THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE PHOTO-OXIDATION OF POLYSTYRENE

By

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PREFACE

The work described in this Thesis was carried out in the period October 1959 to March, 1963, at the University of Glasgow in the department of Physical Chemistry, which is under the supervision of Professor J.M. Robertson, F.R.S.

My thanks are due to the U.S. Rubber Company for the award of a Research Scholarship, during the tenure of which this work was carried out.

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CHAPTER I

Introduction

Ever since synthetic polymers became commercially important materials, attempts have been made to understand the processes which lead to the deterioration of their useful properties. Underlying these efforts has been the desire to identify the primary reactions involved, since it is only by controlling these that undesirable products can be avoided, and that ultimately the life of the polymer can be prolonged.

The overall deterioration process, however, is highly complex and is the result of the simultaneous operation of a large number of environmental factors, such as light, heat, oxygen, radiation, and so on, each of which has a deleterious action on polymers. A study of the overall reaction, therefore, would permit neither the elucidation of the initial stages of the reaction nor the evaluation of the contribution of a specific agency. A much more profitable approach is through the thorough investigation of the constituent reactions, like thermal and photochemical degradation. In these investigations, where the number of variables is minimized, it is often possible to elucidate the various degradation mechanisms, an understanding of which is essential to the fuller explanation of the overall weathering process.

Considerable progress has been made in the field of thermal degradation and the mechanisms of degradation of a large number of polymers have been established. In the field of oxidation, on the other hand, a large amount of effort has been devoted to the technical aspects of the process and this is reflected in the large patent literature on antioxidants for polymers.(1) The fundamental chemical aspects of oxidation, with which this present work is concerned, have been comparatively neglected.

Prerequisite to the determination of the mechanism of oxidation of a polymer are firstly, the unequivocal identification of the reaction product and secondly, an intimate knowledge of the initiation step. It is difficult to fulfil the first of these requirements at low extents of oxidation, since it involves the detection of small concentrations of oxygenated groups attached to the hydrocarbon chains. At higher extents of oxidation, however, smaller molecules are produced, but while these are potentially more readily identifiable, they cannot always be easily accounted for in terms of the original polymer structure. Moreover, at this stage of the process secondary reactions tend to predominate and the initial steps of the reaction are effectively obscured.

These two requirements are thus to a certain extent mutually exclusive, and it is for this reason that extensive studies have been made of the oxidation of model compounds for polymers, i.e. small molecules having the same functional groups as the polymers. These studies have shed some light on the initial steps of oxidation of nylon (2,3) rayon (4,5,6) and rubber. (7-12) Generalizations made on the basis of these results, however, are not always valid, since many reactions which are commonplace in the chemistry of small molecules are not feasible in the macromolecular environment. Structural abnormalities, absent in small molecules, but present in many polymer molecules, can also have a profound effect on the reaction.

Quantitative information about the oxidation of small molecules, e.g. olefins which are model compounds for rubber, is well in advance of that for polymers. It is useful, therefore, before considering the oxidation of polystyrene to discuss olefin oxidation.

Oxidation of Olefins

Although this has been the subject of a vast amount of research for many years, it is only comparatively recently that the chemistry of the process has been elucidated. Perhaps the greatest advances were made by Farmer(15) and Criegee(13,14) who showed independently that the initial product of oxidation of cyclohexene was a hydroperoxide. Farmer proposed that oxidation of olefins proceeded by a chain reaction involving the addition of a molecule of oxygen to the carbon atom adjacent to a double bond, to form a hydroperoxide.

$$-CH_2-CH=CH- + O_2 \longrightarrow -CH(OOH)-CH=CH-$$

Later Farmer and his co-workers(16-20) substantiated this hypothesis with a large amount of experimental evidence. To Bolland, Bateman, Gee and their co-workers(21,22) is due the major credit for establishing the detailed mechanism and kinetics of the reaction. These workers determined rates of oxidation of ethyl linoleate by measuring the oxygen absorbtion, and they found that the rate increased linearly with the amount of oxygen absorbed. They showed that the reaction was initiated by the thermal decomposition of the ethyl linoleate hydroperoxide, the sole product of the early stage of the reaction, and that the autocatalytic nature of the reaction derived from this.

By studying the oxidation in presence of catalysts like benzoyl peroxide,(23) and in presence of actinic light(24) it was established that a square-root relationship existed between the rate of the reaction and the light intensity or catalyst concentration and that the photoreaction had a quantum yield greater than unity. The presence of free radical inhibitors, like phenols and naphthols(25) depressed reaction rates. Similar results were obtained for the oxidation of a number of olefin substrates.(7,8,9,26)

It was thus established beyond any doubt that the oxidation of olefins, as Farmer had postulated proceeded by a radical chain reaction involving hydroperoxides, the experimental observations were accounted for by the following mechanism(27) in which RH represents the olefin,

Initiation

$$\left.\begin{array}{l}\text{Catalysts}\\ 2\text{ROOH}\\ \text{Photo}\end{array}\right\} \longrightarrow R\cdot \text{ or } RO_2\cdot \qquad\qquad r_i$$

Propagation

$R\cdot + O_2 \longrightarrow RO_2\cdot$ $\quad k_2(R\cdot)(O_2)$

$RO_2\cdot + RH \longrightarrow RO_2H + R\cdot$ $\quad k_3(RO_2\cdot)(RH)$

Termination

$$\left.\begin{array}{l} 2R\cdot \\ R\cdot + RO_2\cdot \\ 2RO_2\cdot \end{array}\right\} \longrightarrow \text{Non-radical Products} \qquad \begin{array}{l} k_4(R\cdot)^2 \\ k_5(R\cdot)(RO_2\cdot) \\ k_6(RO_2\cdot)^2 \end{array}$$

An analysis of the above scheme shows that the rate of oxidation is related to the rates of the elementary reactions by the equation

$$-\frac{d(O_2)}{dt} = r_i \frac{k_3}{\sqrt{k_6}} (RH) \frac{k_2 \sqrt{k_6} (O_2)}{k_3\sqrt{k_4}(RH) + k_2\sqrt{k_6}(O_2) + \sqrt{k_4 k_6 r_i}}$$

This relation has been found to apply in the oxidation of a large number of mono-olefins and diolefins,(28-31) so it can be concluded that the mechanism is generally applicable. It is interesting to note that the rate expression obtained for the oxidation of cumene(32,33,34) a model compound for polystyrene, has the same form as the above equation, indicating a close similarity between the mechanism of cumene oxidation and Bolland and Bateman's mechanism.

Various attempts have been made to interpret the oxidation of high polymers in terms of this mechanism and it has been observed(35–39) that the characteristics of rubber and polyethylene oxidations are in some respects analogous to those of their model compounds. Recently(40) it has been shown that the initiation step in the thermal oxidation of polypropylene is the bimolecular decomposition of the hydroperoxide, which is of course the same as the initiation step in Bolland's mechanism. Quantitative information about the oxidation of a large number of polymers is, however, still lacking.

The Oxidation of Polystyrene

(1) Introduction

Compared with the high reactivities of olefins towards oxygen, polymers are in general relatively inert. Mesrobian and Tobolsky(41) investigated the oxidation of a number of polymers, including natural and synthetic rubbers, nylon and polystyrene, measuring the volumes of oxygen absorbed by these polymers when they were heated to 130°C in an oxygen atmosphere. Using the rate of oxygen uptake as a criterion of oxidisibility they showed that while those polymers with double bonds in their backbones, like rubbers were particularly susceptible to oxidative degradation, those which had electrophilic side groups, like chlorine, carbonyl and phenyl (as in polystyrene) were much less reactive. These authors also pointed out a qualitative correlation between ease of polymerization and oxidisibility; generally the more easily polymerized a monomer is, the more stable is its polymer towards oxygen. Of all the polymers examined, polystyrene, having a rate of oxidation of about one twentieth of that of nylon and rubber, was the least reactive towards oxygen.

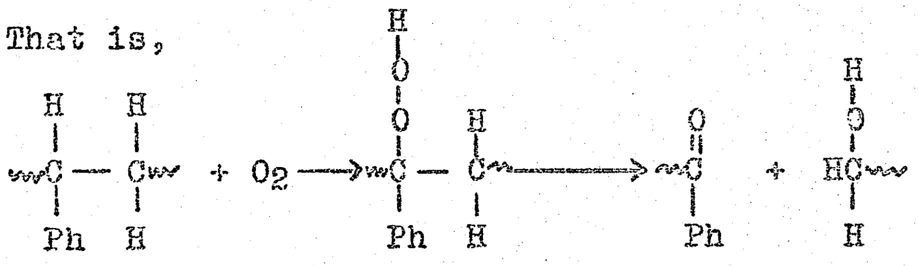
(2) Jellinek's Hydroperoxide Theory

Perhaps the most significant early contribution to the systematic study of the oxidation of polystyrene was made by Jellinek.(42,43) He carried out the bulk oxidation of polystyrene in air in the temperature range 180°C to 280°C, following the progress of the reaction by determining the viscosity molecular weights of the residual material at frequent intervals. On plotting the limiting viscosity versus time of degradation at each temperature he observed a rapid decrease in viscosity at first followed by an eventual tail off. Jellinek attempted to explain his results in terms of the theory of random scission, which predicts a linear relation between the average number of chain breaks per original chain and the time of degradation for the initial stages of the degradation. Straight lines were, however, not obtained, instead a rapid tailing off was observed, and he concluded that inhibitors in the form of antioxidants were formed concurrently with the chain breaks. Earlier work(44,45) had shown that benzaldehyde was formed during the degradation of polystyrene in air, and Jellinek suspecting that this was a possible inhibitor, repeated the oxidations in presence of small amounts of benzaldehyde. The results showed conclusively that benzaldehyde did indeed efficiently inhibit chain scission during oxidative degradation.

To account for the experimental observations, Jellinek, reasoning by analogy with the oxidation of olefins, proposed that the first product of polystyrene oxidation was the hydroperoxide, formed presumably on the tertiary substituted carbon atom, α to the benzene ring. Subsequent decomposition of the hydroperoxide would lead to chain scission and to the production of inhibitors. The reaction scheme can be formulated as follows,

Polystyrene + O_2
↓
Polystyrene hydroperoxide
↓
Chain scission
↓
Inhibitors

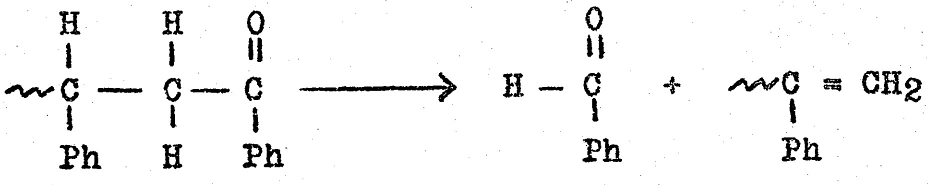
That is,



$$\sim CH(Ph)-CH_2\sim + O_2 \longrightarrow \sim C(OOH)(Ph)-CH_2\sim \longrightarrow \sim C(=O)Ph + HOCH_2\sim$$

Hydroperoxide   Chain scission

Benzaldehyde is then formed by the breaking off of the oxidised chain ends,



$$\sim CH(Ph)-CH_2-C(=O)Ph \longrightarrow H-C(=O)Ph + \sim C(Ph)=CH_2$$

As evidence for the mechanism, Jellinek showed that a rate expression derived on the basis of the above sequence of reactions adequately represented the experimental results. The mechanism of the inhibitory action of the benzaldehyde was not elucidated, but a plausible explanation is that it reacts with the polystyrene hydroperoxide to become itself a hydroperoxide, thus destroying the hydroperoxide and so indirectly preventing chain scission.

(3) Evidence for Jellinek's Theory

(a) Achhammer *et al*(46) exposed polystyrene films to heat and ultra-violet radiation at 60°C and examined their infra-red spectra at frequent intervals. It was observed that an exposure of 70 hours resulted in the appearance of an absorption band in the 1720 $cm.^{-1}$ region and that 100 hours exposure produced a band in the 3450 $cm.^{-1}$ region. These absorbtions were attributed to carbonyl and hydroxyl groups respectively, and their appearance to hydroperoxide decomposition, as suggested by Jellinek. These authors modified Jellinek's hydroperoxide decomposition mechanism in the light of Walsh's(47) results, suggesting that the process was not a molecular but a free radical one, involving the homolytic fission of the O–O bond. The overall interpretation, however, was unchanged.

It was suggested that the carbonyl absorbtion band was due to the combined absorbtions of ketones, aldehydes and acids all of which would be expected to be present simultaneously. Achhammer <u>et al</u>, however, were unable to differentiate between such groups. Recently this has been achieved by Zaitoun(48) who repeated their work and resolved the carbonyl band into aldehyde, ketone and acid absorbtions.

(b) Similar thermal and photo-oxidations of polystyrene were carried out by Achhammer and Wall(49,50) who followed the reactions mass - spectrometrically, estimating the gaseous products evolved as a function of time. Although a large number of compounds was identified, these authors were able to show that comparatively few of them were genuine oxidation products. The presence of benzene, toluene, ethyl alcohol and methyl alcohol was attributed to residual solvent and precipitant (and their impurities) in the polymer. It was established, however, that benzaldehyde, formaldehyde, formic acid, carbon-monoxide, carbon-dioxide and water were the principal products of oxidation, and that their production was compatible with the decomposition of hydroperoxides attached to the carbon atoms α to the phenyl groups. In other words, the products of oxidation were those expected from the reaction mechanism postulated by Jellinek.

(c) That the α-position is associated with the oxidation of polystyrene was demonstrated by Beachell and Nemphos(51) who measured rates of oxygen uptake of polystyrene and of several partially deuterated (in the α and β-positions) polystyrenes. Replacements of the hydrogen on the tertiary substituted carbon atom by deuterium resulted in a large change in the oxidation rate, the hydrogen compound having a rate of oxidation seven times greater. No appreciable isotope effect was observed upon substitution of deuterium into the β-position.

Again these observations can be rationalized in terms of the hydroperoxide theory. It would appear that the rate determining step in the reaction is the fission of the bond between the tertiary carbon and hydrogen during the production of hydroperoxide.

The above evidence together with the observation of Wall(52) that oxidized polystyrene catalyzes the polymerization of methyl methacrylate at 47°C, strongly favours an oxidation mechanism involving hydroperoxides. Direct proof in the form of hydroperoxide detection and isolation, rather than circumstantial evidence is required before it can be stated unequivocally that hydroperoxides are indeed involved. Unfortunately, no such direct proof has yet been obtained in spite of the many attempts that have been made to detect hydroperoxides by the usual analytical methods. Wall(52) concludes that this failure to detect them is a result of hydroperoxide instability; hydroperoxides are presumably decomposed as soon as they are formed. It seems rather more likely, however, that differences in solubility of the hydroperoxide and the reducing agents used to detect it, for example potassium iodide (it is impossible to find a common solvent for polystyrene and potassium iodide) preclude the detection of the low concentrations which are likely to be present.

