xrightarrow{k_{16}} Q + H_2O \qquad (16)$$

$$Q^{*} + Q \xrightarrow{k_4} Q + Q \qquad (4)$$

$$Q^{*} + O_2 \xrightarrow{k_{17}} Q + O_2 \qquad (17)$$

$$Q^{*} \xrightarrow{k_{18}} Q + h\nu' \qquad (18)$$

$$Q^{*} \xrightarrow{k_1} Q' + \text{Solvent} \longrightarrow Q' \longrightarrow Q \qquad (1)$$

The physical deactivations can be described as the deactivation by collision with solvent molecules (3) and (16) involving a number of molecules of water and alcohol, by sensitizer molecules (4) and by dissolved oxygen; by fluorescence (18) and by a non-radiative adiabatic route (1), involving the transference of the excited state Q^{*} to the ground state Q, possibly via intermediate stage Q'.

In this kinetic scheme the rate constants k_{13} and $k_{14} \gg k_2$ and also the rate constants for the reactions of AHO_2 and HO_2 are all $\gg k_2$. Thus, the rate of oxygen uptake of the aqueous solution of sensitizer and reductant could be given by :

$$-\frac{d[AH_2]}{dt} = -\frac{d[O_2]}{dt} = k_2 [Q^*] [AH_2]$$

Detailed kinetic study showed that the processes responsible for deactivation of the photo-excited sensitizer were only (1) and (2) and the expression obtained was :

$$\frac{1}{-\frac{d[O_2]}{dt}} = \frac{1}{I} + \frac{1}{I} \cdot \frac{k_1}{k_2} \cdot \frac{1}{[AH_2]}$$

where I represents the rate of activation and is proportional to the intensity of light. The ratio k_2/k_1 was used as a measure of the reactivity of the reductant to the photo-excited sensitizer and the reactivities of a wide range of reductants were determined. In table 1.9 the relative reactivities (k_2/k_1) of various alcohols per hydroxyl group have been compared. From his work he arrived at the following conclusions :

(i) In the primary alcohols, reactivity increases with the increase in chain length.

(ii) With the glycols, increasing methylation of the carbon atoms in the α position to the hydroxyl groups is found to increase their reactivity.

(iii) Reactivity increases in the monohydric alcohols with increasing alkylation on the α- carbon atom until all the hydrogen atoms are replaced, when a great reduction in reactivity results, i.e., reactivity increases along the series tert-Bu OH $\ll$ Me OH $<$ Et OH $<$ iso-Pr OH.

(iv) Increasing the number of hydroxyl groups in alcohols, decreases the reactivity, i.e. reactivity decreases along the series n-Pr OH $>$ Propylene glycol $>$ glycerol.

When the work was extended to ethers (36), increasing alkylation was found to reduce the reactivity. This effect was attributed to the increase in steric hindrance. With alcohols the increase in inductive effect accompanying the increasing alkylation causes the reactivity to increase. The decreasing reactivity with the increase in hydroxylation in alcohols, is also due to the increasing steric hindrance.

Wells deduced that the photo-excited sodium anthraquinone -2- sulphonate attacks only the C-H bond α to the hydroxyl group, and as mentioned in the section 1.1.1 the reaction proceeds by a simple hydrogen atom transfer,

$$Q^{*} + R_2\,C\,H\,O\,H \longrightarrow \dot{Q}H + R_2\,\dot{C}\,OH$$

and not by slow electron transfer followed by a rapid proton expulsion from the alcohol,

$$Q^{*} + R_2\,CHOH \xrightarrow{\text{Slow}} \overset{\bullet -}{Q} + R_2\,CH\,\overset{+}{O}H$$

$$R_2\,CH\,\overset{+}{O}H \xrightarrow{\text{Fast}} R_2\,\dot{C}\,OH + \overset{+}{H}$$

This deduction has been explained in detail in the following paragraphs.

The increase in reactivity with the increase in alkylation on the α - carbon atom of the simple alcohols is consistent with either of the above mechanisms, because the increasing inductive effect will facilitate the removal of the electron or of the hydrogen atom.

However, tert-butyl alcohol will have different behaviour in relation to simple primary and secondary alcohols depending on whether electron or hydrogen atom transference is rate-controlling. With all alcohols, once the electron or hydrogen atom has been removed the semiquinone radical (or radical ion) is very rapidly oxidized by oxygen,

$$\cdot QH\ (\cdot Q^{-}) + O_2 \longrightarrow Q + HO_2^{\cdot}\ (\cdot O_2^{-})$$

So, for a rapid electron transfer or a rapid hydrogen transfer, a high rate of oxygen uptake or a high observed reactivity ratio will be obtained. In tert-butyl alcohol, with electron transference, the large inductive effect on the α - carbon atom would lead to a high observed reactivity on the $\geqslant$ COH groups, whereas with hydrogen atom transference, the inductive effect cannot influence the reactivity of the $\geqslant$ COH group, due to the absence of a hydrogen atom on the α - carbon atom, and a very low reactivity would be expected. In fact a very low reactivity has been observed, which indicates that the reaction proceeds by a simple hydrogen atom transfer from the alcohol to the quinone.

TABLE 1.9

Comparison of Relative Rates of Hydrogen Transfer from Alcohols to Molecules

Alcohol	Wells (5,6,36) Sod.Anthra-Quinone-2-sulphonate (in water)	Bowen et al. (37, 38, 39) Dichromate ion (in water)	Immamura (40) Eosine (in water)	Atkinson & Di (1) Benzoquinone (in CCl_4)
Methyl	0.12	0.3	0.22	
Ethyl	1.0	1.0	1.0	1.0
n-Propyl	1.53	1.5		0.73
iso-Propyl	2.14	2.0	2.12	0.78
n-Butyl	2.07			
tert-Butyl	0.01			
Ethylene Clycol	0.289			
1:2-Propylene Glycol	0.625			
2:3-Butylene Glycol	1.49			
Glycerol	0.28			

Table 1.9 shows that the values of Wells, Bowen and Immamura are in fair agreement and in general the reactivity of hydrogen atom increases in the order

primary H $<$ secondary H $<$ tertiary H

This trend is similar to that observed in table 1.7 for the relative rate of hydrogen transfer from alcohols to the free radicals.

The results of Atkinson and Di, in disagreement to these workers, show that hydrogen could be removed more easily from ethyl than from propyl alcohols. A reasonable explanation for this difference may be the possibility of a different value of k_2 in the two media, aqueous and non-aqueous, and the various possibilities of solvation of the excited quinone, e.g., hydrogen bo-nding. It is also possible that sodium anthraquinone-2-sulphonate (Wells) may be a more selective reactant than benzoquinone and its derivatives. Scrutton (31) found that tert-butyl alcohol reacted with the various quinones to the same extent as the other alcohols, whereas Wells observed a very low reactivity of tert-butyl alcohol.

Kellmann (41) studied the photochemical reactions of acridine with alcohols (100%) at 365 mμ and determined the relative rates of hydrogen abstraction from the various alcohols by acridine molecules. His figures for the relative reactivities do not refer to the ratio k_2/k_1 of equation 1.4. They were obtained by the ratio

$$\frac{\text{Quantum efficiency for the loss of acridine}}{\text{Concentration of alcohol (moles } l.^{-1}\text{)}}$$

The results are given in table 1.10

TABLE 1.10

Alcohol	ϕ	$\frac{\phi}{[AH_2]} . 10^2$	Relative Reactivity (EtOH =1)
Methyl	0.145	0.585	0.51
Ethyl	0.13	0.765	1.00
n-Propyl	0.091	0.685	0.90
iso-Propyl	0.127	0.974	2.55
tert-Butyl	0.011	0.106	

Wells (42) also determined the reactivities of carbohydrates to photoexcited anthraquinone-2-sulphonate and found that methyl β - D - glucoside (having an axial C-H bond at position 1) was more reactive than the α - anomer (an equatorial C-H bond at position 1), which is contrary to Barton's postulate (43). The reactivities of carbohydrates relative to ethyl alcohol are given in table 1.11.

TABLE 1.11

Carbohydrate	$\frac{k_2}{k_{EtOH}}$
Methyl β -D-glucopyranoside	0.99
Methyl α -D-glucopyranoside	0.58
Methyl α -D-mannopyranoside	0.78
β -D-Mannose	2.04
β -D-Galactose	2.20
α -D-Galactose	0.99
β -D-Glucose	1.57
α -D-Glucose	0.67
α -D-Xylose	0.82

The observation for the methyl glucosides that the β - is more reactive anomer appears to be true also for the free sugars glucose and galactose.

Table 1.11 shows that β-D- galactose is the most reactive of the free sugars. It was presumed that it might be due to a very reactive grouping. The study of the 'upper side' and the 'under side' of the molecule revealed that the 'upper side' has a big cluster of hydroxyl groups, presumably responsible for the hindrance of approach of the larger quinone to few C-H bonds lying on this side.. The 'under side' contains a cluster of three axial hydrogen atoms (at positions 1,3 and 5), and one equatorial hydrogen atom (at position 4), with a comparatively unhindered approach.

Among the D-galactoses and D-glucoses, reactivity decreases in the order β-D-galactose > β-D-glucose > α-D-galactose > α-D-glucose.

This decrease in reactivity can be correlated with the total number of axial and equatorial C-H bonds on the uninhibited under side as shown in Table 1.12.

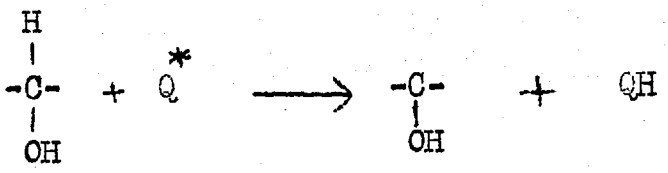
TABLE 1.12

Disposition of C-H Bond at Positions 1-5 of Pyranose Rings of Carbohydrates.

Carbohydrate	Under Side		Upper Side		$\frac{k_2}{k_{EtOH}}$
	Axial	Equatorial	Axial	Equatorial	
β-D-Galactose	3	1	1		2.20
β-D-Mannose	3	1	1		2.04
β-D-Glucose	3		1	1	1.57
α-D-Galactose	2	1	2		0.99
α-D-Glucose	2		2	1	0.67

It can be seen from Table 1.11 that O-methylation at position 1 causes a reduction in reactivity. This is in contradiction to the increased reactivity on methylation at α carbon atom in alcohols, but it is comparable with reduction in reactivity with methylation in ethers, which was attributed to the steric hindrance of reactive hydrogen atoms.

Hence, owing to the inhibition of cluster of large hydroxyl groups on the upper side, hydrogen atoms on the under side of the pyranose ring are attacked by the excited quinone. As most of the C-H bonds on the under side are axial, therefore an axial is attacked in preference to the equatorial C-H bond. On the other hand equatorial hydrogen atoms in cyclohexanediols are more reactive than the axial hydrogen atoms persumably owing to the absence of large number of hydrated hydroxyl groups. Another reason in favour of the preferential attack of the axial C-H bonds on the under side could be that the closer packing of the axial groups might involve greater repulsion in axial than in equatorial positions. Thus in a reaction involving abstraction of hydrogen to form a free radical, such as :



$$\overset{\displaystyle H}{\underset{\displaystyle OH}{-C-}} + \overset{*}{Q} \longrightarrow \underset{\displaystyle OH}{-C-} + QH$$

the repulsion energy of hydrogen will assist the reaction. From the above discussion it was concluded that steric inhibition is the main factor responsible for the variation of reactivity in sugars.

1.4. Flash Photolysis of Quinones

Bridge and Porter (3,4) studied the flash photolysis of wide variety of quinones in various solvents, using unfiltered light. By employing the spectroscopic technique they could detect the existence of following transient species, although not all were present in each case :

QH	the semiquinone free radical,
Q^-	the semiquinone radical ion,
Q^t	the triplet state.

The flash photolysis of duroquinone in viscous solvent like liquid paraffin, produced both the triplet and the semiquinone free radical. With less viscous solvents, such as hexane, 3-methyl pentane and cyclohexane, the triplet was no longer observed, presumably due to its short lifetime. The semiquinone free radical was still present, although in much smaller quantities. Using carbon tetrachloride as solvent, the earliest flashes did not give any evidence of the presence of semiquinone free radical, provided the carbon tetrachloride was free from chloroform. Presence of 1% of chloroform in the solvent produced large quantities of the free radical. Even in pure carbon tetrachloride, the free radical was formed as a result of the repeated flashing, and this was presumably due to hydrogen abstraction from the duroquinone itself.

In ethyl alcohol as solvent, the results were more complicated as they depended on ~~PH~~ pH. The free radical was observed in all the solutions, but the radical ion existed only in alkaline ~~than~~ not in acid alcohol. The conversion of free radical to the radical ion was actually observed in ethyl alcohol, and a rate constant was derived. It was established that the primary reaction of the excited state with the solvent was hydrogen abstraction and not the electron abstraction.

Though the triplet state was observed when duroquinone was flashed in liquid paraffin, it was found that the major part of the reaction with the solvent proceeded via the singlet and not the triplet state.

Flash photolysis of benzoquinone, toluquinone, m- and p-xyloquinone and tri-methylquinone in both liquid paraffin and ethyl alcohol gave only semiquinone free radicals, and the triplet was not detected even in liquid paraffin. When naphthoquinone was flashed in liquid paraffin, a weak triplet was observed.

They presented their observations in terms of the following scheme of reactions :

$$\begin{array}{l}
Q + h\nu \longrightarrow Q^{*}_{S} \\
Q^{*}_{S} \xrightarrow{k_{ST}} Q^{*}_{T} \\
Q^{*}_{T} \xrightarrow{k_{1T}} Q \\
Q^{*}_{S} + AH_2 \xrightarrow{k_{2S}} QH + AH \\
Q^{*}_{T} + AH_2 \xrightarrow{k_{2T}} QH + AH \\
2QH \xrightarrow{k_8} Q + QH_2 \\
QH \xrightarrow{k_{19}} Q^{-} + H^{+} \\
2Q^{-} \xrightarrow{k_{20}} Q + Q^{2-} \\
Q^{-} + H^{+} \xrightarrow{k_{21}} QH \\
QH \overset{K}{\rightleftharpoons} \bar{Q} + H^{+}
\end{array}$$

where Q is duroquinone and AH_2 the solvent (ethanol/ water, ethanol and liquid paraffin).Ethanol/water was referred to the mixture containing equal parts by volume of water and alcohol, and ethanol containing only 4% by volume of water was referred to as ethanol.

Rate constants for the individual steps and the equilibrium constant were obtained, and the values are shown in table 1.13.

TABLE 1.13

Rate Constant	Solvent	Value
k_{ST}	all	$> 5 \times 10^5$ sec.$^{-1}$
k_{1T}	liquid paraffin	$= 0.9 \times 10^4$ sec.$^{-1}$
	ethanol/water	$> 4 \times 10^4$ sec.$^{-1}$
k_{2S}	all	$> 4 \times 10^4$ sec.$^{-1}$
k_{2T}	liquid paraffin	$\ll k_{1T}$
k_8	ethanol/water	$= 7.9 \times 10^4\ \epsilon_{(410)}$ l. mole^{-1} sec.$^{-1}$
		$\approx 8 \times 10^8$ l.mole^{-1} sec.$^{-1}$
	liquid paraffin	$= 4.6 \times 10^4\ \epsilon_{(405)}$ l. mole^{-1} sec.$^{-1}$
		$\approx 5 \times 10^8$ l.mole^{-1} sec.$^{-1}$
k_{19}	ethanol	$= 7.4 \times 10^3$ sec.$^{-1}$
	ethanol/water	$> 4 \times 10^4$ sec.$^{-1}$
k_{20}	ethanol/water	$= 4.6 \times 10^2\ \epsilon_{(435)}$ l. mole^{-1} sec.$^{-1}$
		$\approx 4.6 \times 10^6$ l. mole^{-1} sec.$^{-1}$
k_{21}	ethanol	$> 3 \times 10^{10}$ l.mole^{-1} sec.$^{-1}$
	ethanol/water	$\approx 7.4 \times 10^9$ l.mole^{-1} sec.$^{-1}$
K	ethanol/water	$= 1.2 \times 10^{-6}$ mole l.$^{-1}$
	ethanol	$\approx 10^{-6}$ mole l.$^{-1}$

Bridge (44) determined the quantum efficiency for the formation of intermediate species, using filtered light. With higher light intensity than used previously, ~~be~~ he observed the triplet state with duroquinone in ethyl alcohol. The quantum efficiencies for the formation of triplet and radical ion at different wavelengths are given in table 1.14.

TABLE 1.14

Duroquinone in Ethyl Alcohol

Wavelength mμ	$\phi \times 10^{-4}\,\epsilon$ Triplet	$\phi \times 10^{-4}\,\epsilon$ Radical-ion
400	0.19	0.8
350	0.07	0.11
260	0.01	0.016

The semiquinone radical-ion has $\epsilon = 10^4$ and for the triplet state ϵ lies between 10^3 and 10^5. Using these values for the extinction Coefficient, the absolute quantum efficiency can be calculated. The quantum efficiency is found to decrease with decreasing wavelength, and this trend is also observed with anthraquinone, 2-methylanthraquinone, and 2:6-di SO_3-anthraquinone in ethyl alcohol. This effect was explained on the grounds that the photochemically reactive transition is the weak, long wavelength $n \longrightarrow \pi^*$ transition, at approximately, 400 mμ for the anthraquinones and 450 mμ for duroquinone, rather than the stronger $\pi \longrightarrow \pi^*$ transition which lies at lower wavelength. In an $n \longrightarrow \pi^*$ transition, a non-bonding electron of the carbonyl oxygen atom is raised to an antibonding π molecular orbital resulting in an unpaired electron being left on the oxygen atom. The molecular state may then be either singlet or triplet. This oxygen probably interacts with the solvent via a hydrogen bond, and hence the $n \longrightarrow \pi^*$ transition is in a unique position to initiate an attack by the quinone on the solvent. In fact, it is difficult to see how the other transitions not involving n-electrons could possibly lead direct to the same reaction without internal conversion.

1.5. Association of Alcohol Molecules in Carbon Tetrachloride

The photochemical reactions of toluquinone with alcohols were carried out in carbon tetrachloride, therefore it was desirable to know the extent of association of alcohol molecules in carbon tetrachloride, so that the concentration of monomer could be determined. The infrared spectra of compounds containing OH groups often show a sharp absorption band close to 2.75 µ, most apparent in dilute solution, and a much wider band at about 3 µ for the pure compound or strong solutions. The narrow band is due to vibration of the free OH group and the broad band is characteristic of the vibration of OH groups that are associated by hydrogen bonds.

Recently NMR technique has established the general phenomenon of shift in the OH frequency with change of concentration due to the disturbance of hydrogen bonding equilibrium. The quantitative work on the association of alcohol molecules in carbon tetrachloride is summarized in table 1.15.

TABLE 1.15

Alcohol	Conc.Range Moles $l.^{-1}$	Technique Employed	Model	K	Reference
Phenol	0.0145-0.176	Infrared	Dimer	≃6	Fox and Martin (45)
Ethyl	below 0.0171	Infrared	No association		Errera, Gaspart and Sack (46)
Phenol	above 0.1	NMR	Dimer	13±7	Huggins, Pimentel and Shoolery (47)
Ethyl	0.03 - 17	NMR	Cyclic Dimer	5 ±2	Becker, Liddel and Shoolery (48)
Phenol	above 0.01	NMR	Trimer	4.78	Saunders & Hyne (49)
tert-Butyl	above 0.01	NMR	Trimer	5.6	" "
Methyl	above 0.01	NMR	Tetramer	28.4	" "
Ethyl	reinterpretation of data after Becker et al.		Trimer & Tetramer	5.19 44.9	" " " "

Table 1.15 Cont'd.

Alcohol	Conc. Range Moles $l.^{-1}$	Technique Employed	Model	K	Reference
Ethyl	0.00511 - 1	Infrared	Trimer & Tetramer	10.0 50.0	Coburn & Grunwald (50)
Methyl	below 0.1	NMR	Dimer	7	Connor & Reid (51)
iso-Propyl	0.00625 - 0.2	Infrared	Cyclic Dimer	0.73	Blanks & Prausnitz (52)

Smith, de Maine and de Maine (53) measured the infrared absorption spectra of various alcohols dissolved in carbon tetrachloride.

The equation,

$$N(ROH) \overset{K}{\rightleftharpoons} (ROH)_N$$

was solved for K and N by a computer method. The concentration ranges studied for the various alcohols are given in table 1.16, together with the values of K and N.

TABLE 1.16

Alcohol	Concentration Range Moles $l.^{-1}$	K	N
Methyl	0.0393 - 1.88	0.905	2.38
n-Propyl	0.0213 - 1.018	1.142	2.42
iso-Propyl	0.0208 - 1.00	1.030	2.40
n-Amyl	0.0148 - 0.71	1.005	2.41
Phenyl Ethyl	0.0134 - 0.6434	1.000	2.28

2. EXPERIMENTAL

2. 1. Introduction.

The present work is a kinetic study of the photochemical reactions of P-toluquinone with organic reducing agents using carbon tetrachloride as a solvent. Cyclohexane, which was considered as an alternative solvent, was found to react with toluquinone with a quantum efficiency of 0.5.

The main product in all the reactions studied was toluhydroquinone. In general, the rate of reaction was determined by measuring the yield of toluhydroquinone.

The solutions were irradiated at 365 mμ and 25.0°C in an atmosphere of nitrogen or in vacuum. In studying the reactions of toluquinone with methyl alcohol particular difficulties were experienced in obtaining reproducible results. The trouble was traced to evaporation of the reductant during the passage of 'oxygen free' nitrogen through the solution. The problem was solved by pumping out the solution on a vacuum line before irradiation. For the measurement of light intensity, the potassium ferrioxalate actinometer was used.

Bearing in mind the above requirements, the apparatus and experimental technique were developed, and are described in the following sections.

2.2. Materials

2.2.1. P-Toluquinone (Light's) black tar product was purified by soxhlet extraction with petroleum ether (b.p.30-40°C). The toluquinone was filtered off, and sublimed twice at atmospheric pressure m.p.68°C [lit.(54) m.p.69°C]. (Found C,67.48; H, 4.94%. Calculated for $C_7H_6O_2$:C,68.87; H,4.95%).

P-Toluquinone (Hopkin and Williams), which was comparatively less impure than the Light's product, was purified by recrystallising from petroleum ether (b.p. 30-40°C), and subjecting the resulting crystals to two successive sublimations at atmospheric pressure m.p.68°C [lit.(54) m.p.69°C]. (Found C,68.32;H,4.98%. Calculated for $C_7H_6O_2$: C,68.87;H,4.95%). The amount of toluhydroquinone in the toluquinone sample was determined as follows:

A solution of toluquinone (2.0×10^{-2} mole $l.^{-1}$) in pure cyclohexane was prepared. The solution (1.0 and 2.0 ml) was mixed with 10.0 ml of reagent solution A (section 2.5.2) in two black conical flasks, stirred for half an hour with magnetic stirrers and kept for one hour in the dark. The optical densities of aqueous layers from both the flasks were measured at 510 mμ in 1 cm cells with the reagent solution A as blank. From the optical densities the concentration of toluhydroquinone was found to be 0.86×10^{-5} mole $l.^{-1}$ in the 2.0×10^{-2} mole $l.^{-1}$ toluquinone solution. This corresponds to 0.043% of toluhydroquinone in the toluquinone.

2.2.2. Toluhydroquinone (Light's) was purified by recrystallisation three times from benzene and the resulting crystals were dried under vacuum m.p.124-125°C [lit. (55) m.p. 124-5°C].

2.2.3. Alcohols

iso-Propyl alcohol (Hopkin and Williams AnalaR) was dried with lime and distilled in the atmosphere of dry 'oxygen free' nitrogen. A sample of iso-Propyl alcohol was also dried with Molecular Sieve (Potassium alumino-silicate) before distillation under nitrogen. The purity of alcohol was found to be of the same order in both the cases. This was indicated by the identical figures for the quantum efficiency at the same alcohol concentration.

Methyl alcohol (Hopkin and Williams AnalaR) was dried by Molecular Sieve and then distilled under dry 'oxygen free' nitrogen.

2.2.4. Carbon Tetrachloride (Hopkin and Williams AnalaR) to be used with iso-propyl alcohol was dried by lime before distillation under nitrogen. For the preparation of methyl alcohol solutions, carbon tetrachloride was dried with Molecular Sieve and distilled under nitrogen.

All distillations were carried out with an all glass plain fractionation column, 500 mm. FC 7/43, and was filled with Raschi~~n~~g rings FC 8/06. The septa EX 13/23 was used as a support for the packing. The column was provided with sluice type head FC 15/32, and was attached to the distillation adapter FC 15/2 by means of a clip J.C. 2/12. The column also carried a reflux condenser C5/12 at the top. The bulb of the thermometer was kept just below the level of the side arm. The solvent (600 ml) was distilled, the first 200 ml fraction being rejected, and the next 200 ml having constant boiling point was collected. The purity of each solvent was checked by gas chromatography. Working solutions were prepared by volumetric dilution.

2.2.5. Other Chemicals

Cyclohexane (B.D.H.) for spectroscopy, ferric chloride (AnalaR), ferrous ammonium sulphate (AnalaR), potassium oxalate (AnalaR), sodium acetate (AnalaR), concentrated sulphuric acid (AnalaR) and O-phenanthroline were used without further purification.

2.2.6. Nitrogen

The 'oxygen free' nitrogen was freed from the traces of oxygen by passing it through three wash bottles containing Fieser's solution. One of these wash bottles had a sintered disk at the end of the incoming glass tubing. The Fieser's solution was prepared by dissolving 16g of sodium hydrosulphite, 15g of sodium hydroxide and 0.8g of sodium anthraquinone-2-sulphonate in 100 ml of water. Impurities, i.e., hydrogen sulphide, were removed by passing the gas through sodium hydroxide solution (5%) and lead acetate solution (5%) contained in wash bottles. Finally the gas was passed through a wash bottle containing distilled water. The wash bottle containing sodium hydroxide solution also had a sintered disc at the end of incoming glass tubing.

The gas was then dried by silica gel. Beyond this point the line was divided into two parts by means of a two-way tap. On one side the gas could be used to remove air from the analysis and reaction vessels, while on the other it was saturated with the solvent by passing it through one bubbler (kept in the thermostat), or two bubblers (one of them being outside the thermostat) containing either the same pure solvent or the mixed solvents taken in the same proportion as were used in the experiment.

2.3. Apparatus for Irradiation of Solutions

2.3.1. The Optical Bench

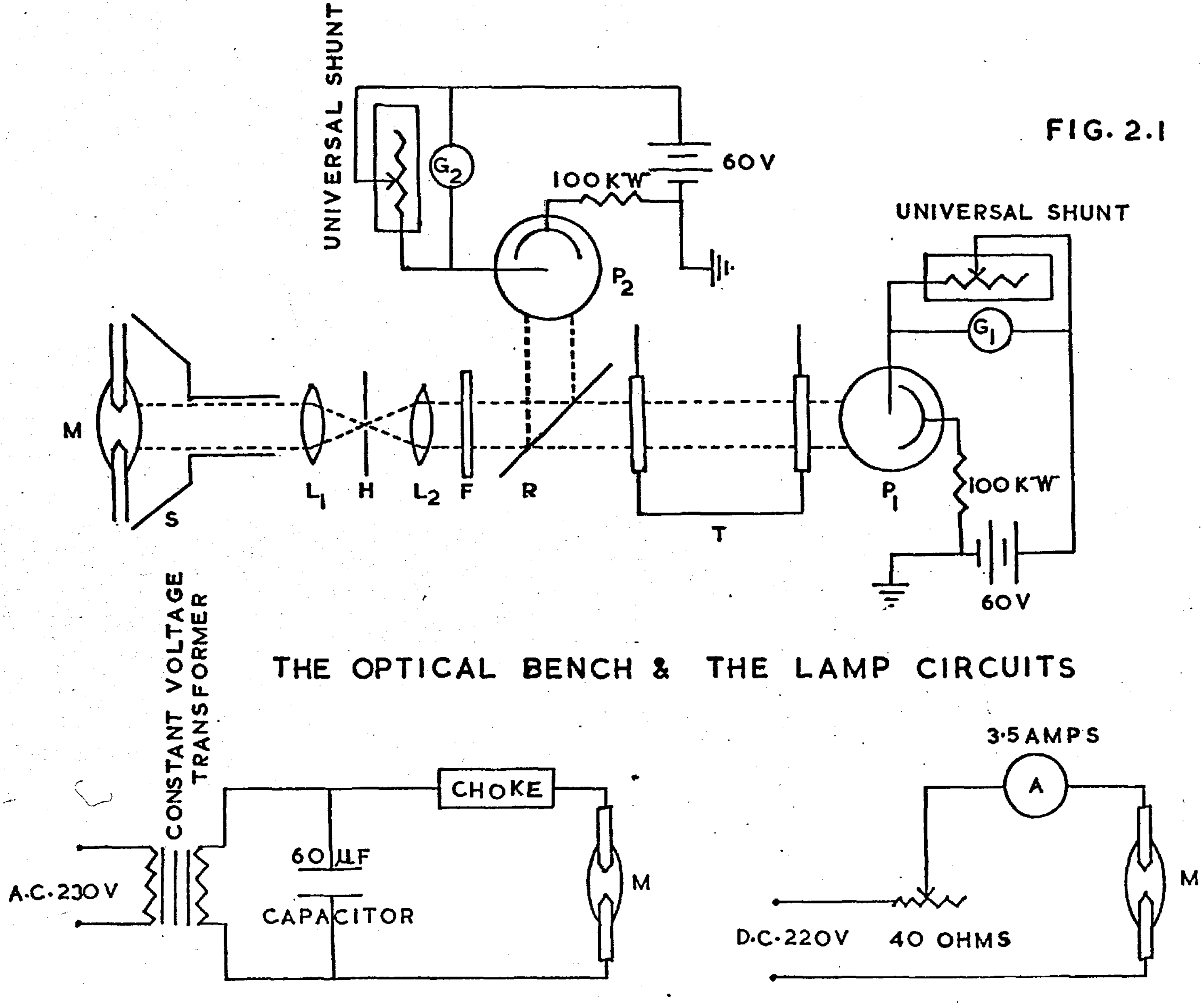
The light source is a 250 watt high pressure mercury lamp M (ME/D Mazda box-type), run on 230 Volts

A.C. mains or 220 volts D.C. mains, circuits being shown in fig. 2.1. Most of the work was carried out on A.C. mains. The lamp gave fairly constant light intensity, about half an hour after it was switched on.

The light from the centre of the arc passed through a cylindrical metal tube (length about 10 cm and diameter 5 cm), attached to the metal shield S. The beam was then focussed on a circular hole H (diameter 2mm) in a metal plate, with the help of quartz lens L_1 (focal length 8cm.). This arrangement gave a point source of light with appreciably constant light intensity. Another quartz lens L_2 was placed at its focal distance (8cm) from the point source to obtain a parallel beam of light.

The monochromatic beam was obtained by passing the light through the filter F, and was allowed to fall on a glass plate R placed at an angle of 45° to the optical axis. A part of the beam was reflected to the photocell P_2, while most of the light passed the thermostat bath containing the reaction vessel, on to the photocell P_1. This arrangement allowed the beam to be checked continuously throughout each run, irrespective of the changes in the intensity of light,

FIG. 2.1



THE OPTICAL BENCH & THE LAMP CIRCUITS

absorbed by the solution in the reaction vessel.

The photocells used were Cintel Q.V.A. 39 photocells, each connected in series with a dry cell operating at 60 volts, a galvanometer (Tinsley type 4500A) and a 100 KΩ resistance. The sensitivity of each galvanometer was varied with the help of universal shunt, connected in the galvanometer circuit.

2.3.2. The Thermostat Bath.

For efficient temperature control, a thermostat tank made of copper, painted on the inside with non-rusting paint, was used. It was fitted with two borosilicate glass windows (thickness 1mm), and the reaction vessel could be placed in the light beam. The tank was filled with distilled water, which was circulated with the help of an efficient stirrer. The heating of water was accomplished by an immersion heater consisting of a spiral of nichrome wire in a glass U-tube. The temperature of the bath was controlled to ± 0.1°C by a mercury-toluene regulator in circuit with a "Sunvic" hot wire switch. A suitable arrangement was made to cover the optical bench (excluding the light source) with a black curtain to prevent the stray light coming in.

2.3.3. Light Filters

The 365 mμ mercury line was isolated by a combination of two filters: (a) A Chance OXI filter (b) Two glasses. The transmission curve for the combination of these filters is given in fig. 2.2. The combination transmits about 61% at 365 mμ, and less than 0.2% at 310 mμ and 405 mμ.

A series of aluminised borosilicate glass filters were used as neutral filters in order to vary the intensity of light in stages.

2.3.4. The Reaction Vessels

Two reaction vessels (1 and 2) were used. The reaction vessel 1 was employed in conjunction with the removal of air from the solution with nitrogen. The reaction vessel 2 was used in conjunction with the degassing of the solution on a vacuum system.

(a) Reaction Vessel 1

The construction of the reaction vessel was based on that used by Atkinson and Di(1). Arrangement was made to transfer the contents of the reaction vessel to the analysis vessel (flask F_1, shown in fig. 2.3) by using the nitrogen pressure. The blank sample required in allowance for any thermal reaction was prepared by

TRANSMISSION OF 365Mμ FILTERS

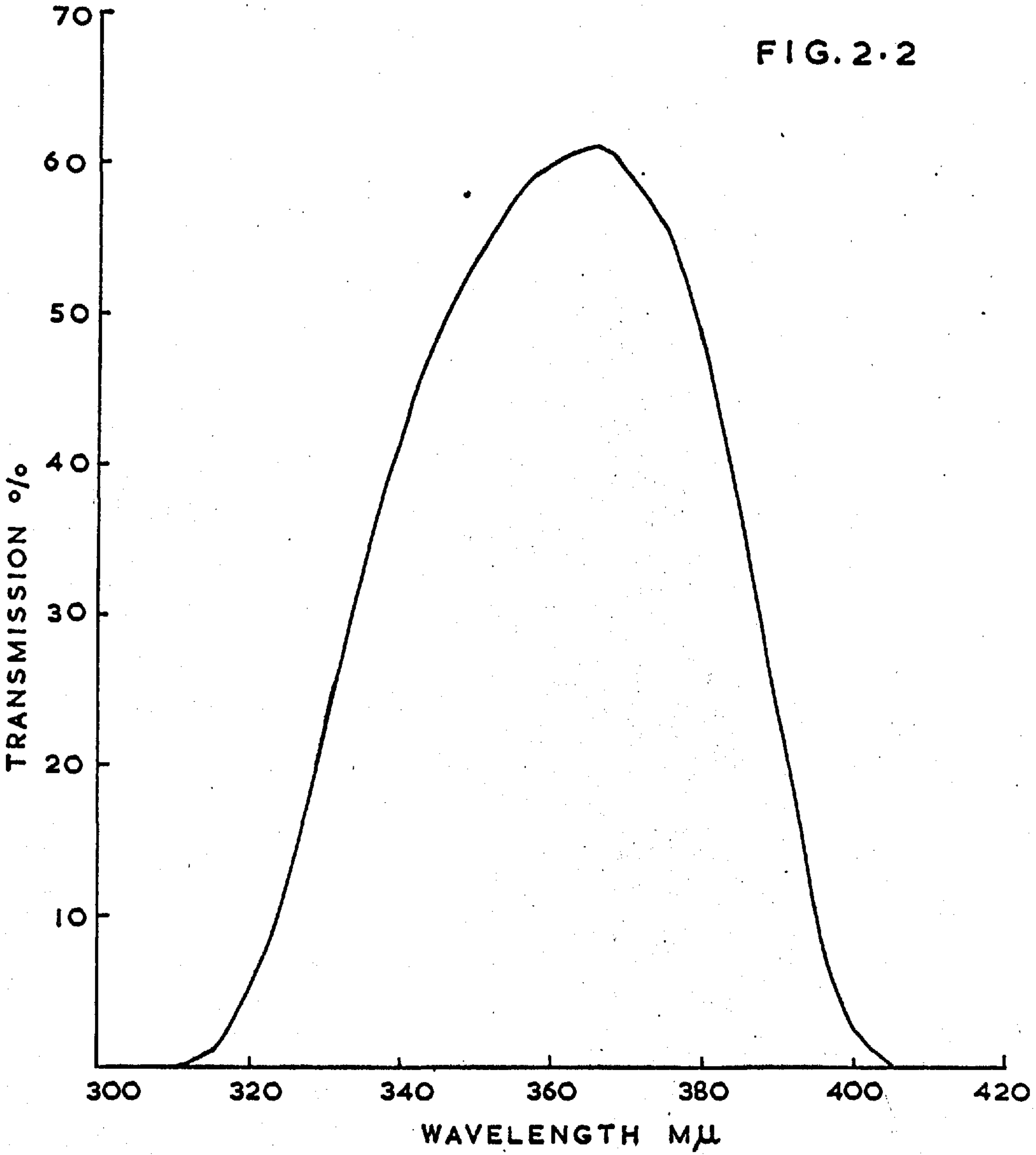
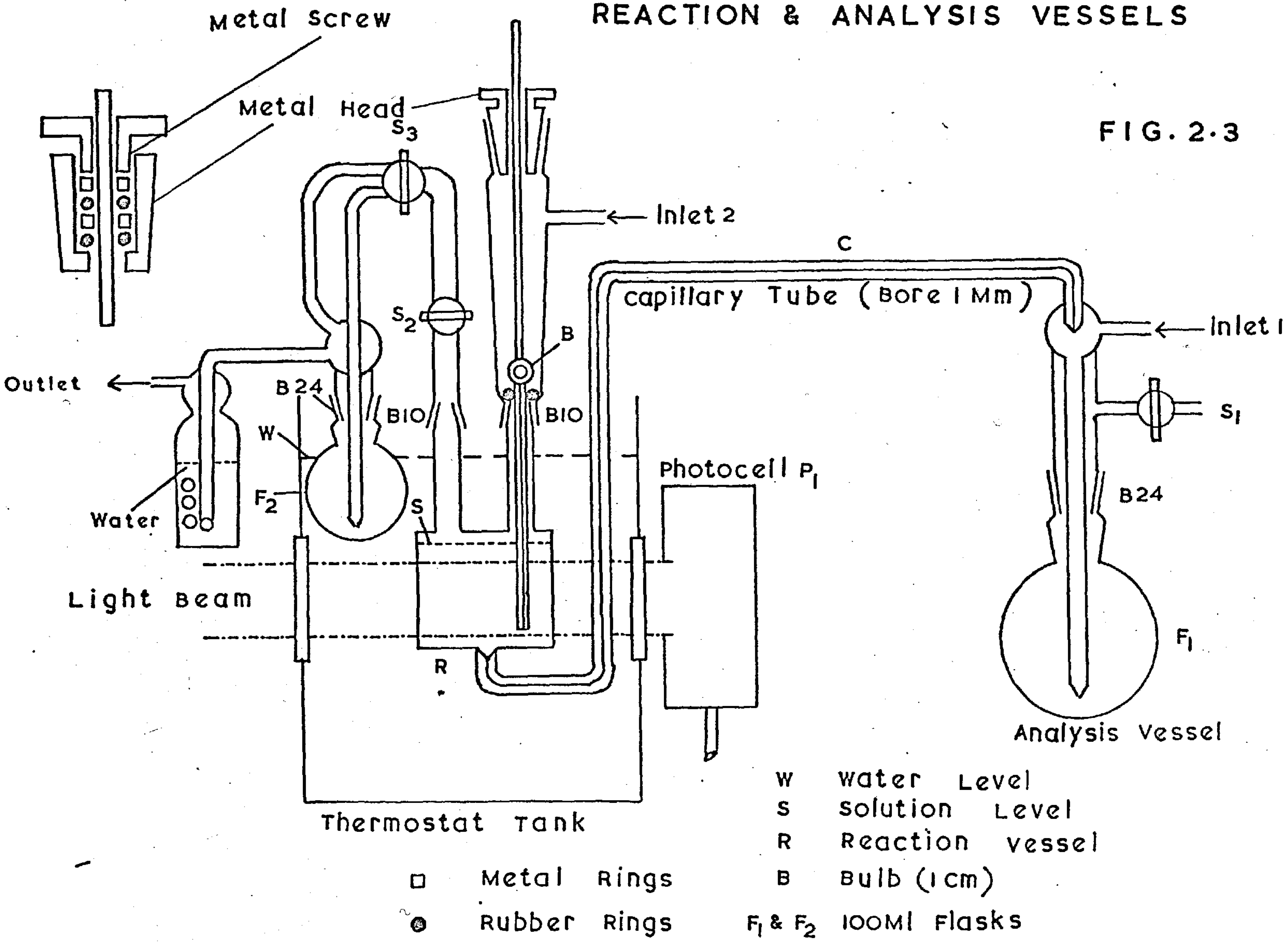


FIG. 2·2

REACTION & ANALYSIS VESSELS

FIG. 2·3



passing the nitrogen after leaving the reaction vessel through the same volume of the reactants, in flask F_2. The flask F_2 was placed alongside the reaction vessel in the thermostat, but not in the path of light.

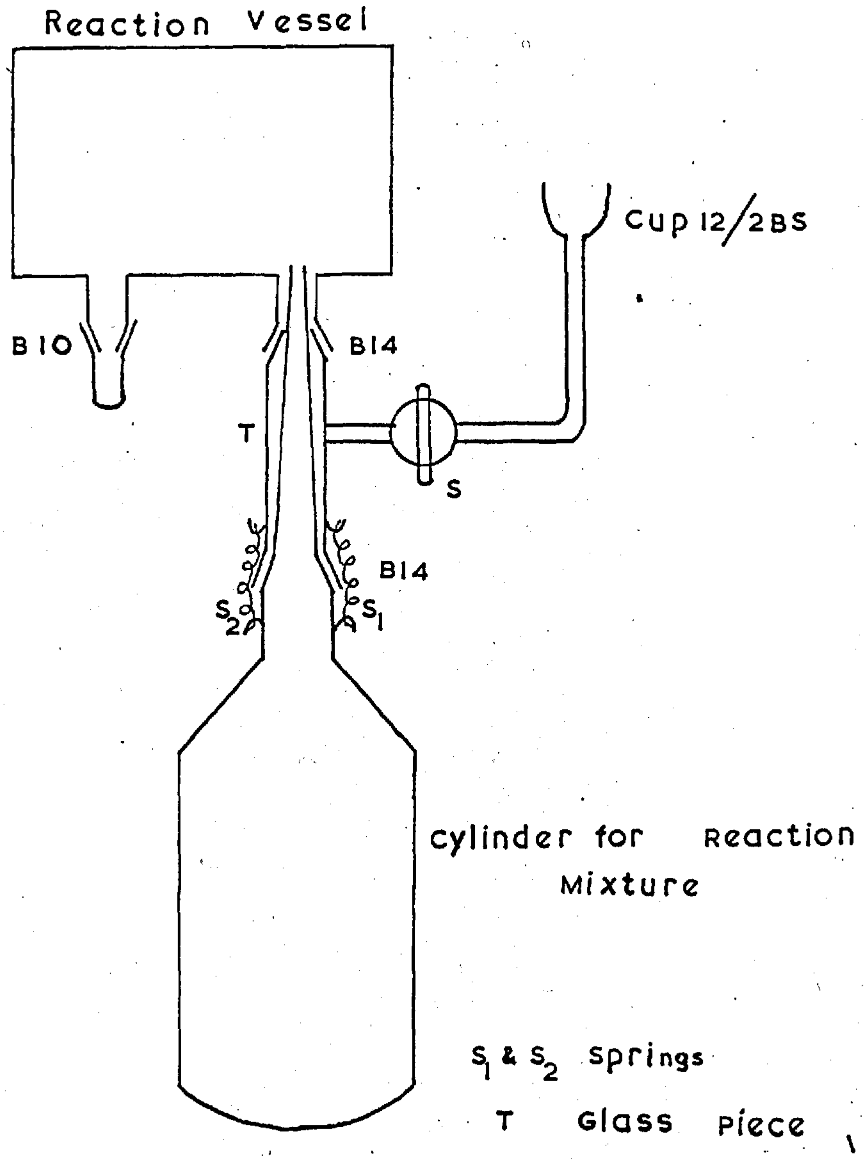
The reaction vessel, shown in fig. 2.3, was a cylinder (length 4 cm and diameter 3.5 cm) with two flanged ends, where borosilicate glass windows were sealed with the help of an adhesive prepared from Araldite D and Hardener 951 of Aero Research Limited. The vessel was provided with two side tubes, carrying standard B10 joints. A retractable gas bubbling tube was fixed to one of the joints and a stopcock to the other. This arrangement provided a means of passing nitrogen saturated with solvent through the solution, and then retracting the gas bubbling tube without admitting air to the reaction vessel. A capillary tube (bore 1 mm) from the bottom of the reaction vessel, was led into the analysis vessel. The flasks F_1 and F_2 were painted black to protect the solution from stray light.

(b) Reaction Vessel 2

The apparatus, shown in fig.2.4, was designed for degassing the solution on a vacuum system in a separate vessel and then transferring the solution to

APPARATUS FOR DEGASSING OF SOLUTION ON A VACUUM LINE

FIG. 2·4



the reaction vessel. Arrangement was made that the solution did not come in contact with grease to avoid any possible contamination.

The reaction vessel was a cylinder of the same dimensions as mentioned in the description of reaction vessel 1. Sealing of the borosilicate glass windows to the two flanged ends was also done with the help of an adhesive described before. The vessel was provided with two side tubes. One side tube had a standard B10 cone, which was closed, and the other carried a B14 socket. A cylinder capable of accomodating about 60 ml of carbon tetrachloride was joined to the reaction vessel via a glass piece as shown in the fig. 2.4. The glass piece was attached to the cup 12/2BS through the stop-cock S. The cylinder and glass piece were provided with hooks. The stopcock and standard joints were greased with Apiezon N grease.

2.3.5. Degassing and Irradiation of Solution

(a) Procedure when nitrogen was used

Air was removed from the analysis vessel, the capillary tube C and the reaction vessel by passing nitrogen for 20 minutes, using the inlet 1 with stopcock S_1 closed and stopcock S_2 open. The solution to be irradiated (40 ml) was pipetted into the reaction vessel and the nitrogen stream was changed over to that saturated with solvent which was passed through the solution for 45 minutes by means of bubbling tube and inlet 2. After leaving the reaction vessel, nitrogen was led through flask F_2 containing 40 ml of the solution. The passage of gas through the solution was ascertained by connecting the flask F_2 to a wash bottle containing water. The rate of passage of nitrogen was adjusted by the rate of gas bubbles. The gas bubbling tube was then retracted. The passage of nitrogen was stopped, and the solution was irradiated for the required time. After irradiation the solution was transferred to the analysis vessel by closing the stopcock S_2, opening the stopcock S_1 and using the nitrogen pressure from inlet 2. The analysis vessel and flask F_2 were removed from the apparatus, stoppered and shaken before the solution was analysed. The analysis procedure has been described in section 2.4.

(b) Procedure when Vacuum System was used

The reaction mixture (40 ml) was pipetted into the cylinder, and was held to the glass piece by means of two springs. The various parts of the apparatus were joined together as shown in the fig.2.4.

The unit was clamped in a stand just below the side arm of the glass piece. The attachment to the vacuum line was given via the cup 12/2BS, Apiezon N grease was used at this joint and a clip JC 2/12 was employed to keep the unit attached. The solution was protected from light by wrapping the cylinder with aluminium foil. The solution was frozen by gradually dipping the cylinder in liquid nitrogen contained in the Dewar flask. The level of liquid nitrogen was kept just below the B14 joint. Then the length of glass tubing between stopcock S and cup 12/2BS was evacuated for three minutes. This was followed by opening of the stopcock S to degas the remaining unit. At this stage only the rotary oil pump was on. When the stopcock S had been kept opened for 5 minutes, the mercury diffusion pump was also switched on. The degassing process was continued for 10 minutes when the stopcock S was closed. The Dewar flask was removed and the mixture was melted. The melting was accomplished by leaving the mixture at room temperature. The solution was again frozen and the degassing operation was repeated for 10 minutes with both the pumps on. The degassing process was also repeated for the third time. But it was found that the same solution gave almost identical figures for the quantum efficiency, whether the degassing process was repeated twice or thrice. So the degassing process was repeated only twice in the majority of the measurements. After the completion of degassing the unit was detached from the vacuum line, and the mixture was melted. When the solution attained the room temperature, it was transferred to the reaction vessel by inverting the unit. The reaction vessel was fixed in the stand to place it in the light beam. The solution was irradiated for a measured time. The stand along with the whole apparatus was taken out of the thermostat. The vacuum was released by opening the stopcock S. The solution was transferred to a round bottomed (100 ml) flask, painted black, through the standard B10 cone after removing the grease. The flask was stoppered and shaken before the analysis of solution was performed. Section 2.4 deals with the analysis of the solution.

It was found that the toluquinone solution in carbon tetrachloride containing methyl alcohol (0.988 Mole $l.^{-1}$) does not undergo significant thermal reaction during this procedure. So in the measurements at alcohol concentrations, 0.988 mole $l.^{-1}$ and below the solution placed in the cupboard at room temperature, was used as blank. At high concentrations of alcohol it was necessary to degas the blank in order to allow for the thermal reaction.

2.4. Analysis of Hydroquinone

The oxidation of hydroquinone by ferric ions has been studied by Baxendale and Hardy (56,57). They found that the reaction proceeds as follows :-

$$Fe^{+++} + QH_2 \xrightleftharpoons[k_2]{k_1} Fe^{++} + QH + H^{+}$$

$$Fe^{+++} + QH \xrightleftharpoons[k_2]{k_2} Fe^{++} + Q + H^{+}$$

It is clear from above that if the Fe^{++} ions formed in the reaction are removed efficiently, the hydroquinone may be quantitatively oxidized by Fe^{+++} ions.

Kolthoff, Lee and Leussing (58) established a quantitative estimation of Fe^{++} ions in aqueous solution by converting the Fe^{++} ions to the stable coloured complex 'ferroin' with O-phenanthroline, and measuring the colour intensity at the absorption peak (510 mμ). It was shown that not less than 99% of the Fe^{++} ions form the complex, if the ratio of the concentration of O-phenanthroline to the concentration of hydrogen ions is greater than 0.035.

Taking the above references into consideration, Atkinson and Di(1) developed a method of analysis of benzohydroquinone solution in carbon tetrachloride.

The hydroquinone was first extracted into water, and the aqueous solution was then treated with excess Fe^{+++} ions and O-phenanthroline to form 'ferroin'.

This method of extraction, when applied to the toluhydroquinone solution in carbon tetrachloride, did not give reproducible results, presumably due to the thermal reaction in water. A high yield of hydroquinone formation was noticed. In order to avoid the change of hydroquinone in carbon tetrachloride, it was thought advisable to do the analysis immediately after irradiation. A solution containing excess ferric chloride in acetate buffer and O-phenanthroline was used to extract the hydroquinone from the carbon tetrachloride layer. The hydroquinone reduced the Fe^{+++} ions to Fe^{++} ions, which were converted to 'ferroin' by O-phenanthroline. The concentration of buffer in the ferric chloride solution was chosen to give the correct P^H for the formation of 'ferroin' without carbon tetrachloride producing precipitation. The analysis in the atmosphere of nitrogen was found to give the same results as the analysis in air. Therefore, a sample from the irradiated solution was pipetted in air into the analysis solution in a separate flask. A similar procedure was adopted for the blank.When there were two liquid layers the reacted sample and the blank were stirred simultaneously for half an hour with the help of magnetic stirrers. When the mixture of sample and reagent was homogeneous no magnetic stirring was used. After stirring the solutions were kept for an hour in the dark before the measurement of the optical density. The above periods of stirring and standing were found to be suitable for the quantitative estimation of toluhydroquinone. The optical density of the aqueous layer from the irradiated sample was compared with the blank at 510 mμ in 1 cm cells using a Unicam 500 spectrophotometer.

2.5. Reagent solution for determination of Toluhydroquinone

2.5.1. Stock Solutions

The stock solutions of ferric chloride and O-phenanthroline were prepared in water. The ferric chloride solution was made by mixing 2.0 N sulphuric acid (100 ml) with 2.0 N sodium acetate solution (150 ml) and dissolving in this hydrated ferric chloride to make the solution 5×10^{-2} M in ferric chloride. The pH of the resulting solution was adjusted to 3.1 to 3.2 with 2.0 N sulphuric acid.

2.5.2. Preparation of Reagent solution

The reagent solution A was a mixture of :-

(a) ferric chloride solution in acetate buffer (5×10^{-2}M, ~~PH~~pH3.1-3.2),

(b) 0-Phenanthroline solution (0.1% in water),

(c) distilled water.

The percentages by volume of (a), (b), and (c) in the reagent solution were :

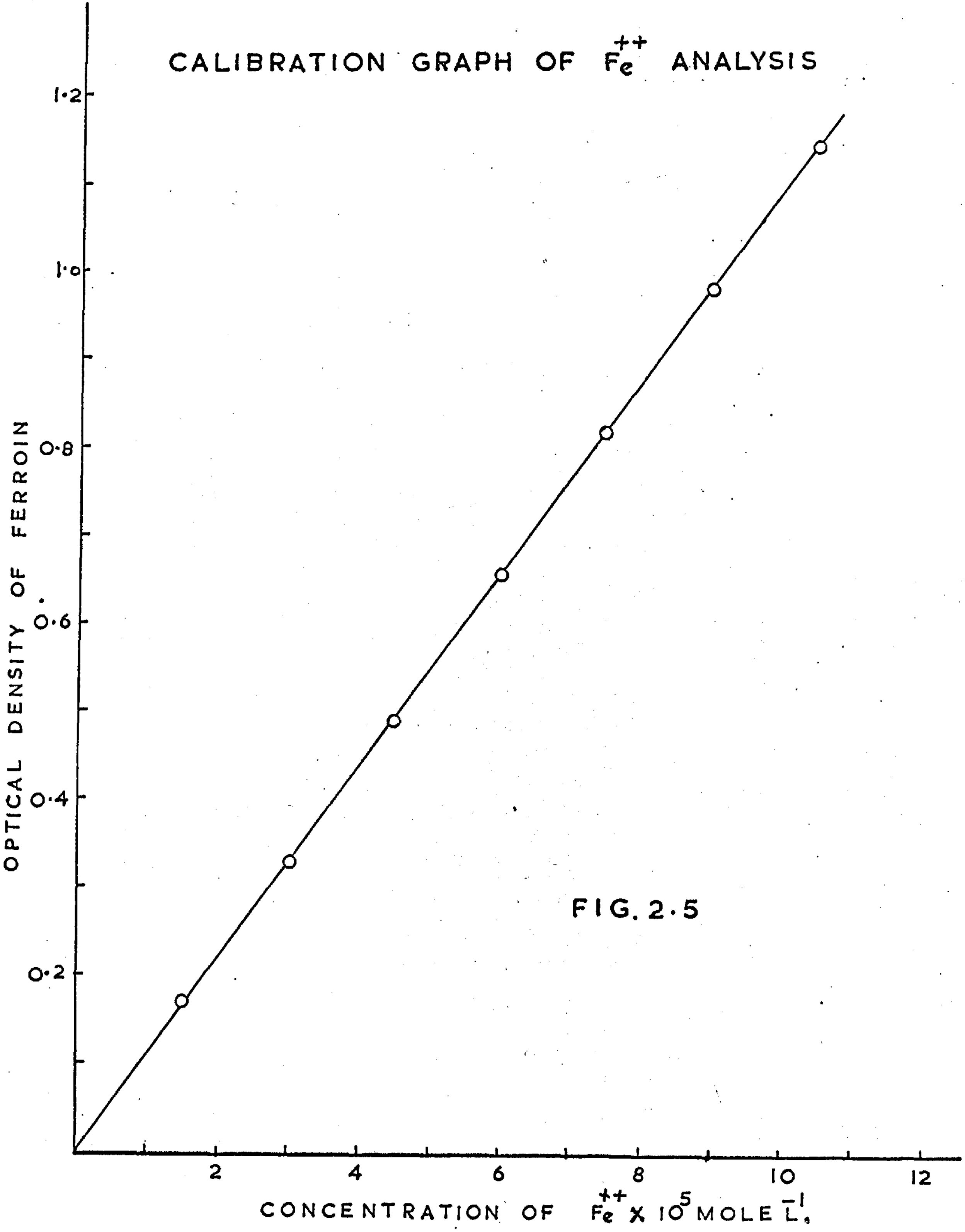
(a) 10% (b) 50% (c) 40%

Thus 10.0 ml of reagent solution A consisted of ferric chloride solution (1.0 ml), 0-phenanthroline solution (5.0 ml), and distilled water (4.0 ml).

The normal procedure was to treat 10.0 ml of reagent solution A with 1.0 or 2.0 ml of the solution to be analysed. When the concentration of toluhydroquinone was high lower aliquot portions were taken. Care was taken to keep the optical density of the final solution within the limits of 0.1 and 1.0. The amount of the solution for analysis per 10.0 ml of the reagent solution was normally limited to 2.0 ml to avoid the introduction of an excessive proportion of alcohol into the reagent. When the solution to be analysed consisted largely of carbon tetrachloride erratic results were obtained if more than 1.0 ml of the solution was taken with 10.0 ml of the reagent. The modified reagent solution, reagent solution B, which was used in these circumstances, will be described in section 2.6.2.

2.6. Calibration of Hydroquinone Analysis

First of all a figure for the extinction coefficient of 'ferroin' was required. So a calibration graph relating optical densities to ferrous iron concentrations was prepared. The test solution used for the measurement of optical density consisted of 5.0 ml of 0.1 N sulphuric acid containing the required amount of ferrous iron together with 1.0 ml of O-phenanthroline solution (0.1% in water), 2.5 ml of acetate buffer (pH 4.5) and 1.5 ml of distilled water, the total volume of test solution being 10.0 ml. Blank sample was a similar solution to which no ferrous iron had been added. The buffer solution was prepared by mixing 1.0 N sulphuric Acid (180 ml) with 1.0 N sodium acetate solution (300 ml) and diluting with distilled water to 500 ml. The final pH of the solution was adjusted to 4.5 with 1.0 N sulphuric acid. Half an hour was allowed between mixing and taking the optical density. The figures for the optical densities determined at 510 mµ were plotted against ferrous iron concentrations, and a straight line was obtained as shown in fig 2.5. The



CALIBRATION GRAPH OF Fe^{++} ANALYSIS

FIG. 2·5

figures for the optical densities are given in table 2.1. The value for the extinction coefficient of 'ferroin' was found to be 11080 by using the relation:

$$\log \frac{I_0}{I} = \epsilon c l$$

Hatchard and Parker (59) obtained a value of 11050 for the extinction coefficient. The value of 11080 was used in this work.

TABLE 2.1

Analysis of Ferrous Solution (0.594×10^{-3} mole $l.^{-1}$) in 0.1 N Sulphuric Acid

Conc. of Ferrous in Test Solution Mole $l.^{-1} \times 10^{5}$	Optical Density of 'Ferroin' i.e., $\log \frac{I_0}{I}$	$\epsilon = \frac{\log \frac{I_0}{I}}{c l}$
1.49	0.170	11440
2.97	0.330	11100
4.46	0.492	11040
5.94	0.660	11100
7.43	0.822	11060
8.92	0.985	11050
10.40	1.150	11060

Average ϵ = 11080

ϵ Extinction coefficient of 'ferroin'.

c   Concentration of ferrous in test solution

l   Thickness of solution (1 cm)

Knowing the value of extinction coefficient, the above relation could be used to calculate optical densities for solutions prepared from known amounts of toluhydroquinone. In doing this it was assumed that the reaction of the reagent with toluhydroquinone is :-

$$\begin{tikzcd}
QH_2 + 2\,Fe^{+++} \arrow[r] & QH_2^{++} \arrow[d] & + \; 2\,Fe^{++} \\
& Q + 2\,H^{+} &
\end{tikzcd}$$

Thus the concentration of toluhydroquinone is half the concentration of ferrous iron.

2.6.1. Calibration Results in 100% Alcohol

The method of analysis was first calibrated using solutions of toluhydroquinone in iso-propyl alcohol. 2ml portions of each solution were pipetted immediately into one of a series of 50 ml conical flasks, each containing 10.0 ml of reagent solution A. The flasks were painted black in such a manner that a gap was left on one side.

Fig. 2.6 is the calibration graph obtained for toluhydroquinone in iso-propyl alcohol. The optical densities of the solutions were plotted against the concentrations of toluhydroquinone, and a straight line

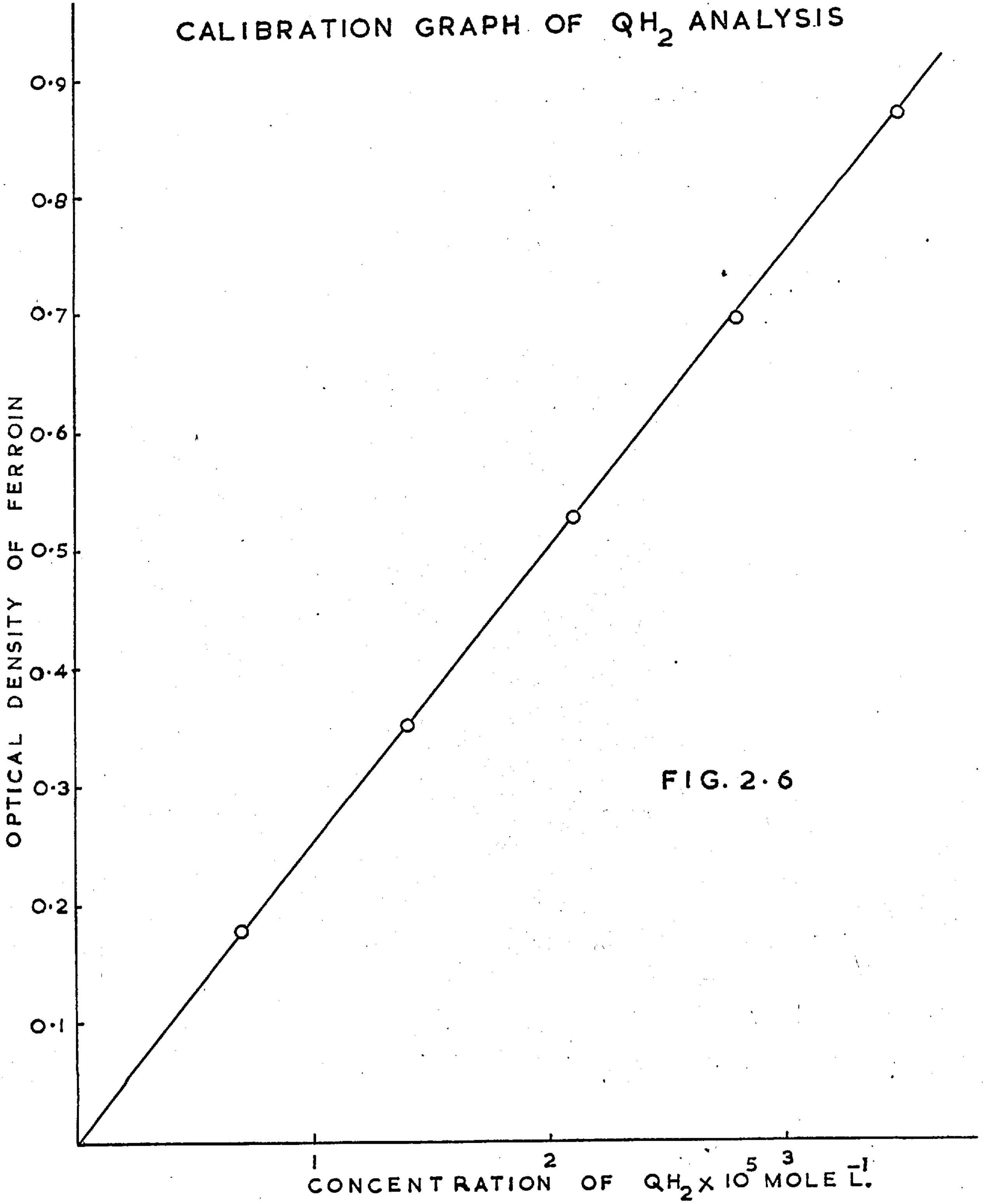

CALIBRATION GRAPH OF QH_2 ANALYSIS
OPTICAL DENSITY OF FERROIN
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
1
2
3
CONCENTRATION OF $QH_2 \times 10^5$ MOLE L^{-1}.

FIG. 2·6

was obtained. The optical densities of the solutions were taken after one hour standing in the dark. The blank against which the optical densities were compared, consisted of 2.0 ml of iso-propyl alcohol in 10.0 ml of reagent solution A. The figures for the optical densities are given in table 2.2, together with the optical densities, using a value of 11080 for the extinction coefficient. The volume of the final solution resulting from mixing 2.0 ml of iso-propyl alcohol with 10.0 ml of distilled water was determined.

TABLE 2.2.

Analysis of Toluhydroquinone (9.515×10^{-4} mole $l.^{-1}$) in iso-Propyl Alcohol

QH_2 Conc. in Final Solution Mole $l.^{-1}$ x 10^5	Opt. Density Experimental	Opt. Density Calculated	QH_2% Theoretical
0.793	0.178	0.176	101
1.59	0.353	0.352	100
2.38	0.528	0.527	100
3.17	0.696	0.703	99
3.96	0.870	0.879	99

This proves that the analysis of toluhydroquinone in iso-propyl alcohol is reproducible.

The method of analysis was checked in the presence of toluquinone and the analysis was again found to give a quantitative estimation of toluhydroquinone. A blank containing the same concentration of toluquinone was used. The analysis results are given in table 2.3.

TABLE 2.3

Analysis of Toluhydroquinone (12.3 x 10^{-5} mole $1.^{-1}$) and Toluquinone (2.0 x 10^{-2} mole $1.^{-1}$) in iso-Propyl Alcohol

Vol. Reaction Liquid in ml	Vol. Reagent Soln. A in ml	Opt. Density Experimental	Opt. Density Calculated	QH_2% Theoretical
1.0	10.0	0.248	0.248	100
2.0	10.0	0.457	0.457	100

2.6.2. Calibration Results for Solutions of Toluhydroquinone in Carbon Tetrachloride

Some loss of toluhydroquinone in carbon tetrachloride solution was found after standing for several hours in air. This was presumed to be caused by aerial oxidation. Solutions of toluhydroquinone were therefore used without delay.