The Colouration of Polystyrene

(1) Introduction

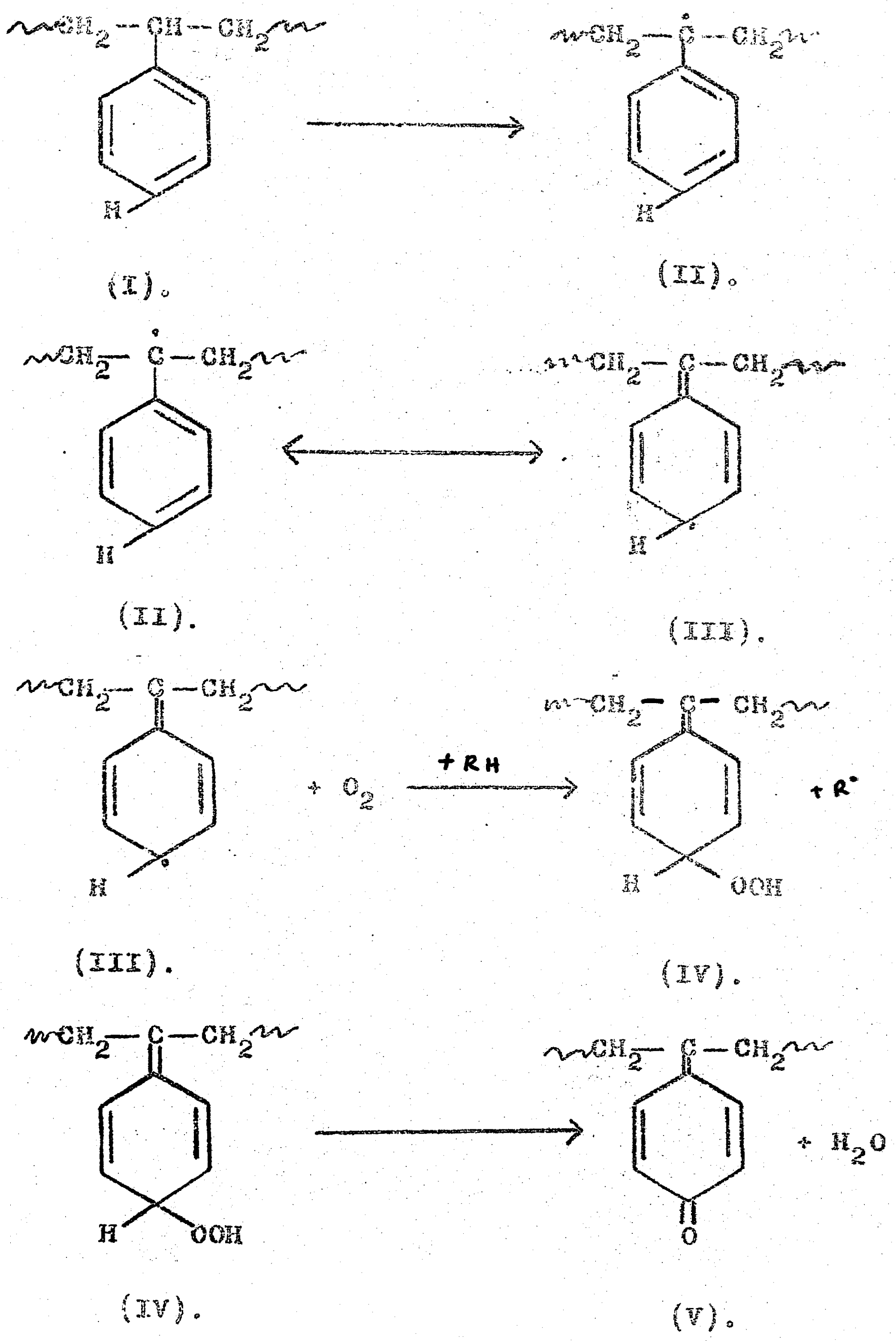
Perhaps the most obvious manifestation of oxidation of polystyrene is the yellowish discolouration.

Matheson and Boyer(53) investigated the formation of colour, exposing polystyrene films to heat and ultraviolet radiation and obtaining their visible and ultraviolet absorbtion spectra at frequent intervals. Expressing discolouration as the absorbance of 3650Å radiation, these authors showed that colour development was concomitant with carbonyl formation, and that the process was accelerated by monomer and by sulphur compounds. This effect is no doubt a consequence of the enhanced absorbtion of the activating radiation by these compounds. It was suggested by these authors that the chromophores were probably unsaturated aldehydes and ketones, but neither the nature of these compounds nor the mode of their formation was given.

(2) Achhammer's Theory of Colouration

The first attempt to explain the colouration of polystyrene was made by Achhammer(49) who suggested that the colour was due to the presence of quinonoid structures, which were formed from hydroperoxides. According to Achhammer these compounds are produced by the mechanism shown in figure 1.

FIGURE 1.

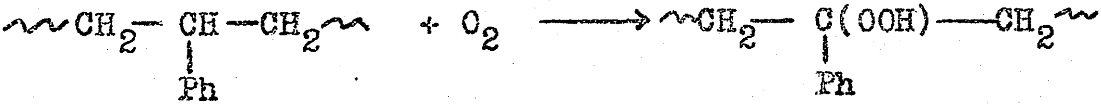


A double bond shift in the initially formed radical (II) gives rise to the radical (III) which reacts with oxygen to form the secondary hydroperoxide (IV), subsequent dehydration of which produces the quinomethane (V).

(3) Wall's Theory of Colouration

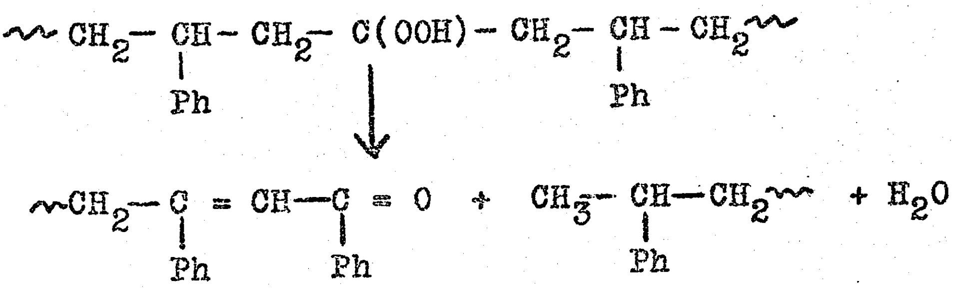
An alternative, yet essentially similar theory of colouration was promulgated by Wall(54,55) to account for the changes produced in the visible and ultra-violet spectra of polystyrene films as a result of photo-oxidation. In addition to finding a progressive decrease in transmission of the 3400Å line as a result of oxidation, Wall found that this transmission continued to decrease after the light source had been removed; in other words there was a dark reaction leading to the formation of chromophores. Re-exposure of the films to the light, however, resulted in a rapid initial increase in transmission at 3400Å, which was followed by a decrease, the rate of decrease, however, being the same as that observed before interruption.

A closer examination of the ultra-violet spectrum of the coloured material revealed that it was similar to that of benzalacetophenone, a yellow-coloured compound, which Lutz and Jordan(56) had shown underwent a cis-trans isomerization on irradiation with sunlight. Corresponding to this isomerization, an increase in the transmission of the 3400Å region of the spectrum was observed. Wall, recognising that this effect was reminiscent of the removal of the post-irradiation effect by subsequent irradiation, mentioned above, suggested that the chromophores in oxidised polystyrene were compounds, the structures of which were closely related to that of benzalacetophenone and that their precursors were hydroperoxides. During exposure to ultra-violet radiation and oxygen the hydroperoxide is formed



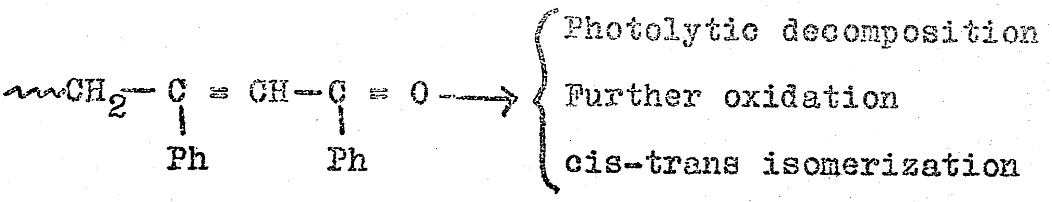
$$\sim CH_2-\underset{\displaystyle Ph}{\underset{|}{CH}}-CH_2\sim + O_2 \longrightarrow \sim CH_2-\underset{\displaystyle Ph}{\underset{|}{C}}(OOH)-CH_2\sim$$

On subsequent dark storage the hydroperoxide decomposes to produce the group which has a high absorbtion in the ultra-violet region.



$$\sim CH_2-\underset{\displaystyle Ph}{\underset{|}{CH}}-CH_2-C(OOH)-CH_2-\underset{\displaystyle Ph}{\underset{|}{CH}}-CH_2\sim$$
$$\downarrow$$
$$\sim CH_2-\underset{\displaystyle Ph}{\underset{|}{C}}=CH-\underset{\displaystyle Ph}{\underset{|}{C}}=O + CH_3-\underset{\displaystyle Ph}{\underset{|}{CH}}-CH_2\sim + H_2O$$

Finally during subsequent irradiation several reactions, each of which would result in a decrease in ultra-violet absorbtion, can occur,



$$\sim CH_2-\underset{Ph}{C}=CH-\underset{Ph}{C}=O \longrightarrow \left\{\begin{array}{l}\text{Photolytic decomposition}\\ \text{Further oxidation}\\ \text{cis-trans isomerization}\end{array}\right.$$

(4) Merits and Demerits of the two Theories.

While Wall's theory accounts satisfactorily for his observations, it is obvious that they can also be explained by Achhammer's theory since the hydroperoxide decomposition leading to the formation of the quinonoid compounds could constitute the dark reaction and these compounds would be equally susceptible to photolysis and further oxidation. The ultra-violet spectra of the two possible compounds would also be essentially similar, and it is therefore not possible to use ultra-violet absorption characteristics as a means of distinguishing them.

Wall's theory accounts immediately for chain scission, whereas Achhammer's predicts that it would be a secondary reaction, presumably brought about by the photolysis of the quinomethane. This, however, is perhaps a rather naive objection, considering the potential complexity of the system.

Since the production of chromophores, according to Achhammer, involves the dehydration of the hydroperoxide in which the hydrogen in the para-position is removed, it would be reasonable to expect a decrease in the rate of chromophore formation on substitution of deuterium into the para-position. Wall(57) has measured the rates of increase of absorbance at 3400Å on oxidation for a series of deuterated polystyrenes, including the α, β and para-duetero isomers. The results show that isotope effects are appreciable only when the hydrogen in the α-position is substituted. This indicates that the α-position is the key point of attack in the oxidation, which is of course, predicted by both theories. The absence of an isotope effect in the oxidation of the para-isomer suggests that the quinomethanes may not be present. The result, however, is inconclusive and would require confirmation in the form of a product analysis. The presence of HDO, for example, in the volatile products would be strong evidence for the validity of Achhammer's hypothesis.

At the moment it is not possible to say unambiguously which structure is indeed the chromophore, however, considering the similarity of the mechanisms of their formation, it is highly probable that both these structures are present.

Aims of the Present Work

An examination of the literature on polystyrene oxidation reveals that a disproportionate amount of attention has been paid to the secondary reactions, for example, carbonyl formation, colouration, benzaldehyde formation, etc. The initial phases of the oxidation reaction, however, have been comparatively neglected. Another very obvious feature is the large variety of conditions under which previous oxidations have been carried out, for example, thermal oxidation at temperatures ranging from 60°C to 280°C, thermal and photo-oxidations of commercial polystyrenes, containing platicizers and other impurities, oxidation at a variety of oxygen pressures, and so on. In other words, previous workers have exercised little or no control over the various variables, like oxygen pressure, temperature, light intensity, and so on, each of which must surely play an important part in determining not only the rate but also the mechanism of the reaction. Because of this it is difficult to evaluate the data obtained, and even more difficult to compare the results of one worker with those of another.

The need for the present work follows naturally from those criticisms of previous work. The aim of this work is to make a quantitative study of the oxidation of polystyrene, care being taken to exercise a strict control over the various variables, so that the effect of, for example light intensity on the rate of oxidation can be uniquely defined.

Obviously far more accurate data can be obtained from a study of the initial stages of the reaction where secondary reactions are not predominant. This, however, limits the number of methods which can be used to follow the reactions. In this work rates of oxidation are determined by a direct method, namely by measuring oxygen absorbtion by the polymer. In order to minimize the complicating side reactions resulting from the decomposition of thermo-labile groups at elevated temperatures, the oxidation is carried out at room temperature and is photo-initiated.

CHAPTER 2

APPARATUS AND EXPERIMENTAL TECHNIQUES

Section 1: Preparation and Characterisation of Polymers.

Section 2: Oxidation Apparatus.

Section 3: Photochemical Techniques.

Section 4: Analytical Methods.

1. Preparation of the Polymer (S_1)

(a) Introduction

Since it was not known initially whether the rate of oxidation of polystyrene would be a function of its molecular weight, or whether the reaction would be affected by the presence of initiator fragments at the chain ends, it was decided to prepare one sufficiently large polymer sample by thermal polymerization and to use it throughout the subsequent investigations of the oxidation reaction. In order to avoid the incorporation of oxygenated structures, possible photo-active sites, in the chains during polymerization the polymer was prepared under high vacuum conditions. By taking these precautions it was ensured that pure polystyrene was obtained, and thus the possibility of ambiguities arising from the presence of impurities was minimized.

The effect of molecular weight on the reaction rate was investigated and a series of polymers having different molecular weights was prepared. This is described in detail later.