A series of solutions containing both toluhydroquinone and toluquinone in carbon tetrachloride were prepared. Analyses were performed in which 1.0 or 2.0 ml of the solution was added to 10.0 ml of reagent solution A in conical flasks. The solutions were stirred for half an hour with the help of magnetic stirrers, and then kept in the dark for one hour, to allow the two liquid layers to separate. The aqueous layer was removed by means of a pipette and the optical density was compared against a blank. The blank was prepared in a similar way, using a solution containing the same concentration of toluquinone and alcohol in carbon tetrachloride but in the absence of toluhydroquinone. Analysis results are shown in table 2.4.

TABLE 2.4

Analysis of Toluhydroquinone in presence of Toluquinone (2.0×10^{-2} mole l^{-1}) in Carbon Tetrachloride containing iso-Propyl Alcohol

Hours After preparation	Reaction Liquid		Vol. Reaction Liquid in ml	Vol. Reagent Soln. A in ml	Opt.D. Experimental	Opt. D. Calculated	QH_2% Theoretical
	QH_2 Conc. Mole $l^{-1}\times10^{5}$	iso-ProH Mole l^{-1}					
0.5	3.58	0.0262	1.0	10.0	0.079	0.079	100
1.0	3.58	0.0262	2.0	10.0	0.155	0.158	98
2.5	3.58	0.0262	1.0	10.0	0.076	0.079	96
3.0	3.58	0.0262	2.0	10.0	0.149	0.158	94
3.5	3.58	0.0262	3.0	10.0	0.211	0.237	89
5.0	3.58	0.0262	1.0	10.0	0.079	0.079	100
5.0	3.58	0.0262	2.0	10.0	0.126	0.158	80
0.0	7.17	0.0524	2.0	10.0	0.305	0.316	97

Table 2.4 indicates that the analysis was unreliable when more than 1.0 ml of the reaction liquid was used with 10.0 ml of reagent solution. Further evidence of this unre-liability was obtained from analyses after the photochemical runs.

During experiments in which methyl alcohol in carbon tetrachloride was used as reactant, it was found that there was no variation between the analyses on 1.0 ml and 2.0 ml of solution. Following this a new formula for the reagent solution was evolved.

Reagent solution B was made up as follows :- Reagent solution B was similar to reagent solution A with the only difference that 1.0 ml of methyl alcohol was added to the reagent solution A before pipetting the reaction liquid into it. The results obtained in the analysis of standard solutions, using reagent solution B, are given in table 2.5. In connection with these measurements the volumes of the aqueons layer resulting from mixing 1.0 ml of methyl alcohol and 1.0 or 2.0 ml of the reaction liquid with 10.0 ml of distilled water were determined. This provided the volume appropriate to the calculation of the expected optical density, for the various samples of toluhydroquinone.

TABLE 2.5

Analysis of Toluhydroquinone in presence of Toluquinone (2.0 x 10^{-2} mole $l.^{-1}$) in Carbon Tetrachloride containing iso-Propyl Alcchol.

Reaction Liquid		Vol. Reaction Liquid in ml	Vol. Reagent Soln. B in ml	Opt.D. Experimental	Opt.D. Calculated	QH_2 % Theoretical
QH_2 Conc. Mole $l.^{-1}$ x10^5	Iso-PrOH Mole $l.^{-1}$					
32.3	0.236	2.0	10.95	1.39	1.42	98
25.1	0.183	2.0	10.95	1.12	1.11	101
17.9	0.131	2.0	10.95	0.781	0.790	99
10.8	0.0786	2.0	10.95	0.471	0.474	99
9.27	0.131	1.0	10.95	0.188	0.188	100
9.27	0.131	2.0	10.95	0.376	0.376	100
7.17	0.0524	1.0	10.95	0.158	0.158	100
7.17	0.0524	2.0	10.95	0.307	0.316	97
3.58	0.0262	2.0	10.95	0.156	0.158	99
1.79	0.0131	2.0	10.95	0.078	0.079	99

The results given in table 2.5 show an error that is in general not more than 2%.

Analysis with reagent solution B was also checked in the presence of formaldehyde and no interference with the estimation of toluhydroquinone was found.

During the course of photochemical measurements, observations were made on the possible effect of air on the toluhydroquinone or ferrous ion during the analysis procedure. Parallel analyses were performed with and without displacement of air from the conical flasks by nitrogen. The results in table 2.6, show that no advantage was gained by displacing the air.

TABLE 2.6

Analysis of Toluhydroquinone in presence of Toluquinone (2.0×10^{-2} mole $l.^{-1}$) in Carbon Tetrachloride containing Alcohol

Reaction Liquid			Vol. Reaction Liquid in ml	Vol. Reagent Soln. A in ml	Opt.D Experimental in Air	Opt.D. Experimental in Nitrogen
QH_2 Conc. Mole $l.^{-1}$ $\times10^5$	Iso-PrOH Mole $l.^{-1}$	MeOH Mole $l.^{-1}$				
5.74	0.0131		1.0	10.0	0.127	0.121
6.84	0.0131		1.0	10.0	0.146	0.142
4.69	0.0131		1.0	10.0	0.104	0.100
17.2		12.4	1.0	10.0	0.380	0.380
14.2		12.4	1.0	10.0	0.314	0.308

2.7. Calculations of the Yield of Toluhydroquinone

Let the volume of test solution i.e. the aqueous layer including any alcohol added or extracted $= V_1$ ml

Volume of irradiated solution used in the preparation of the test solution $= V_2$ ml

($V_2 = 1.0$ or 2.0)

Optical density of test solution in 1 cm cell $= D$

Quantity of ferrous iron in the test solution $= \frac{D \times V_1}{\epsilon \times 10^3}$ moles

(ϵ =extinction coefficient of 'ferroin')

Equivalent quantity of toluhydroquinone in V_2 ml of irradiated solution $= \frac{D \times V_1}{2\epsilon \times 10^3}$ moles

Therefore, the quantity of toluhydroquinone in 40 ml of irradiated solution $= \frac{D \times V_1 \times 40}{2\epsilon \times 10^3 \times V_2}$ moles

$= R$ moles.

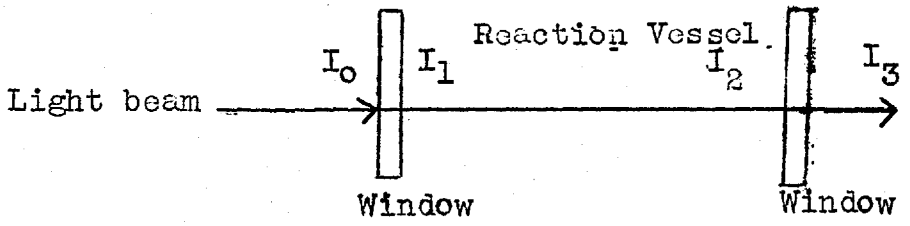
2.8. Actinometry

The intensity of light was measured by using the potassium ferrioxalate actinometer of Hatchard and Parker (59). The actinometer is based on the decomposition of potassium ferrioxalate by irradiation with light, and determination of the ferrous ions produced by the spectrophotometric method, described in section 2.6.

40 ml of potassium ferrioxalate solution (6 x 10^{-3}mole l^{-1}) were pipetted into the reaction vessel, and air removed with nitrogen for 45 minutes. The solution was then irradiated, and transferred to the analysis vessel (flask F_1, fig.2.3). The flask F_1 was removed from the apparatus and the solution (1 to 3 ml) was pipetted into a series of 10 ml graduated flasks for the estimation of ferrous ions as described in section 2.6. The optical densities of the test solutions were compared against the corresponding blanks. The blanks were prepared by the similar procedure from 40 ml of the same potassium ferrioxalate solution in flask F_2, which was placed in the thermostat alongside the reaction vessel with nitrogen passing through it as mentioned in section 2.3.4. The intensity of light entering the reaction vessel was calculated. The quantum efficiency used was 1.21 for 365 mμ.

The photocell response was calibrated in terms of the intensity of light entering the reaction vessel. The calibration was repeated from time to time.

2.9. Calculations of the Intensity of Light Absorbed by the Solution



Symbols to be used.

Photocell deflection for no cell in beam,	D_o	
Photocell deflection for solvent in cell,	D_m	
Photocell deflection for solution in cell,	D_n	
Fraction of light lost at each window,	α	
Light intensity of beam reaching front Window,	I_o	Einstein per sec.
Intensity behind front window,	I_1	" " "
Intensity behind solution,	I_2	" " "
Intensity of light absorbed,	I_a	" " "

Relations

$I_o = \beta D_o$, and for solution, $I_3 = \beta D_n$

where β is determined by actinometry.

$$I_1 = I_o(1-\alpha)$$

$$I_3 = I_2(1-\alpha)$$

For solvent in Cell, $I_2 = I_1$

$$\therefore \quad I_3 = I_o (1-\alpha)^2$$

Dividing by β ,

$$D_m = D_o (1 - \alpha)^2 \text{ and } (1 - \alpha) = \left(\frac{D_m}{D_o}\right)^{\frac{1}{2}} \qquad \text{(A)}$$

This equation is used to calculate $(1 - \alpha)$.

Measurement with the actinometer for the actinometer solution gives l_a.

$$\begin{aligned} I_a &= I_1 - I_2 \\ &= I_o (1 - \alpha) - \frac{I_3}{(1-\alpha)} \\ &= \beta D_o (1 - \alpha) - \frac{\beta D_n}{(1-\alpha)} \qquad \text{(B)} \end{aligned}$$

Equation (B) is used to determine β .

For 0.006 M potassium ferrioxalate at 365 mμ, with a cell length over 1 cm,

$$D_n = 0$$

When β is known the above equation (B) may be used to calculate I_a from D_o and D_n.

3. RESULTS

3.1. Photochemical Reactions of Toluquinone with various Reducing Agents

Solutions of toluquinone in pure solvents (carbon tetrachloride, cyclohexane or iso-propyl alcohol) or in mixed solvents (carbon tetrachloride mixed with cyclohexane, iso-propyl alcohol or methyl alcohol) were irradiated in the absence of air at 25°C and with light of wavelength 365 $m\mu$. The concentration of toluquinone in most of the experiments was such that light absorption was not complete and hence the absorption took place throughout the length of the reaction vessel. The duration of illumination was usually sufficient to produce the necessary amount of toluhydroquinone for accurate analysis. The consumption of toluquinone was usually less than 2%.

The quantum efficiency (ϕ) for the formation of toluhydroquinone was given by :-

$$\phi = \frac{R}{t \times I}$$

where

R Number of moles of toluhydroquinone formed in 40 ml of irradiated solution.

t Time of irradiation in seconds.

I Intensity of light in einsteins per second, absorbed by the solution in the reaction vessel.

The methods of calculating the yield of toluhydroquinone and the intensity of light absorbed by the solution have been given in sections 2.7 and 2.9.

In order to remove air from the toluquinone solutions before irradiation, either nitrogen gas (which had been bubbled through one or two solvent bubblers in the nitrogen flow line) or a vacuum line was employed. The removal of air with nitrogen worked satisfactorily in studying the reactions of toluquinone with cyclohexane or iso-propyl alcohol. This procedure gave irreproducible results with methyl alcohol due to its loss during the passage of nitrogen. Outgassing on a vacuum line led to consistent results.

In the photochemical experiments the irradiated solution was analysed for toluhydroquinone using the procedure described in section 2.5.2. The optical density of the aqueous layer was measured against a blank produced by applying the same procedure to a portion of unirradiated solution. This unirradiated solution was the same toluquinone solution as was irradiated. For example, when the removal of air was done with nitrogen, the blank sample was prepared by passing the nitrogen stream leaving the reaction vessel through 40 ml of the toluquinone solution in a black flask, kept alongside the reaction vessel in the thermostat, but outside the light beam.

In solutions of methyl alcohol not exceeding 0.988 mole $l.^{-1}$ and of iso-propyl alcohol not exceeding 1.31 mole $l.^{-1}$, there was no significant thermal reaction. Under these circumstances the optical density of a blank prepared by removing air with nitrogen was the same as that of one prepared by outgassing on a vacuum system or by merely standing in air in the dark. To save time the blank to be used when the solution was degassed on a vacuum line was normally prepared from a sample of solution that had been kept in the dark, without degassing.

When the concentration of methyl alcohol exceeded the above limit, in the analysis of the liquid after reaction in vacuum, the optical density was measured against water. A similar experiment was then performed in which a similar solution was given the same treatment, except that it was kept in the dark. The difference between the two optical densities gave the optical density resulting from photochemical reaction. It was difficult in the procedure to give the solutions exactly the same thermal treatment. Thus when the thermal reaction was fast, results obtained by outgassing on the vacuum system could not have a high accuracy.

3.2. Carbon Tetrachloride

Solutions of toluquinone in carbon tetrachloride were irradiated in nitrogen, using one solvent bubbler in the nitrogen flow line (section 2.2.6). Although there is no hydrogen in carbon tetrachloride, a reducing substance was formed, possibly by the reaction of an impurity in carbon tetrachloride, with toluquinone. For convenience this reducing substance is treated in calculations and in discussion in the present section as if it is toluhydroquinone.

3.2.1. Variation of Toluhydroquinone yield with Time

The results are shown in table 3.1.

TABLE 3.1

Toluquinone (2.0×10^{-2} mole $l.^{-1}$) in Carbon tetrachloride, 365 mμ, 25.0°C

Time of Irrad. Seconds	I Einst.$Sec.^{-1}$ $\times 10^{9}$	IT Einst. $\times 10^{6}$	QH_2 Produced Moles $\times 10^{7}$	∅
2000	2.08	4.16	4.95	0.119
4000	2.18	8.72	6.68	0.077
6000	2.15	12.9	9.31	0.072
8000	2.22	17.8	10.1	0.057
10000	2.09	20.9	10.8	0.052

Toluhydroquinone produced is plotted against the light absorbed in fig. 3.1. A curve is obtained showing that the quantum efficiency of toluhydroquinone formation decreases as the reaction proceeds.

There are two explanations for the decrease in quantum efficiency during a run that must be considered. The first is that the reaction is between toluquinone and an impurity which is steadily consumed. The second possibility is that the product of the reaction, possibly toluhydroquinone, retards the reaction. These possibilities are examined in sections 3.2.2 and 3.2.3.

3.2.2. Effect of (i) Toluquinone concentration and (ii) added Toluhydroquinone on Quantum Efficiency

Solutions of toluquinone either of variable concentrations or with added toluhydroquinone were irradiated in nitrogen using one solvent bubbler in the nitrogen flow line (section 2.2.6). The results are given in table 3.2.

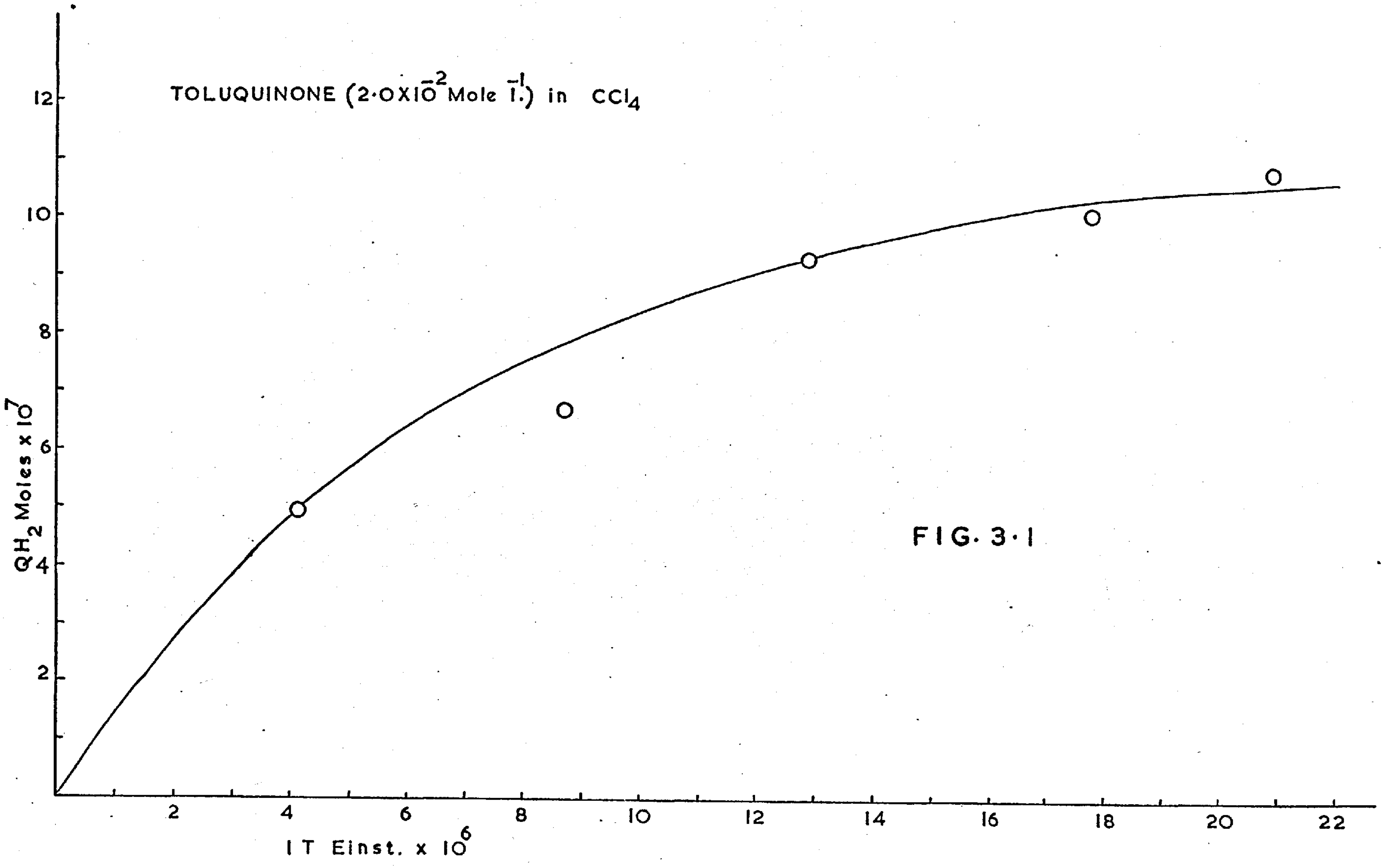

TOLUQUINONE ($2{\cdot}0 \times 10^{-2}$ Mole l^{-1}.) in CCl_4

FIG. 3·1

TABLE 3.2

Toluquinone and Toluhydroquinone in Carbon Tetrachloride, 365 mμ, 25.0°C

Toluquinone Mole $l.^{-1}$ x10^2	Toluhydroquinone Mole $l.^{-1}$ x10^5	Time of Irrad. Seconds	I Einst. $Sec.^{-1}$ x10^9	QH_2 Produced Moles x10^7	ø
0.5	-	7200	0.980	3.83	0.054
1.0	-	7200	1.45	5.63	0.054
2.0	2.39	3600	1.62	1.95	0.033
2.0	1.61	5400	1.88	2.74	0.027
2.0	-	5400	0.322	1.23	0.071
2.0	-	5400	0.307	1.26	0.076

Table 3.2 indicates that

(i) there is no variation of quantum efficiency with change in toluquinone concentration, and

(ii) the quantum efficiency has been significantly reduced by the addition of 2x10^{-5} mole $l.^{-1}$ toluhydroquinone.

The analysis described in section 2.2.1 shows that a typical sample of toluquinone contained 0.86x10^{-5} mole $l.^{-1}$

(0.043%) of toluhydroquinone. This corresponds to toluhydroquinone (3.44×10^{-7} moles) present in the reaction vessel at the start of experiment.

In normal runs in the presence of reactants such as alcohols the final concentration of toluhydroquinone was usually about five times the concentration added in the above experiments. In these circumstances the contribution to the quantum efficiency by reaction with carbon tetrachloride is small.

3.2.3. Removal of Impurity from Carbon Tetrachloride

In order to find out whether the quantum efficiency of reaction of toluquinone with carbon tetrachloride was due to the presence of an impurity in carbon tetrachloride or to the reaction of toluquinone with carbon tetrachloride itself, the following experiment was performed.

A toluquinone solution (2.0×10^{-2} mole $l.^{-1}$) in carbon tetrachloride (Hopkin and Williams AnalaR) was irradiated at 365 mμ and 25.0°C for 6000 seconds. The irradiated solution was then distilled with an all glass fractionation column described in section 2.2.4, under nitrogen. The solution (100 ml) was distilled, the first fraction of 20 ml was rejected and the next 60 ml were collected. A toluquinone solution (2.0×10^{-2} mole $l.^{-1}$) was prepared in this sample of carbon tetrachloride and irradiated in nitrogen, using one solvent bubbler in the nitrogen flow line (section 2.2.6) at 2.164×10^{-9} einst.sec.^{-1}, for 2000 seconds. Toluhydroquinone (1.715×10^{-7} moles in 40 ml of solution) was formed with a quantum efficiency of 0.04. This figure for the quantum efficiency is lower than the value (0.119) obtained from the corresponding run in table 3.1, when the solution was also irradiated for 2000 seconds. This provides evidence that the reaction observed is at least partly a reaction with an impurity in the carbon tetrachloride, which is destroyed in the photochemical reaction.

In the preparation of carbon tetrachloride for use in subsequent photochemical experiments it was not purified by this procedure due to the following reasons.

(i) As mentioned in section 3.2.2, in normal runs in the presence of reactants such as alcohols, the final concentration of toluhydroquinone formed in the reaction was such that the reaction between toluquinone and carbon tetrachloride would be of no significance.

(ii) It was not convenient to purify carbon tetrachloride by this procedure.

3.3. Cyclohexane

3.3.1. Thermal Reaction

Toluquinone solution (2.0×10^{-2} mole l.^{-1}) in cyclohexane was prepared. Immediately after preparation 1.0 and 2.0 ml of the solution were mixed with 10.0 ml of reagent solution A (section 2.5.2) in two conical flasks. The mixtures were stirred by magnetic stirrers for half an hour, and allowed to stand for one hour in the dark. The optical densities of aqueous layers from both the samples were measured against water at 510 mµ in one cm cells. The figures for the optical densities were 0.325 (for 1 ml sample) and 0.330 (for 2 ml). The main bulk of the toluquinone solution was kept in a dark cupboard in air at 20°C for three hours. It was analysed using the procedure described above. The optical densities of the aqueous layers from both the samples measured against water, were found to be exactly the same as the corresponding figures above. This shows that there is no thermal reaction of toluquinone with cyclohexane.

3.3.2 Effect of Toluquinone Concentration and Intensity of Light on . . . Quantum Efficiency

Solutions of toluquinone in cyclohexane were irradiated in nitrogen using one solvent bubbler in the nitrogen flow line (section 2.2.6). The results are shown in table 3.3.

TABLE 3.3

Toluquinone in Cyclohexane, 365 mμ, 25.0°C

Toluquinone Mole l^{-1}.x10^2	Time of Irrad. Seconds	I Einst. Sec^{-1}.x10^9	QH_2 Produced Moles x 10^7	∅
2.00	5460	2.09	57.4	0.503
2.11	3600	2.11	37.2	0.491
1.73	5400	0.131	3.30	0.469
1.66	3600	1.97	34.7	0.488

The quantum efficiency may be taken as 0.49±0.015. This figure is considerably larger than that for carbon tetrachloride. Obviously cyclohexane cannot be used as a solvent in studying the photochemical reactions of toluquinone with other substances.

Table 3.3 does not give evidence of any variation of quantum efficiency with either toluquinone concentration or light intensity absorbed in the range studied.

3.3.3 Effect of Cyclohexane Concentration on Quantum Efficiency

Solutions of toluquinone in carbon tetrachloride containing cyclohexane were irradiated in nitrogen, using two solvent bubblers in the nitrogen flow line (section 2.2.6).

A solution of toluquinone in carbon tetrachloride containing cyclohexane (0.093 mole l.$^{-1}$) was also irradiated in vacuum. The results are given in table 3.4.

TABLE 3.4

Toluquinone (2.0x10^{-2} mole l.$^{-1}$) in Carbon Tetrachloride containing Cyclohexane, 365 mμ, 25.0°C

Cyclohexane Mole l.$^{-1}$ i.e. $[AH_2]$	Log ~~Log~~ $[AH_2]$	Time of Irrad. Seconds	I Einst. Sec.$^{-1}$ x10^{9}	QH_2 Produced Moles x10^{7}	Ø
9.3	0.969	5460	2.09	57.4	0.503≠
4.65	0.668	3600	1.50	23.1	0.428
0.93	$\bar{1}.969$	3600	1.67	20.7	0.343
0.465	$\bar{1}.668$	3600	1.81	22.1	0.339
0.279	$\bar{1}.446$	3600	1.57	20.1	0.357
0.093	$\bar{2}.969$	7200	1.62	34.6	0.296
0.093	$\bar{2}.969$	3600	1.80	19.3	0.298✱
0.0558	$\bar{2}.747$	7200	1.75	34.2	0.271
0.0093	$\bar{3}.969$	7200	1.72	21.8	0.177
0.0		For yields of QH_2 probably less than (section 3.2)	$>$	10.0, the Ø	is 0.05

≠ Pure cyclohexane.
✱ Solution was irradiated in vacuum.

The quantum efficiencies have been plotted against the logarithms of cyclohexane concentrations in fig. 3.2. Table 3.4 shows that

(i) there is agreement between an experiment performed after removal of air with nitrogen and one performed after degassing on a vacuum system,

(ii) the quantum efficiency is constant for cyclohexane concentrations in the range 0.279 to 0.93 mole $l.^{-1}$. With cyclohexane concentration below 0.279 mole $l.^{-1}$, the quantum efficiency decreases with decrease in cyclohexane concentration, and

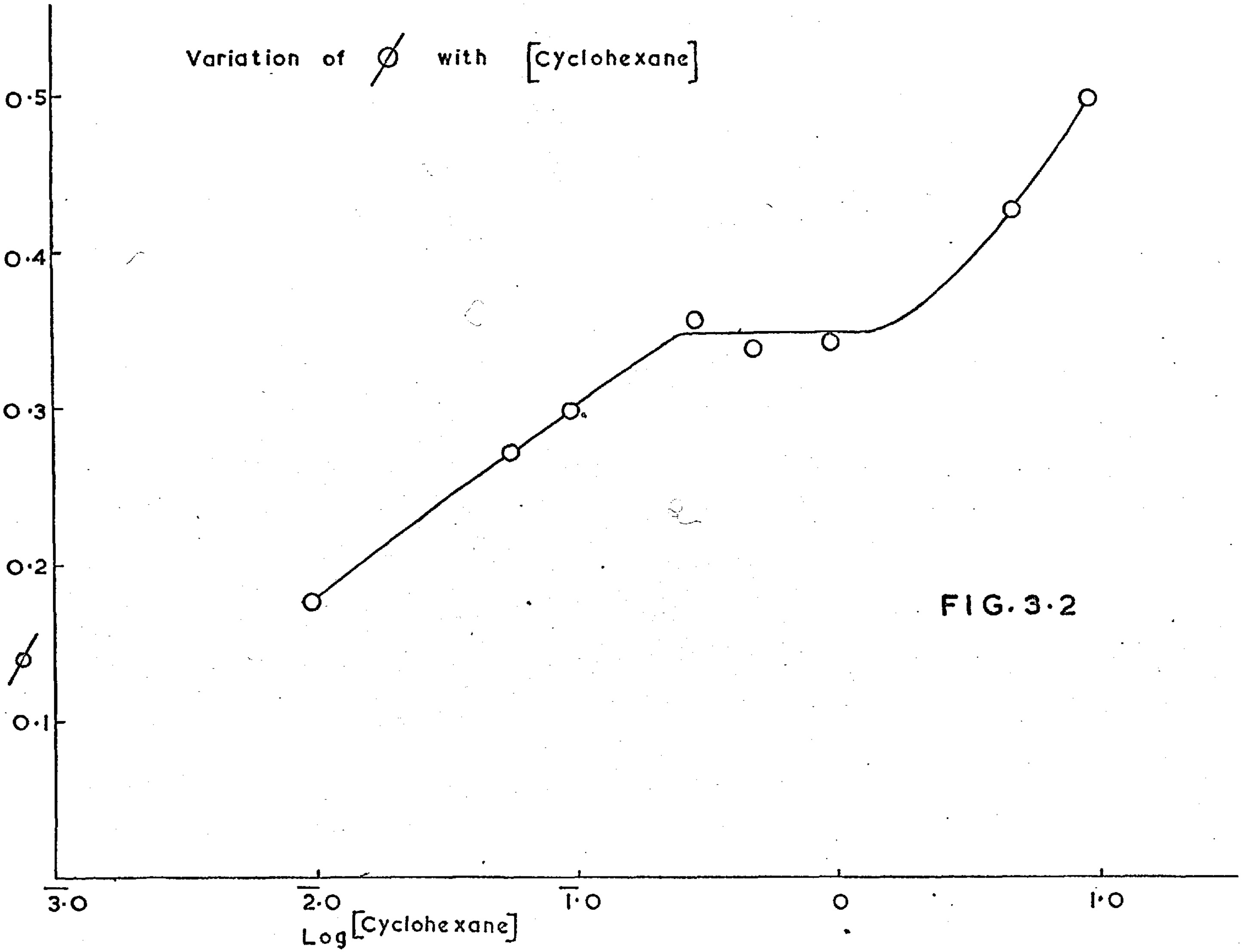
(iii) there is a fall in quantum efficiency when the concentration of cyclohexane is reduced from pure cyclohexane (9.3 mole $l.^{-1}$) to 0.93 mole $l.^{-1}$ in carbon tetrachloride. This may be attributed to the cage effect, which is more effective in carbon tetrachloride (M.Wt.153.84) than in cyclohexane (M.Wt.84.16). The cage effect may lead to the recombination of free radicals within the solvent cage. The mechanism can be described as follows :-

$$Q + h\nu \longrightarrow Q^{*}$$

$$Q^{*} + AH_2 \xrightarrow{k_{2A}} (QH.AH) \qquad (2A)$$

$$(QH.AH) \xrightarrow{k_{-2A}} Q + AH_2 \qquad (-2A)$$

$$(QH.AH) \xrightarrow{k_{2B}} QH + AH \qquad (2B)$$



Variation of ϕ with [Cyclohexane]

FIG. 3·2

In the absence of a cage effect k_{-2A} is zero and the reaction can be written as :

$$Q^{*} + AH_2 \xrightarrow{k_2} QH + AH \qquad (2)$$

Reaction (2B) will be followed by reactions of free radicals as indicated in the mechanism given in section 4.2. The results indicate that k_{-2A} may be very low in cyclohexane but significant in carbon tetrachloride.

A graph of reciprocals of the cyclohexane concentration (range 27.9×10^{-2} to 0.93×10^{-2} mole l^{-1}) against the quantum efficiency, has been plotted in fig 3.3 and a straight line is obtained. The results that are plotted in fig. 3.3 are given in table 3.5.

TABLE 3.5

cyclohexane Mole $l^{-1}\times10^{2}$ i.e. $[AH_2]\times10^{2}$	$\frac{1}{[AH_2]}$	I Einst. $Sec^{-1}\times10^{9}$	ϕ	$\frac{1}{\phi}$
27.9	3.58	1.57	0.357	2.80
9.3	10.8	1.62	0.296	3.38
9.3	10.8	1.80	0.298	3.36
5.58	17.9	1.75	0.271	3.69
0.93	108.0	1.72	0.177	5.65

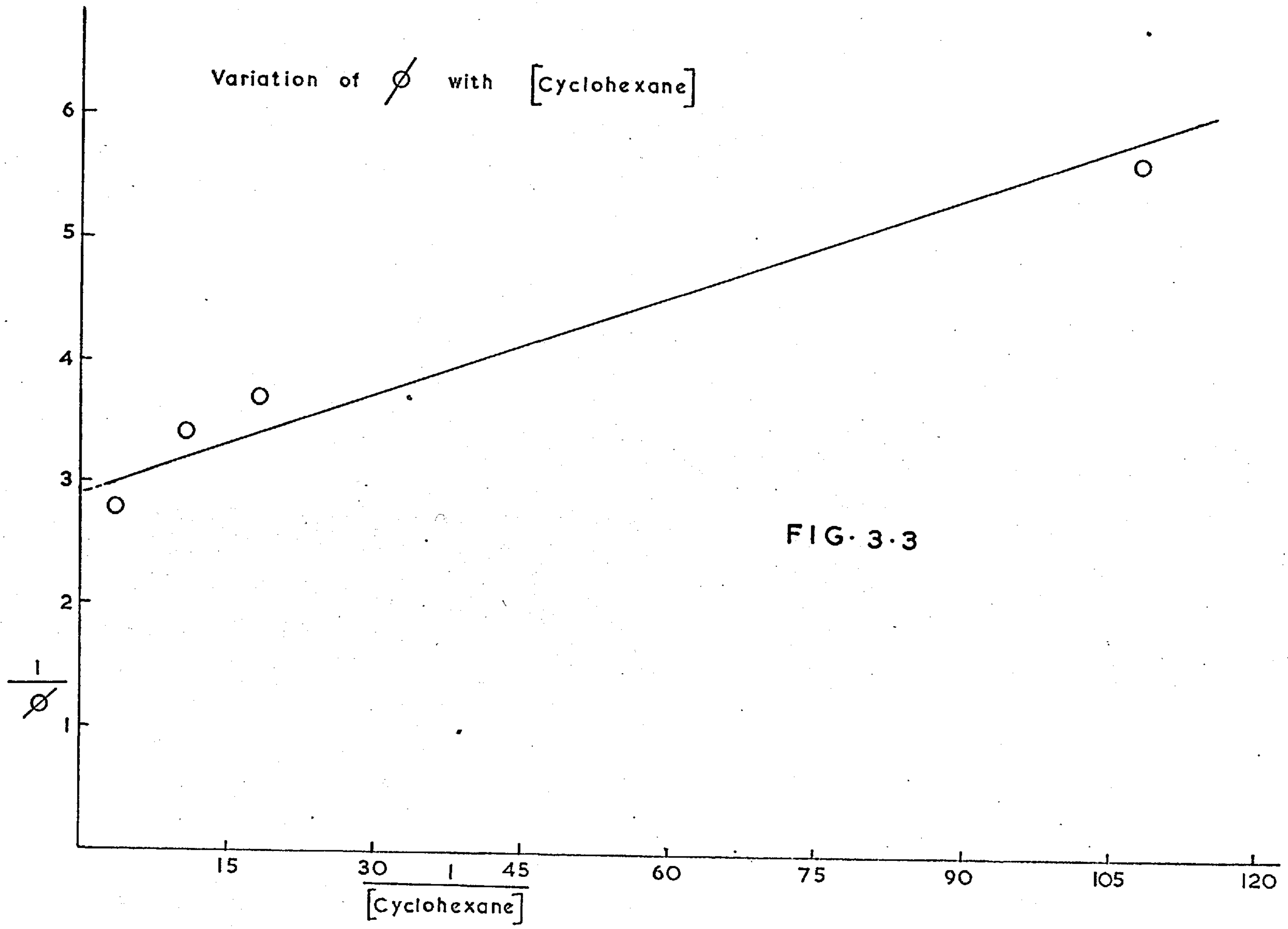

Variation of ϕ with [Cyclohexane]

FIG. 3.3

Taking the constant value of 0.35 in the range of cyclohexane concentration 0.279 to 0.93 mole l^{-1}. as ϕ_2 and the quantum efficiency for reaction with carbon tetrachloride as ϕ_o (i.e. 0.05), a graph of $\frac{\phi - \phi_o}{\phi_2 - \phi}$ against cyclohexane concentration is plotted in fig. 3.4 using the results shown in table 3.6. The plot is linear.

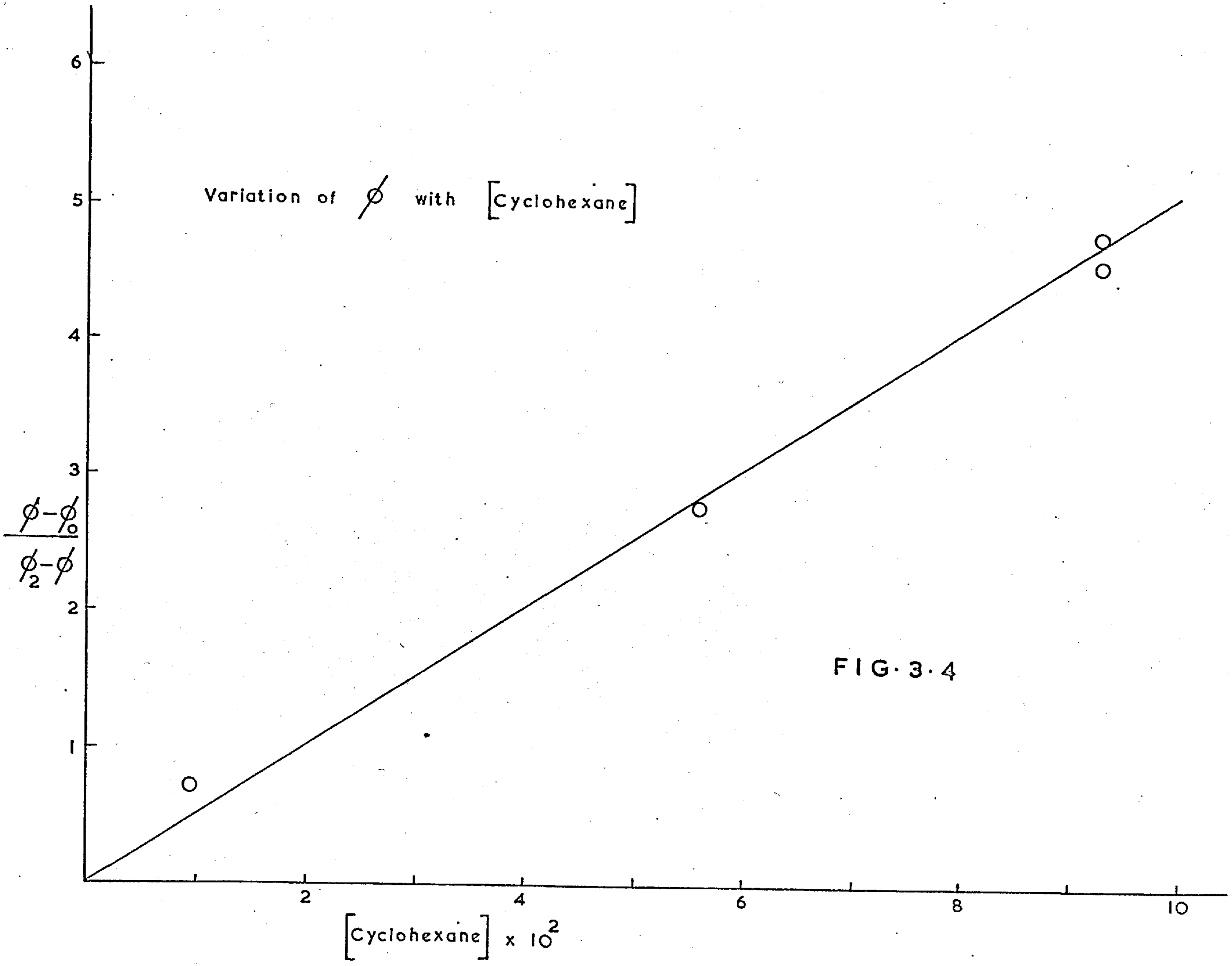
TABLE 3.6

Cyclohexane Mole l^{-1}.x10^2 i.e. $[AH_2]$ x10^2	I Einst. Sec^{-1}.x10^9	ϕ	$\frac{\phi - \phi_o}{\phi_2 - \phi}$
9.3	1.62	0.296	4.56
9.3	1.80	0.298	4.77
5.58	1.75	0.271	2.80
0.93	1.72	0.177	0.734

3.4. iso-Propyl Alcohol

3.4.1. Thermal Reaction

A solution of toluquinone (2.0x10^{-2} mole l^{-1}.) in iso-propyl alcohol was found to form toluhydroquinone in the dark. The reaction was found both with a sample left in air at room temperature (20°C), and with a sample which


Variation of ϕ with [Cyclohexane]
$\frac{\phi-\phi_0}{\phi_2-\phi}$
1
2
3
4
5
6
2
4
6
8
10
[Cyclohexane] x 10^2

FIG·3·4

had nitrogen passing through it at 25.0°C.

Toluquinone (2.0×10^{-2} mole $l.^{-1}$) in iso-propyl alcohol was kept in the dark, in air, at room temperature (20°C), and analysed for toluhydroquinone initially and at different time intervals. In the measurement of optical density the blank sample consisted of iso-propyl alcohol and reagent solution A (section 2.5.2) taken in the same relevant proportions. The results are given in table 3.7. The rate of toluhydroquinone formation was found to be 1.85×10^{-9} mole $l.^{-1}$ $sec.^{-1}$

TABLE 3.7

Toluquinone (2.0×10^{-2} mole $l.^{-1}$) in iso-Propyl Alcohol, Thermal Reaction in Air at 20°C in the Dark

Hours After Preparation	QH_2 Produced Moles $\times 10^7$ (in 40 ml of solution)
43.0	95.9
94.0	277.0

3.4.2. Effect of Toluquinone Concentration and Intensity of Light on Quantum Efficiency

Solutions of toluquinone in iso-propyl alcohol were irradiated in nitrogen using one solvent bubbler in the nitrogen flow line (section 2.2.6). The results are shown in table 3.8.

TABLE 3.8

Toluquinone in iso-Propyl Alcohol, 365 mμ, 25.0°C

Toluquinone Mole l^{-1}	Time of Irrad. seconds	I Einst. Sec^{-1} x10^9	QH_2 Produced Moles x10^7	∅
0.5	3600	0.733	28.9	1.10
0.5	3600	0.668	23.1	0.961
1.0	3600	0.967	32.2	0.925
2.0	1800	1.96	36.3	1.03
2.0	3600	8.69	310.0	0.991

Table 3.8 indicates that the quantum efficiency is independent of toluquinone concentration and intensity of light in the range studied.

It is clear from table 3.8 that the yield of toluhydroquinone produced photochemically is about ten times (first four experiments) and fifty times (last experiment) than that could be obtained thermally if calculated on the basis of the rate of thermal reaction (section 3.4.1). Hence there is no serious interference by the thermal reaction even if the method of preparation of blank does not properly allow for the thermal reaction during irradiation. Within the experimental error the quantum efficiency may be taken as 1.00 ± 0.05.

3.4.3. Effect of added Toluhydroquinone on Quantum Efficiency

Solutions of toluquinone with added toluhydroquinone in iso-propyl alcohol were irradiated in nitrogen using one solvent bubbler in the nitrogen flow line (section 2.2.6) and table 3.9 illustrates the results.

TABLE 3.9

Toluquinone (2.0×10^{-2} mole $l.^{-1}$) with added Toluhydroquinone (QH_2) in iso-Propyl Alcohol, 365 mμ, 25.0°C

Initial amount of QH_2 in Reaction vessel Moles $\times10^7$	Time of Irrad. Seconds	I Einst. Sec^{-1} $\times10^9$	QH_2 Produced Moles $\times 10^7$	∅
19.0	1800	9.28	157.0	0.938
38.0	1800	8.53	147.0	0.955

It is clear from tables 3.8 and 3.9 that the product, toluhydroquinone does not retard the photochemical reaction between toluquinone and iso-propyl alcohol.

3.4.4. Variation of Toluhydroquinone Yield with Time

Solutions of toluquinone in carbon tetrachloride containing iso-propyl alcohol were irradiated in nitrogen using one or two solvent bubblers in the nitrogen flow line (section 2.2.6). Solutions were also irradiated in vacuum. The results are shown in table 3.10.

TABLE 3.10

Toluquinone (2.0×10^{-2} mole $l.^{-1}$) in Carbon Tetrachloride containing iso-Propyl Alcohol, 365 mμ, 25.0°C

iso-Propyl Alcohol Mole $l.^{-1}$	Time of Irrad. Seconds	I Einst. $Sec.^{-1} \times 10^{9}$	I T Einst. $\times 10^{6}$	QH_2 Produced Moles $\times 10^{7}$	ϕ
1.31	3600	2.05	7.38	30.0	0.406*
1.31	3600	2.00	7.20	30.7	0.426*
1.31	7200	1.61	11.6	46.9	0.405
0.131	3600	2.17	7.81	38.4	0.492*
0.131	2400	1.78	4.27	22.6	0.529
0.131	1800	1.70	3.06	15.4	0.503
0.0131	1800	6.70	12.1	38.5	0.319
0.0131	1800	3.22	5.79	17.7	0.306
0.0131	3600	2.52	9.09	26.1	0.287≠
0.0131	3600	2.63	9.45	26.9	0.285*
0.0131	12600	0.309	3.90	11.6	0.299*
0.0131	5400	1.39	7.53	24.2	0.322
0.0131	5400	1.36	7.32	24.2	0.331
0.0131	5400	1.18	6.35	21.5	0.338
0.0131	3600	1.13	4.08	13.0	0.318

* Solutions were irradiated in vacuum.

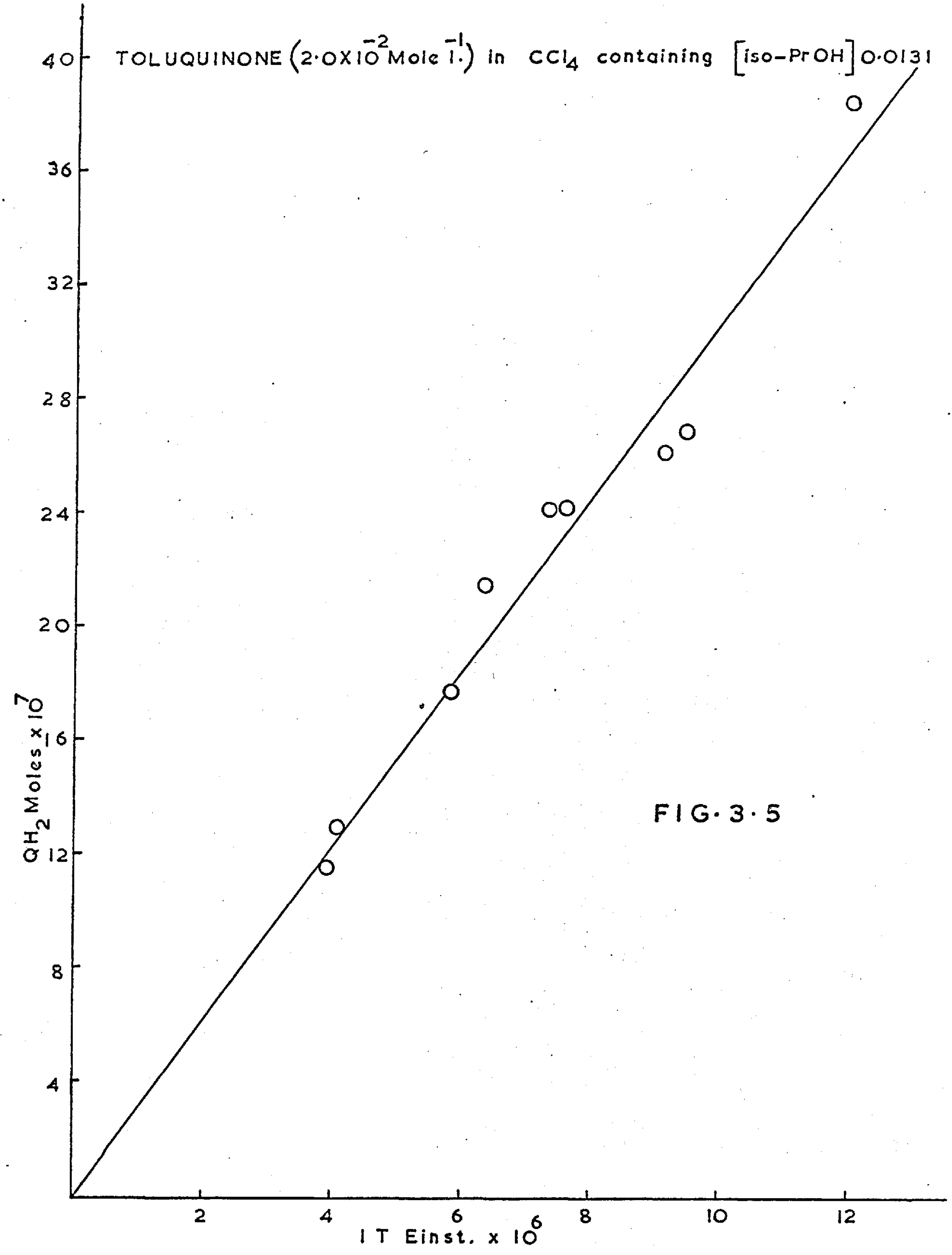
≠ Two solvent bubblers in the nitrogen flow line were used.

At iso-propyl alcohol concentration, 0.0131 mole l.$^{-1}$ the toluhydroquinone produced has been plotted against the light absorbed in fig. 3.5. A straight line is obtained indicating both, a linear variation of toluhydroquinone yield with time, and that the quantum efficiency is independent of light intensity in the range studied.

Table 3.10 shows that at iso-propyl alcohol concentrations, 1.31, 0.131 and 0.0131 mole l.$^{-1}$, the results obtained after removal of oxygen with nitrogen and after degassing on a vacuum line are in agreement.

3.4.5. Effect of iso-Propyl Alcohol Concentration and Intensity of Light on Quantum Efficiency

Solutions of toluquinone in carbon tetrachloride containing iso-propyl alcohol were irradiated in nitrogen using one or two solvent bubblers in the nitrogen flow line (section 2.2.6). In further experiments the vacuum method for degassing of solution was used. The results are given in tables 3.11 and 3.12.


TOLUQUINONE $(2{\cdot}0 \times 10^{-2}$ Mole $l.^{-1})$ in CCl_4 containing [iso-PrOH] 0·0131
QH_2 Moles $\times 10^7$
40
36
32
28
24
20
16
12
8
4
2
4
6
8
10
12
I T Einst. $\times 10^6$

FIG·3·5

TABLE 3.11

Toluquinone ($2.0x10^{-2}$ mole $l.^{-1}$) in Carbon Tetrachloride containing iso-Propyl Alcohol, 365 mμ, 25.0°C

Experiment	Iso-Propyl Alcohol Mole $l.^{-1}$	Time of Irrad. Seconds	I Einst. $Sec.^{-1}x10^{9}$	QH_2 Produced Moles x 10^{7}	ø
1	13.1	see section 3.4.2.			1.00±0.05
2	6.55	2400	1.40	20.1	0.598
3	6.55	2400	1.32	19.7	0.622
4	1.31	1800	7.56	68.3	0.502≠
5	1.31	3600	2.05	30.0	0.406*
6	1.31	3600	2.00	30.7	0.426*
7	1.31	7200	1.61	46.9	0.405
8	1.31	9000	0.205	15.5	0.840*
9	0.655	5400	1.55	42.5	0.508*
10	0.655	12600	0.223	19.5	0.694*
11	0.131	3600	2.17	38.4	0.492*
12	0.131	2400	1.78	22.6	0.529
13	0.131	1800	1.70	15.4	0.503
14	0.131	10800	0.188	13.8	0.680*
15	0.0917	1800	7.17	66.4	0.515≠
16	0.0917	3600	2.15	34.8	0.450*
17	0.0655	3600	1.86	25.9	0.387*
18	0.0393	1800	6.98	58.4	0.465
19	0.0393	3600	2.16	23.6	0.303*
20	0.0393	3600	2.07	22.6	0.303*
21	0.0131	from fig. 3.5			0.300

TABLE 3.12

Toluquinone (2.0×10^{-2} mole $l.^{-1}$) in Carbon Tetrachloride containing iso-Propyl Alcohol, 365 mμ, 25.0°C

Experiment	Iso-Propyl Alcohol Mole $l.^{-1}$ $\times 10^3$	Time of Irrad. Seconds	I Einst. $Sec.^{-1} \times 10^9$	QH_2 Produced Moles $\times 10^7$	ø
22	6.55	1800	7.59	25.4	0.186*
23	6.55	1800	7.30	28.0	0.213≠
24	6.55	1800	6.91	24.0	0.193≠
25	6.55	7200	2.07	20.1	0.135*
26	6.55	7200	1.93	15.8	0.114*
27	6.55⌿	1800	4.71	19.5	0.230≠
28	3.93	1800	6.94	24.0	0.192
29	3.93	1800	6.73	22.5	0.186≠
30	3.93	7200	1.77	12.9	0.101*
31	3.93	7200	1.72	14.8	0.120*
32	2.62	1800	6.86	20.0	0.162
33	1.70	1800	6.64	16.8	0.141
34	1.70	1800	6.15	15.5	0.140
35	1.31	1800	6.81	16.4	0.134
36	1.18	1800	6.22	12.1	0.108
	0.0	For yields of QH_2 > 10.0, the ø is probably less than 0.05 (section 3.2)			

In tables 3.11 and 3.12

≠ Two solvent bubblers in the nitrogen flow line were used.

* Solutions were irradiated in vacuum.

⌿ Toluquinone concentration (1.0×10^{-2} mole $l.^{-1}$).

The results given in Tables 3.11 and 3.12 lead to the following conclusions.

(a) Comparison of results obtained after different methods of removal of oxygen.

(i) 1.31 mole $l.^{-1}$ alcohol

The figure for the quantum efficiency in experiment 5 (0.406), degassed on a vacuum line, is in agreement with the figure for quantum efficiency (0.405) in experiment 7, deoxygenated by passing nitrogen.

(ii) 0.131 mole $l.^{-1}$ alcohol

Comparable quantum efficiencies are those for experiment 11, vacuum method, 0.492, and experiment 13, nitrogen method, 0.503.

(iii) 0.0131 mole $l.^{-1}$ alcohol

In section 3.4.4 it was shown that the two methods for removal of oxygen led to similar quantum efficiencies at this concentration.

(iv) 6.55×10^{-3} mole $l.^{-1}$ alcohol

Comparable quantum efficiencies are those for experiment 22, vacuum method, 0.186 and experiment 24, nitrogen method, 0.193.

(b) Variation of quantum efficiency with light intensity.

The range of light intensity covered was 0.2×10^{-9} to

8.7×10^{-9} einst. sec.$^{-1}$.

(i) Pure alcohol, 13.1 mole l.$^{-1}$

It is clear from table 3.8 that the quantum efficiency is independent of light intensity in the range 0.7×10^{-9} to 8.7×10^{-9} einst. sec.$^{-1}$

(ii) 6.55 mole l.$^{-1}$ alcohol

The effect of variation of light intensity on the quantum efficiency was not studied.

(iii) 1.31 mole l.$^{-1}$ alcohol

The quantum efficiency is a function of light intensity, in the range 0.2×10^{-9} to 7.6×10^{-9} einst. sec.$^{-1}$ Results 8 and 5,6,7, indicate that the quantum efficiency decreases with an increase in light intensity from 0.2×10^{-9} to 2×10^{-9} einst. sec.$^{-1}$ However in the range 2×10^{-9} to 7.6×10^{-9} einst. sec.$^{-1}$ the quantum efficiency increases significantly with increase in light intensity. The results are plotted in fig 3.6.

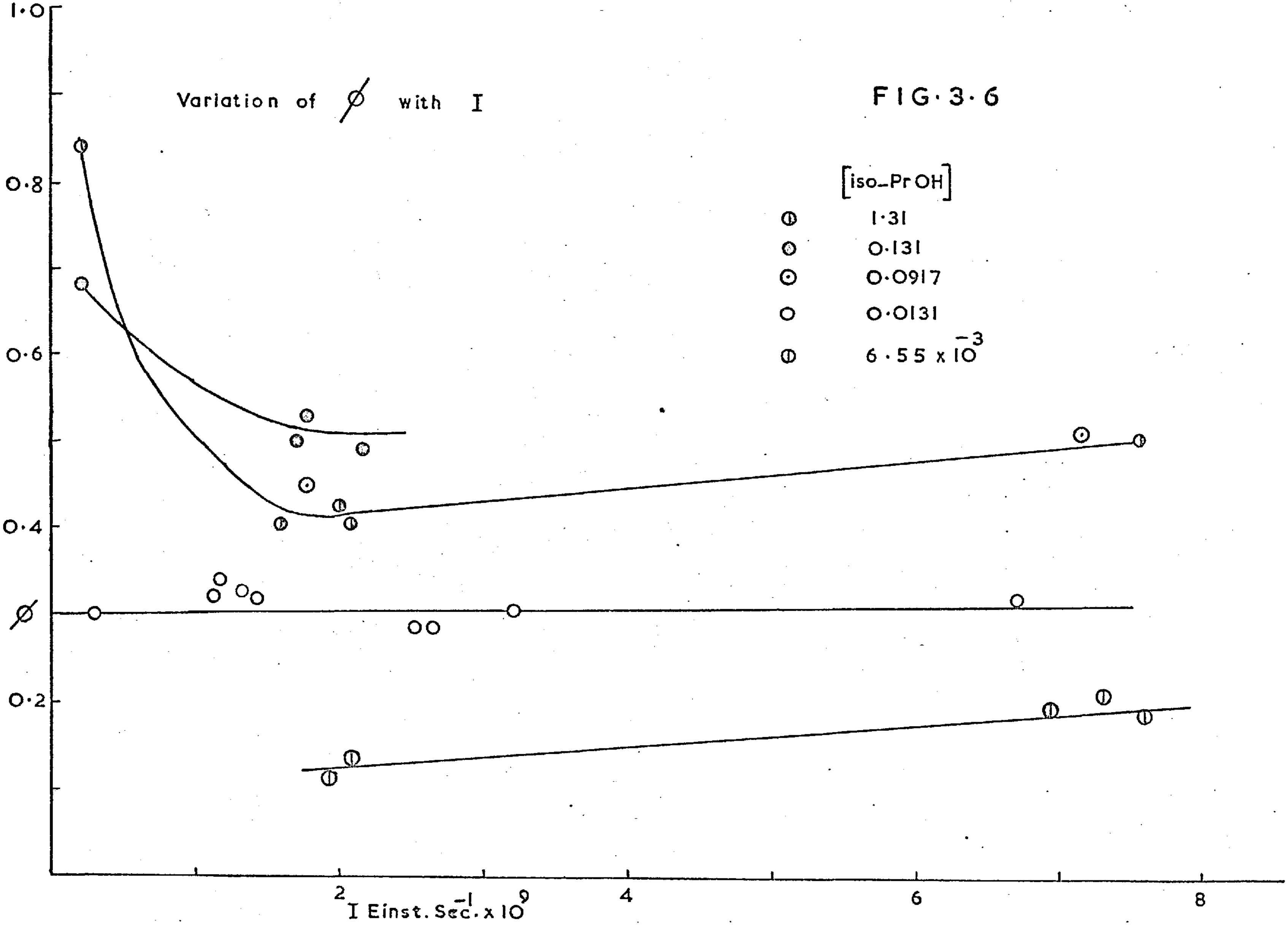
(iv) 0.655 mole l.$^{-1}$ alcohol

The light intensity range covered was from 0.2×10^{-9} to 1.6×10^{-9} einst. sec.$^{-1}$ The results, 9 and 10, show a decrease in the quantum efficiency with the increase in light intensity.

(v) 0.131 mole l.$^{-1}$ alcohol

In the light intensity range 0.2×10^{-9} to

FIG·3·6


Variation of Ø with I
[iso-PrOH]
1·31
0·131
0·0917
0·0131
6·55 x 10^{-3}
1·0
0·8
0·6
0·4
0·2
Ø
2
4
6
8
I Einst. Sec.$^{-1}$ x 10^{9}

$2x10^{-9}$ einst. $sec.^{-1}$ it is found that the quantum efficiency decreases with increasing light intensity. The results have been plotted in fig 3.6.

(vi) 0.0917 mole $1.^{-1}$ alcohol

Two experiments, 15 and 16, show that the quantum efficiency increases when the light intensity is increased from $2x10^{-9}$ to $7x10^{-9}$ einst. $sec.^{-1}$ The results are plotted in fig. 3.6.

(vii) 0.0393 mole $1.^{-1}$ alcohol

The results 18, 19 and 20, indicate that the quantum efficiency increases with the increase of light intensity from $2x10^{-9}$ to $7x10^{-9}$ einst. $sec.^{-1}$

(viii) 0.0131 mole $1.^{-1}$ alcohol

The results given in table 3.10 cover the whole range of light intensity ($0.3x10^{-9}$ to $7x10^{-9}$ einst. $sec.^{-1}$). The variation of the quantum efficiency with light intensity appears to be small, and with-in the possible range of experimental error. The results have been plotted in fig. 3.6.

(ix) $6.55x10^{-3}$ mole $1.^{-1}$ alcohol

In table 3.12, runs 22 to 26, show that in the light intensity range 2×10^{-9} to 7.6×10^{-9} einst. sec.$^{-1}$, there is increase of the quantum efficiency with the increase of light intensity. Run 27 appears to show that the quantum efficiency increases when the toluquinone concentration is reduced from 2×10^{-2} to 1×10^{-2} mole l.$^{-1}$

(x) 3.93×10^{-3} mole l.$^{-1}$ alcohol

Experiments 30 and 31, when compared with 28 and 29, show that in the light intensity range 1.7×10^{-9} to 7×10^{-9} einst. sec.$^{-1}$ the quantum efficiency increases with increasing light intensity.

(xi) Alcohol concentrations below 3.93×10^{-3} mole l.$^{-1}$

The effect of varying light intensity on the quantum efficiency was not studied.

(xii) Summary

In pure alcohol (13.1 mole l.$^{-1}$) the quantum efficiency does not vary with light intensity. At 1.31 mole l.$^{-1}$ alcohol and below (see fig. 3.6) two regions of light intensity can be distinguished. From 0.2×10^{-9} to 2×10^{-9} einst. sec.$^{-1}$ the quantum efficiency falls with increasing light intensity, when the alcohol concentration is within the range 0.131 to 1.31 mole $l.^{-1}$ From $2x10^{-9}$ to $7x10^{-9}$ einst. $sec.^{-1}$, there is a marked increase in the quantum efficiency with light intensity at all alcohol concentrations from 1.31 mole $l.^{-1}$ down to $3.93x10^{-3}$ mole $l.^{-1}$, with the exception that at 0.0131 mole $l.^{-1}$ no increase was noticed. It appears to be established that there is little variation of quantum efficiency with higher light intensity at 0.0131 mole $l.^{-1}$ alcohol, but the point at low intensity must be regarded with suspicion. It seems surprising that it is not higher than the figure at medium intensity. Further observations in these conditions are obviously required.

(c) Variation of quantum efficiency with alcohol concentration.

Tables 3.11 and 3.12 show that the quantum efficiency is a function of light intensity. Therefore, t~~h~~o study the effect of alcohol concentration on the quantum efficiency, measurements at constant light intensity were required. The majority of measurements in table 3.11 and 3.12 correspond to two light intensities, $1.8 \pm 0.4x10^{-9}$ and

$7.0 \pm 0.5 \times 10^{-9}$ einst. sec.$^{-1}$, at different alcohol concentrations.

The results at light intensity, $1.8 \pm 0.4 \times 10^{-9}$ einst. sec.$^{-1}$ are given in table 3.13.

TABLE 3.13

iso-PrOH Mole l.$^{-1}$ i.e. $[AH_2]$	I Einst. Sec.$^{-1}$ x 10^9	ϕ
13.1	see section 3.4.2	1.00 ± 0.05
6.55	1.40	0.598
1.31	2.00	0.426
0.655	1.55	0.508
0.131	2.17	0.492
0.0917	2.15	0.450
0.0655	1.86	0.387
0.0393	2.07	0.303
0.0131	2.52	0.287$\neq$
0.655$\ast$	2.07	0.135
0.393$\ast$	1.77	0.101
0.0	For yields of $QH_2 > 10.0 \times 10^{-7}$ moles, the ϕ is probably less than 0.05 (section 3.2).	

$\neq$ see table 3.10

$\ast$ $[AH_2] \times 10^2$

A graph of the quantum efficiency against alcohol concentration has been plotted in figs. 3.7(a) and (b), which show that the quantum efficiency increases with the increase in alcohol concentration from 0.393×10^{-2} to 0.131 mole l.$^{-1}$ The quantum efficiency appears to be constant in the concentration range 0.131 to 0.655 mole l.$^{-1}$ Above 0.655 mole l.$^{-1}$ alcohol, there is a significant dip in the quantum efficiency at 1.31 mole l.$^{-1}$ Beyond 1.31 mole l.$^{-1}$ alcohol the quantum efficiency increases and in 100% alcohol the quantum efficiency is 1.00±0.05.

The occurrence of a dip in the curve is peculiar. Therefore, consideration was given to possible sources of error that might be responsible for this peculiarity.

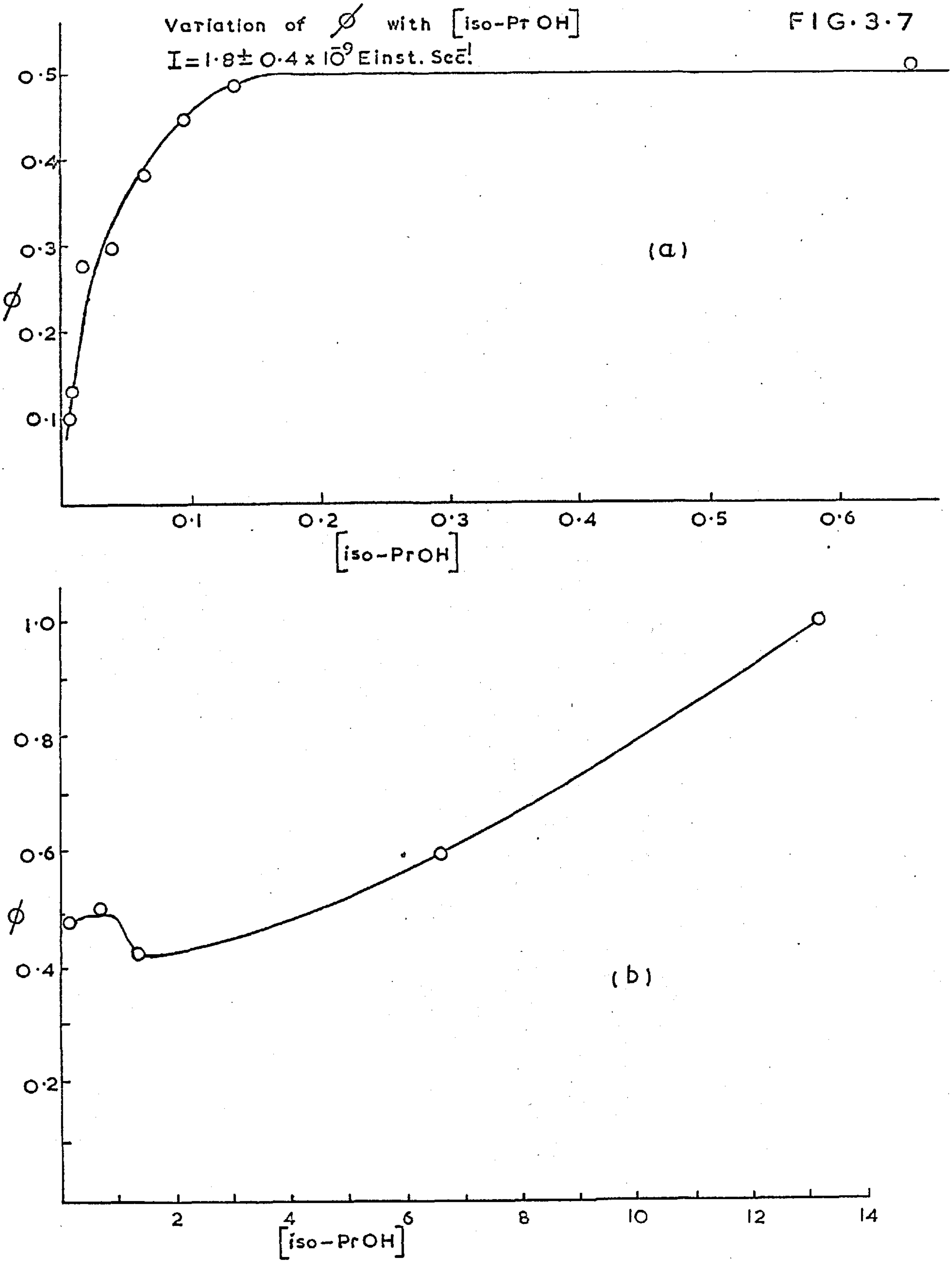
(i) Impure samples of toluquinone and iso-propyl alcohol.