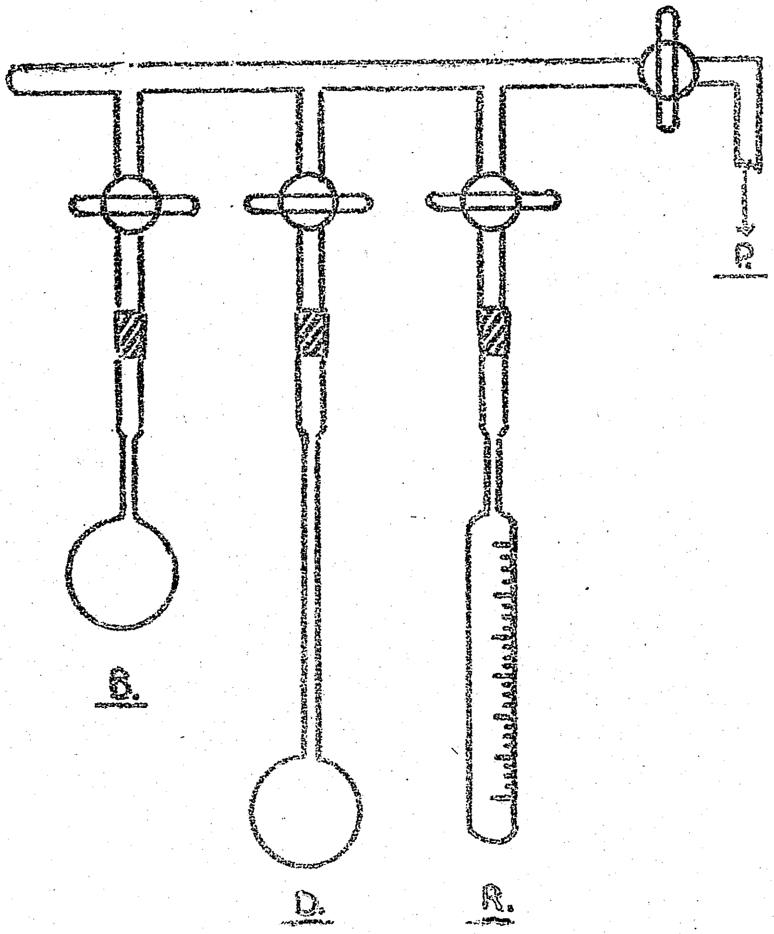
(b) Purification of the Monomer

Styrene monomer (Forth Chemicals Ltd.) contained 0.1% p-tert-butylcatechol as inhibitor. This was removed by washing the monomer several times with dilute potassium hydroxide solution. After washing several times with water and drying over anhydrous magnesium sulphate for 24 hours, the monomer was fractionally distilled under reduced pressure, the middle fraction (b.p. 68°C at 15 mm Hg) only being retained.

(c) Filling of the dilatometer

The high-vacuum apparatus used for filling the dilatometer shown in figure 2 was evacuated to 10^{-5} torr by a mercury diffusion pump backed by a rotary oil-pump, Styrene monomer was introduced into the reservoir tube and degassed three times under high vacuum by the alternate freezing and thawing technique. Before distilling any monomer into the dilatometer the first 10 ml. was eliminated by distillation into the bulb, B. After the required amount of styrene had been distilled into the dilatometer it was sealed off under high vacuum.

FIGURE 2.



APPARATUS FOR FILLING DILATOMETERS.

B-Bulb, D-Dilatometer, R-Reservoir., P-to pumps.

(d) Polymerization

The polymerization was carried out at 90°C in a water thermostat controlled to ± 0.05°C by a Sunvic H.V.S. type relay actuated by a mercury-toluene regulator. The contraction during polymerization at 90°C, 18.5% for 100% polymerization, was obtained by extrapolation of Melville and Valentine's data$^{(58)}$, a linear relationship between contraction during polymerization and temperature of polymerization being assumed.

(e) Isolation and Drying of the Polymer

Polymerization was stopped at 10% conversion by immersing the dilatometer in a freezing mixture. The polymer-monomer mixture was then dissolved in Analar benzene and the polymer precipitated by adding this solution to methyl alcohol. The resulting polymer was filtered off and dried under high vacuum for several days at 25°C. It was found, however, that this treatment did not satisfactorily remove the last traces of benzene from the polymer, and it seemed probable that under the conditions necessary to achieve this, partial oxidation of the polymer might occur.

It was essential that the polymer to be oxidised should be completely free from both solvent and precipitant and it was found possible to achieve this by reprecipitating in methyl alcohol from Analar chloroform solution. The polymer was obtained as a fine, flocculent precipitate which soon coagulated. After decantation of the supernatant liquid the polymer was partially dried in air at 25°C and ground to a fine powder which was dried under high vacuum at 30°C for several days.

2. Measurement of Molecular Weight

(a) Osmotic Pressure Measurement

The number-average molecular weight of the polymer was obtained from osmotic pressure data, the latter being measured using a modified Fuoss-Mead osmometer with a bacterial cellulose membrane.(59) The osmometer was thermostatted by means of a water jacket through which water was pumped from a tank maintained at 25°C ± 0.05°C by a mercury-toluene regulator and Sunvic H.V.S. type relay. Analar benzene was used as solvent, and cell constants were obtained before and after each determination.

Before each measurement the cell was washed out six times with the solvent and six times with the solution under examination. Measurements were carried out on the stock solution (0.9 gm./100 ml. benzene) and on a series of solutions obtained by dilution of the stock solution. Solution concentrations were determined by evaporating a known weight of solution in an air oven at 110°C for 24 hours.

(b) Relation between Osmotic Pressure and Molecular Weight.

The osmotic pressure of a polymer solution is related to the molecular weight of the polymer by the Van't Hoff equation,

$$\pi V = \frac{W}{M} RT$$

where π is the osmotic pressure, V is the volume of solution, M is the molecular weight, W is the weight of solute, R is the gas constant (0.082 litre atm.), and T is the Absolute temperature. The molecular weight was calculated by applying this equation at infinite dilution.

i.e. $\left(\frac{\pi}{C}\right)_{c \to 0} = \frac{RT}{M}$ where C is the concentration in gm./litre and $(\pi/C)_{c \to 0}$ is the limiting value of π/C.

But π was measured in cm. of benzene and C, in gm. of polymer per 100 gm. benzene. Assuming that the density of the solution is the same as that of the solvent (the error involved is within the experimental error of the measurement) and inserting appropriate values, the above equation becomes

$$M = \frac{10330 \times RT}{(\pi/C)_{C \to 0}}$$

in which π is in cm. of benzene and C in gm. per 100 gm. benzene. The value of $(\pi/C)_{C \to 0}$ was obtained from a least-squares analysis of the $\pi/C - C$ data. The number average molecular weight of the polymer was found to be 493×10^3.

3. Preparation of Polymers of Different Molecular Weights

3. Preparation of Polymers of Different Molecular Weights

In order to investigate the possible effect of molecular weight on the rate of oxidation, a number of polymers of different molecular weights was required. These were prepared by polymerizing styrene in presence of different amounts of initiator, 2,2'-azoisobutyronitrile. The techniques used were the same as those for the preparation of the thermal polymer, with the exception that the initiator, purified by recrystallization from Analar chloroform, was introduced into the dilatometers in chloroform solution and the solvent removed at the water pump before distillation of the monomer was commenced.

4. Determination of Molecular Weights of these Polymers

The molecular weights of these polymers were obtained from viscosity data determined by means of a P.C.L. Suspended Level Viscometer. The measurements were carried out in a water bath maintained at 25°C ± 0.05°C by means of a mercury-toluene regulator and Sunvic relay.

Times of flow for a 0.5% chloroform solution and for several dilutions were obtained for each polymer. Corresponding specific viscosities were calculated and the limiting viscosity numbers obtained by extrapolation of the graph of $\frac{\eta_{sp}}{C}$ versus C to zero concentration. The molecular weights were then calculated from the equation,

$[\eta] = K(M_v)^{\alpha}$ in which $K = 1.12 \times 10^{-4}$ and $\alpha = 0.73$ for this system at 25°C(60). The following table summarizes data obtained.

Table 1

Polymer	Temperature of polymerization	% Polymerization	Initiator concentration(%)	Molecular weight
No.1	60°C	10	0.002	3.3×10^5
No.2	60°C	10	0.01	2.14×10^5
No.3	60°C	10	0.1	1.86×10^5
No.4	60°C	10	0.2	1.59×10^5
No.5	60°C	10	0.4	1.5×10^5

5. Preparation of Films

(a) Introduction

The polystyrene was oxidised in the form of films of accurately known surface area and thickness. Similar experiments carried out on the powdered polymer would have yielded conflicting and erratic results, on account of the large number of uncontrollable variables associated with such a system, for example surface area of the powder, particle size, layer thickness, and so on.

Several standard methods are available for preparing polymer films, for example, melting, moulding, pressing, etc., but each suffers from the disadvantage that the polymer may become partially degraded, or oxidised during the formation of the film. It was found, however, that polystyrene films could be cast satisfactorily from solution, by solvent evaporation, a process which involved no degradation or oxidation, and this technique was adopted.

(b) Formation of Films

A small amount of the polymer (15 mgs.) was dissolved in A.R. chloroform (3 mls.) and the solution filtered. Considerable losses of solvent by evaporation were incurred in this process and it was necessary to make the filtrate up to 3 mls. again by addition of chloroform in order to prevent premature film formation. The resulting solution was then poured into a 30 ml. beaker containing 20 ml. of carefully purified mercury.

After 24 hours at room temperature the chloroform had evaporated leaving a film on the mercury surface. Addition of a few c.c. of water released the film completely free from adhering mercury droplets. In order to reduce the possibility of contamination of the films with residual impurities, like dust from the mercury, the first six films prepared were rejected.

No advantage was gained by accelerating the drying process. Evaporation of the solvent under reduced pressure in a desiccator invariably led to bubble formation in the films, and evaporation in an air stream or at elevated temperatures yielded opaque films as a result of premature precipitation of the polymer.

6. Drying of Films

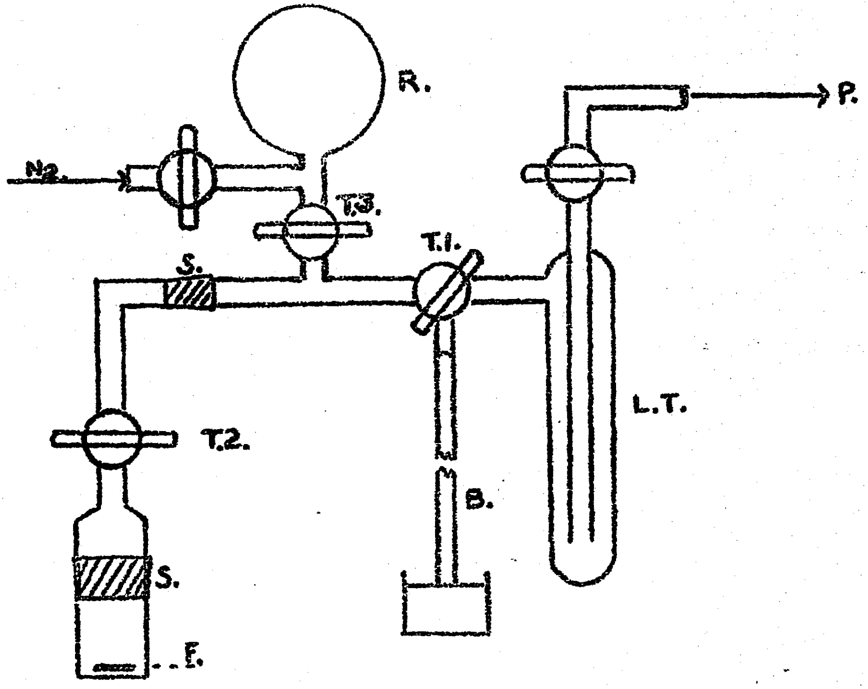
(a) Introduction

In order to eliminate the possibility of the casting solvent participating in the subsequent oxidation reactions, it was necessary to remove it completely from the films, since traces of impurities are sufficient to alter the course of photochemical and radical reactions. It has already been pointed out that polystyrene can be freed satisfactorily from chloroform by continuous pumping under high vacuum for several days, however a much faster, equally efficient, yet non-destructive method of removing solvent was required and to this end the following technique was evolved.

(b) Apparatus

The apparatus used is shown in figure 3. The films were placed in the socket, S, which was then attached to a high-vacuum system and the whole of the apparatus pumped at 10^{-5} torr for half an hour. During this time nitrogen was introduced into the reservoir, R, via a liquid nitrogen trap. T_1 was closed and the drying unit isolated from the pumping system. The socket was then filled with nitrogen at 300 mm Hg, T_2 and T_3 closed and the former immersed in a beaker of water, the temperature of which was kept at 45°C. After 1/2 hour the nitrogen and solvent released during heating were pumped off and the system pumped at 10^{-5} torr for 10 minutes. This process was repeated

FIGURE 3.



APPARATUS FOR DRYING FILMS.

F-Film, R-Reservoir, S-Socket, T_1, T_2, T_3-Stopcocks,

B-Barometer, L.T-Liquid Nitrogen Trap, P-toPumps.

several times.

That this treatment actually led to the complete removal of the solvent was verified by weighing the film after each cycle; normally no further change in weight was distinguishable after the third cycle. It could be argued that the chloroform was occluded in the polymer and that this treatment would never remove it satisfactorily. However, infra-red spectra of the film were obtained after each cycle and it was found that the chloroform absorbtion at 1218 cm.$^{-1}$, quite distinct in the spectrum of an undried film, had disappeared completely after two cycles. This is shown in figure 4. Films were stored in the socket under high vacuum till required.

7. Determination of Film Thickness

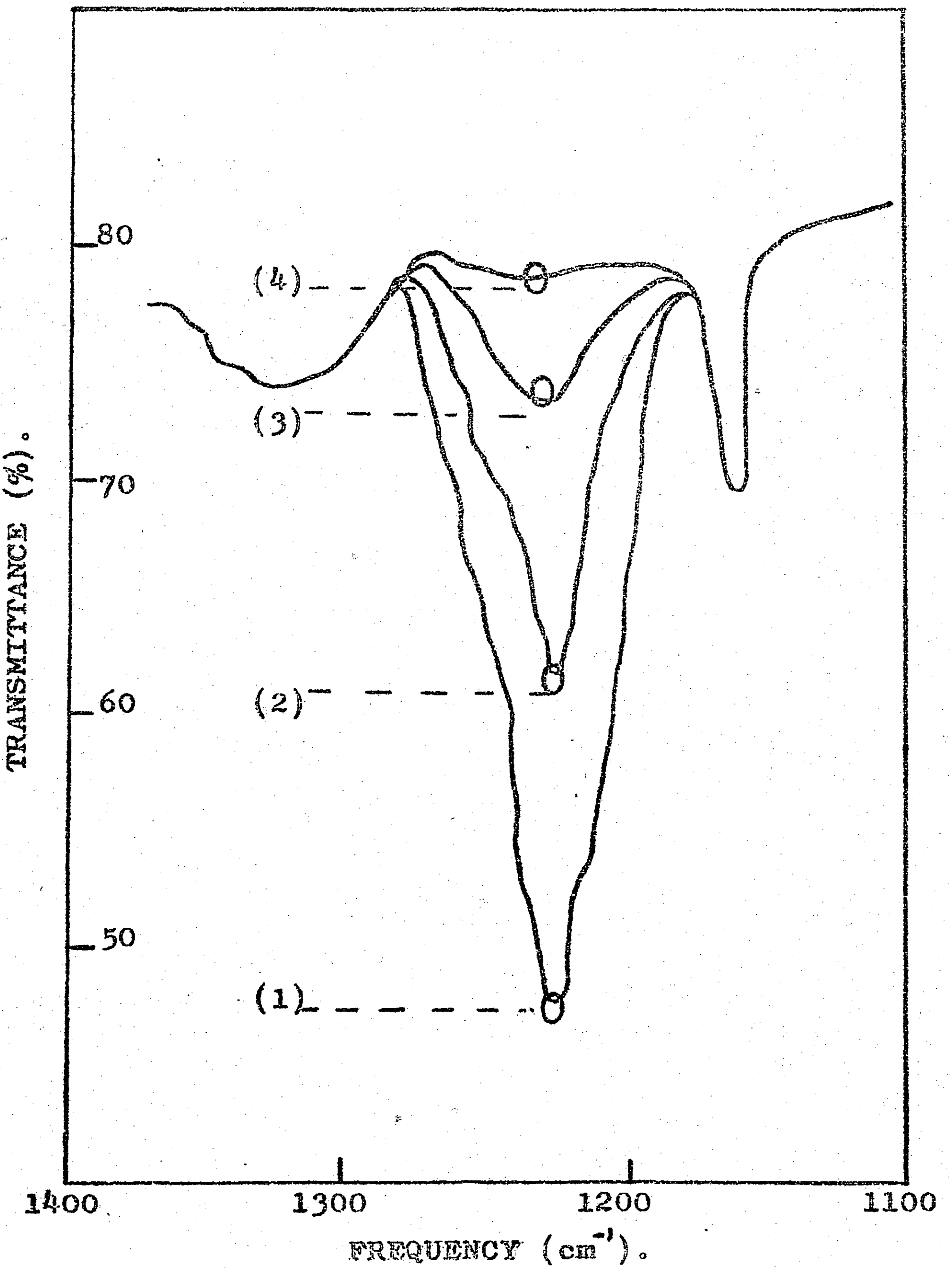
The thickness of a uniform film is related to its weight by the equation,

$$w = d\ A\ t \qquad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

in which w is the weight, t, the thickness, A the area and d, the density of the polymer (1.054 g./c.c.).(1)

FIGURE 4.