The samples of toluquinone and iso-propyl alcohol were the same as were used in the majority of experiments. Hence the toluquinone and iso-propyl alcohol cannot be held responsible for this peculiarity.

(ii) Incomplete removal of air from the solution.

The presence of this dip has been confirmed ...

FIG. 3.7



Variation of ϕ with [iso-PrOH]

$I = 1{\cdot}8 \pm 0{\cdot}4 \times 10^{-9}$ Einst. Sec^{-1}

by three experiments 5,6 and 7. In experiments 5 and 6 the solutions were degassed on a vacuum line. In experiment 7 air from the solution was removed with nitrogen. So the incomplete removal of air from the solution cannot be the reason for the peculiarity.

(iii) Error in preparation of the solution.

In each of the three experiments fresh solution of toluquinone was used. There was a long time interval between experiments. There is no possibility that the same error could have been made in all the three experiments.

(iv) Error in measurement of light intensity.

Table 3.14 gives the calibration figures of light intensity at different time intervals and the quantum efficiencies at alcohol concentrations 6.55, 1.31, 0.655 and 0.131 mole $l.^{-1}$

TABLE 3.14

Table	Experiment	Date	Intensity Calibration Figure (einst. $sec.^{-1}$ per scale division) $x10^{12}$	iso-Propyl Alcohol Mole $l.^{-1}$	ϕ
3.11	12	31.7.62	1.46	0.131	0.529
3.11	13	7.8.62	1.44	0.131	0.503
3.11	2	30.8.62	1.46	6.55	0.598

Table 3.14 Contd.

<table>
<tr><th>Table</th><th>Experiment</th><th>Date</th><th>Intensity Calibration Figure (einst. sec.$^{-1}$ per scale division) x 10^{12}</th><th>iso-Propyl Alcohol Mole l.$^{-1}$</th><th>ϕ</th></tr>
<tr><td>3.11</td><td>3</td><td>31.8.62</td><td>1.46</td><td>6.55</td><td>0.622</td></tr>
<tr><td>3.11</td><td>7</td><td>6.9.62</td><td>1.47</td><td>1.31</td><td>0.405</td></tr>
<tr><td colspan="6">The following experiments were performed using the new housings for the photocells, which had bigger holes for the entry of the light beam</td></tr>
<tr><td>3.11</td><td>6</td><td>22.5.64</td><td>0.847</td><td>1.31</td><td>0.426</td></tr>
<tr><td>3.11</td><td>5</td><td>25.5.64</td><td>0.847</td><td>1.31</td><td>0.406</td></tr>
<tr><td>3.11</td><td>11</td><td>13.5.64</td><td>0.847</td><td>0.131</td><td>0.492</td></tr>
<tr><td>3.11</td><td>9</td><td>16.7.64</td><td>0.856</td><td>0.655</td><td>0.508</td></tr>
</table>

Experiments 12 and 13 at 0.131 mole l.$^{-1}$ alcohol were performed in 1962 using nitrogen method for the removal of air from the solutions. The figures for the quantum efficiency are in agreement with the one obtained in experiment 11 at the same alcohol concentration. Experiment 11 was performed after about two years and the solution was degassed on a vacuum line.

The figure for the quantum efficiency in experiment 7 at 1.31 mole l.$^{-1}$ alcohol is in agreement with those obtained in experiments 5 and 6 at the same concentration. Experiment 7 was performed in 1962 when air from the solution was removed with nitrogen. Experiments 5 and 6 were carried out after a gap of about two years using a vacuum line for degassing of the solution.

Above agreement between the experimental results at 0.131 and 1.31 mole $1.^{-1}$ alcohol rules out the following possible sources of error :

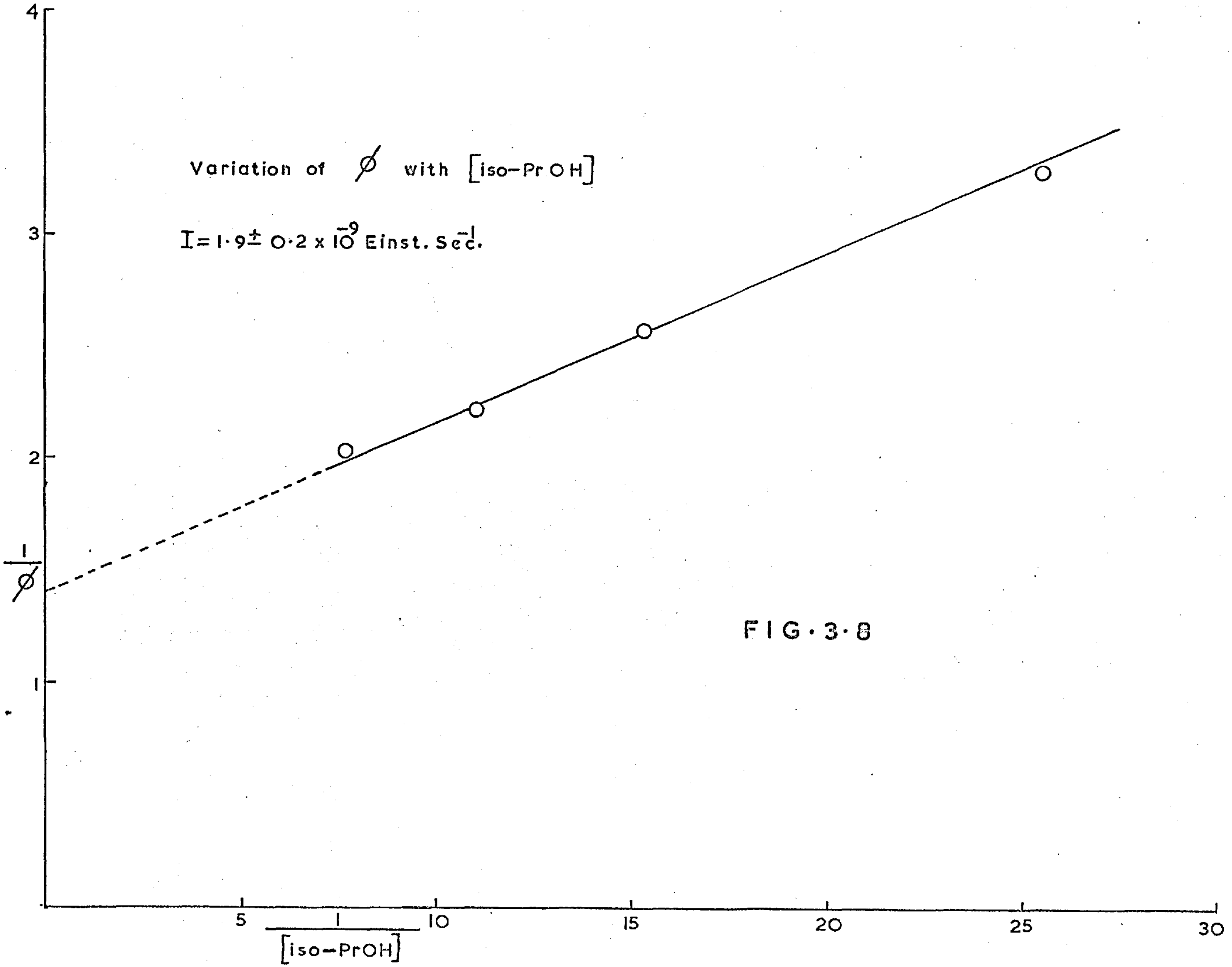
(a) Error in preparation of solution, and

(b) incomplete removal of air from solution.

Experiments 2 and 3 at 6.55 mole $1.^{-1}$ were performed in 1962 using the nitrogen method for removal of air from the solutions. Experiment 9 at 0.655 mole $1.^{-1}$ alcohol was carried out in 1964 when the solution was degassed on a vacuum line.

Table 3.14 shows that there is no error in the light calibration figures used in the experiments at alcohol concentrations 6.55, 1.31, 0.655 and 0.131 mole $1.^{-1}$

For the light intensity, $1.9 \pm 0.2 \times 10^{-9}$ einst. sec.^{-1} the reciprocal of quantum efficiency is plotted (fig.3.8) against the reciprocal of alcohol concentration in the range 0.131 to 0.0393 mole $1.^{-1}$ A straight line is obtained. Extrapolation to high alcohol concentration gives a quantum efficiency of 0.714 (ϕ_2). The results below 0.0393 mole $1.^{-1}$ alcohol do not fall on this line. Table 3.15 lists the results that are plotted in fig.3.8.



Variation of ϕ with [iso-PrOH]

$I = 1{\cdot}9 \pm 0{\cdot}2 \times 10^{-9}$ Einst. Sec^{-1}.

FIG·3·8

TABLE 3.15

iso-PrOH Mole l.$^{-1}$ i.e. $[AH_2]$	$\frac{1}{[AH_2]}$	I Einst. Sec.$^{-1}$ x 10^9	ϕ	$\frac{1}{\phi}$
0.131	7.63	2.17	0.492	2.03
0.0917	10.9	2.15	0.450	2.22
0.0655	15.3	1.86	0.387	2.58
0.0393	25.5	2.07	0.303	3.30

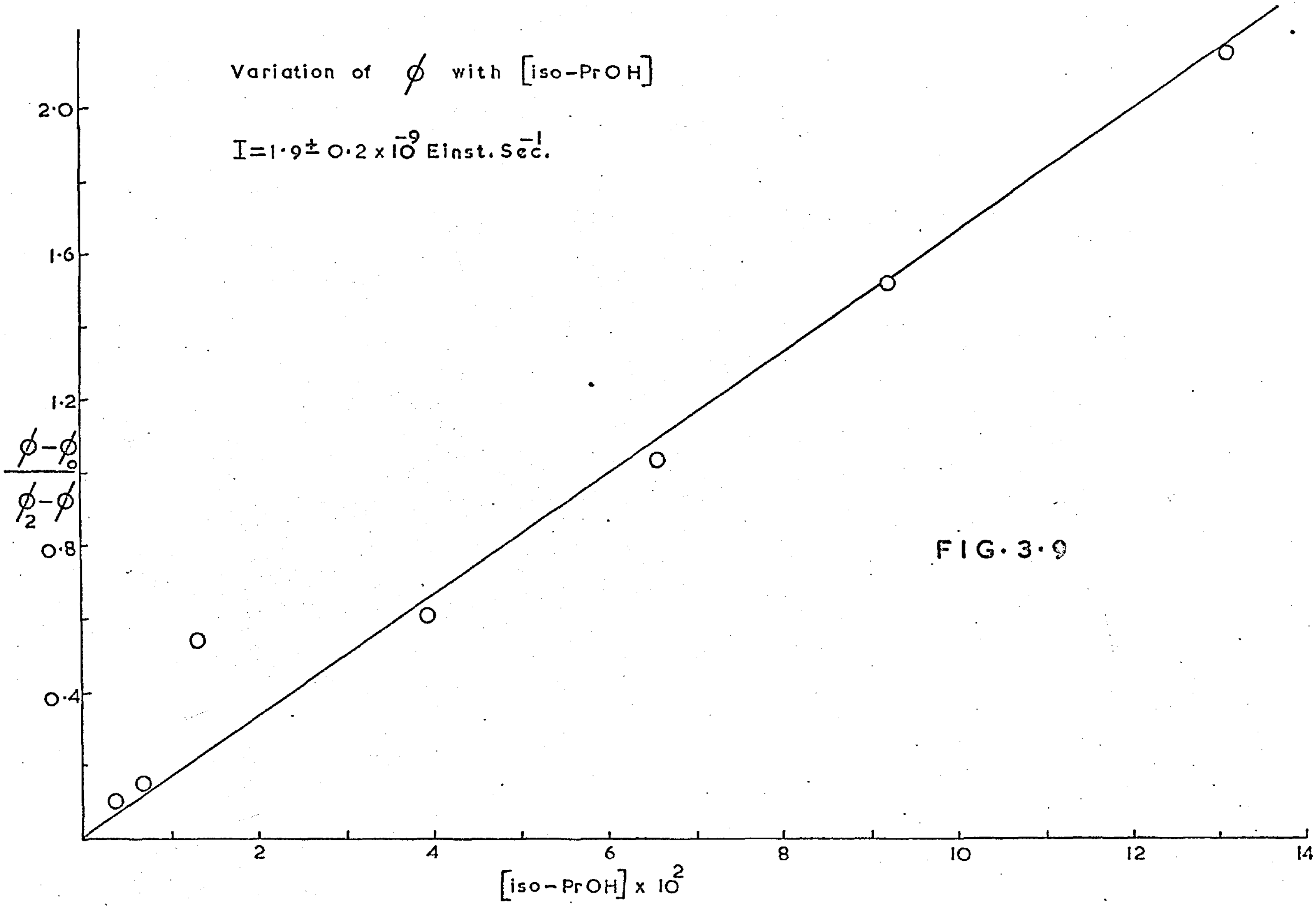
A graph of $\frac{\phi - \phi_0}{\phi_2 - \phi}$ against $[AH_2]$ is plotted in fig. 3.9 using the results shown in table 3.16. The points lie on a straight line with the exception of one at 0.0131 mole l.$^{-1}$ alcohol.

TABLE 3.16

iso-PrOH Mole l.$^{-1}$ i.e. $[AH_2]$	I Einst. Sec.$^{-1}$ x 10^9	ϕ	$\frac{\phi - \phi_0}{\phi_2 - \phi}$ *
0.131	1.70	0.503	2.15
0.0917	2.15	0.450	1.52
0.0655	1.86	0.387	1.03
0.0393	2.07	0.303	0.616
0.0131	2.52	0.287	0.555
0.655≠	2.07	0.135	0.147
0.393≠	1.77	0.101	0.083

* $\phi_0 = 0.05$

≠ $[AH_2] \times 10^2$

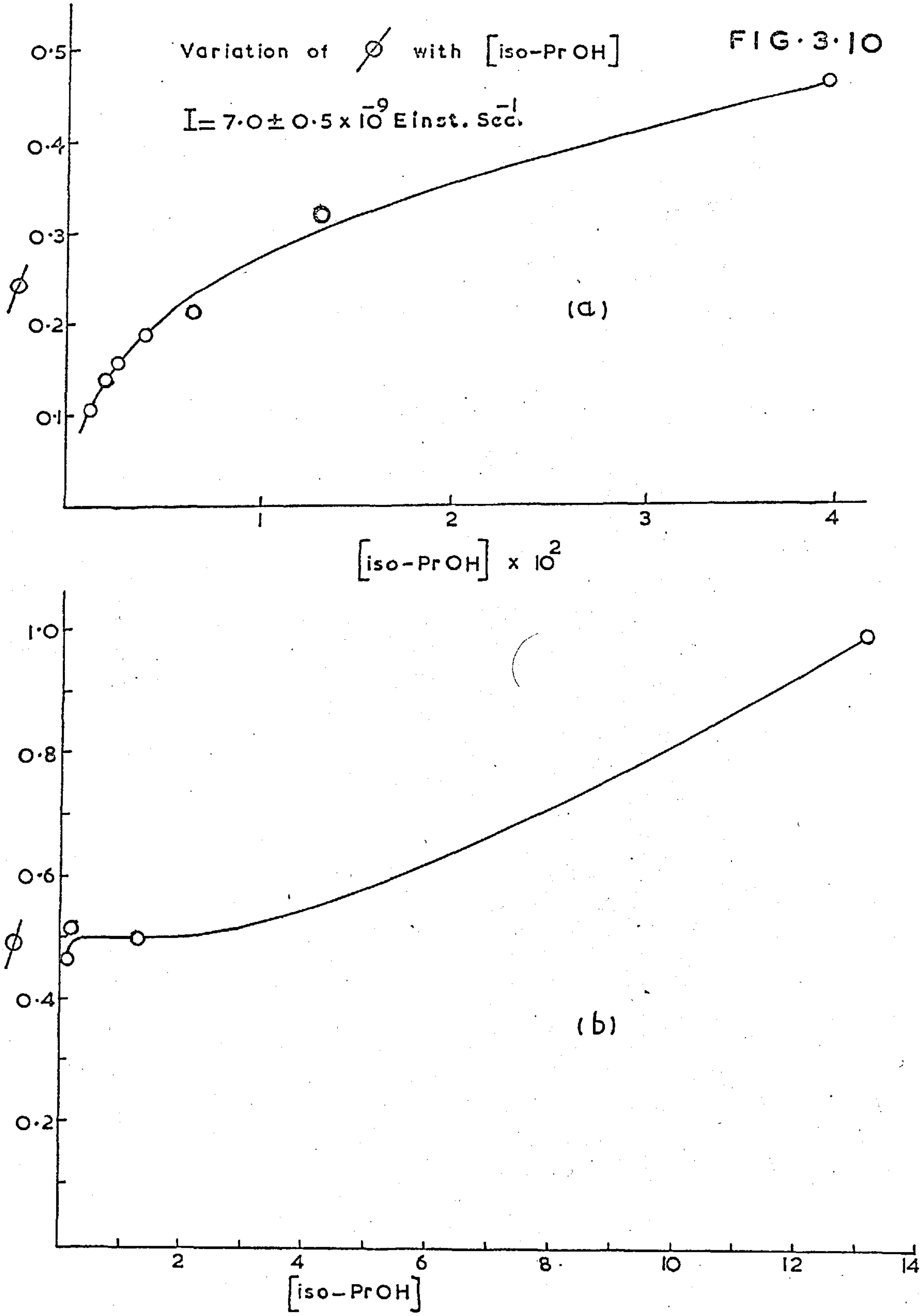

Variation of ∅ with [iso-PrOH]
I = 1·9 ± 0·2 x 10⁻⁹ Einst. Sec⁻¹
2·0
1·6
1·2
0·8
0·4
(∅ − ∅₀)/(∅₂ − ∅)
2
4
6
8
10
12
14
[iso-PrOH] x 10²

FIG·3·9

The results at light intensity, 7.0±0.5x10^{-9} einst. sec.$^{-1}$ are given in table 3.17. A graph of the quantum efficiency against alcohol concentration has been plotted in figs. 3.10 (a) and (b). It is clear from the above figs. that the quantum efficiency increases with increasing alcohol concentration from 0.118x10^{-2} to 9.17x10^{-2} mole l.$^{-1}$ In the range 9.17x10^{-2} to 1.31 mole l.$^{-1}$ alcohol the quantum efficiency appears to be constant. There is no dip in the graph at 1.31 mole l.$^{-1}$ alcohol in contrast to behaviour at light intensity, 1.8±0.4x10^{-9} einst. sec.$^{-1}$ (fig. 3.7). Above 1.31 mole l.$^{-1}$ alcohol the quantum efficiency in 100% alcohol is 1.00±0.05.

TABLE 3.17

iso-PrOH Mole l.$^{-1}$ x 10^2 i.e. $[AH_2]$ x10^2	I Einst. Sec.$^{-1}$ x 10^9	ϕ
13.1*	section 3.4.2	1.00±0.05
1.31*	7.56	0.502
9.17	7.17	0.515
3.93	6.98	0.465
1.31	6.70	0.319



FIG·3·10

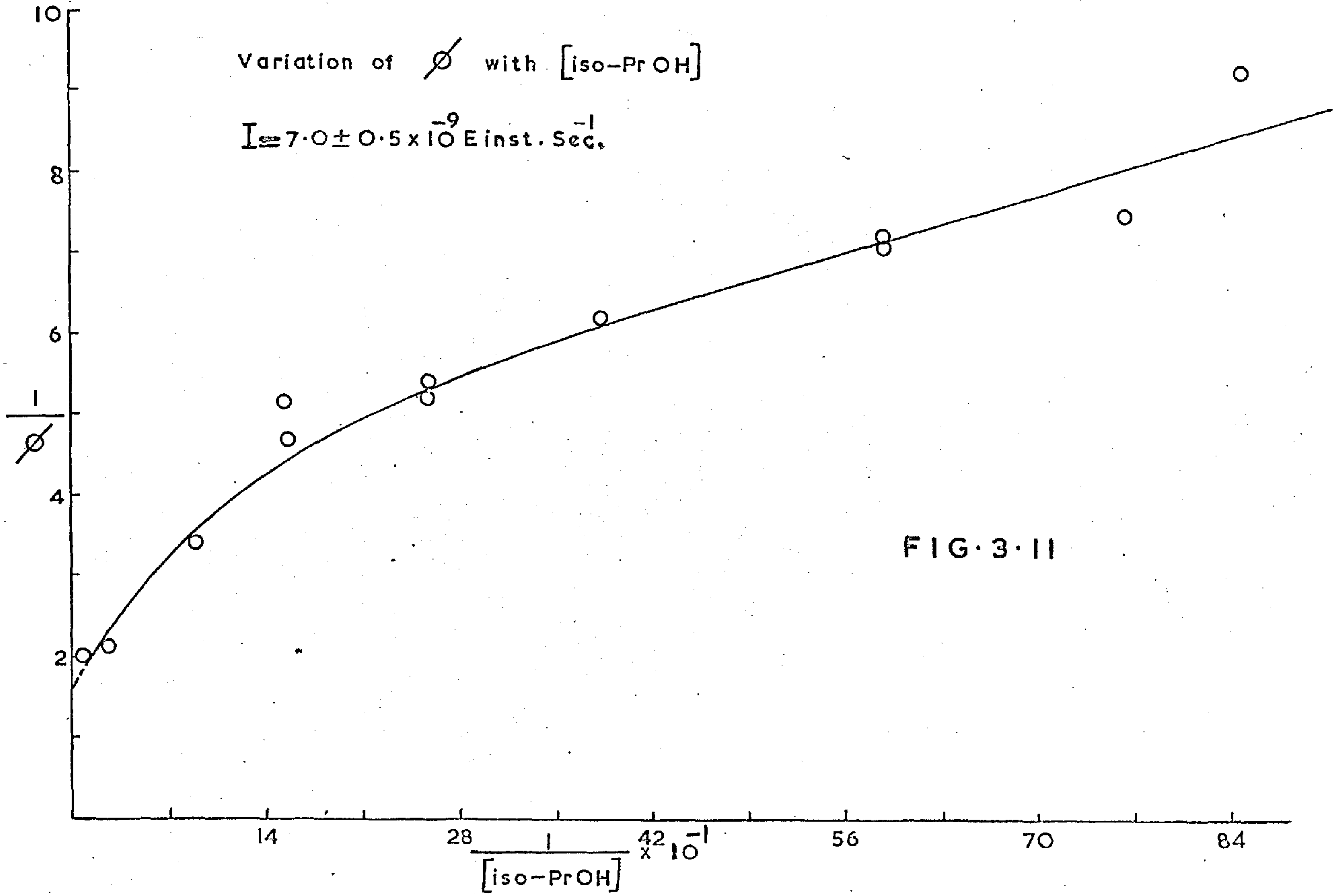
Variation of ϕ with [iso-PrOH]
$I = 7.0 \pm 0.5 \times 10^{-9}$ Einst. Sec.$^{-1}$
ϕ
0·1
0·2
0·3
0·4
0·5
1
2
3
4
(a)
[iso-PrOH] × 10^2
ϕ
0·2
0·4
0·6
0·8
1·0
2
4
6
8
10
12
14
(b)
[iso-PrOH]

Table 3.17 Contd.

iso-PrOH Mole $l.^{-1}$ $\times 10^2$ i.e. $[AH_2]$ x 10^2	I Einst. $Sec.^{-1}$ x 10^9	∅
0.655 0.655 0.655	7.59 7.30 6.91	0.186 0.213 0.193
0.393 0.393	6.94 6.73	0.192 0.186
0.262	6.86	0.162
0.170 0.170	6.64 6.15	0.141 0.140
0.131 0.118	6.81 6.22	0.134 0.108
0.0	For yields of $QH_2 > 10.0 \times 10^{-7}$ moles, the ∅ is probably less than (Section 3.2)	0.05

x $[AH_2]$ x 10^0

A graph of the reciprocal of quantum efficiency against the reciprocal of alcohol concentration for the above light intensity is plotted (fig. 3.11). A curve is obtained. Extrapolation to high alcohol concentration


Variation of Ø with [iso-PrOH]
I = 7·0 ± 0·5 x 10⁻⁹ Einst. Sec⁻¹
10
8
6
4
2
1/Ø
14
28
42
56
70
84
1/[iso-PrOH] x 10⁻¹

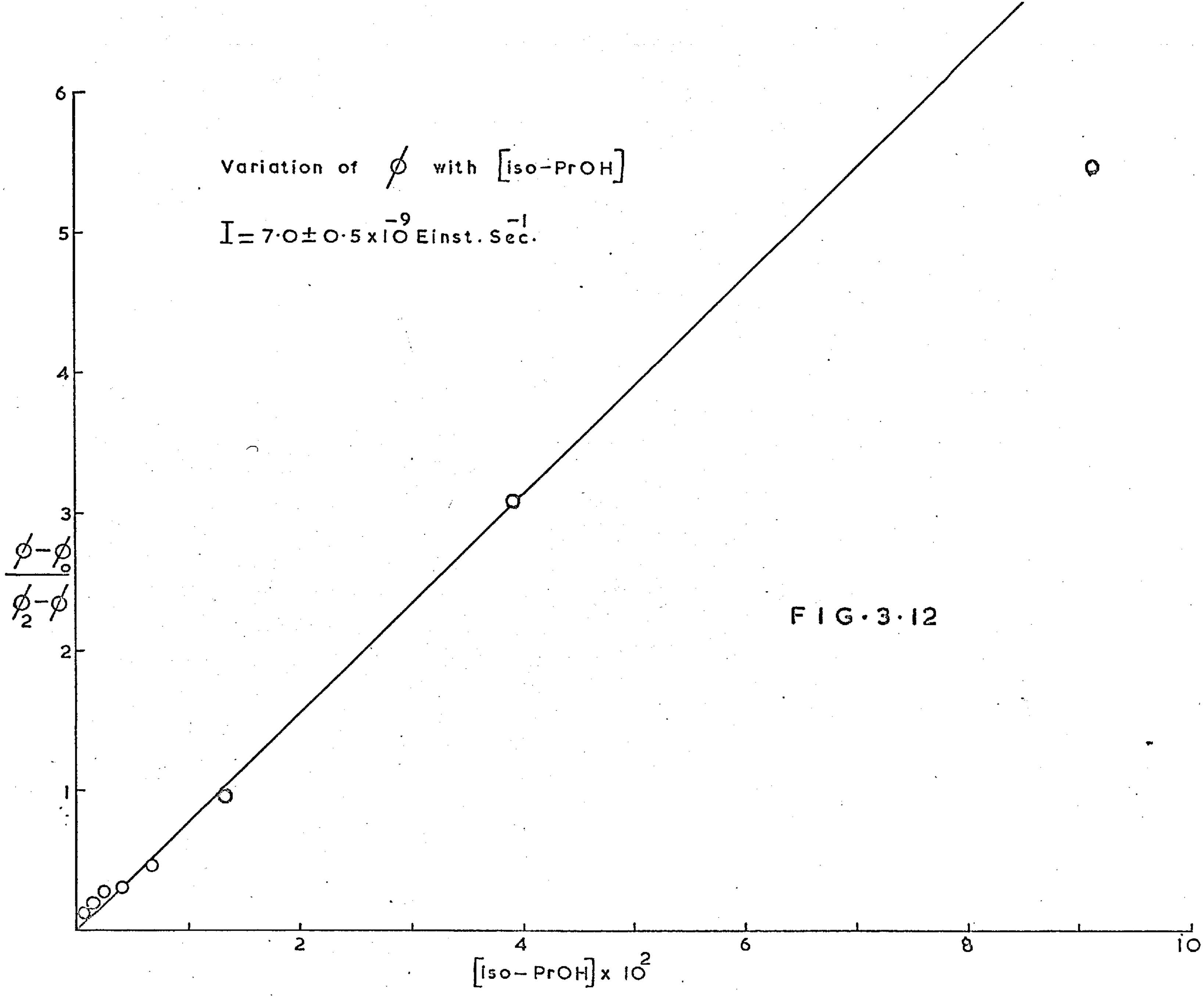
FIG·3·11

gives a quantum efficiency of 0.6 (ϕ_2). Table 3.18 shows the results that are plotted in fig. 3.11.

TABLE 3.18

iso-PrOH Mole $l.^{-1} \times 10^2$ i.e. $[AH_2] \times 10^2$	$\frac{1}{[AH_2]}$	I Einst. $Sec.^{-1}$ $\times 10^9$	ϕ	$\frac{1}{\phi}$
9.17	10.9	7.17	0.515	1.94
3.93	25.5	6.98	0.465	2.15
1.31	76.3	6.70	0.319	3.13
0.655	153.0	7.30	0.213	4.70
0.655	153.0	6.91	0.193	5.18
0.393	255.0	6.94	0.192	5.21
0.393	255.0	6.73	0.186	5.38
0.262	382.0	6.86	0.162	6.17
0.170	587.0	6.64	0.141	7.09
0.170	587.0	6.15	0.140	7.14
0.131	763.0	6.81	0.134	7.46
0.118	848.0	6.22	0.108	9.26

A graph of $\frac{\phi - \phi_0}{\phi_2 - \phi}$ against $[AH_2]$ is plotted in fig. 3.12 using the results given in table 3.19. Within the experimental error the points lie on a straight line.