REMOVAL OF CHLOROFORM FROM A POLYSTYRENE FILM.



(1)-Undried film, (2)-Same film vacuum dried for one hour, (3)-Same film, one cycle of drying treatment, (4)-Two cycles.

The areas of several pieces of film were determined accurately by placing them on squared paper and counting the number of squares covered. The corresponding weights were then obtained and the thicknesses found from equation (1). It was found that the films had a uniform thickness throughout and that the above relation was accurately obeyed. Using the data obtained by this technique, a relation between thickness and absorbtion of the 2537Å line was derived. The latter measurement proved to be rapid and very sensitive (on account of the high extinction coefficient of polystyrene at 2537Å) and it was used to check the thickness of a film prior to oxidation.

8. Choice of Film Thickness

The film thickness chosen for oxidation studies was determined by considering two properties of the polymer, viz. (a) Absorbance of the 2537Å line and (b) diffusion of oxygen into the polymer.

(a) Absorbance of 2537Å line

Because of the very high extinction coefficient of polystyrene for the 2537Å line, the incident light intensity is reduced to less than 1% by passage through a film 0.01 mm thick. It follows then that the photo-initiation at this and at greater depths in a film will be negligible compared with that at the surface and it was therefore unnecessary to use films as thick as 0.01 mm.

(b) Diffusion of oxygen

Before attempting to obtain quantitative information from a gas-solid reaction, it must be established that the reaction is not diffusion controlled. Measurements by Barrer(61) and Stannett(62) indicate that the rate of diffusion of oxygen into polystyrene at 28°C and 600 mm Hg of oxygen is 7×10^{-7} c.c./cm.^{2}/mm/min. For a film 0.01 mm thick, with a diffusion path of 0.005 mm, the rate of diffusion is 10^{-4} c.c./cm.^{2}/min. Early oxidation experiments indicated that this figure was greater than the rate of oxidation by a factor of five. In order to be completely certain, however, and especially since thinner films still had sufficient mechanical strength, it was decided to use films 0.0044 mm in thickness.

SECTION 2

Oxidation Apparatus

1. Introduction

The need to study the photo-oxidation at room temperature has already been stressed. Preliminary experiments, however, indicated that the rate of the reaction was very slow and the volumes of oxygen absorbed were too small to be measured accurately with the type of apparatus which had been used successfully in similar investigations with olefins(7). In developing an alternative technique for measuring oxygen consumption, the following factors were considered.

2. Factors Influencing the Choice of Apparatus

(a) Transmission of ultra-violet radiation

It was soon realised that the reaction was very sensitive to the wavelength of the radiation used, for example, the rate of oxidation in presence of 2537 Å radiation was greater than that in presence of a similar intensity of 3650 Å radiation by a factor of about forty Thus in order to have a reasonable time scale, it was decided to use 2537 Å radiation.

Pyrex glass, however, is opaque to such radiation, so the apparatus must include at least a fused silica window. Initially such windows were attached to pyrex tubes with " Araldite" , but this adhesive rapidly deteriorated on irradiation. These reaction vessels were later replaced by fused silica tubes with flattened ends, which were ground and polished to an optical finish.

(b) Effect of Mercury

A mercury-free atmosphere is required within the oxidation apparatus for the following two reasons.

(i) Mercury vapour, the pressure of which is appreciable at room temperature (1.4×10^{-3} torr), absorbs its resonance radiation strongly, thus the intensity reaching the polymer will be considerably attenuated. Some idea of the extent of this effect can be had from the data obtained by Noyes(65) who showed that a one cm. column of air containing mercury vapour at 25°C is sufficient to reduce the incident intensity of 2537 Å radiation to about 20%.

(ii) Another consequence of mercury absorbing 2537 Å radiation is the production of ozone in an oxygen atmosphere. Mercury absorbs the radiation to produce excited atoms according to the equation,

$$Hg(6\,{}^1S_0) + h\nu\ (2537\ \text{Å}) \longrightarrow Hg^*\ (6\ {}^3P_1)$$

In the absence of collisions these atoms become deactivated by fluorescing. Oxygen, however, quenches this fluorescence and concurrently atomic oxygen and ozone are produced(70).

$$Hg^*(6\ {}^3P_1) + O_2 \longrightarrow O + HgO$$
$$O + O_2 + M \longrightarrow O_3 + M$$

It is quite conceivable that the action of ozone on the polymer will be different to that of oxygen and it is thus essential that the above reactions are not permitted to occur.

(c) Manometric Fluid

As a consequence of the undesirable properties just mentioned, mercury was considered unsuitable as a manometric fluid. The suitability of alternative fluids was assessed from four points of view.

(i) The Density of the Fluid

Absolute pressure can be defined as

$P = \rho g h$ were ρ is the density of the fluid, g is the gravitational constant, h is the height of the column and P is the pressure.

It follows that,

$$\frac{dh}{dP} = \frac{1}{\rho g}$$

In other words, the sensitivity of the fluid to small changes in pressure, and ultimately the accuracy of a measurement with the fluid, is inversely proportional to its density. Since small pressure changes were anticipated during oxidation a low density fluid was preferred.

(ii) Vapour-Pressure of the Fluid

Apart from its more obvious and undesirable participation in the reaction, a fluid which has an appreciable vapour pressure at room temperature is particularly unsuitable on account of the opacity to 2537 Å radiation (all the potential manometric fluids absorb 2537 Å radiation strongly). A substance with a low vapour pressure was thus essential.

(iii) Response to Pressure Changes

The response of a liquid in a tube to small pressure changes depends largely on its viscosity and surface tension; for example a substance with a low surface tension tends to wet the glass, causing tailing and a substance with a high viscosity tends to respond only sluggishly. A substance combining the desirable properties of low viscosity and high surface tension is therefore required.

(iv) Lack of Reactivity

Since the surface of the fluid is to be exposed to ultra-violet radiation in oxygen, a compound which can withstand these conditions without serious modification is required. In this connection certain silicone fluids are entirely unsuitable on account of their tendency to become rubbery on irradiation.

Choice of Manometric Fluid

Several substances having combinations of these properties were examined and Table 2 shows some of the relevant properties. From the table it can be seen that two substances in particular, silicone oil and di-octyl sebacate, best fulfil the requirements. Although the latter has a lower vapour pressure, the former is preferred on the grounds of higher sensitivity, it being considered that the loss of light intensity incurred when 10^{-6} torr of silicone oil is replaced by 10^{-5} torr of

TABLE 2

Substance	Density (gm/cc. at 25°C)	Sensitivity (Hg = 1)	Boiling Point (°C at 5 torr)	Vapour Pressure (torr)	Surface Tension	Viscosity
Di-butyl phthalate	1·051	12·9	182	10^{-4}	low	high
Di-butyl sebacate	0·94	15·9	200	7×10^{-5}	fairly high	high
Di-octyl sebacate	0·92	16·25	240	10^{-5}	fairly high	low
Silicone Oil	1·1	12·3	?	10^{-6}	low	low

di-octyl sebacate is negligible, and is certainly more than compensated for by the resultant gain in sensitivity.

(d) Temperature Control

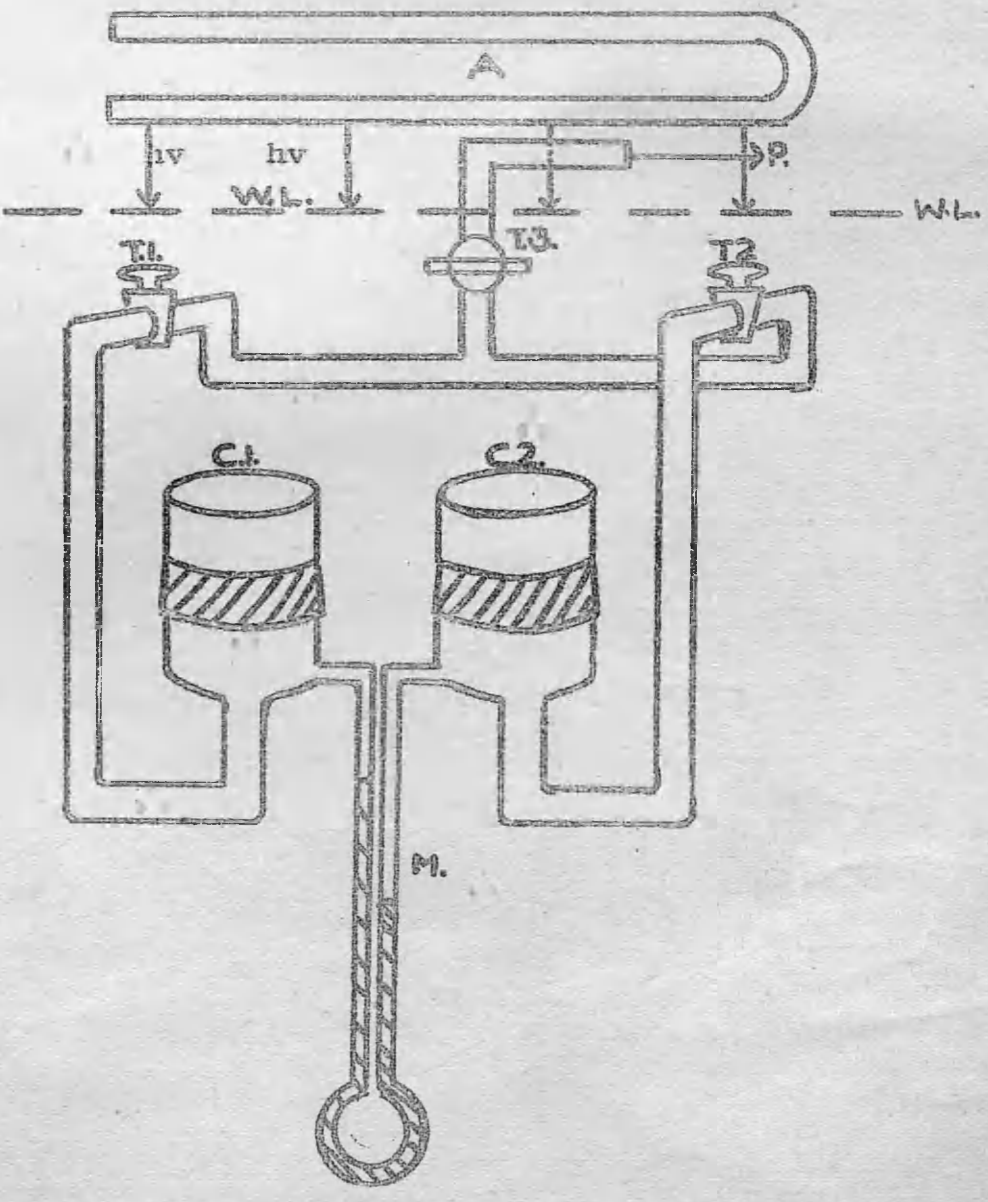
It is futile to attempt accurate pressure measurements with a di-octylsebacate manometer if adequate thermostatting of the whole apparatus is not provided. Maintainance of uniform temperature throughout an apparatus however, usually imposes a restriction on its size and consequently on the size of the sample which can be introduced into it. Obviously in this case, where the volume of oxygen consumed by the polymer is very small, it is desirable to use large areas of film. These, however, require relatively large apparatus.

It was decided to compromise and to use a small apparatus which can be accurately thermostatted and which can accommodate relatively large areas of film, that is the ratio of the film area to the apparatus volume is relatively large.

3. The Oxidation Apparatus

The apparatus shown in figure 5 consists essentially of two cells of equal volume joined by a differential

FIGURE 5



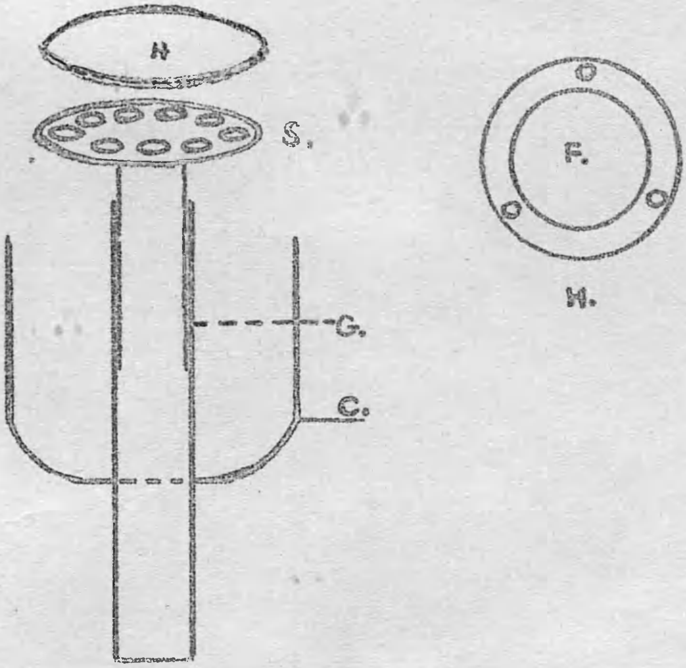
OXIDATION APPARATUS.

C_1, C_2- Fused-silica cells, M-Manometer, A-Low-pressure mercury arc, T_1, T_2, T_3-Stopcocks, W.L.-Water level, P-to pumps.

manometer. The lower parts of the cells are constructed from B40 Pyrex cones and the upper parts consist of B40 fused silica sockets (Thermal Syndicate Limited) with flattened ends through which the ultra-violet radiation is transmitted. The cells are independently joined to the oxygen supply and high vacuum system, and can be isolated from these and from each other by closing stop-cocks, T_1 and T_2. The films are oxidised in C_1, while C_2 which is under the same conditions of temperature, pressure, radiation, etc., acts as a compensating volume. In this way variations in pressure arising from small fluctuations in the ambient temperature are balanced out. The manometer is constructed from heavy-wall constant-bore Pyrex tubing having a volume per cm. of 0.165 c.c.

The arrangement of the film inside C_1 is shown in figure 6. The film is placed between two brass O-rings which are screwed together and then placed on the platform, S, which consists of a brass disc, perforated to allow the oxygen to have free access to the underside of the film. The disc is in turn supported on a glass tube, G, round which the glass cup, C, is sealed. The purpose of the latter is to contain absorbants to remove volatile material

FIGURE 6.



ARRANGEMENT OF FILMS IN C_1

F-Film, H-Holder, S-Perforated brass support, G-Glass support, C-glass cup which contains absorbants for water and carbon dioxide.

produced during oxidation.

Because a certain amount of space is occupied by this supporting equipment, the effective volume of C_1 is less than that of C_2, and in order to avoid any corresponding pressure changes, it is necessary to introduce identical apparatus (with the exception of the film) into C_2. This will also compensate for possible oxygen absorbtion by the brass holder and ring in C_1.

The lamp, with its arc in a horizontal position, is mounted vertically above the apparatus, both cells being uniformly and equally irradiated. The lamp - cell distance is kept constant throughout the work.

The following advantages accrue from using this system.

4. Advantages of the System

(a) Since the film is mounted between the brass rings, the surface area exposed to oxygen and radiation is accurately known and can be kept constant throughout the experiments.

(b) The film is held rigidly and warping is thus made impossible.

(c) Since the position of the film in the cell is automatically fixed by means of the supports, and since the lamp is placed at the same distance above the cells, the intensity of radiation incident on the film is constant.

(d) The incorporation of a compensating volume in the apparatus minimizes spurious pressure changes. Pressure changes associated with the supporting equipment are also balanced out.

(e) Possible oxygen absorbtion by the manometric fluid will also be balanced out, since the surfaces of the fluid in the two limbs will be exposed to the same conditions.

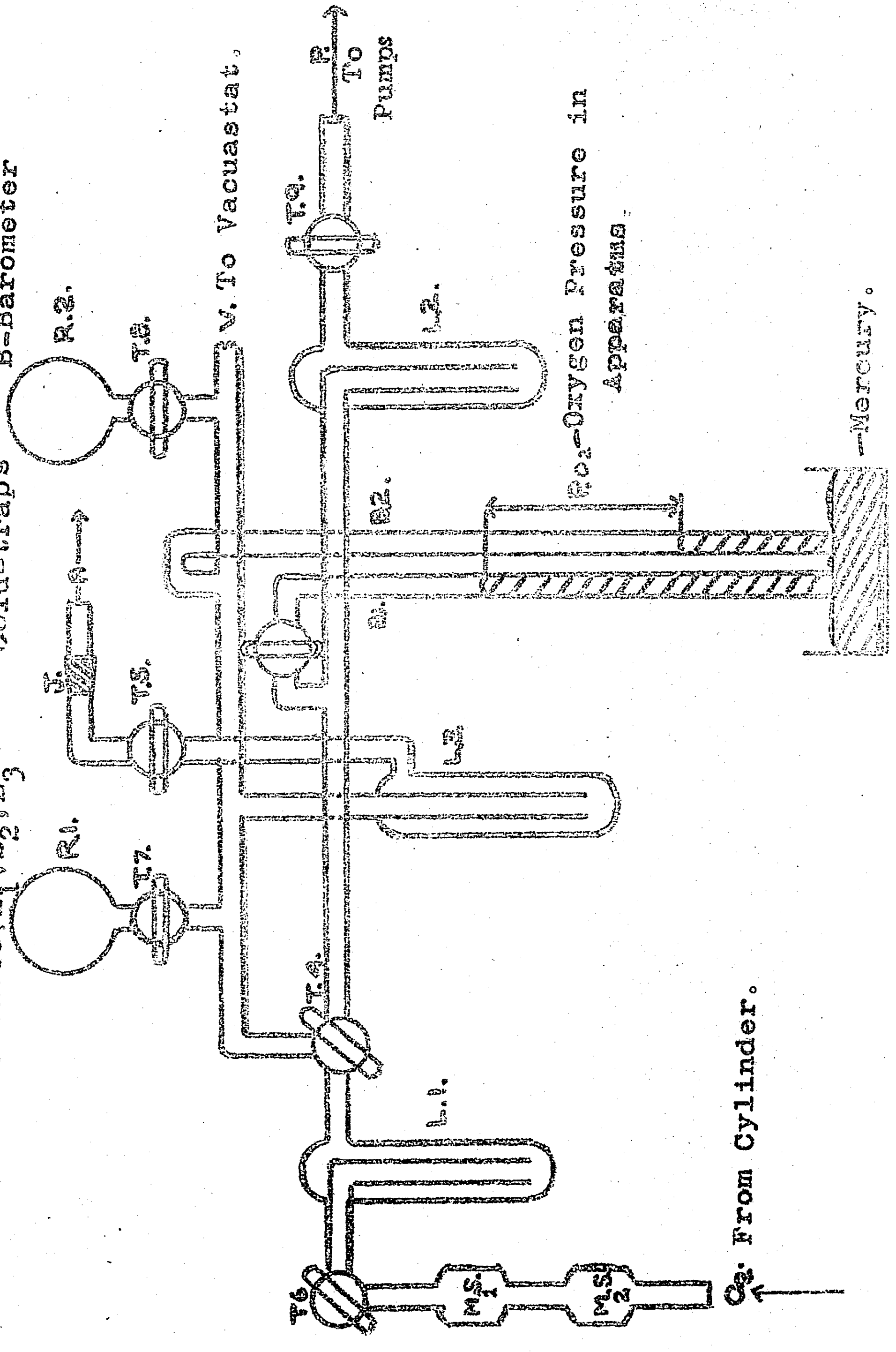
(f) The use of the low density manometric fluid makes the apparatus extremely sensitive.

5. The Vacuum System and Oxygen Supply

The system shown in figure 7 is used to evacuate the oxidation apparatus and to supply it with oxygen. Evacuation is achieved by a mercury diffusion pump backed by a rotary oil pump, and the pressure in the system is measured on the "Vacuastat" pressure gauge, V.

FIGURE 7.

VACUUM SYSTEM AND OXYGEN SUPPLY.



R_1, R_2, Reservoirs, T_4 to T_9 Stopcocks, J-Ground glass Joint, A-to apparatus, M.S.-Molecular sieves tubes, L_1, L_2, L_3 Cold-traps B-Barometer

Oxygen is supplied to the apparatus from the reservoirs, R_1, R_2, and not directly from a cylinder, since it is extremely difficult to obtain reproducible pressures in the apparatus using the latter technique. R_1 is filled with oxygen at 700 mm Hg and R_2 with oxygen at a pressure of about 20 mm Hg greater than that required in the apparatus. The apparatus is then pressurized to within 5 mm Hg of that pressure required with oxygen from R_1 and T_7 is closed T_8 is then opened and oxygen at a comparatively lower pressure is admitted to adjust the total pressure in the apparatus to that desired.

6. Operation of the Apparatus

After removing the fused silica sockets from the cells, a mounted film and the supporting equipment is placed in C_1 and similar equipment is placed in C_2. The sockets are then replaced care being taken to smear silicone high vacuum grease on the lower surfaces of the cones and sockets only, in order to avoid the presence of the grease inside the cells, and hence its possible oxidation. The apparatus is immersed to the level shown in figure 5 in the water in a thermostat, maintained at 28°C by a mercury-toluene regulator and Sunvic Relay, and it is then connected to the vacuum system through a ground glass joint, J. Stopcocks, T_1, T_2, T_3, and T_5 are opened and the whole system evacuated and pumped out for ten minutes. T_9 is then closed, T_6, T_7 and T_8 opened and the entire system is flushed several times with oxygen which is drawn from a cylinder through two tubes, MS_1, MS_2, containing types 4A and 5A Linde molecular sieves (30 mesh) and a trap, L_1, immersed in " Drikold" at -78°C. The impurities present in the cylinder oxygen which could conceivably affect the oxidation reactions, (water and carbon-dioxide) are thus removed. A similar trap, L_3, adjacent to the oxidation apparatus removes the mercury vapour from the oxygen before it enters the cells.

The reservoirs are then filled to the required pressures, those being indicated on the barometers, B_1, B_2. The stopcocks, T_6, T_7 and T_8 are closed and the system evacuated. T_4 is closed so as to isolate the section containing the reservoirs, and the oxidation apparatus is then filled from R_1 and R_2, the working pressure being indicated as the difference in the levels of mercury in the two barometers, B_1 and B_2. Stopcocks T_3 and T_5 are closed and the apparatus is left for half an hour, during which time the oxygen assumes the temperature of the water bath. and the pressure of oxygen throughout the apparatus becomes uniform. After this T_1 and T_2 are closed so as to isolate the cells from each other and the apparatus is given a further half hour to settle down. At this time the lamp is also switched on, care being taken to avoid irradiation of the film. By allowing the lamp to run for about half an hour before the reaction begins, it is ensured that the output has become sufficiently stable. It was found that if these precautions were not taken reproducible results could not be obtained.

After the settling down period is complete the lamp is placed above the cells and the reaction is started. As the oxidation proceeds, the volume of oxygen in C_1 is diminished and a corresponding change of pressure results. The pressures in C_1 and C_2 are now no longer equal and the levels of the di-octyl sebacate in the two limbs of the manometer change, the level in the limb attached to C_1 rising and that in the limb attached to C_2 falling by an equal amount. The reaction is followed by measuring pressure differences at ten-minute intervals, using a cathetometer. The corresponding amount of oxygen absorbed is calculated as follows.

If V(cc) is the volume of C_1 and C_2, P(cm.Hg) is the original pressure of oxygen in C_1 and C_2 (initially the two pressures are equal), d(gm./cc) is the density of the manometric fluid, d_M is the density of mercury, r is the radius of the manometer tubing, 2h(cm.) is the observed pressure difference and T(^oA) is the temperature at which the reaction takes place, then the original number of moles of oxygen (n_o) in C_1 and C_2 is given by the equation,

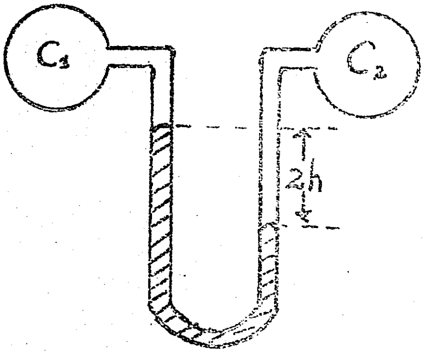
$$n_o = \frac{PV}{RT} \quad \text{where R (cm Hg, cc) is the gas constant}$$

After Reaction

The new pressure in C_2 (P2) is found by applying Boyle's Law (this is valid since the number of molecules in C_2 remains constant)

$$\text{i.e.} \quad PV = P2(V + \pi r^2 h)$$

$$\therefore P_2 = \frac{PV}{V + \pi r^2h}$$



The new pressure in C_1, P_1, is related to this pressure by the equation,

$$P_1 = P_2 - \frac{2hd}{d_M}$$
$$= \frac{PV}{V + \pi r^2h} - \frac{2hd}{d_M}$$

The new volume of oxygen in C_1, V_1, is given by the equation,

$$V_1 = V - \pi r^2h$$

It follows then that the number of moles of oxygen, n_1, left after reaction is given by the relation,

$$n_1 = \frac{P_1V_1}{RT}$$
$$= \frac{1}{RT}\left[(V - \pi h r^2)\left(\frac{PV}{V+ \pi r^2h} - \frac{2hd}{d_M}\right)\right]$$
$$= \frac{1}{RT}\left(\frac{PV^2}{V+\pi r^2h} - \frac{PV \quad r^2h}{V+\pi r^2h} - \frac{2hdV}{d_M} + \frac{2h^2d \pi r^2}{d_M}\right)$$

The extent of reaction is then given by $n_0 - n_1$,

i.e. $n_0 - n_1 = \frac{1}{RT}\left[PV - \frac{PV^2}{V+\pi r^2h} + \frac{PV \quad r^2h}{V+\pi r^2h} + \frac{2hdV}{d_M} - \frac{2h^2d \pi r^2}{d_M}\right]$

Some idea of the sensitivity of the system can be obtained from the following information. The smallest pressure difference which can be read is 0.002 cm, i.e. h = 0.001 cm. This corresponds to an absorbtion of 1.9×10^{-8} moles of oxygen when the oxygen pressure is 600 mm.Hg. The technique is also a micro one, since the normal sample weight is 5×10^{-3} g.

SECTION 3

Photochemical Techniques

(1) The Ultra-violet Lamps

(a) Introduction

The need to use short-wave ultra-violet radiation (2537 Å) has already been justified, and the source of this was a Hanovia " Chromatolite" lamp. In order to investigate the effect of longer wave ultra-violet radiation on the reaction, however, an Osram 125W MB type mercury vapour lamp was used.