Variation of ϕ with [iso-PrOH]

$I = 7{\cdot}0 \pm 0{\cdot}5 \times 10^{-9}$ Einst. Sec^{-1}

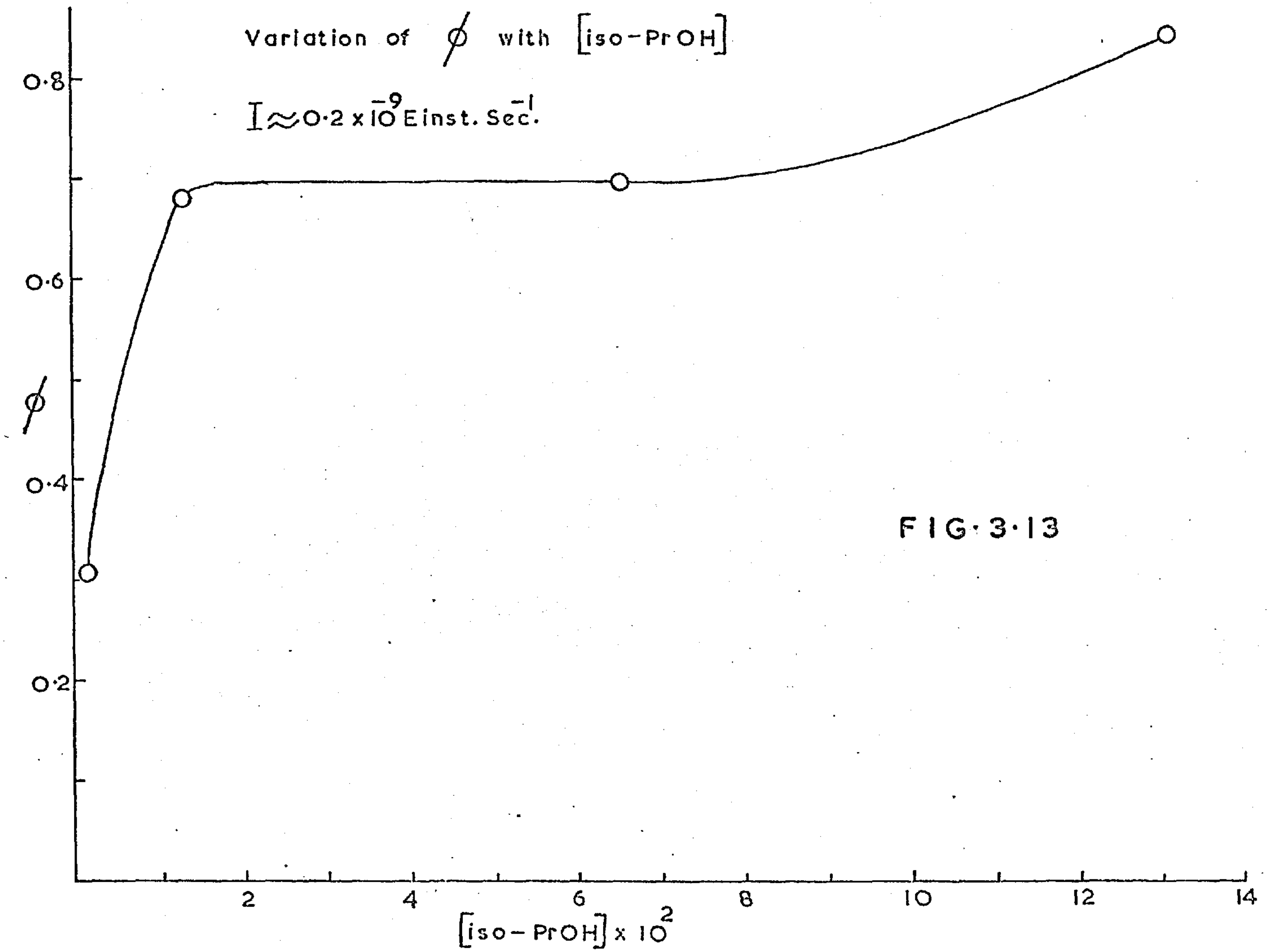
FIG·3·12

TABLE 3.19

iso-PrOH Mole l.$^{-1}$ x10^{2} i.e. $[AH_2]$ x10^{2}	I Einst. Sec.$^{-1}$ x 10^{9}	ϕ	$\frac{\phi - \phi_0^*}{\phi_2 - \phi}$
9.17	7.17	0.515	5.47
3.93	6.98	0.465	3.07
1.31	6.70	0.319	0.957
0.655	7.30	0.213	0.421
0.655	6.91	0.193	0.351
0.393	6.94	0.192	0.348
0.393	6.73	0.186	0.329
0.262	6.86	0.162	0.256
0.170	6.64	0.141	0.198
0.170	6.15	0.140	0.196
0.131	6.81	0.134	0.180
0.118	6.22	0.108	0.118

* $\phi_0 = 0.05$

The results at light intensity, $\approx$ 0.2x10^{-9} einst. sec.$^{-1}$ one given in table 3.20. A graph of the quantum efficiency against alcohol concentration is plotted in fig. 3.13. It shows that the quantum efficiency increases



Variation of ϕ with [iso-PrOH]

$I \approx 0{\cdot}2 \times 10^{-9}$ Einst. Sec^{-1}.

FIG·3·13

with increase in alcohol concentration from 0.0131 to 0.131 mole $l.^{-1}$ The quantum efficiency appears to be constant at a value of about 0.7 in the alcohol concentration range 0.131 to 0.655 mole $l.^{-1}$ Beyond 0.655 mole $l.^{-1}$ alcohol the quantum efficiency increases to 0.840 at 1.31 mole $l.^{-1}$ alcohol. . The quantum efficiency **in 100% iso-propyl alcohol** is 1.00±0.05.

TABLE 3.20

iso-PrOH Mole $l.^{-1}$ i.e. $[AH_2]$	I Einst. $Sec.^{-1}$ $\times 10^9$	ϕ
13.1	see section 3.4.2	1.00±0.05
1.31	0.205	0.840
0.655	0.223	0.694
0.131	0.188	0.680
0.0131	0.309	0.299
0.0	For yields of $QH_2 > 10.0\times10^{-7}$ moles, the ϕ is probably less than 0.05 (section 3.2)	

3.5. Methyl Alcohol

3.5.1. Thermal Reaction

During the study of reactions of toluquinone with methyl alcohol, tests were made to find out whether there was any thermal reaction. In this regard experiments were performed under the following conditions.

(i) Reaction in pure methyl alcohol in the atmosphere of nitrogen.

A run was carried out in which 40 ml of toluquinone solution (2.0×10^{-2} mole $l.^{-1}$) in pure methyl alcohol were left in the reaction vessel at 25.0°C for one hour, in the dark, with nitrogen passing through it using one solvent bubbler in the nitrogen flow line. Then 1.0 ml of the solution was mixed with 10.0 ml of reagent solution A (section 2.5.2) in a black conical flask. After one hour the optical density of the solution was measured against water at 510 mμ in one cm cells. It was found that the solution had the optical density > 2. This indicates a fast thermal reaction of toluquinone with pure methyl alcohol. Because of the fast thermal reaction, photochemical measurements in pure methyl alcohol, using the nitrogon method for removal of air were not carried out.

(ii) Reaction in pure methyl alcohol under vacuum.

A toluquinone solution (2.0×10^{-2} mole $l.^{-1}$) in pure methyl alcohol was prepared. The solution (40 ml) was degassed on a vacuum line using the apparatus shown in fig. 2.4. The procedure for degassing has been described in section 2.3.5. After the degassing the frozen stuff in the cylinder (fig. 2.4) was melted so that the solution could be irradiated after transferring it to the reaction vessel. As the melting of frozen stuff commenced, the cylinder (fig. 2.4) cracked. This may be due to the expansion when the frozen stuff starts melting. The experiment was repeated with a fresh solution of toluquinone (2.0×10^{-2} mole $1.^{-1}$) in pure methyl alcohol. The frozen stuff was melted slowly and carefully. In spite of care the cylinder (fig. 2.4) cracked as the melting started. Because of this difficulty a photochemical measurement in pure methyl alcohol using the vacuum method of degassing could not be carried out.

(iii) Reaction in solution of methyl alcohol in carbon tetrachloride.

Table 3.21 gives the amount of toluhydroquinone formed as a result of the thermal reaction in solutions of toluquinone in carbon tetrachloride containing methyl alcohol. The amount of toluhydroquinone in the toluquinone (analysis described in section 2.2.1) has also been shown in table 3.21. In these circumstances the blank was 10.0 ml of reagent solution A (section 2.5.2) to which no toluquinone had been added.

TABLE 3.21

Toluquinone ($2.0x10^{-2}$mole $1.^{-1}$) in Carbon Tetrachloride containing Methyl Alcohol

Hours After Preparation	Methyl Alcohol Mole $1.^{-1}$	Toluhydroquine Mole $1.^{-1}x10^{5}$
2.0	12.4	2.44 in air at 20°C in the dark
2.0	12.4	4.15≠
2.0	2.47	2.12 "
2.0	2.47	3.39≠
2.0	0.988	0.72 "
2.0	0.988	0.99≠
Amount of toluhydroquinone in toluquinone ≈0.90x10^{-5} mole $1.^{-1}$		

≠ Solutions were degassed on a vacuum line and kept in the thermostat at 25.0°C for half an hour.

Table 3.21 indicates that (i) there is no significant thermal reaction at alcohol concentration, 0.988 mole $1.^{-1}$, and (ii) some toluhydroquinone is produced in the solution of toluquinone in carbon tetrachloride containing 2.47 mole $1.^{-1}$ and 12.4 mole $1.^{-1}$methyl alcohol, whether the solution is kept in air at room temperature (20°C) in the dark or it is degassed on a vacuum line. Table 3.21 also shows that more of the toluhydroquinone is formed in the sample of solution which is degassed on a vacuum line.

In the photochemical measurements at 0.988 mole $1.^{-1}$alcohol and below the blank solution was prepared from a sample of the solution that had been kept in the dark, without degassing. When the concentration of alcohol in the solution was 2.47 mole $1.^{-1}$ or above, irradiated solution was analysed and the optical density was measured against water. Then a solution containing the same concentration of toluquinone and methyl alcohol in carbon tetrachloride was prepared and treated similarly, except that it was kept in the dark. The difference between the two optical densities was taken as optical density resulting from photochemical reaction.

3.5.2. Effect of Methyl Alcohol Concentration on Quantum Efficiency

Solutions of toluquinone in carbon tetrachloride containing methyl alcohol were irradiated in nitrogen using one solvent bubbler in the nitrogen flow line (section 2.2.6). The results are shown in table 3.22.

TABLE 3.22

Toluquinone (2.0x10^{-2} mole l.$^{-1}$) in Carbon Tetrachloride containing Methyl Alcohol, 365 mμ, 25.0°C

Methyl Alcohol Mole l.$^{-1}$	Time of Irrad. Seconds.	I Einst. Sec.$^{-1}$ x10^{9}	QH_2 Produced Moles x 10^{7}	ø
12.4	1800	3.63	74.4	1.14
12.4	1800	3.25	68.6	1.17
2.47	2700	3.27	84.5	0.957
2.47	1800	2.90	59.0	1.13
1.24	1800	3.05	56.8	1.03
0.741	1800	2.81	49.8	0.984
0.741	1800	2.74	46.7	0.947
0.494	2700	1.98	48.0	0.900
0.494	2700	1.78	47.3	0.982
0.247	3600	2.60	28.0	0.299
0.247	3600	2.74	61.6	0.624
0.148	3600	1.96	31.1	0.440
0.124	3600	2.10	26.5	0.352
0.0988	5400	3.32	34.4	0.192
0.0988	5400	3.29	38.5	0.216

It is clear from table 3.22 that the results are satisfactory in the concentration range 12.4 to 0.494 mole 1.$^{-1}$ alcohol. Below 0.494 mole 1.$^{-1}$ alcohol the results are irreproducible. Therefore, special attention was given to purification of the reactants. Frequent recalibration of light intensity was made. The solutions, used to purify 'oxygen free' nitrogen, were renewed very often.

After the purification of reactants the solutions of toluquinone in carbon tetrachloride containing methyl alcohol were irradiated in nitrogen using one solvent bubbler in the nitrogen flow line (section 2.2.6). The results are given in table 3.23.

TABLE 3.23

Toluquinone (2.0×10^{-2} mole 1.$^{-1}$) in Carbon Tetrachloride containing Methyl Alcohol, 365 mμ, 25.0°C

Methyl Alcohol Mole 1.$^{-1}$	Time of Irrad. Seconds	I Einst. Sec.$^{-1}$ x 10^9	QH_2 Produced Moles x 10^7	ø
1.24	1800	2.57	46.4	1.00
0.741	1800	2.35	40.3	0.953
0.494	1800	2.18	37.7	0.963
0.494	1800	2.18	36.7	0.935
0.346	1800	1.99	34.7	0.969
0.346	5400	2.04	69.5	0.630
0.346	5400	2.21	35.2	0.295
0.247	3600	2.18	20.9	0.267
0.247	5400	2.15	52.3	0.541

Table 3.23 also shows that the results at high concentrations from 1.24 to 0.494 mole $1.^{-1}$ alcohol are consistent. Below 0.494 mole $1.^{-1}$ alcohol the results are erratic.

The reason for inconsistent results was found as follows :

A solution of methyl alcohol, 0.346 mole $1.^{-1}$ in carbon tetrachloride was prepared. The infrared spectrum of a portion of this solution was recorded. The infrared spectrum of another portion of the solution was recorded after passing nitrogen, using one solvent bubbler in the nitrogen flow line (section 2.2.6), through the solution for 45 minutes and then over the surface of solution for $1\frac{1}{2}$ hours. When these spectra were compared, it was found that practically the whole of the methyl alcohol was lost from the portion that had been treated with nitrogen.

It will be seen later that the results in tables 3.22 and 3.23 below 0.494 mole $1.^{-1}$ alcohol are not only irreproducible but also the figures for the quantum efficiency are considerably lower than those obtained after degassing the solutions on a vacuum system (see section 3.5.3).

3.5.3 Effect of Methyl Alcohol Concentration and Intensity of Light on Quantum Efficiency

Solutions of toluquinone in carbon tetrachloride containing methyl alcohol were irradiated in vacuum. The results are shown in tables 3.24, 3.25 and 3.26.

TABLE 3.24

Toluquinone (2.0×10^{-2} mole $l.^{-1}$) in Carbon Tetrachloride containing Methyl Alcohol, 365 mμ, 25.0°C

Experiment	Methyl Alcohol Mole $l.^{-1}$	Time of Irrad. Seconds	I Einst. Sec.$^{-1}$ $\times 10^9$	QH_2 Produced Moles $\times 10^7$	ϕ
1	12.4	1800	1.82	44.4	1.12
2	2.47	900	3.16	36.0	1.11
3	2.47	1800	1.67	35.1	0.943
4	2.47	1800	1.62	32.6	0.857
5	2.47	7200	0.377	37.2	1.09
6	0.988	1800	2.86	54.7	1.07
7	0.988	9000	0.334	38.4	1.28
8	0.618	1800	3.09	55.3	0.995
9	0.618	9000	0.349	32.3	1.03
10	0.494	1800	2.65	46.0	0.967
11	0.494	1800	2.50	41.8	0.928
12	0.494	1800	1.83	39.7	1.20

The results given in tables 3.24, 3.25 and 3.26 lead to the following conclusions.

(a) Variation of quantum efficiency with light intensity.

The range of light intensity covered was from 0.01×10^{-9} to 3×10^{-9} einst. $sec.^{-1}$

(i) 12.4 mole $l.^{-1}$ alcohol

The effect of varying light intensity on the quantum efficiency was not studied. The value of quantum efficiency at light intensity, 1.8×10^{-9} einst. $sec.^{-1}$ is above one (1.12).

(ii) 2.47 mole $l.^{-1}$ alcohol

The light intensity was varied from 0.4×10^{-9} to 3×10^{-9} einst. $sec.^{-1}$ The results 2,3, 4 and 5 are not reproducible. The inconsistency may be due to the thermal reaction (section 3.5.1). It has been mentioned in section 3.1 that although the blank solution was also degassed on a vacuum line to allow for the thermal reaction yet it is very difficult to give the solutions exactly the same thermal treatment. Therefore, consideration will be given to data at alcohol concentration 0.988 mole $l.^{-1}$ and below. There was no significant thermal reaction in solutions of methyl alcohol not exceeding 0.988 mole $l.^{-1}$ (section 3.5.1).

(iii) 0.988 mole $l.^{-1}$ alcohol

Experiments 6 and 7 show that the quantum efficiency decreases when light intensity is increased from 0.3×10^{-9} to 2.9×10^{-9} einst. sec.$^{-1}$ The quantum efficiency is plotted against $\frac{1}{I^{\frac{1}{2}}}$ in fig. 3.14.

(iii) 0.618 mole l.$^{-1}$ alcohol

In the light intensity range 0.3×10^{-9} to 3×10^{-9} einst. sec.$^{-1}$ it is found that the quantum efficiency decreases with increasing light intensity.

(v) 0.494 mole l.$^{-1}$ alcohol

Experiments 10 and 11, when compared with 12 show that the quantum efficiency decreases with increase in light intensity from 1.8×10^{-9} to 2.7×10^{-9} einst. sec.$^{-1}$

TABLE 3.25

Toluquinone (2.0×10^{-2} mole l.$^{-1}$) in Carbon Tetrachloride containing Methyl Alcohol, 365 mμ, 25.0°C

Experiment	Methyl Alcohol Mole l.$^{-1}$	Time of Irrad. Seconds	I Einst. Sec.$^{-1}$ $\times10^{9}$	QH_2 Produced Moles $\times10^{7}$	Ø
13	0.395	1800	3.25	55.3	0.946
14	0.395	10800	0.374	41.6	1.03
15	0.346	1800	2.44	41.8	0.953
16	0.346	1800	1.77	34.8	1.10
17	0.321	1800	1.59	27.4	0.954
18	0.296	1800	1.49	24.6	0.916
19	0.296	1800	1.42	24.8	0.969

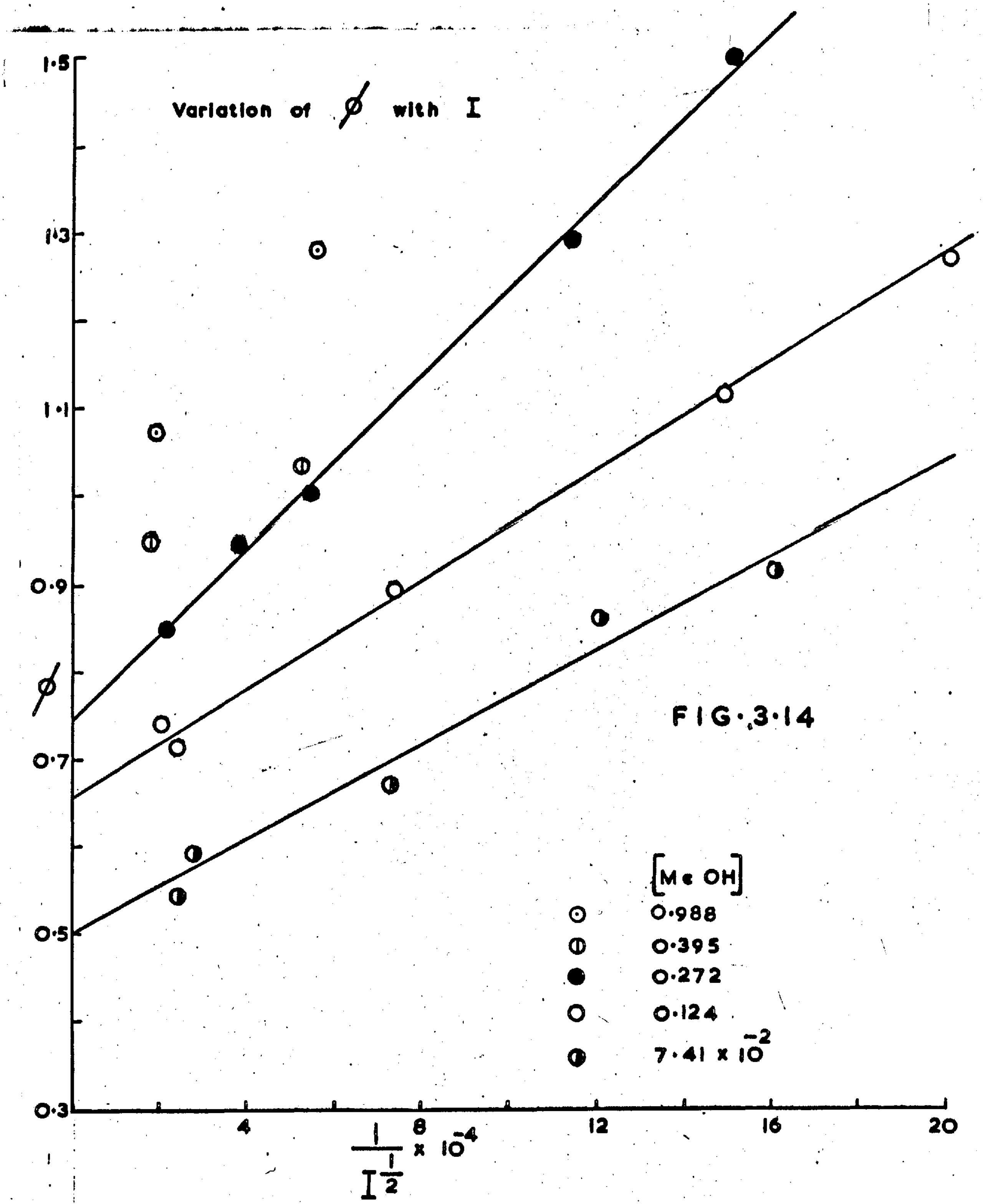

Variation of Ø with I

FIG. 3·14

Table 2.25 Contd.

Experiment	Methyl Alcohol Mole $l.^{-1}$	Time of Irrad. Seconds	I Einst. $Sec.^{-1}$ $x\ 10^{9}$	QH_2 Produced Moles $x10^{7}$	ϕ
20	0.272	1800	2.23	33.9	0.846
21	0.272	3600	0.676	23.0	0.946
22	0.272	7200	0.342	24.6	1.00
23	0.272	14400	0.077	14.4	1.29
24	0.272	10800	0.044	7.13	1.50
25	0.222	2700	1.68	41.2	0.908
26	0.198	3600	1.48	44.5	0.835
27	0.173	1800	2.52	35.3	0.779
28	0.173	10800	0.231	22.8	0.914
29	0.148	3600	1.77	44.4	0.696
30	0.124	1800	2.52	33.9	0.745
31	0.124	3600	1.72	44.3	0.714
32	0.124	10800	0.185	17.9	0.894
33	0.124	21600	0.045	10.7	1.11
34	0.124	21600	0.025	6.86	1.27

(vi) 0.395 mole $l.^{-1}$ alcohol

Experiments 13 and 14 indicate that the quantum efficiency decreases with increase in light intensity from $0.4x10^{-9}$ to $3x10^{-9}$ einst. $sec.^{-1}$ The quantum efficiency is plotted against $\frac{1}{I^{\frac{1}{2}}}$ in fig. 3.14.

(vii) 0.346 mole $l.^{-1}$ alcohol

The results, 15 and 16 obtained at light intensity $2.4x10^{-9}$ and $1.8x10^{-9}$ einst. $sec.^{-1}$ respectively suggest that the quantum efficiency decreases when the light intensity is increased.

(viii) 0.321 and 0.296 mole l.$^{-1}$ alcohol

The variation of quantum efficiency with light intensity was not studied.

(ix) 0.272 mole l.$^{-1}$ alcohol

In experiments 20 to 24 the range of light intensity covered was from 0.04x10^{-9} to 2x10^{-9} einst. sec.$^{-1}$ The results show that the quantum efficiency decreases with increasing light intensity. A graph of quantum efficiency against $\frac{1}{I^{\frac{1}{2}}}$ is plotted in fig. 3.14 and a straight line is obtained.

(x) 0.222 and 0.198 mole l.$^{-1}$ alcohol

The change in quantum efficiency through change in light intensity was not studied.

(xi) 0.173 mole l.$^{-1}$ alcohol

The results 27 and 28 show that there is decrease in the quantum efficiency with increase in light intensity from 0.2x10^{-9} to 2.5x10^{-9} einst. sec.$^{-1}$

TABLE 3.26

Toluquinone (2.0×10^{-2} mole l.$^{-1}$) in Carbon Tetrachloride containing Methyl Alcohol, 365 mμ, 25.0°C

Experiment	Methyl Alcohol Mole l.$^{-1}$ x 10^2	Time of Irrad. Seconds	I Einst. Sec.$^{-1}$ x 10^9	QH_2 Produced Moles x 10^7	ϕ
25	9.88	3600	1.71	39.3	0.639
36	9.88	3600	1.70	38.7	0.633
37	7.41	3600	1.73	33.5	0.538
38	7.41	5400	1.37	43.8	0.590
39	7.41	10800	0.192	13.8	0.666
40	7.41	18000	0.070	10.8	0.859
41	7.41	18000	0.039	6.41	0.913
42	6.92	2700	2.43	35.1	0.534
43	5.93	5400	1.58	37.3	0.437
44	4.94	3600	2.42	34.5	0.396
45	4.94	3600	2.26	36.3	0.445
46	4.94	86400	0.0125	5.42	0.502
47	3.95	3600	2.09	26.4	0.351
48	2.47	7200	1.57	32.3	0.285
49	1.24	7200	2.13	24.6	0.161
50	1.24	7200	2.10	22.3	0.147
51	0.618	5400	3.27	19.7	0.112
52	0.618	21600	0.356	8.57	0.112
53	0.247	7200	1.61	12.8	0.111
54	0.0	For yields of $QH_2 > 10.0$, the ϕ is probably less than 0.05 (section 3.2)			

(xii) 0.124 mole $l.^{-1}$ alcohol

Results 30 to 34 indicate that the quantum efficiency decreases with an increase in light intensity from 0.03×10^{-9} to 2.5×10^{-9} einst. $sec.^{-1}$ The quantum efficiency is plotted against $\frac{1}{I^{\frac{1}{2}}}$ in fig. 3.14 and a straight line is obtained.

(xiii) 9.88×10^{-2} mole $l.^{-1}$ alcohol

The effect of variation of light intensity on the quantum efficiency was not studied.

(xiv) 7.41×10^{-2} mole l^{-1} alcohol

In experiments 37 to 41 the light intensity range covered was from 0.04×10^{-9} to 1.7×10^{-9} einst. $sec.^{-1}$ The results indicate that the quantum efficiency decreases with increasing light intensity. The quantum efficiency is plotted against $\frac{1}{I^{\frac{1}{2}}}$ in fig. 3.14. Within the experimental error the points lie on a straight line.

(xv) 6.92×10^{-2} and 5.93×10^{-2} mole $l.^{-1}$ alcohol

The effect of varying light intensity on the quantum efficiency was not studied.

(xvi) 4.94×10^{-2} mole $l.^{-1}$ alcohol

Experiments 44 and 45, when compared with experiment 46 show that the quantum efficiency has been decreased by the increase in light intensity from 0.01×10^{-9} to to 2.4×10^{-9} einst. $sec.^{-1}$

(xvii) 3.95×10^{-2}, 2.47×10^{-2} and 1.24×10^{-2} mole $l.^{-1}$ alcohol

The variation of quantum efficiency with light intensity was not studied.

(xviii) 0.618×10^{-2} mole $l.^{-1}$ alcohol

Experiments 51 and 52 show that the quantum efficiency is independent of light intensity in the range 0.4×10^{-9} to 3×10^{-9} einst. $sec.^{-1}$

(xix) 0.247×10^{-2} mole $l.^{-1}$ alcohol

The effect of varying light intensity on the quantum efficiency was not studied.

(xx) Summary

There is thermal reaction above 2.47 mole $l.^{-1}$ alcohol. It is difficult to draw any conclusion from the results regarding the effect of light intensity on the quantum efficiency. From 0.988 mole l^{-1} to 0.247×10^{-2} mole $l.^{-1}$ alcohol the effect of light intensity on the quantum efficiency has been studied at different alcohol concentrations. The results show that above 0.618×10^{-2} mole $l.^{-1}$ alcohol the quantum efficiency is a function of light intensity. The trend is similar at all alcohol concentrations that the quantum efficiency decreases with increase in light intensity. The quantum efficiency is independent of light intensity at 0.618×10^{-2} mole $l.^{-1}$ alcohol.

Table 3.27 lists the results that are plotted in fig. 3.14. It is apparent from Fig. 3.14 that the value of the quantum efficiency at infinite light intensity increases with increase in alcohol concentration.

TABLE 3.27

MeOH Mole l.$^{-1}$ i.e. $[AH_2]$	I Einst. Sec.$^{-1}$ x 10^{9}	ϕ	$\frac{1}{I^{\frac{1}{2}}}$ x 10^{-4}
0.988	2.86	1.07	1.87
0.988	0.334	1.28	5.47
0.395	3.25	0.946	1.75
0.395	0.374	1.03	5.17
0.272	2.23	0.846	2.12
0.272	0.676	0.946	3.85
0.272	0.342	1.00	5.41
0.272	0.077	1.29	11.4
0.272	0.044	1.50	15.1
0.124	2.52	0.745	1.99
0.124	1.72	0.714	2.41
0.124	0.185	0.894	7.35
0.124	0.045	1.11	14.9
0.124	0.025	1.27	20.0
7.41*	1.73	0.538	2.40
7.41*	1.37	0.590	2.70
7.41*	0.192	0.666	7.22
7.41*	0.070	0.859	12.0
7.41*	0.039	0.913	16.0

* $[AH_2]$ x10^{2}

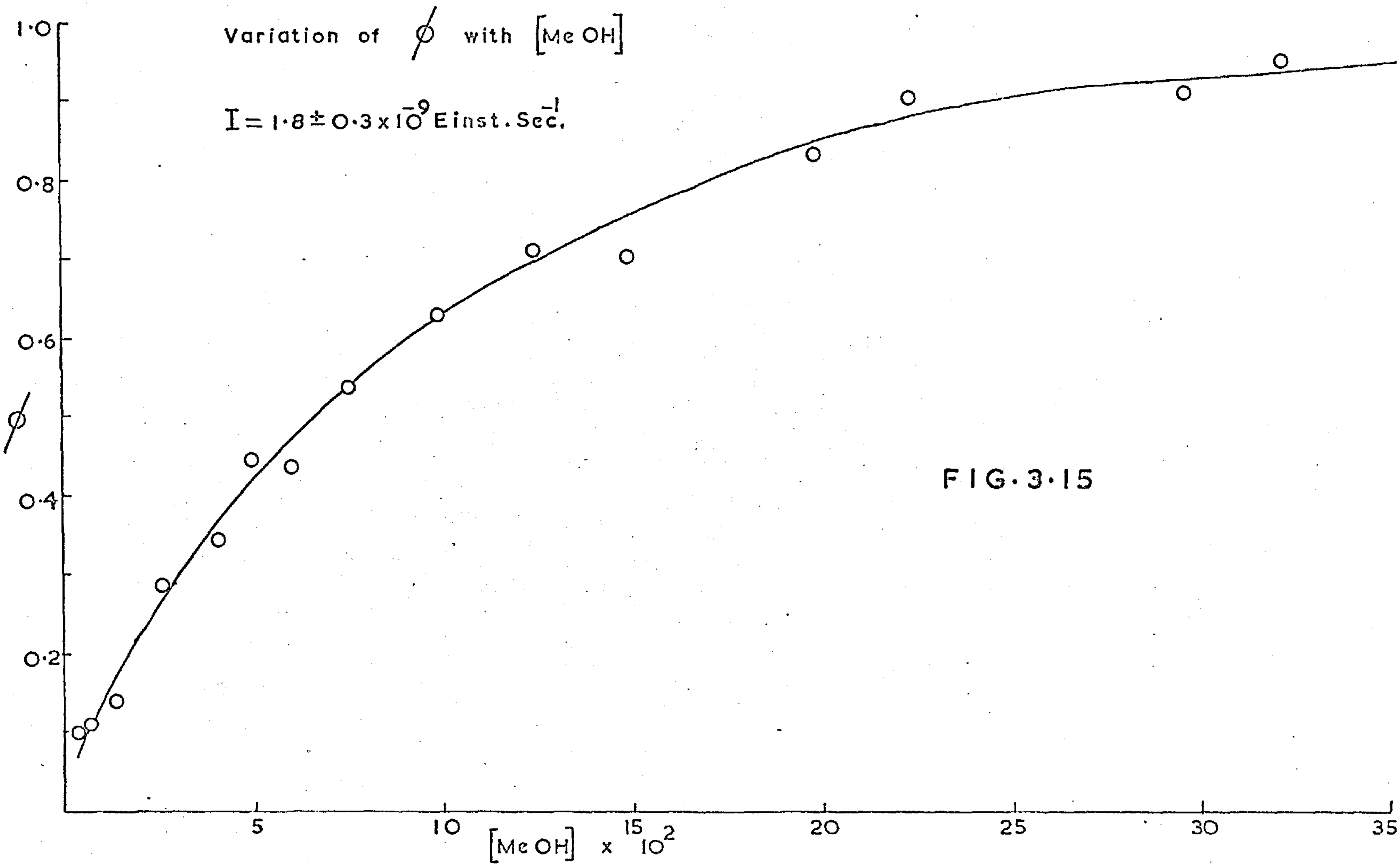
(b) Variation of quantum efficiency with alcohol concentration.

Tables 3.24, 3.25 and 3.26 show that the quantum efficiency is dependent on light intensity. Therefore, to study the effect of alcohol concentration on the quantum efficiency the results at different alcohol concentrations but at approximately constant light intensity ($1.8 \pm 0.3 \times 10^{-9}$ einst. sec.$^{-1}$) were considered. The results are given in table 3.28. The quantum efficiency is plotted against alcohol concentration in fig. 3.15.

TABLE 3.28

MeOH Mole $l.^{-1} \times 10^2$ i.e. $[AH_2^-] \times 10^2$	I Einst. Sec.$^{-1}$ $\times 10^9$	ϕ
32.1	1.59	0.954
29.6	1.49	0.916
22.2	1.68	0.908
19.8	1.48	0.835
14.8	1.77	0.696
12.4	1.72	0.714
9.88	1.70	0.633
7.41	1.73	0.538
5.93	1.58	0.437
3.95	2.09	0.351
2.47	1.57	0.285
1.24	2.10	0.147
0.247	1.61	0.111

It is clear from fig. 3.15 that the quantum efficiency increases with increase in alcohol concentration from 0.247×10^{-2} to



Variation of ϕ with [MeOH]

$I = 1{\cdot}8 \pm 0{\cdot}3 \times 10^{-9}$ Einst. Sec.$^{-1}$

FIG. 3.15

32.1×10^{-2} mole $l.^{-1}$ This trend of increasing quantum efficiency with increase in alcohol concentration also occurs from 32.1×10^{-2} to 0.988 mole $l.^{-1}$ Above 0.988 mole $l.^{-1}$ alcohol the thermal reaction is responsible for the irreproducibility of the results, as mentioned already in section 3.1.