(b) Output of the Hanovia Lamp

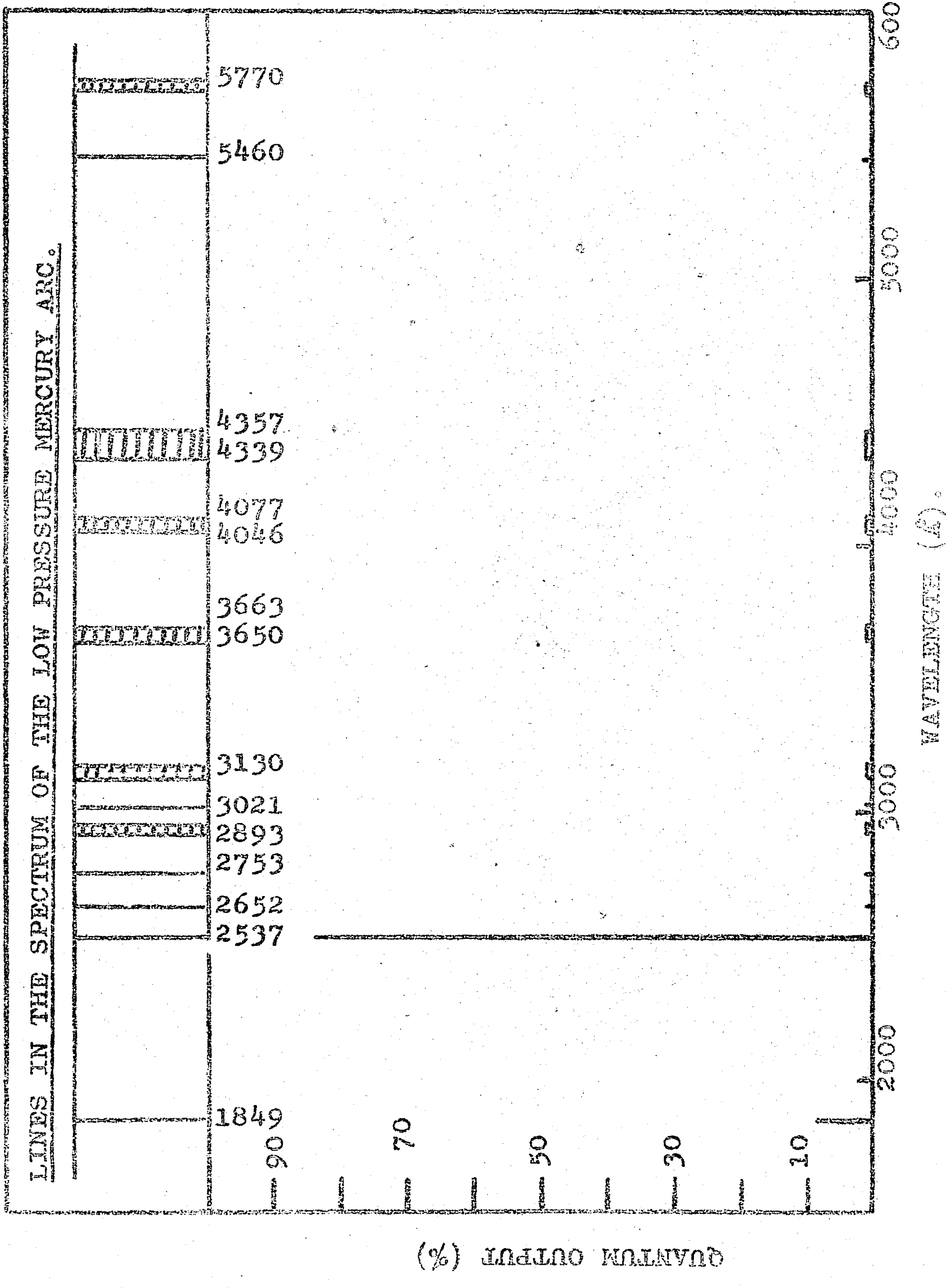
This lamp employed a low pressure mercury arc to produce a typical mercury emission spectrum, the intensities of the two resonance lines at 1849 Å and 2537 Å being much greater than those of all the other wavelengths present. The output of this lamp is shown in figure 8.

(c) The Osram Lamp

The ultra-violet radiation was provided by a medium pressure mercury arc. The arc which is produced between tungsten electrodes in a silica tube is in turn surrounded by a lead glass envelope which acts as an efficient filter

FIGURE 8

OUTPUT OF THE HANOVIA LAMP.



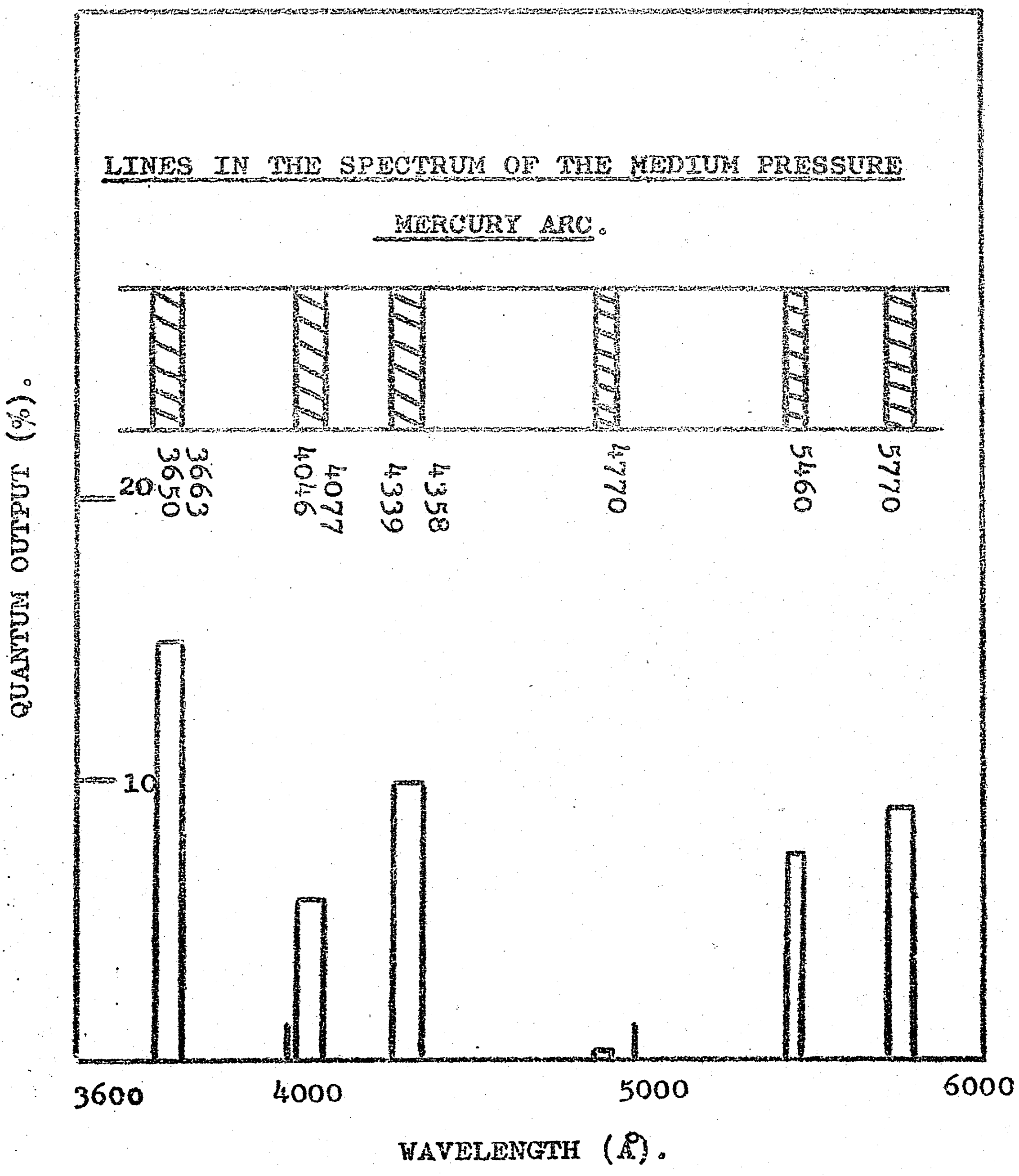
removing all radiation with a wavelength shorter than 3200 Å. The output of the lamp is shown in figure 9.

2. Determination of Absolute Numbers of Quanta Produced by the Lamps

(a) Introduction

In order to calculate quantum yields for oxidation the absolute numbers of quanta of each active wavelength must be known. The ideal way in which to obtain this information would be to use filter systems to monochromatize the radiation from the sources and then measure the numbers of quanta of the particular wavelengths using uranyl-oxalate-oxalic acid actinometry. In practice, however, it is impossible to obtain a filter system which does not also absorb the monochromatic radiation, and it is therefore necessary to measure the total effective quantum outputs of the sources, that is the total numbers of quanta produced by the lamps which are capable of photolyzing the actinometric solution (all quanta with wavelengths less than 5000 Å)(66). From the total number, the numbers of quanta with particular wavelengths can be found as follows. If N is the total effective number of quanta produced by the

FIGURE 9.



OUTPUT OF THE OSRAM LAMP.

lamp per unit time, then the number of molecules of oxalic acid, (U) decomposed per unit time is given by

$$U = N \sum_{0}^{n} F_\lambda A_\lambda \phi_\lambda \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (X)$$

(The summation being carried out over all the n wavelengths shorter than 5000 Å)

where F_λ is the fraction of the radiation emitted at wavelength λ ,

ϕ_λ is the quantum yield at wavelength λ

A_λ is the absorbtion of wavelength λ by the actinometric solution

A_λ is found from the equation,

$$A_\lambda = Io_\lambda (1 - e^{-kcl}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (Y)$$

in which Io_λ is the incident intensity of radiation of wavelength, λ , c is the concentration of uranyl oxalate, l is the thickness of the layer of actinometric solution, and k is the extinction coefficient, values of which were obtained from the data of Noyes(65).

It follows then that the absolute number of quanta with wavelength λ (Q_λ) is related to the total effective number by the relation

$$Q_\lambda = \frac{E_\lambda \quad A_\lambda \quad \phi_\lambda}{\sum_n E_\lambda \quad A_\lambda \quad \phi_\lambda} \; N \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (Z)$$

(b) Actinometry(63,64)

The actinometry was carried out in the oxidation apparatus in the thermostat at 28°C, since it would have been virtually impossible to reproduce otherwise the exact radiation conditions obtaining during oxidation.

Uranyl oxalate was prepared by mixing hot equivalent solutions of AnalaR oxalic acid and uranyl nitrate. The crude oxalate was washed several times with water and dried thoroughly in air at 110°C for three hours. Actinometric solutions were prepared by mixing 5 ml. 0.006M uranyl oxalate and 10 ml. 0.01M oxalic acid in a 30 ml. beaker. The very dilute uranyl oxalate was considered essential on account of its very high extinction coefficient for 2537 Å radiation (2900)(65). Higher concentrations would have resulted in 90% absorbtion of the incident 2537 Å intensity within the first 0.01 mm. of photolyte, thus concentration gradients would have been set up and irregular results obtained. The solution was then acidified (2 ml. concentrated sulphuric acid) and titrated against standard potassium permanganate at 85°C. Similar solutions were prepared, introduced into the oxidation apparatus in beakers and irradiated for known lengths of time, care being taken to agitate them gently during the irradiation. The beakers were removed and their contents titrated against the permanganate in the manner described above.

Volumes of permanganate corresponding to oxalic acid decomposed were then obtained by difference and the numbers of molecules of acid decomposed were then calculated. Before applying equation (X) it is necessary to compute $\sum F_\lambda \; \phi_\lambda \; A_\lambda$. The values of ϕ_λ are obtained from the data of Noyes and Leighton(65), those of A_λ calculated from the equation (Y) (c and l being determined by direct measurement) and those of F_λ from figures 8 and 9. N is then found and from it, by application of equation (Z), the required numbers are calculated. Tables 3 and 4 summarize relevant information.

Table 3 - Output of Hanovia Lamp

λ (Å)	F_λ	ϕ_λ	A_λ	$F_\lambda A_\lambda \phi_\lambda$	Q_λ (einsteins/sec./cm.^{2})
*1849	0.084	-	-	-	-
2537	0.84	0.62	1.0	0.520	3.1×10^{-9}
2652	0.0018	0.58	1.0	0.0011	6.5×10^{-12}
2753	0.0010	0.58	1.0	0.0058	3.45×10^{-12}
2893	0.003	0.58	1.0	0.00174	1.05×10^{-11}
2967	0.001	0.57	1.0	0.0057	3.45×10^{-12}
3021	0.0052	0.57	1.0	0.003	1.82×10^{-11}
3130	0.0052	0.56	0.94	0.0027	1.65×10^{-11}
3650	0.0056	0.56	0.62	0.0019	1.15×10^{-11}
3663	0.0056	0.53	0.11	0.0003	1.82×10^{-12}
4046	0.0067	0.56	0.56	0.0021	1.28×10^{-11}
4077	0.0067	0.58	0.56	0.0021	1.28×10^{-11}
4339	0.0032	0.58	0.19	0.0003	1.65×10^{-12}
4357	0.0080	0.58	0.10	0.0005	3.1×10^{-13}
4358	0.016	0.56	0.10	0.001	6.2×10^{-12}

$$\sum F_\lambda \quad O_\lambda \quad A_\lambda$$
$$= 0.5284$$

* 1849 Å radiation is completely absorbed by air and therefore contributes nothing to the photolysis.

Table 4 - Output of Osram Lamp

λ (Å)	F_λ	ϕ_λ	A_λ	$F_\lambda\ A_\lambda\ \phi_\lambda$	Q_λ (einsteins/sec./cm.^{2})
3650	0.15	0.56	0.62	0.052	2.5×10^{-8}
3663	0.15	0.55	0.11	0.0088	4.6×10^{-9}
4046	0.059	0.56	0.56	0.0185	9.65×10^{-9}
4077	0.059	0.58	0.56	0.0185	9.65×10^{-9}
4339	0.095	0.58	0.19	0.011	5.7×10^{-9}
4357	0.095	0.58	0.10	0.006	3.16×10^{-9}
4358	0.095	0.56	0.10	0.006	3.16×10^{-9}

$$\sum F_\lambda\ \phi_\lambda\ A_\lambda = 0.1208$$

(3) Transmission of the Ultra-violet Radiation

(a) Introduction

The output of the lamps traversed two inches of air, 1 cm. of water, 2 mm. fused silica and 1 cm. of oxygen (inside the cell) before finally impinging on the films. The nature of the radiation eventually reaching the film was modified to some extent by the absorbtion characteristics of these media, and it is therefore worthwhile to examine these characteristics.

(b) Transmission by Air

An examination of the composition of air reveals that the only component which is capable of absorbing the ultra-violet radiation produced by these sources is oxygen, the other constituents being completely transparent in this region of the spectrum. The oxygen absorbtion spectrum consists of two sets of bands, the one system converging at 2400 Å, and the more important Schumann-Runge system, having a threshold wavelength at 2000 Å and converging towards 1761 Å (67,68). Corresponding to these two absorbtions are two photo-dissociations of oxygen moleculse,

$$O_2 + h\nu \longrightarrow O(^3P) + O('D)$$

and

$$O_2 + h\nu \longrightarrow 2O(^3P)$$ respectively; ozone is produced concurrently according to the equations,

$$O('D) + O_2 + M \longrightarrow O_3 + M$$

$$O(^3P) + O_2 + M \longrightarrow O_3 + M$$

M being the necessary third body.

It is obvious then that only the 1849 Å line has an energy associated with it which exceeds the threshold energy for the photo-dissociation of oxygen; it is thus the only line which is absorbed by the air. Noyes(65) has pointed out that 1 cm. of air is sufficient to absorb this line completely.

(c) Water

The absorbtion spectrum of 1 cm. of water is shown in figure 10. With the exception of 1849 Å radiation, water in transparent to all wavelengths.

(d) Fused Silica. The transmission of fused silica is shown in figure 11, it is similar to that of water.

FIGURE 10

ULTRA-VIOLET ABSORBTION OF WATER (1cm.)

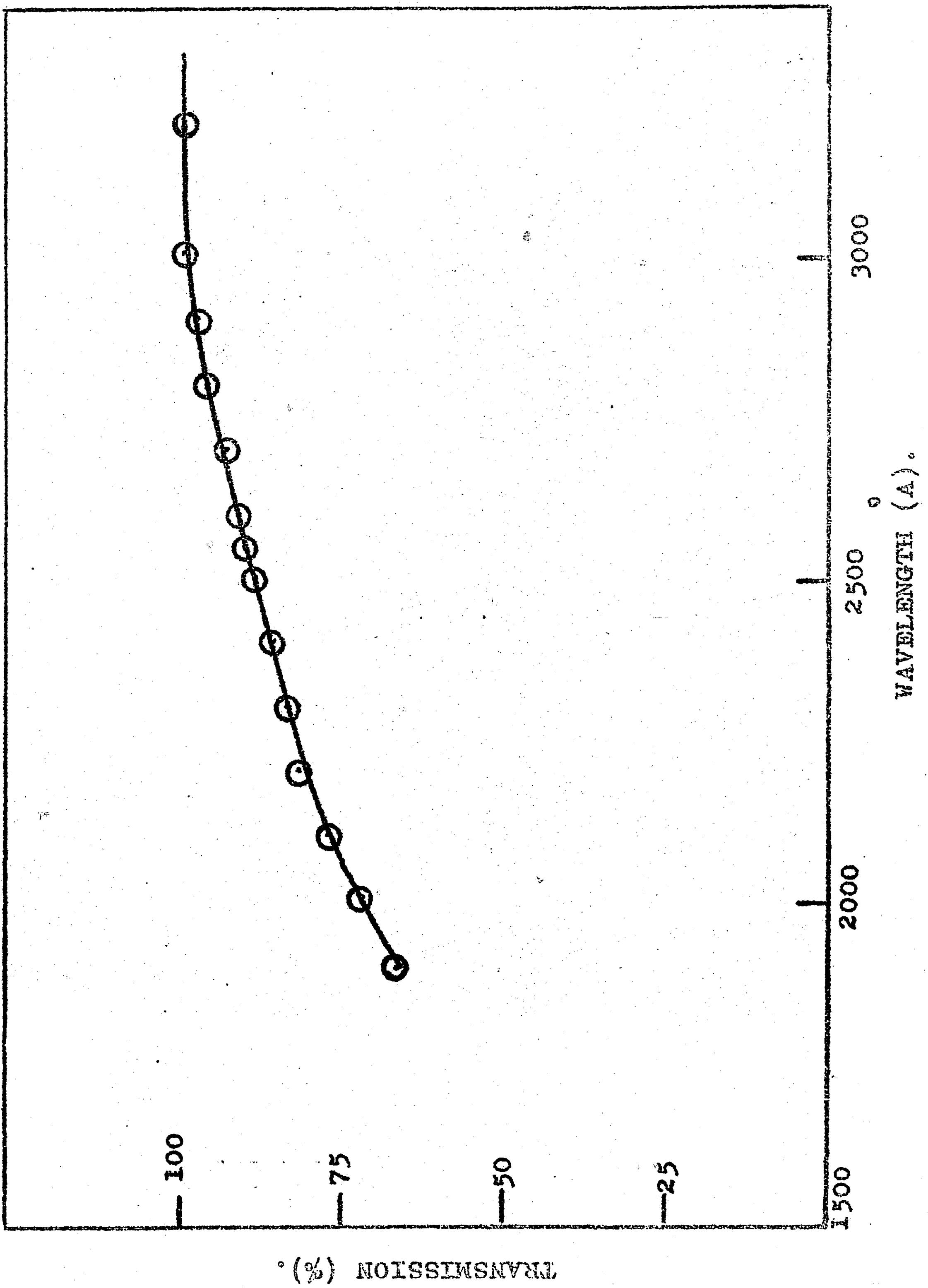
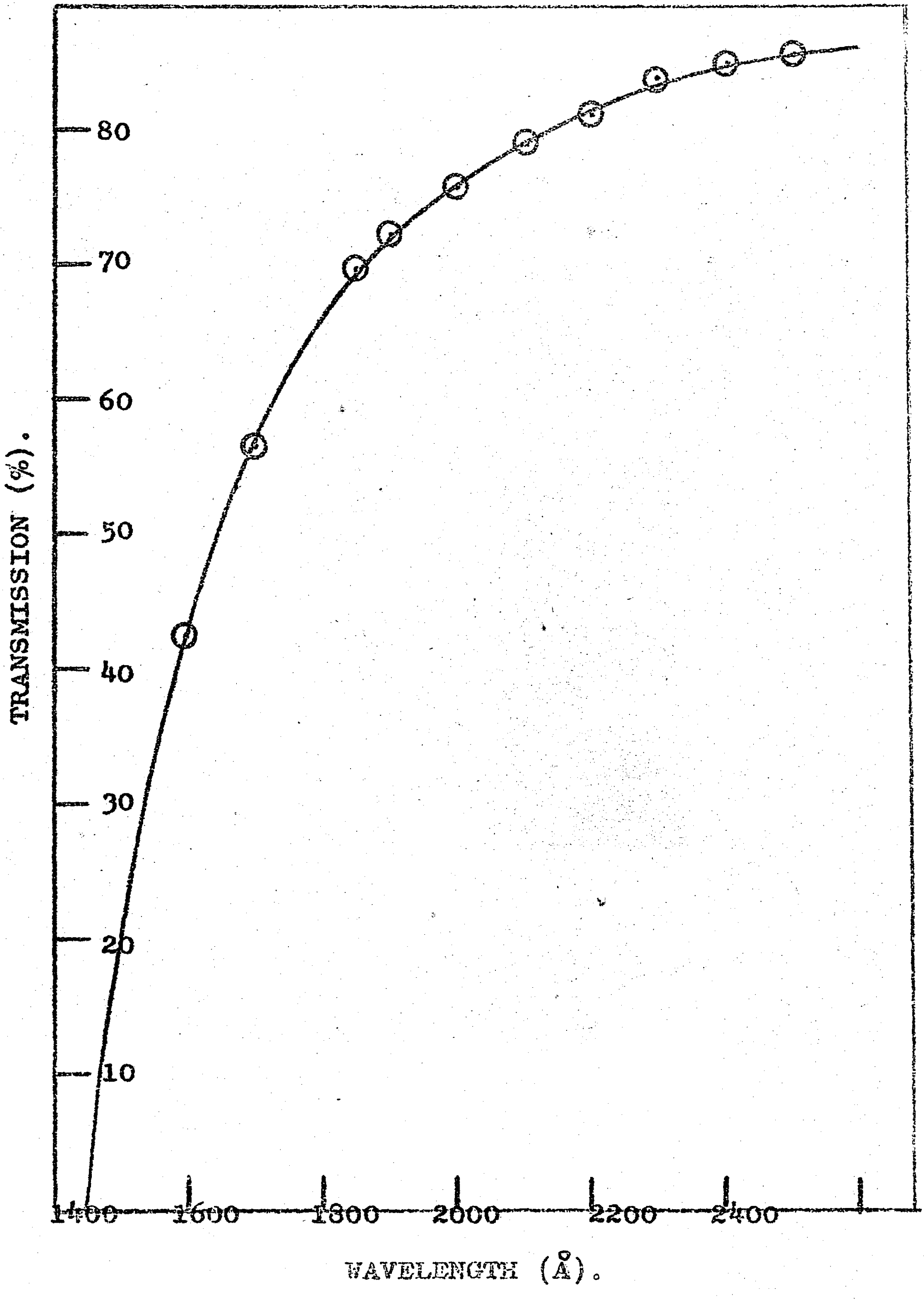


FIGURE 11.

ABSORBTION SPECTRUM OF FUSED SILICA (2mm.).



(e) Monochromaticity of the source

It has been shown that 93% of the output of this lamp is composed of the mercury resonance radiation with wavelengths of 1849 Å and 2537 Å, and that in traversing the arc to polymer path the intensity of the former is reduced to an extremely low value. The intensity of the latter, however, is only slightly attenuated. This means then that since the intensities of the longer wavelength radiation are negligible compared with that of the 2537 Å, that the radiation reaching the polymer is virtually monochromatic (2537 Å).

It is fortunate that the 1849 Å line is so strongly absorbed by the air, since photolysis of the oxygen in the cell would occur yielding ozone, which could conceivably alter the course of the reaction by degrading the polymer. A direct and very sensitive test for ozone (potassium iodide) was applied, and it showed that the amount of ozone accumulating in the cell during an hour's irradiation was not sufficient to be detected by this method.
It appeared then that ozone, if present at all, would not have a sufficiently high concentration to affect the reaction to any significant extent.

(4) The Ultra-Violet Spectrum of Polystyrene

In a photochemical study the ultra-violet absorption characteristics of the photolyte must be investigated and the nature of the absorbing groups established. Figure 12 shows the absorbtion spectrum of a 0.0044 mm. film of polystyrene. The absorbtion pattern is a very simple one, the benzene rings attached to the main chain being the chromophoric groups.

(5) Verification of Lambert's Law

Before attempting to obtain quantitative information from rates of oxidation of various thicknesses of polystyrene films, it had to be established that the intensity of radiation was indeed exponentially attentuated throughout the film, that is that Lambert's Law was applicable, If this law is obeyed,

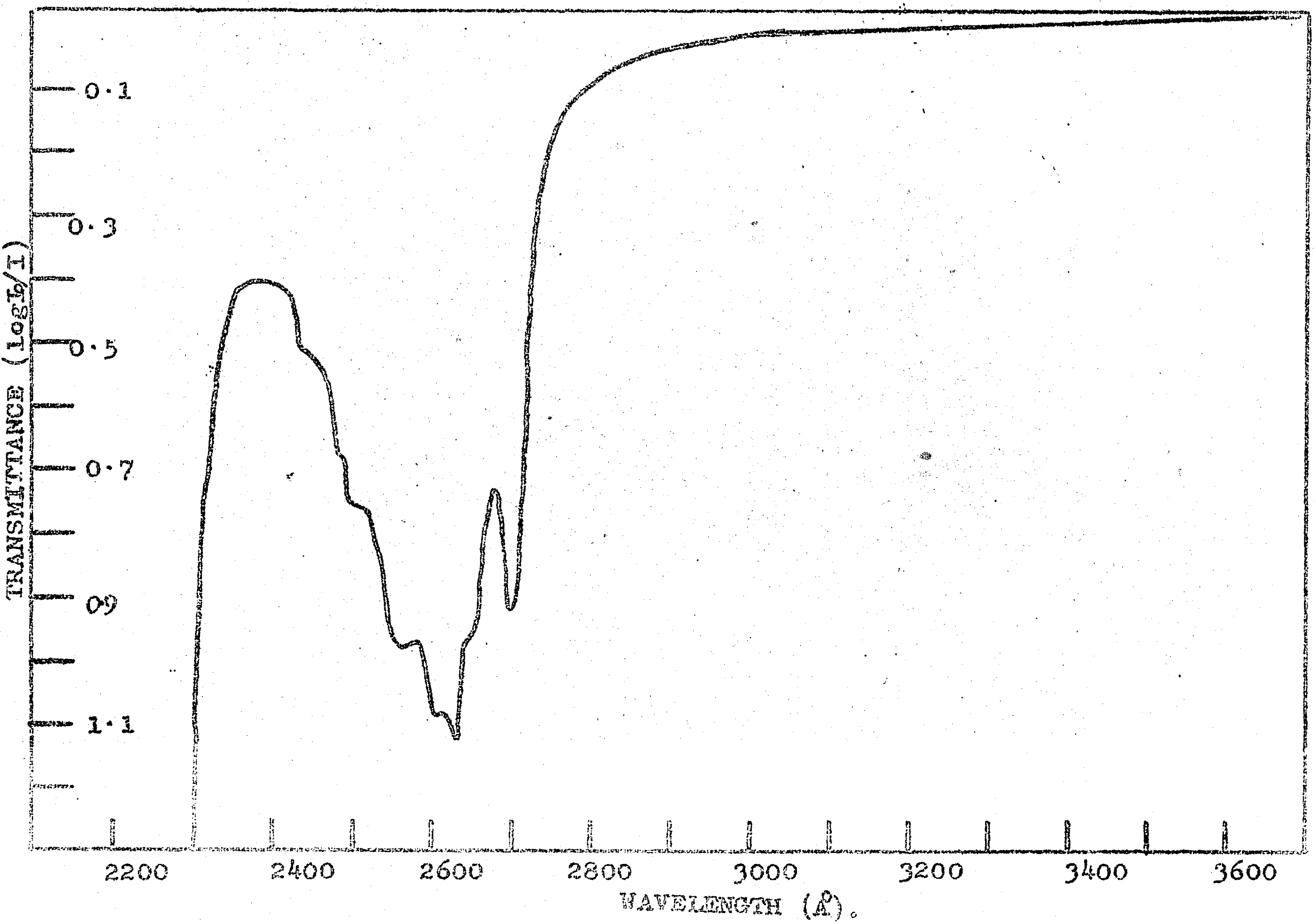
$It = Io\ e^{-ul}$ where It, Io are the transmitted and incident intensities of radiation of a given wavelength, u is the extinction coefficient, and l is the thickness.

In other words, optical density

$$= \log_{10} \frac{Io}{It} = k\,l \quad (k = \frac{u}{2.303})$$

FIGURE 12.