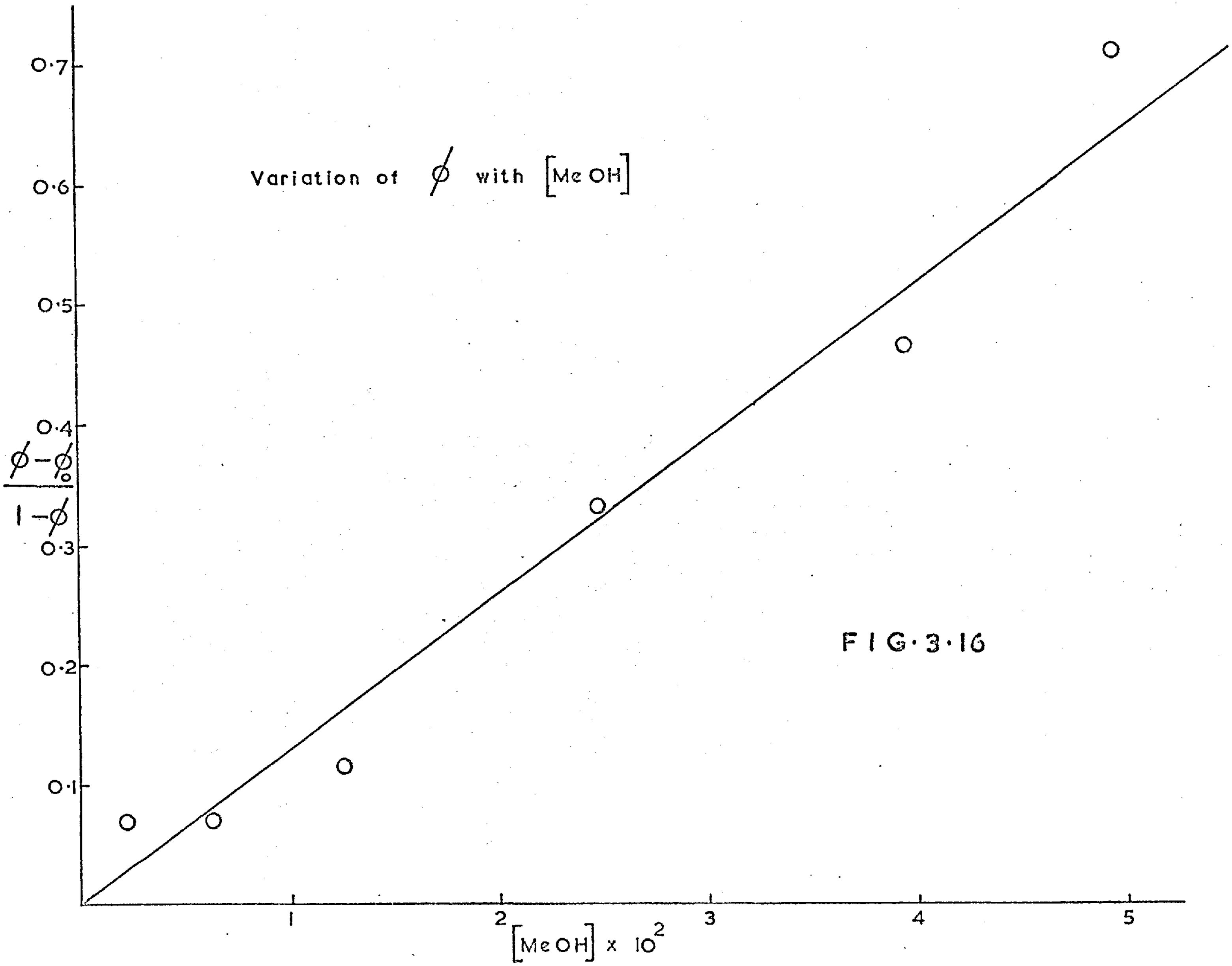
Taking $\phi_2 = 1$ and $\phi_0 = 0.05$ a graph of $\frac{\phi - \phi_0}{\phi_2 - \phi}$ against $[AH_2]$ is plotted in fig. 3.16 using the results shown in table 3.29. A straight line in the concentration range 0.247×10^{-2} to 4.94×10^{-2} mole $l.^{-1}$ alcohol is obtained.

TABLE 3.29

MeOH Mole $l.^{-1}$ x 10^2 i.e. $[AH_2]$ x10^2	I Einst. $Sec.^{-1}$ x 10^9	ϕ	$\frac{\phi - \phi_0}{\phi_2 - \phi}$
4.94	2.26	0.445	0.712
3.95	2.09	0.351	0.464
2.47	1.57	0.285	0.329
1.24	2.10	0.147	0.114
0.618	3.27	0.112	0.070
0.247	1.61	0.111	0.069

3.5.4. Effect of Toluquinone Concentration on Quantum Efficiency

Solutions with different concentrations of toluquinone in carbon tetrachloride containing methyl alcohol were



Variation of ϕ with [MeOH]

FIG·3·16

irradiated in vacuum. The results are shown in table 3.30.

TABLE 3.30

Toluquinone in Carbon Tetrachloride containing Methyl Alcohol, 365 mμ, 25.0°C

Toluquinone Mole. l.$^{-1}$ x 10^2	Methyl Alcohol Mole l.$^{-1}$	Time of Irrad. Seconds	I Einst. Sec.$^{-1}$ x10^9	QH_2 Produced Moles x10^7	ϕ
2.0	0.247	3600	1.72	54.0	0.874
6.0	0.247	1800	3.16	50.0	0.879
0.67	0.124	1800	1.60	23.6	0.818
6.0	0.124	1800	2.98	40.7	0.758

Table 3.30 indicates that the quantum efficiency is independent of toluquinone concentration.

4. DISCUSSION

4.1. Maximum Quantum Efficiency and Mechanism

Toluquinone is reduced to toluhydroquinone in the photochemical reaction with iso-propyl alcohol /Scrutton (31)7. In the systems described here, there was no evidence of formation of side products from the toluquinone. Atkinson and Di (1) detected the presence of a side product in the photochemical reactions of benzoquinone with ethyl and propyl alcohols. This side product was thought to be present in small quantities. No side product was observed by Scrutton (31) in the reaction of toluquinone with iso-propyl alcohol. It will be assumed that toluquinone is reduced to toluhydroquinone only. The product from methyl alcohol was formaldehyde. The product from iso-propyl alcohol was not analysed but it was assumed to be the same as in the corresponding reaction with benzoquinone i.e. acetone /Ciamician and Silber (22)7.

Evidence has been presented in section 1.1 that the photochemical reactions of quinones with alcohols proceed by a hydrogen atom transfer to the excited quinone. The reactive excited state may be either the triplet or the singlet state. First the relationship between maximum quantum efficiency and mechanism will be discussed for reactions initiated by the singlet state only.

(i) A maximum quantum efficiency of 0.5 will be given by the following sequence of reactions :

$$Q + h\nu \longrightarrow Q^{*}_{S}$$

$$Q^{*} + AH_2 \xrightarrow{k_2} QH + AH \qquad (2)$$

$$QH + QH \xrightarrow{k_8} Q + QH_2 \qquad (8)$$

$$AH + AH \xrightarrow{k_9} A + AH_2 \text{ or } (AH)_2 \qquad (9)$$

In this sequence free radicals are lost by bimolecular reactions between like radicals.

(ii) A maximum quantum efficiency of 1 will be obtained by the sequence :

$$Q + h\nu \longrightarrow Q^{*}_{S}$$

$$Q^{*}_{S} + AH_2 \xrightarrow{k_2} QH + AH \qquad (2)$$

$$QH + QH \xrightarrow{k_8} Q + QH_2 \qquad (8)$$

$$Q + AH \xrightarrow{k_{11}} QH + A \qquad (11)$$

Here the alcoholic radical, AH is reactive towards Q and reaction (9) is omitted. The product, A, must now be an aldehyde or a ketone depending on whether the alcohol is primary or secondary.

(iii) If reactions (2), (8), (9) and (11) all take place i.e.,

$$\begin{array}{lllllll} Q & + & h\nu & \longrightarrow & Q_S^* & & \\ Q_S^* & + & AH_2 & \xrightarrow{k_2} & QH & + AH & (2) \\ QH & + & QH & \xrightarrow{k_8} & Q & + QH_2 & (8) \\ AH & + & AH & \xrightarrow{k_9} & A & + AH_2 & (9) \\ Q & + & AH & \xrightarrow{k_{11}} & QH & + A & (11) \end{array}$$

the maximum quantum efficiency will be between 0.5 and 1. An increase in light intensity will move the quantum efficiency towards 0.5.

(iv) The quantum efficiency can be more than 1 if the processes involved are :

$$\begin{array}{llllllll} & Q & + & h\nu & \longrightarrow & Q_S^* & & \\ & Q_S^* & + & AH_2 & \xrightarrow{k_2} & QH & + AH & (2) \\ & QH & + & QH & \xrightarrow{k_8} & Q & + QH_2 & (8) \\ \text{or} & AH & + & AH & \xrightarrow{k_9} & A & + AH_2 & (9) \\ & Q & + & AH & \xrightarrow{k_{11}} & QH & + A & (11) \\ & QH & + & AH_2 & \xrightarrow{k_{12}} & QH_2 & + AH & (12) \end{array}$$

Reactions (11) and (12) provide the cycle of a chain reaction. The chain length will be large and the quantum efficiency will be more than 1 if reactions (8) and (9) become relatively unimportant. The chain length will decrease with increase in light intensity.

(v) A maximum quantum efficiency of 1 can also be obtained by the combination of processes :

$$Q + h\nu \longrightarrow Q_S^*$$

$$Q_S^* + AH_2 \xrightarrow{k_2} QH + AH \qquad (2)$$

$$AH + AH \xrightarrow{k_9} A + AH_2 \qquad (9)$$

$$QH + AH_2 \xrightarrow{k_{12}} QH_2 + AH \qquad (12)$$

Here the semiquinone, QH, is reactive towards alcohol. When the alcohol concentration is reduced, the quantum efficiency will decrease from the maximum value due to increasing influence from

$$QH + QH \xrightarrow{k_8} Q + QH_2 \qquad (8)$$

In the above discussion the reactive species has been assumed to be the singlet state. On the other hand if the reactive species is the triplet state, the maximum quantum efficiency will be given by

$$\phi_{max.} = \frac{k_{ST}}{k_{1S} + k_{ST}} \times n = m \times n$$

where,

n = 0.5 or 0.5-1 or 1 or unlimited as for the various mechanisms given above.

k_{ST} and k_{1S} are the rate constants for the reactions :

$$Q_S^* \xrightarrow{k_{ST}} Q_T^* \qquad (ST)$$

$$Q_S^* \xrightarrow{k_{1S}} Q \qquad (1S)$$

where,

Q_S^{*} Excited quinone in singlet state.

Q_T^{*} Excited quinone in triplet state.

Whichever of the excited states i~~n~~s reactive, lower values of quantum efficiency are obtained if quenching processes of the following types are involved:

$$Q^{*} + AH_2 \xrightarrow{k_3} Q + AH_2 \qquad (3)$$

$$Q^{*} + Q \xrightarrow{k_4} Q + Q \qquad (4)$$

$$Q^{*} + QH_2 \xrightarrow{k_5} Q + QH_2 \qquad (5)$$

In the present work the concentrations of quinone were not sufficiently high for reaction (4). For the present, reaction (5) will be left out of consideration, though it influences the photochemical reactions of duroquinone and chloranil [Scrutton (31)].

At low alcohol concentrations, the competition between

$$Q^{*} \xrightarrow{k_1} Q \quad \text{internal conversion} \qquad (1)$$

and $$\overset{*}{Q}+AH_2 \xrightarrow{k_2} QH+AH \qquad (2)$$

will lead to a fall in quantum efficiency. The efficiency of formation of semiquinone free radicals will be given by,

$$\phi_r = \frac{k_2 [AH_2]}{k_1 + k_2 [AH_2]} \qquad (4A)$$

It will be m times for reaction of the triplet state (for m see page 161).

Even when the alcohol concentration is high there can be some loss of quantum efficiency because of the cage effect. The cage effect of solvent can be expressed by the following equations :

$$Q^* + AH_2 \xrightarrow{k_{2A}} (QH \cdot AH) \qquad (2A)$$

$$(QH \cdot AH) \xrightarrow{k_{-2A}} Q + AH_2 \qquad (-2A)$$

$$(QH \cdot AH) \xrightarrow{k_{2B}} QH + AH \qquad (2B)$$

k_{-2A} refers to the recombination of free radicals in the solvent cage. The efficiency of formation of free radicals will be given by,

$$\phi_c = \frac{k_{2B}}{k_{2B} + k_{-2A}} \qquad (4B)$$

k_{2B} may depend on the molecular weight of the solvent molecule, being lower for heavy solvent molecule.

From equations (4A) and (4B) the overall efficiency of formation of semiquinone free radicals will be :

$$\phi_{rc} = \phi_r \phi_c$$

It will be m times for reaction of triplet state.

$$\therefore \quad \frac{1}{\phi_{rc}} = \frac{k_1}{\phi_c k_2[AH_2]} + \frac{1}{\phi_c}$$

The various different mechanisms, (i) to (v), pages 159 to 161 show how different relationships between ϕ_{rc} and the resultant ϕ_{QH_2} can arise. If ϕ_{QH_2} = constant x ϕ_{rc} (constant being 0.5 or 1), then a graph of $\frac{1}{\phi}$ against $\frac{1}{AH_2}$ will be a straight line at low alcohol concentrations and the quantum efficiency will be independent of light intensity.

On the other hand mechanisms of type (iii) and (iv) give a relation,

$$\phi_{QH_2} = f\,(I,\ AH_2,\ Q) \times \phi_{rc}$$

and each such system must be considered individually.

Carbon tetrachloride, solvent, gives a photochemical reaction with toluquinone and the product of reaction has been assumed to be toluhydroquinone (section 3.2). So the reaction will be written :

$$Q\ (+S) \xrightarrow{k_6} QH_2$$

There is no accurate way suitable for allowing for the reaction with carbon tetrachloride in the presence of alcohol. The contribution of reaction (6) decreases during a run because of inhibition of the reaction by toluhydroquinone. This possibly runs through the mechanism :

$$\begin{array}{lcl} Q^{*}(+S) & \longrightarrow & QH + x \\ QH+QH & \longrightarrow & Q + QH_2 \\ x + QH_2 & \longrightarrow & S + QH \end{array}$$

In the following sections reaction (6) will be included in the mechanism. Its contribution will be judged from extrapolation of results taken in the presence of alcohol. In general this leads to a quantum efficiency of about 0.05 for the reaction in pure carbon tetrachloride, a value corresponding to appreciable inhibition of the reaction by toluhydroquinone.

4.2. Reaction of Toluquinone with Cyclohexane

The photolysis of toluquinone in cyclohexane yields toluhydroquinone.

The maximum quantum efficiency in 100% cyclohexane (9.3 mole $l.^{-1}$) is 0.49±0.015, which is independent of toluquinone concentration and light intensity.

The fall in quantum efficiency from 0.49±0.015 to 0.35 when the concentration of cyclohexane is reduced from 100% to 10% with carbon tetrachloride, has been attributed to the cage effect (section 3.3). It cannot be caused by variation in k_1, the rate constant for internal conversion because already at 0.279 mole $l.^{-1}$ (3%) cyclohexane concentration the quantum efficiency has reached a steady value, corresponding to efficient reaction of the excited state with cyclohexane.

The fall in quantum efficiency at very low cyclohexane concentrations is that expected in a system in which internal conversion,

$$Q^{*} \xrightarrow{k_1} Q \qquad (1)$$

is competing with reaction,

$$Q^{*} + AH_2 \xrightarrow{k_2} QH+AH \qquad (2)$$

For the concentration range 27.9×10^{-2} to 0.93×10^{-2}

mole $l.^{-1}$ cyclohexane, values of $\frac{1}{\phi}$ have been plotted against $\frac{1}{[AH_2]}$ and a straight line is obtained (Fig.3.3).

There is also a reaction of toluquinone with carbon tetrachloride, apparently giving hydroquinone.

As the maximum quantum efficiency is about 0.5 and there is evidence for loss of efficiency by the cage effect in carbon tetrachloride the probable reaction mechanism is (i) of section 4.1 with the addition of allowance for the cage effect, and of reactions (1) and (6) at low cyclohexane concentration and for the reaction of toluquinone with carbon tetrachloride respectively. α is included to cover the possibility that two different excited singlet states are formed, one of which does not react. For cyclohexane α is one but it will be retained below to make the treatment generally applicable. The reactant is almost certainly the singlet state because it is unlikely that the triplet state could be formed with 100% efficiency. Because of the cage effect (see page 163), $k_2 = k_{2A}\ \phi_c$ where ϕ_c changes for major variations in the solvent composition. The mechanism is :

$$Q \quad + \quad h\nu \longrightarrow Q_S^{*} \quad \text{Rate} = \alpha\ [I]$$

$$Q_S^{*} \xrightarrow{k_1} Q \quad \text{internal conversion} \qquad (1)$$

$$\left.\begin{array}{l} Q_S^{*} + AH_2 \xrightarrow{k_{2A}\,\phi_c} QH + AH \\ Q_S^{*} + AH_2 \xrightarrow{k_{2A}(1-\phi_c)} Q + AH_2 \end{array}\right\} \quad (2)$$

$$Q_S^{*} \ (+S) \xrightarrow{k_6} QH_2 \qquad (6)$$

$$QH + QH \xrightarrow{k_8} Q+QH_2 \ ; \ -\frac{d[QH]}{dt} = k_8[QH]^2 \qquad (8)$$

$$AH + AH \xrightarrow{k_9} A+AH_2 \ ; \ -\frac{d[AH]}{dt} = k_9[AH]^2 \qquad (9)$$

$[I]$ is the light absorbed in einst. l.$^{-1}$ sec.$^{-1}$
Assuming a stationary concentration of Q^{*}

$$\alpha[I] = k_1[Q^{*}] + k_{2A}[Q^{*}][AH_2] + k_6[Q^{*}]$$

$$\therefore \quad [Q^{*}] = \frac{\alpha[I]}{k_1+k_6+k_{2A}[AH_2]} \qquad (4.2.1)$$

At a stationary concentration of QH radicals,

$$\frac{d[QH]}{dt} = 0 = k_{2A}\,\phi_c\,[Q^{*}][AH_2] - k_8[QH]^2$$

$$\text{or} \quad [QH]^2 = \frac{k_{2A}\phi_c\,[Q^{*}][AH_2]}{k_8} \qquad (4.2.2)$$

From reaction steps (6) and (8)

$$\frac{d[QH_2]}{dt} = k_6[Q^{*}] + \tfrac{1}{2}k_8[QH]^2 \qquad (4.2.3)$$

Substituting the values of $[Q^{*}]$ and $[QH]^2$ in equation (4.2.3)

$$\frac{d[QH_2]}{dt} = \frac{k_6\,\alpha[I]}{k_1+k_6+k_{2A}[AH_2]} + \frac{k_{2A}\phi_c\,\alpha[I]\,[AH_2]}{2(k_1+k_6+k_{2A}[AH_2])}$$

$$= \frac{(2k_6 + k_{2A}\,\phi_c\,[AH_2])\,\alpha[I]}{2(k_1+k_6+k_{2A}[AH_2])}$$

$$\phi = \frac{d\,[QH_2]}{dt} \Big/ [I] = \frac{(2k_6 + k_{2A}\,\phi_c\,[AH_2])\,\alpha}{2(k_1 + k_6 + k_{2A}\,[AH_2])} \qquad (4.2.4)$$

$$\text{When } [AH_2] = 0, \phi = \frac{k_6\,\alpha}{k_1 + k_6} = \phi_o \qquad (4.2.5)$$

$$\text{When } [AH_2] \text{ is high, } \phi_2 = \tfrac{1}{2}\,\alpha\,\phi_c \qquad (4.2.6)$$

From equation (4.2.4),

$$(k_1+k_6)\,\phi + k_{2A}\,[AH_2]\,\phi = k_6\alpha + \tfrac{1}{2}\,k_{2A}\,\phi_c\,\alpha\,[AH_2]$$

$$\text{or } \phi + \frac{k_{2A}}{k_1+k_6}\,[AH_2]\,\phi = \frac{k_6\alpha}{k_1+k_6} + \tfrac{1}{2}\,\phi_c\alpha\frac{k_{2A}}{k_1+k_6}\,[AH_2]$$

$$\text{or } \frac{\phi - \phi_o}{\frac{1}{2}\,\phi_c\alpha - \phi} = \frac{k_{2A}}{k_1 + k_6}\,[AH_2]$$

$$\text{or } \frac{\phi - \phi_o}{\phi_2 - \phi} = \frac{k_{2A}}{k_1+k_6}\,[AH_2] \qquad (4.2.7)$$

Where ϕ_2 is constant only if ϕ_c is constant. In pure cyclohexane, $\phi_2 = 0.49 \pm 0.015 = \frac{1}{2}\alpha\phi_c$. Thus $\alpha = 1$ and $\phi_c = 0.98 \pm 0.03$ for pure cyclohexane. In 0.279 to 0.93 mole $1.^{-1}$ cyclohexane in carbon tetrachloride, ϕ is constant at 0.35 and therefore $\phi = \phi_2 = 0.35$. With $\alpha = 1$, $\phi_c = 0.7$.

Taking $\phi_2 = 0.35$ and $\phi_o = 0.05$, a graph of $\frac{\phi - \phi_o}{\phi_2 - \phi}$ against $[AH_2]$ for 0 to 0.93 mole $1.^{-1}$ cyclohexane has been plotted in fig. 3.4. A straight line is obtained whose slope, $\frac{k_{2A}}{k_1+k_6} = 50.8 \text{ l. mole}^{-1}$.

It is important now to consider whether or not the values of ϕ_c given above are reasonable. In pure cyclohexane $\phi = 0.49 \pm 0.015$. Taking the lowest permitted value, 0.47 for ϕ_2, $\phi_c = 0.94$. This can be written as:

$$\phi_c = \frac{\frac{k_{2B}}{k_{-2A}}}{\frac{k_{2B}}{k_{-2A}} + 1} = 0.94$$

from which, $\frac{k_{2B}}{k_{-2A}} = 15.8$.

k_{2B} is dependent on the molecular weight of the solvent molecule, being lower for heavy solvent molecule. The molecular weight of carbon tetrachloride is 1.83 times that of cyclohexane. Therefore, it may be assumed that the value of k_{2B} in carbon tetrachloride solution will be about half the value in pure cyclohexane.

When $\frac{k_{2B}}{k_{-2A}}$ is halved, ϕ_c will be given as :

$$\phi_c = \frac{7.9}{7.9+1} = 0.88$$

$$\therefore \quad \phi_2 = 0.44 \qquad (\alpha = 1)$$

Experimental results show that at 0.279 mole l^{-1} cyclohexane in carbon tetrachloride $\phi_c = 0.7$. This corresponds to a value for $\frac{k_{2B}}{k_{-2A}}$ of 2.33. A change in the ra~~d~~tio, $\frac{k_{2B}}{k_{-2A}}$ from 15.8 to 2.33 for a change from pure cyclohexane to solution in carbon tetrachloride is not reasonable. As shown above a change from 15.8 to 7.9 would be reasonable, though even then the 15.8 is derived by using the lowest permissible value for ϕ_2 in cyclohexane.

Thus it is desirable to consider an alternative mechanism in which the maximum quantum efficiency is 1 and the value of about 0.5 in pure cyclohexane arises because the cage effect is already reducing ϕ in that solvent. The alternative mechanism is (ii) of section 4.1 with the addition of allowance for the cage effect, internal conversion [reaction (1)], and reaction (6), the reaction with solvent.

$$Q + h\nu \xrightarrow{\qquad} Q_S^{*} \quad \text{Rate} = \alpha\,[I]$$

$$Q_S^{*} \xrightarrow{k_1} Q \quad \text{internal conversion} \qquad (1)$$

$$\left.\begin{aligned} Q_S^{*} + AH_2 &\xrightarrow{k_{2A}\,\phi_c} QH + AH \\ Q_S^{*} + AH_2 &\xrightarrow{k_{2A}(1-\phi_c)} Q + AH_2 \end{aligned}\right\} \qquad (2)$$

$$Q_S^{*}\ (+S) \xrightarrow{k_6} QH_2 \qquad (6)$$

$$QH + QH \xrightarrow{k_8} Q + QH_2 ;\ -\frac{d\,[QH]}{dt} = k_8\,[QH]^2 \qquad (8)$$

$$Q + AH \xrightarrow{k_{11}} QH + A \qquad (11)$$

By applying the stationary state treatment,

$$\phi = \frac{(k_6 + k_{2A}\,\phi_c\,[AH_2])\,\alpha}{k_1 + k_6 + k_{2A}\,[AH_2]} \qquad (4.2.8)$$

when $[AH_2] = 0$, $\phi = \dfrac{k_6\alpha}{k_1+k_6} = \phi_o = 0.05$

when $[AH_2]$ is high, $\phi_2 = \phi_c\alpha$

In pure cyclohexane, $\phi_2 = 0.49 \pm 0.015 = \phi_c\alpha$

With $\alpha = 1$, $\phi_c = 0.49 \pm 0.015$.

From 0.279 to 0.93 mole $l.^{-1}$ cyclohexane, ϕ is constant at 0.35 and therefore $\phi = \phi_2 = 0.35$. With $\alpha = 1, \phi_c = 0.35$.

From equation (4.2.8) and substituting for ϕ_o and ϕ_2 we get,

$$\frac{\phi - \phi_o}{\phi_2 - \phi} = \frac{k_{2A}}{k_1+k_6}[AH_2]$$

Again from fig. 3.4, $\dfrac{k_{2A}}{k_1+k_6} = 50.8$ l. mole^{-1}

As the value of k_6 is small, the ratio $\dfrac{k_{2A}}{k_1+k_6}$ is close to tho ratio between the rate constant for reaction of the excited state and that for internal conversion. The significance of the figures obtained will be discussed later.

The values of ϕ_c derived from this second mechanism must now be examined to see if they are reasonable.

In pure cyclohexane,

$$\phi_c = 0.49, \quad \frac{k_{2B}}{k_{-2A}} = 0.96$$

At 0.279 mole $l.^{-1}$ cyclohexane in carbon tetrachloride,

$\phi_c = 0.35$

This will correspond to a value of 0.54 for $\frac{k_{2B}}{k_{-2_A}}$.

Reduction of the ratio from 0.96 in pure cyclohexane to 0.54 in carbon tetrachloride solution is reasonable. Hence the more likely mechanism for the reaction of toluquinone with cyclohexane is the second one given above. The key step in this mechanism is,

$$Q + AH \xrightarrow{k_{11}} QH + A \qquad (11)$$

in which radicals, AH are lost by reaction with quinone.

Inclusion of reaction step (11) in the scheme is not unusual. Pitts, Jr. and co-workers (60) propose this type of reaction in the mechanism for photolysis of benzophenone in iso-propyl alcohol. As a result of reaction between the alcoholic free radical and the benzophenone the quantum efficiency for formation of acetone is close to one. Bolland and Cooper (7) include a reaction of this type in the mechanism proposed for the autoxidation of ethyl alcohol photosensitized by anthraquinone - 2:6- disulphonate.

4.3. Reaction of Toluquinone with iso-Propyl Alcohol

The maximum quantum efficiency in 100% iso-propyl alcohol is about 1, and it does not appear to be dependent on toluquinone concentration or light intensity. The product, toluhydroquinone does not retard the photolysis of toluquinone in pure iso-propyl alcohol.

There is no retardation of the reaction by toluhydroquinone at 1.31, 0.131 and 0.0131 mole $l.^{-1}$ iso-propyl alcohol in carbon tetrachloride.

In the solutions of iso-propyl alcohol in carbon tetrachloride, the effect of light intensity on the quantum efficiency is very complicated.

The experimental resultscorrespond to the following three light intensities :

(i) medium, $1.8 \pm 0.4 \times 10^{-9}$ einst. $sec.^{-1}$
(ii) low, $\approx 0.2 \times 10^{-9}$ einst. $sec.^{-1}$
(iii) high, $7.0 \pm 0.5 \times 10^{-9}$ einst. $sec.^{-1}$

Fig. 3.7 is a graph of quantum efficiency against alcohol concentration at medium light intensity. This shows that the quantum efficiency increases with increase in alcohol concentration to a figure of 0.5 at 0.131 mole $l.^{-1}$ alcohol. A most unexpected feature is that beyond 0.131 mole $l.^{-1}$ alcohol there is a minimum at 1.31 mole $l.^{-1}$ alcohol in this graph.

Fig. 3.8 shows that in the range 0.0393 to 0.131 mole l.$^{-1}$ alcohol the reciprocal of quantum efficiency varies linearly with the reciprocal of alcohol concentration. The straight line extrapolates to the quantum efficiency, 0.714, which may be regarded as the quantum efficiency that would be observed at about 1.31 mole l.$^{-1}$ alcohol and above if it were not for two additional features in the behaviour of the reaction. One feature is the minimum mentioned above. The other is the increase in quantum efficiency to about 1 in going from 50% to 100% alcohol.

When the results at medium light intensity are compared with those at low light intensity, ≈ 0.2×10^{-9} einst. sec.$^{-1}$ it can be seen (fig. 3.6 and table 3.11) that except at 0.0131 mole l.$^{-1}$ alcohol the quantum efficiency increases with decrease in light intensity. The results at low light intensity indicate that the quantum efficiency levels off at a figure of about 0.7 (fig 3.13) in the range of alcohol concentration, 0.131 to 0.655 mole l.$^{-1}$ This is the same asymptote as for ≈ 2×10^{-9} einst. sec.$^{-1}$ intensity but it is reached at a lower alcohol concentration.

The results at high light intensity, $7.0 \pm 0.5 \times 10^{-9}$ einst. sec.$^{-1}$ have been plotted in fig. 3.10.

This shows that the quantum efficiency rises asymptotically with increase in alcohol concentration to a figure of above 0.5 at 0.0917 mole $l.^{-1}$ Although the asymptote for this range of concentration is not above 0.6 (see fig.3.11), there is a further rise to a quantum efficiency of about 1 in undiluted iso-propyl alcohol.

An unexpected feature of results at high light intensity is that the quantum efficiencies are slightly higher than those at medium light intensities. Thus the trend observed from 0.2×10^{-9} to 2×10^{-9} einst. $sec.^{-1}$ is not continued up to 7×10^{-9} einst. $sec.^{-1}$ No explanation for this change in trend has been found.

As mentioned above the extrapolated values of quantum efficiency in dilute solution rise asymptotically to values of less than one. This may be attributed to the loss of quantum efficiency by the cage effect. In undiluted iso-propyl alcohol the quantum efficiency is close to one, indicating that the cage effect then has little importance.

The mechanism may be similar to that given on pages 167 & 168 with the addition of reaction,

$$QH + AH_2 \xrightarrow{k_{12}} QH_2 + AH \qquad (12)$$

which allows the quantum efficiency to rise above 0.5 and introduces a variation of quantum efficiency with light intensity.

It will be seen that this mechanism does not explain many features of the results but it provides a basis for discussion. It is the mechanism found by Atkinson and Di (1) to fit the results on the photochemical reactions of benzoquinone with alcohols. The mechanism is :-

$$
\begin{array}{llll}
Q + h\nu & \xrightarrow{\qquad} & Q_S^{*} \quad \text{Rate} = \alpha[I] & \\
Q_S^{*} & \xrightarrow{k_1} & Q \quad \text{internal conversion} & (1) \\
Q_S^{*} + AH_2 & \xrightarrow{k_{2A}\,\phi_c} & QH + AH & \multirow{2}{*}{\Big\}\ (2)} \\
Q_S^{*} + AH_2 & \xrightarrow{k_{2A}\,(1-\phi_c)} & Q + AH_2 & \\
Q_S^{*}\ (+S) & \xrightarrow{k_6} & QH_2 & (6) \\
QH+QH & \xrightarrow{k_8} & Q + QH_2 ; -\dfrac{d[QH]}{dt} = k_8[QH]^2 & (8) \\
AH+AH & \xrightarrow{k_9} & A+AH_2 ; -\dfrac{d[AH]}{dt} = k_9[AH]^2 & (9) \\
QH+AH_2 & \xrightarrow{k_{12}} & QH_2 + AH & (12)
\end{array}
$$

By applying the stationary state treatment we obtain,

$$
\frac{\phi-\phi_o}{\phi_2-\phi} = \frac{k_{2A}}{k_1+k_6}\left[AH_2\right] - \frac{k_8}{2k_{12}^2}\cdot\frac{k_{2A}^2}{(k_1+k_6)^2}\cdot\frac{[I]}{\left(1+\dfrac{k_{2A}[AH_2]}{k_1+k_6}\right)^2}\cdot\frac{\phi_2^2}{\phi_2-\phi} \tag{4.3.1}
$$

where,

$\phi_o = \dfrac{k_6\,\alpha}{k_1+k_6} = 0.05$, the quantum efficiency for reaction with carbon tetrachloride.

$\phi_2 = \phi_c \alpha$, the value of quantum efficiency at high values of $\dfrac{[AH_2]^2}{[I]}$.

According to equation (4.3 .1) a graph of $\dfrac{\phi - \phi_0}{\phi_2 - \phi}$ against $[AH_2]$ at very low light intensity should be a straight line. There will be deviations in this relation with the increase in light intensity, because the significance of second term in the equation will increase with increase in light intensity.

Taking $\phi_2 = 0.714$ (from fig. 3.8) and $\phi_0 = 0.05$, the results at medium light intensity, $1.9 \pm 0.2 \times 10^{-9}$ einst. sec.$^{-1}$ are plotted in the form $\dfrac{\phi - \phi_0}{\phi_2 - \phi}$ against $[AH_2]$ in fig. 3.9. The points lie on a straight line with the exception of one at 0.0131 mole l.$^{-1}$ alcohol, the ratio, $\dfrac{k_{2A}}{k_1 + k_6} = 16.7$ l. mole.$^{-1}$ Points above 0.131 mole l.$^{-1}$ alcohol have been excluded because they obviously fall low (see above). The point plotted for 0.0131 mole l.$^{-1}$ alcohol is at a light intensity of 2.5×10^{-9} einst. sec.$^{-1}$ and this may be partly responsible for it not lying on the line. However it must be accepted that results at low alcohol concentrations may deviate from the line.

At low light intensity, 0.3×10^{-9} einst. sec.$^{-1}$, there is one measurement at 0.0131 mole $l.^{-1}$ alcohol which gives a quantum efficiency sufficiently below the asymptote for it to be used in calculating $\frac{k_{2A}}{k_1+k_6}$. This ratio was calculated according to the relation,

$$\frac{k_{2A}}{k_1+k_6} = \frac{\phi - \phi_o}{\phi_2 - \phi} \times \frac{1}{[AH_2]} \qquad (4.3.2)$$

taking $\phi_2 = 0.714$, $\phi_o = 0.05$ and ϕ at 0.0131 mole $l.^{-1}$ alcohol, 0.299 (see table 3.10). The value of $\frac{k_{2A}}{k_1+k_6}$ is 46 l. $mole.^{-1}$

However it has been mentioned above that this measurement must be regarded with suspicion. It is possible that ϕ is low, in which case the value of the ratio will be above 46 l. $mole.^{-1}$

The results at high light intensity, $7.0 \pm 0.5 \times 10^{-9}$ einst. $sec.^{-1}$, plotted in fig. 3.12, taking $\phi_2 = 0.6$ and $\phi_o = 0.05$, give $\frac{k_{2A}}{k_1+k_6} = 78.6$ l. $mole.^{-1}$ The plot is linear within experimental error and is applicable to alcohol concentrations below 0.131 mole $l.^{-1}$

It is possible to make a rough assessment of the value of $\frac{k_{12}}{k_8^{\frac{1}{2}}}$ by fitting equation 4.3.1 to points at the two lower light intensities and at 0.131 mole $l.^{-1}$ alcohol. With $\frac{k_{2A}}{k_1+k_6} = 46.0$ l. $mole.^{-1}$, $\phi_2 = 0.714$ and $\phi_o = 0.05$, the value obtained for $\frac{k_{12}}{k_8^{\frac{1}{2}}}$ is 76.0×10^{-5} $l.^{\frac{1}{2}}$ $mole^{-\frac{1}{2}}$ $sec.^{-\frac{1}{2}}$

(i) The mechanism does not explain the low value of quantum efficiency at medium light intensity at 1.31 mole $l.^{-1}$ alcohol.

(ii) It does not provide an explanation for the slight increase in the quantum effifiency in going from medium to higher light intensities.

(iii) In strong alcohol solutions it would give an asymptotic value of quantum efficiency independent of light intensity. The results at medium and low intensities lead to the asymptote of about 0.7. The asymptote at high intensity is lower at 0.6.

(iv) Above the asymptote the quantum efficiency should vary with ϕ_c (page 163) but be independent of light intensity. In 100% iso-propyl alcohol ϕ_c is one and the quantum efficiency is independent of light intensity. Because of the fast thermal reaction it was not possible to carry out accurate measurements at very high concentrations of alcohol.

The best test of the mechanism would be to fit the results quantitatively to the equation showing the variation of quantum efficiency with light intensity /Atkinson and Di (1)/. When looked at over the whole range of light intensity equation 4.3.1 does not hold properly though qualitatively the results in certain ranges follow the same pattern.

(v) According to the mechanism the graph of $\frac{\phi - \phi_0}{\phi_2 - \phi}$ against $[AH_2]$ should be a straight line at low light intensity. It is interesting to note that the results at high light intensity also give the same relationship, though the slope changes with light intensity as predicted.

To understand the behaviour of the system further work is required. When it was found that the photochemical reactions of toluquinone with methyl alcohol obey a simple theory it was considered worthwhile to divert attention towards the study of that system.

In the discussion of this system the association of methyl alcohol molecules in carbon tetrachloride will be considered. It is worthwhile to mention here, that for 0.136 mole $l.^{-1}$ iso-propyl alcohol in carbon tetrachloride the concentration of monomer is 0.120 mole $l.^{-1}$ The results that have been used above in trying to fit a mechanism are taken at concentrations below 0.136 mole $l.^{-1}$ alcohol.

4.4. Reaction of Toluquinone with Methyl Alcohol

The maximum quantum efficiency is above 1, which indicates that the reaction takes place by a chain process.

The fall in quantum efficiency at very low alcohol concentrations in the range 1.24×10^{-2} to 0.247×10^{-2} mole $l.^{-1}$ can be explained by the usual assumption that the internal conversion,

$$Q^{*} \xrightarrow{k_1} Q \qquad (1)$$

is competing with reaction,

$$Q^{*} + AH_2 \xrightarrow{k_2} QH+AH \qquad (2)$$

A quantum efficiency above 0.5 can be explained by introduction of either of the following two reactions :

$$Q + AH \xrightarrow{k_9} QH + A \qquad (9)$$

$$QH + AH_2 \xrightarrow{k_{12}} QH_2 + AH \qquad (12)$$

(see mechanisms (ii) and (v) of section 4.1)

When the quantum efficiency is above 1, both the above reactions must be included in the scheme. It will be shown that the results can be fitted without the assumption of any loss of quantum efficiency through the cage effect. Therefore the reaction mechanism is (iv) of section 4.1 including the reactions (1), internal conversion and (6), for reaction with solvent.

$$Q + h\nu \longrightarrow Q_S^* \qquad \text{Rate} = \alpha[I]$$

$$Q_S^* \xrightarrow{k_1} Q \quad \text{internal conversion} \tag{1}$$

$$Q_S^* + AH_2 \xrightarrow{k_2} QH + AH \tag{2}$$

$$Q_S^* \ (+S) \xrightarrow{k_6} QH_2 \tag{6}$$

$$QH + QH \xrightarrow{k_8} Q + QH_2 ; -\frac{d[QH]}{dt} = k_8[QH]^2 \tag{8}$$

$$Q + AH \xrightarrow{k_{11}} QH + A \tag{11}$$

$$QH + AH_2 \xrightarrow{k_{12}} QH_2 + AH \tag{12}$$

Assuming a stationary concentration of Q^*

$$\alpha[I] = k_1[Q^*] + k_2[Q^*][AH_2] + k_6[Q^*]$$

$$\therefore [Q^*] = \frac{\alpha[I]}{k_1 + k_6 + k_2[AH_2]} \tag{4.4.1}$$

At a stationary concentration of QH radicals,

$$\frac{d[QH]}{dt} = 0 = k_2[Q^*][AH_2] + k_{11}[Q][AH] - k_8[QH]^2 - k_{12}[QH][AH_2] \tag{4.4.2}$$

At a stationary concentration of AH radicals, $\frac{d[AH]}{dt} = 0 =$

$$k_2[Q^{*}][AH_2] + k_{12}[QH][AH_2] - k_{11}[Q][AH] \qquad (4.4.3)$$

From equations (4.4.2) and (4.4.3),

$$k_8[QH]^2 = 2 k_2 [Q^{*}][AH_2]$$

$$\text{or} \quad [QH] = \left\{ \frac{2k_2[Q^{*}][AH_2]}{k_8} \right\}^{\frac{1}{2}} \qquad (4.4.4)$$

From reaction steps (6), (8) and (12),

$$\frac{d[QH_2]}{dt} = k_6[Q^{*}] + \tfrac{1}{2}k_8[QH]^2 + k_{12}[QH][AH_2] \qquad (4.4.5)$$

Substituting the values of $[Q^{*}]$ and $[QH]$ in equation (4.4.5),

$$\frac{d[QH_2]}{dt} = \frac{k_6\alpha[I]}{k_1+k_6+k_2[AH_2]} + \frac{k_2[AH_2]\alpha[I]}{k_1+k_6+k_2[AH_2]} + k_{12}[AH_2]\left\{\frac{2k_2[AH_2]\alpha[I]}{k_8(k_1+k_6+k_2[AH_2])}\right\}^{\frac{1}{2}} \qquad (4.4.6)$$

$$\emptyset = \frac{d[QH_2]}{dt} \Big/ [I] = \frac{k_6\alpha}{k_1+k_6+k_2[AH_2]} + \frac{k_2[AH_2]\alpha}{k_1+k_6+k_2[AH_2]} + k_{12}[AH_3]\left\{\frac{2k_2[AH_2]\alpha}{k_8[I](k_1+k_6+k_2[AH_2])}\right\}^{1/2}$$

$$= \frac{(k_6+k_2[AH_2])\alpha}{k_1+k_6+k_2[AH_2]} + \frac{k_{12}}{k_8^{\frac{1}{2}}}[AH_2]\left\{\frac{2k_2[AH_2]\alpha}{k_1+k_6+k_2[AH_2]}\right\}^{\frac{1}{2}} \cdot \frac{1}{[I]^{\frac{1}{2}}} \qquad (4.4.7)$$

Equation (4.4.7) expresses $\emptyset$ as a function of alcohol concentration and intensity of light.

According to equation (4.4.7) at constant alcohol concentration, a plot of $\emptyset$ against $\frac{1}{[I]^{\frac{1}{2}}}$ or $\frac{1}{I^{\frac{1}{2}}}$ should give a straight line, whose intercept $= \frac{(k_6+k_2[AH_2])\alpha}{k_1+k_6+k_2[AH_2]}$ (4.4.8) and slope $= \frac{k_{12}}{k_8^{\frac{1}{2}}} \left[AH_2\right] \left\{ \frac{2k_2 \left[AH_2\right] \alpha}{k_1+k_6+k_2 \left[AH_2\right]} \right\}^{\frac{1}{2}}$ (4.4.9)

$[I]^{\frac{1}{2}}$ is the light absorbed per litre and I, the light absorbed in the reaction vessel, in units, einst. sec.$^{-1}$

When $\left[AH_2\right] = 0, \quad \phi = \frac{k_6 \alpha}{k_1+k_6} = \phi_o$ (4.4.10)

In equation (4.4.7), when $\left[AH_2\right]$ is low or when the light intensity approaches infinity, the second term will vanish and

$$\phi = \frac{(k_6+k_2 \left[AH_2\right]) \alpha}{k_1+k_6+k_2\left[AH_2\right]} \qquad (4.4.11)$$

or $\frac{\phi - \phi_o}{\alpha - \phi} = \frac{k_2}{k_1+k_6} \left[AH_2\right]$ (4.4.12)

According to equation (4.4.12) a graph of $\frac{\phi - \phi_o}{\alpha - \phi}$ against $\left[AH_2\right]$ has a slope, $\frac{k_2}{k_1+k_6}$. To examine this function the experimental results in the range 4.94x10^{-2} to 0.247x10^{-2} mole l.$^{-1}$ alcohol were used. The quantum efficiency is not significantly dependent on light intensity at 4.94x10^{-2} mole l.$^{-1}$ alcohol while it is independent of light intensity at 0.247x10^{-2} mole l.$^{-1}$ alcohol. ϕ_o was taken as 0.05. A straight line was obtained when α was taken as one (see fig. 3.16). This provides some justification for neglecting the cage effect in the mechanism given above. From the slope, the ratio $\frac{k_2}{k_1+k_6}$=13.0 l. mole.$^{-1}$

Above 4.94×10^{-2} mole $l.^{-1}$ alcohol the values of quantum efficiency were calculated at different alcohol concentrations by using the equation (4.4.11) with $\frac{k_6}{k_1+k_6} = \phi_0 = 0.05$, $\frac{k_2}{k_1+k_6} = 13.0$ l.mole^{-1} and $\alpha = 1$. These values of quantum efficiency correspond to figures at infinite light intensity. These calculated values (see table 4.1, $\phi_{[AH_2]}$) were plotted on the ordinate of graphs of ϕ against $\frac{1}{I^{\frac{1}{2}}}$ (fig. 4.1, shown as A). It was found that all these figures were higher than those obtained

TABLE 4.1

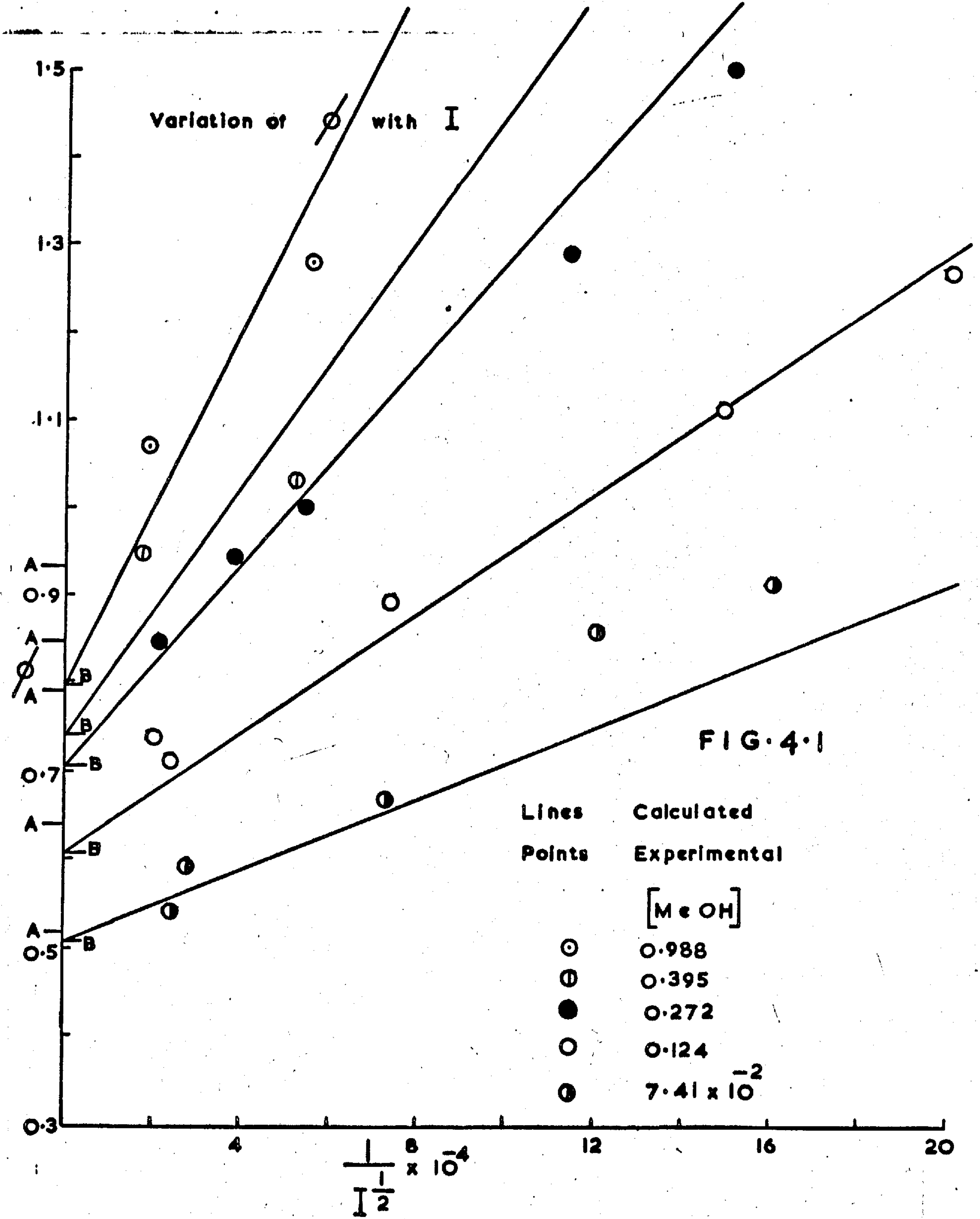
Calculated values of quantum efficiency at infinite light intensity

$$\phi = \frac{(k_6+k_2\ [AH_2])}{k_1+k_6+k_2[AH_2]}$$

$$\frac{k_6}{k_1+k_6} = \phi_0 = 0.05 \quad , \quad \alpha = 1$$

$$\frac{k_2}{k_1+k_6} = 13.0 \text{ l. mole}^{-1} \quad \text{(from fig. 3.16)}$$

Methyl Alcohol Mole $l.^{-1}$ i.e. $[AH_2]$	$\phi_{[AH_2]}$	Methyl Alcohol Mole $l.^{-1}$ i.e. $[M]$	$\phi_{[M]}$
0.988	0.931	0.281	0.796
0.395	0.845	0.203	0.739
0.272	0.791	0.172	0.707
0.124	0.636	0.108	0.605
0.0741	0.516	0.071	0.506


FIG·4·1

Variation of ϕ with I
1·5
1·3
1·1
0·9
0·7
0·5
0·3
A
B
ϕ
4
8
12
16
20
$\frac{1}{I^{\frac{1}{2}}} \times 10^{-4}$
Lines Calculated
Points Experimental
[MeOH]
⊙ 0·988
⦶ 0·395
● 0·272
○ 0·124
◐ $7\cdot41 \times 10^{-2}$

by extrapolation of the experimental results at the corresponding alcohol concentrations. This led to the postulation that the rate of reaction is affected by association of alcohol molecules in carbon tetrachloride. For the equilibrium,

$$N(MeOH) \underset{}{\overset{K}{\rightleftharpoons}} (MeOH)_N$$

various values of K and N have been suggested by various workers on the basis of studies over various ranges of alcohol concentration in carbon tetrachloride. A summary of quantitative work on the association of alcohol molecules in carbon tetrachloride is given in tables 1.15 and 1.16. For the present purpose the results of Saunders and Hyne (46) were the most satisfactory ones to use. From the relevant total alcohol concentration the concentration of monomer, $[M]$ was calculated using their values of $N = 4$, $K = 28.4$. Fig. 3.16 and the constants derived from it were not affected by the assumption that only monomer was reactive. Values of quantum efficiency corresponding to infinite light intensity were calculated at different alcohol concentrations above 4.94×10^{-2} mole $l.^{-1}$ using $[M]$ instead of $[AH_2]$ in equation (4.4.11). These values are given in table 4.1 as $^{\phi}[M]$ and are plotted on the ordinate of graphs of ϕ against $\frac{1}{I^{\frac{1}{2}}}$ (fig. 4.1, shown as B). It can be seen from fig. 4.1 that these values fit fairly well to the experimental results.

Using the calculated value of quantum efficiency, $\phi_{[M]}$ at $[M] = 0.108$ mole l^{-1} ($[AH_2] = 0.124$) as intercept in the graph of ϕ against $\frac{1}{I^{\frac{1}{2}}}$ a straight line fitting to the experimental results at this alcohol concentration was drawn (fig. 4.1), [note I is the light absorbed in the reaction vessel, [I] is the light absorbed per litre, in units, einst. sec.$^{-1}$]. From the slope of the line and making use of equation (4.4.9), the ratio $\frac{k_{12}}{k_8^{\frac{1}{2}}} = 14.4\times10^{-5}$ $l.^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$, when $\frac{k_2}{k_1+k_6} = 13.0$ l. mole^{-1} and $\alpha = 1$. This value of 14.4×10^{-5} $l.^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$ for the ratio $\frac{k_{12}}{k_8^{\frac{1}{2}}}$ was used to calculate the slopes at other alcohol concentrations so that the positions of theoretical lines in fig. 4.1 could be determined at various alcohol concentrations. While drawing the theoretical lines at various alcohol concentrations the calculated values of quantum efficiency, $\phi_{[M]}$ at infinite intensity (table 4.1) were used as intercepts. From fig. 4.1 it is clear that the theoretical lines fit fairly well to the experimental results.

Calculated values of quantum efficiency at various alcohol concentrations and at light intensity, 1.8×10^{-9} einst. sec.$^{-1}$ are given in table 4.2. These values are plotted against the alcohol concentrations, $[M]$ in fig. 4.2. The experimental figures for the quantum efficiency have also been plotted on this graph. The calculated curve fits reasonably to the experimental results.

TABLE 4.2

$$\phi = \frac{(k_6 + k_2[AH_2])\alpha}{k_1 + k_6 + k_2[AH_2]} + \frac{k_{12}}{k_8^{\frac{1}{2}}}[AH_2]\left\{\frac{2k_2[AH_2]\alpha}{k_1 + k_6 + k_2[AH_2]}\right\}^{\frac{1}{2}} \cdot \frac{1}{[I]^{\frac{1}{2}}}$$

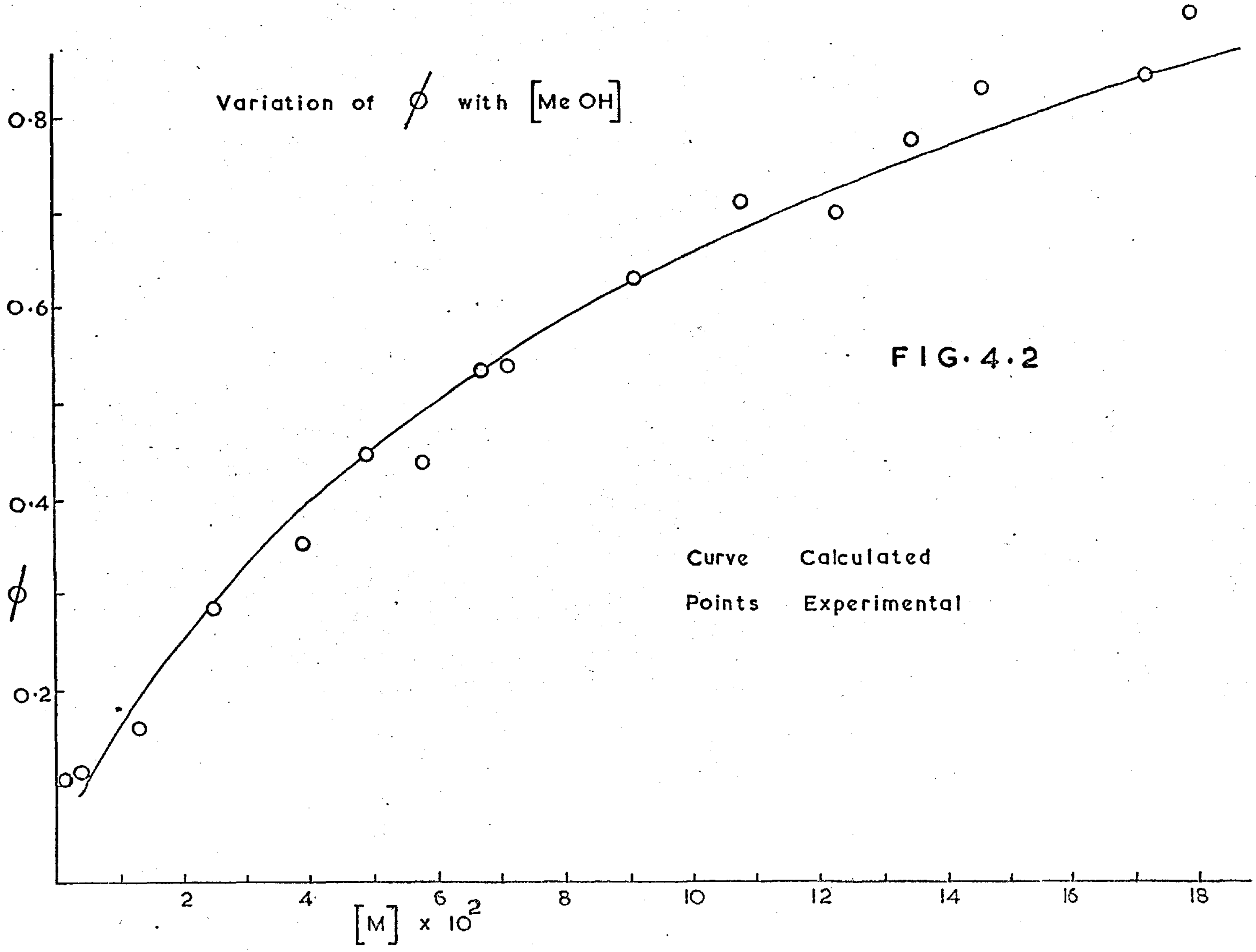
$$\alpha = 1, \quad \frac{k_2}{k_1 + k_6} = 13.0 \text{ l. mole.}^{-1}, \quad \frac{k_{12}}{k_8^{\frac{1}{2}}} = 14.40\times10^{-5} \text{ l.}^{\frac{1}{2}} \text{ mole}^{-\frac{1}{2}} \text{ sec.}^{-\frac{1}{2}}$$

Assumption: monomer-tetramer model, and $[AH_2]$ replaced by $[M]$

$[I] = 4.5\times10^{-8}$ einst. sec.$^{-1}$ l.$^{-1}$

($I = 1.8\times10^{-9}$ einst. sec.$^{-1}$)

Methyl Alcohol Mole l.$^{-1}$ i.e. $[AH_2]$	$[M]$	ϕ
0.0124	0.0124	0.186
0.0247	0.0247	0.293
0.0395	0.0392	0.393
0.0494	0.0488	0.448
0.0593	0.058	0.495
0.0692	0.067	0.536
0.0741	0.071	0.553



Variation of φ with [Me OH]

FIG. 4.2

Table 4.2 contd.

Methyl Alcohol Mole $l.^{-1}$ i.e. $[AH_2]$	$[M]$	ϕ
0.0988	0.091	0.629
0.124	0.108	0.684
0.148	0.123	0.727
0.173	0.135	0.759
0.198	0.146	0.786
0.222	0.156	0.809
0.247	0.164	0.827
0.272	0.172	0.844
0.296	0.179	0.858
0.321	0.186	0.872

Therefore, the proposed mechanism gives a reasonable fit to the experimental results. Special features of the mechanism are the reactions of both the free radicals,

$$Q + AH \xrightarrow{k_{11}} QH + A \qquad (11)$$

$$QH + AH_2 \xrightarrow{k_{12}} QH_2 + AH \qquad (12)$$

This mechanism is not a new one. Walker (61), during studies on the oxidation of ethyl alcohol by phenanthrenequinone, found a chain mechanism involving reactions of type (11) and (12).

4.5. Ratios of Rate Constants

The ratios of rate constants for the photochemical reactions of toluquinone with cyclohexane, iso-propyl and methyl alcohols are given in table 4.3. As k_6 is small, the ratio $\frac{k_{2A}}{k_1+k_6}$ or $\frac{k_2}{k_1+k_6}$ is close to the ratio between the rate constant for reaction of the excited state and that for internal conversion i.e. $\frac{k_2}{k_1}$. The ratio, $\frac{k_2}{k_1}$ is a measure of the reactivity of the excited quinone molecule towards the reducing agent. Therefore, the values of this ratio for the various reducing agents will lead to the comparison of the ease of removal of hydrogen atoms by the excited - - - - - - - - - - -

TABLE 4.3

Ratios of Rate Constants

Reductant	Present work Toluquinone (in $C\ Cl_4$)		Atkinson and Di (1) Benzoquinone (in $C\ Cl_4$)		Wells (5,6,36) Sod. anthraquinone -2-sulphonate (in water)
	$\frac{k_2}{k_1}$ l. mole.$^{-1}$	$\frac{k_{12}}{k_8^{\frac{1}{2}}}$ l$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$ x10^5	$\frac{k_2}{k_1}$ l. mole^{-1}.	$\frac{k_{12}}{k_8^{\frac{1}{2}}}$ l$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$ x10^5	$\frac{k_2}{k_1}$ l. mole^{-1}
MeOH	13.0	14.4			0.054
EtOH			2631.0	860.0	0.445
n-PrOH			1923.0	922.0	0.682
iso-PrOH	dependent on light intensity (i)16.7≭ (ii)(46.0)/ (iii)78.6≠	 (76.0)	2041.0	883.0	0.952
Cyclohexane	50.8				

≭ I = 1.9±0.2x10^{-9} einst.sec.$^{-1}$
/ I = 0.3x10^{-9} einst. sec.$^{-1}$
≠ I = 7.0±0.5x10^{-9} einst. sec.$^{-1}$

quinone molecule from the reducing agents. The ratio $\frac{k_{12}}{k_8^{\frac{1}{2}}}$ is a measure of the reactivity of the semiquinone radical towards the reducing agent, and thus the values will provide a means of comparing the ease of removal of hydrogen atoms by free radical attack on reducing agents. These ratios have been compared in table 4.3.

Values of the ratios, $\frac{k_{2A}}{k_1+k_6}$ for the reaction of toluquinone with iso-propyl alcohol depend on light intensity and the most authentic values will be those obtained from the results at very low light intensity. As mentioned earlier, only one measurement at low light intensity has been used to calculate the ratio $\frac{k_{2A}}{k_1+k_6}$ i.e. $\frac{k_2}{k_1}$. This measurement has been considered doubtful and so the ratio derived from it will not be dependable. However, the ratios at different light intensities are put in table 4.3 for comparison.

The conclusions from table 4.3 are :

(i) The value of ratio $\frac{k_2}{k_1}$ for the reactions of iso-propyl alcohol with various quinones decreases in the order

benzoquinone $>$ toluquinone $>$ sodium anthraquinone -2-sulphonate. The decrease in the value of the ratio is caused either by a decrease in the value of k_2 or an increase in k_1. It seems most likely that the differences should be allocated to k_2 rather than k_1. On this assumption the reactivities of the excited states of these quinone molecules towards iso-propyl alcohol decrease in the order given above. Table 4.3 also shows that in reaction with methyl alcohol the excited state of toluquinone is more reactive than that of sodium anthraquinone-2-sulphonate.

(ii) The value of ratio $\frac{k_{12}}{k_8^{\frac{1}{2}}}$ for the reaction of toluquinone with iso-propyl alcohol is lower than the value for the reaction of benzoquinone with iso-propyl alcohol. The value of ratio $\frac{k_{12}}{k_8^{\frac{1}{2}}}$ depends on the value of k_{12}, where k_{12} is the rate constant for the reaction of semiquinone free radical with the reductant molecule and k_8 is the rate constant for disproportionation reaction of semiquinone free radicals. Thus the values of ratio $\frac{k_{12}}{k_8^{\frac{1}{2}}}$ given in table 4.3 indicate that the benzosemiquinone free radical is more reactive than the tolusemiquinone free radical towards iso-propyl alcohol.

Bridge and Porter (3,4) obtained a value of 8×10^8 l. mole^{-1} sec.$^{-1}$ for k_8, the rate constant for the disproportionation reaction of the semiduroquinone free radicals, produced on flash photolysis of duroquinone in aqueous ethyl alcohol solution. If it is assumed that Bridge and Porter's value of k_8 for duroquinone is similar to that of toluquinone, the value of k_{12} for toluquinone is calculated to be 4.07 l. mole^{-1} sec.$^{-1}$

(iii) The reactivity of excited state of toluquinone towards cyclohexane is similar to its reactivity towards iso-propyl alcohol.

4.6. Future Work

The present work deals with only the reactions of toluquinone with cyclohexane, iso-propyl and methyl alcohols at 365 mμ. For the future work the following suggestions may be considered.

(i) The reaction mechanism suggested for the reactions of toluquinone with cyclohexane gives a possible maximum quantum efficiency of 1. The actual quantum efficiency of about 0.5 in pure cyclohexane has been assumed to be low due to the cage effect,which operates in pure cyclohexane as well as in solutions of cyclohexane in carbon tetrachloride. It would be worthwhile to investigate this system using inert solvents of lower molecular weights. Scrutton (31), during his studies on the reactions of quinones looked for other solvents. He found that tert-butyl alcohol was reactive with various quinones, though it was expected to be inert (section 1.3). Similarly benzene and toluene were also found to give photochemical reactions with chloranil. So far no solvent has been found that is both as unreactive as carbon tetrachloride and capable of dissolving quinones and cyclohexane.

(ii) Further measurements on the reactions of toluquinone with iso-propyl alcohol might clarify some features of the results which have not been explained by the mechanisms discussed above for this system.

(iii) The chain mechanism proposed for the reactions of toluquinone with methyl alcohol fits the experimental results in a reasonable fashion. On the other hand iso-propyl alcohol gives a quantum efficiency of about 1 with toluquinone. Therefore, it will be interesting to study the reactions of methyl alcohol with other quinones in order to correlate the results.

(iv.) Valuable information may be obtained by studying these reactions at other wavelengths.

(v) Reactions of toluquinone with other alcohols may provide interesting results.

Wells (5,6,36) found that in alcohols the reactivity increases with increasing alkylation on the α- carbon atom until all hydrogen atoms are replaced, when a great reduction in reactivity occurs. This led him to deduce that the excited sodium anthraquinone -2- sulphonate attacks specifically the α- carbon atom. This deduction does not appear to be applicable to the reactions of benzoquinone and its derivatives. Atkinson and Di (1) showed that ethyl alcohol is more reactive than propyl alcohols towards excited benzoquinone. Scrutton (31) found that tert-butyl alcohol reacted with various quinones with quantum efficiencies similar to the corresponding reactions with other alcohols. He also found that cyclohexane, benzene and toluene react with chloranil. The present work also shows that cyclohexane gives a considerable reaction with toluquinone. In view of the above, it is concluded that benzoquinone and its derivatives are not specifically reactive towards the α- carbon atom of alcohols whereas sodium anthraquinone -2- sulphonate may be a specific reactant. This means that sodium anthraquinone -2- sulphonate is less reactive and can abstract only the α- hydrogen atom in alcohol molecule. It appears that it is unable to abstract the hydrogen atom of CH_3 group in tert-butyl alcohol because the reaction shows a very low reactivity. On the other hand a high reactivity of benzoquinone and its derivatives towards tert-butyl alcohol (Scrutton) indicates that they are more energetic than sodium anthraquinone -2- sulphonate and can abstract the hydrogen atom of CH_3 group. They can also abstract the hydrogen atoms from cyclohexane, benzene and toluene molecules.

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