ULTRA-VIOLET SPECTRUM OF POLYSTYRENE FILM (0·0044mm. thick)



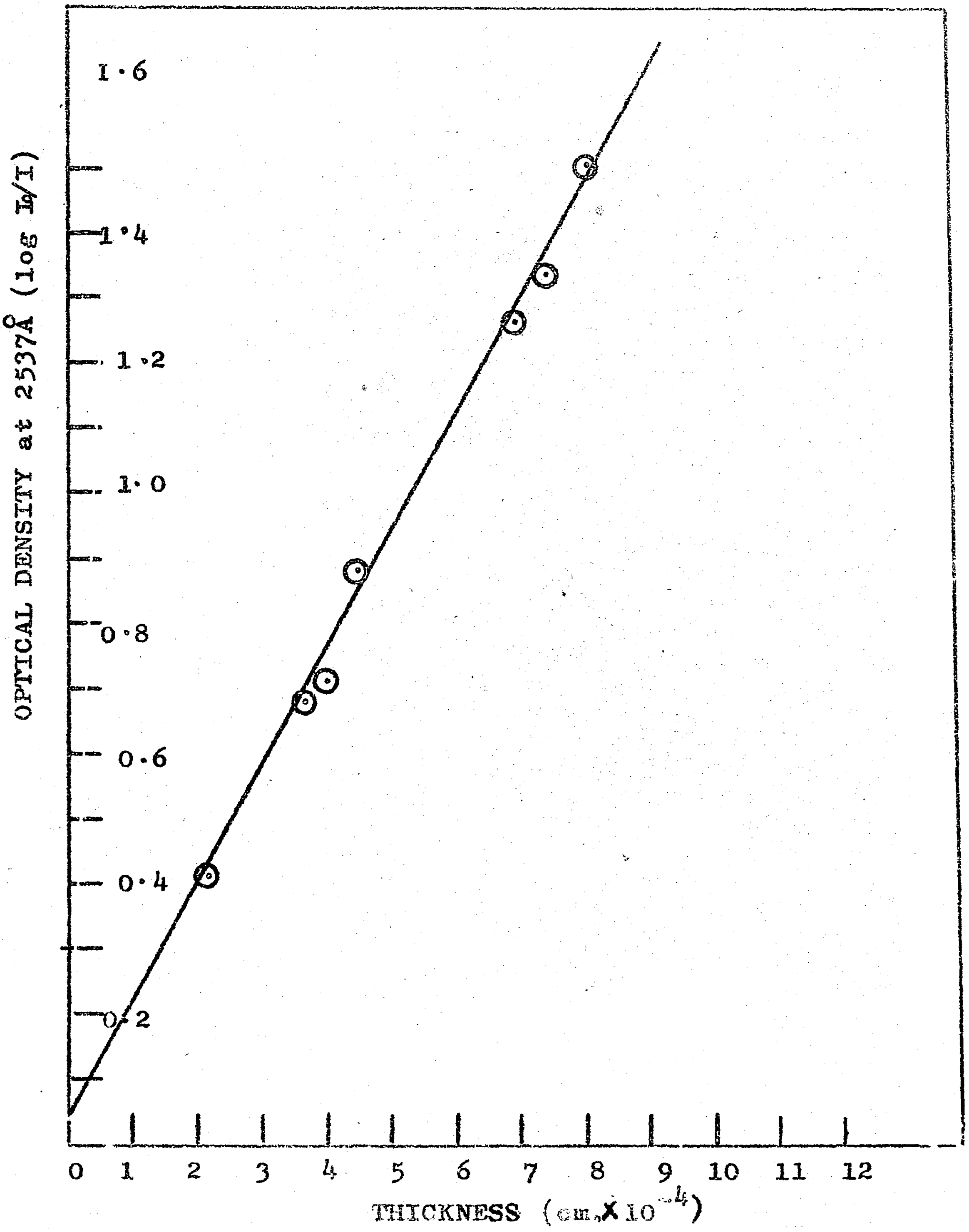
The optical densities of films of various thicknesses were obtained for 2537 Å radiation. The results are shown in figure 13. It can be concluded that since a linear relationship exists between optical density and film thickness, that Lambert's Law is in fact obeyed. The value of the absorbtion (extinction) coefficient, obtained by a least-squares analysis of the data is 1825 (cm. units).

(6) Estimation of Scattered Intensity

An examination of figure 13 shows that when the line is extrapolated to zero thickness it does not pass through the origin, there is, in fact a small intercept on the optical density axis. This absorbtion at zero film thickness can be associated with a loss of 2537 Å radiation through scattering and reflection at the film surface, and allowance must be made for this when quantum yields are being calculated. The actual value of this scattered intensity is 1.2% of the incident intensity of 2537 Å radiation.

FIGURE 13.

VERIFICATION OF LAMBERT'S LAW.



SECTION 4

Analytical Techniques

(1) Infra-red Spectroscopy

Infra-red absorbtion spectra of polystyrene films were measured using a Perkin-Elmer Model 237 Spectrophotometer. Although most of the measurements were made on films which were much thinner than the optimum film thickness (0.075 mm.) for infra-red analysis, it was found that this instrument gave perfectly satisfactory results. Films were usually mounted in the brass O-rings to prevent warping during the measurement period.

(2) Ultra-violet Spectroscopy

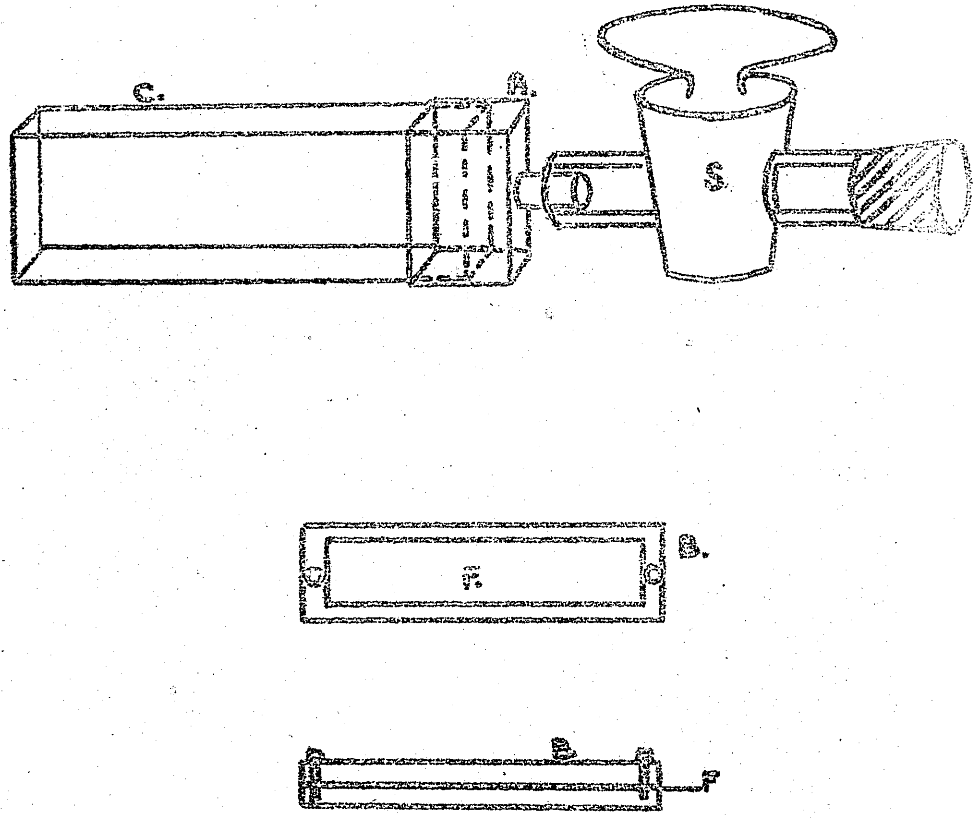
Ultra-violet absorbtion spectra were determined using a Perkin-Elmer Model 137 recording ultra-violet spectrophotometer. Films were supported on the brass rings during measurements, in order to prevent warping which can lead to artifically high absorbtions.

In order to investigate instantaneous changes in ultra-violet absorbtion during irradiation in vacuum, nitrogen or oxygen it was necessary to modify the measurement technique as follows. Films (0.0044 mm. thick) mounted on rectangular brass holders, were introduced into 2 mm. fused silica cuvettes which were then sealed to 1 mm. Pyrex stop-cocks through metal adaptors as shown in figure 14. This apparatus was then attached to a high vacuum system and thoroughly degassed. In the case of subsequent irradiation under high vacuum conditions the degassing was continued for 24 hours, and in the case of irradiation in presence of oxygen or nitrogen the apparatus was pressurized with the appropriate gas. The stop-cocks were closed and the units removed from the vacuum system and mounted under the source of ultra-violet radiation. In order to obtain the instantaneous ultra-violet spectra the units were placed in the spectrophotometer, the cuvette being placed in the slot as in normal measurements on solutions.

The advantages of being able to make a series of measurements under standard conditions in this way are threefold.

(1) Films which have been irradiated in nitrogen or under high vacuum conditions are not brought into contact with atmospheric oxygen during measurements. Thus the spectral changes observed are entirely the results of irradiation, and not of a combination of irradiation

FIGURE 14.



APPARATUS FOR INVESTIGATING INSTANTANEOUS CHANGES IN ULTRA-VIOLET AND VISIBLE SPECTRA.

C-Cuvette, A-Brass adaptor, F-Film, S-Stopcock, B-Brass holder.

and subsequent oxidation.

(2) The progress of the reaction can be followed virtually continuously, since the time required to make a measurement and return the apparatus to the appropriate radiation conditions is negligible.

(3) Films which become progressively more brittle on irradiation do not require to be handled; thus damage is avoided and films remain intact throughout the investigations.

(3) Colourimetric Analysis

The extent of colouration of polystyrene films during irradiation and oxidation was determined using an E.E.L. " Spectra" colourimeter, the sample compartment and lid of which were modified to accommodate the apparatus shown in figure 14. The techniques of irradiation and measurement were the same as those just described.

(4) Gas Analysis

(a) Introduction

Irradiation of polystyrene under high vacuum conditions and in nitrogen leads to the production of non-condensable (at -196°C) gaseous material which was suspected to be a mixture of hydrogen and methane. The possibility of carbon monoxide and carbon dioxide also being present was not excluded, in spite of the fact that neither can be immediately be accounted for in terms of the polymer structure.

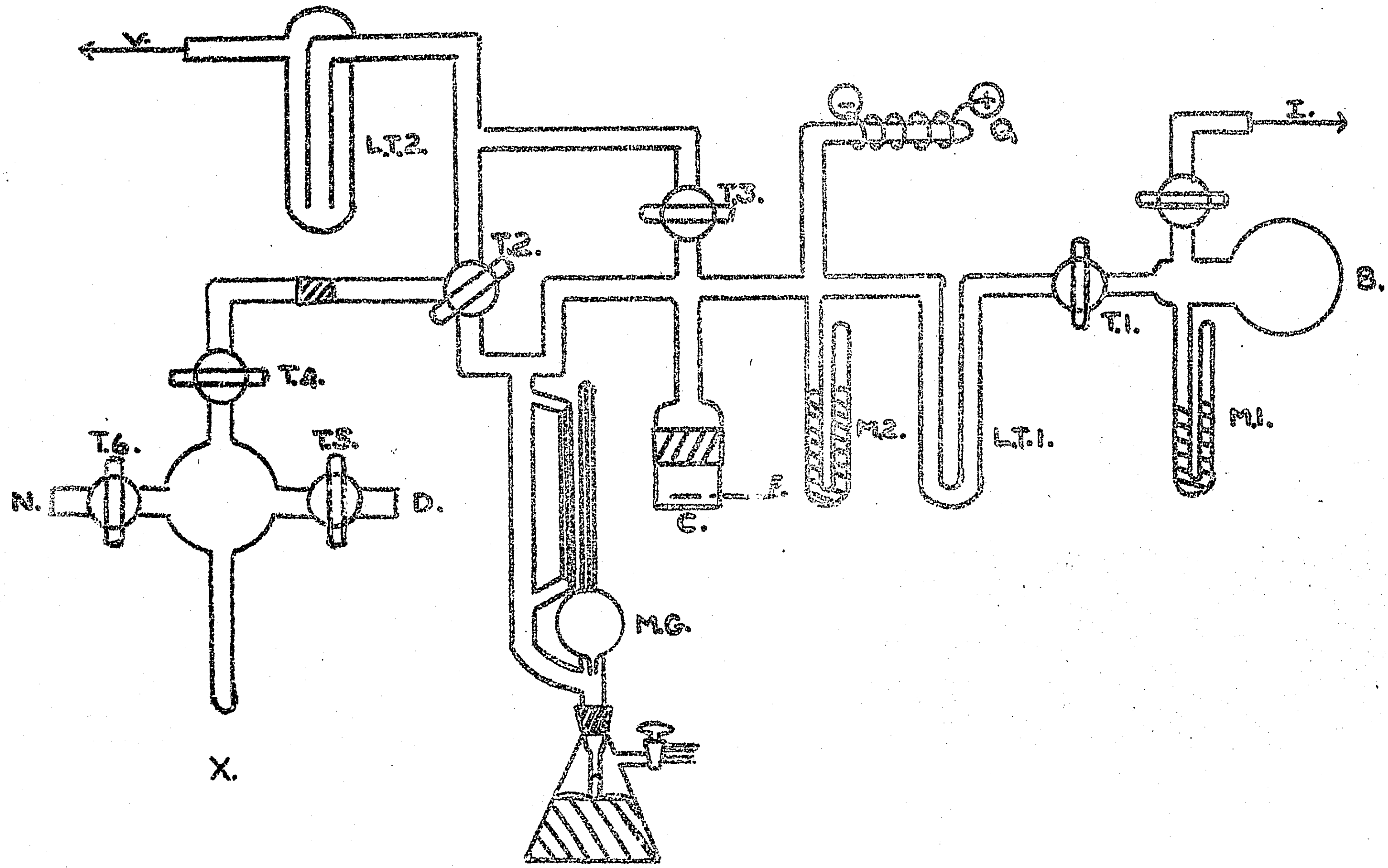
Since the total pressure of the gases is extremely small, conventional gas analysis techniques(69) are not sufficiently sensitive and it was therefore necessary to modify the existing techniques so that they could be applied at low pressures.

(b) Apparatus

The apparatus shown in figure 15 forms part of the high vacuum system already referred to. The gaseous materials are produced in the fused silica cell, C, by the irradiation of polystyrene films with 2537 Å radiation, and the resulting pressure is measured on the McLeod guage, M.G. By passing the mixture over cupric oxide (M.A.R. grade) heated to 300°C ± 3°C in the quartz furnace, it is possible to oxidize hydrogen and carbon monoxide selectively to water and carbon dioxide respectively, and on increasing

FIGURE 15.

GAS-ANALYSIS APPARATUS.



L.T.-Liquid nitrogen Traps, T_1 to T_6-Stopcocks, V-To vacuum, F-Film, C-Fused silica cell, Q-Silica Furnace, D-To Chromatographic column, I-Gas inlet, M.G.-M^{c}Leod gauge. X-Sampler for gas chromatography, M_1, M_2-Manometers, N-To nitrogen supply B-Bulb.

the combustion temperature to 350°C methane can be similarly oxidised.

The furnace consists of a quartz tube round which Nichrome tape (20 Ω per yard) and asbestos were wound. The Nichrome is heated electrically, power being supplied from a "Variac" transformer.

(c) Calibration of the Apparatus

The apparatus was calibrated for quantitative analysis as follows. After evacuating the entire system to 10^{-6} torr, stop-cocks T_1, T_2, T_3 were closed (the key of T_2 in a horizontal position) and nitrogen was introduced into the bulb, B and its pressure recorded on the manometer, M_1. The volume of B, that is, that volume separated from the remainder of the apparatus by T_1, had been previously determined accurately by weighing it empty and again full of water. T_1 was opened and the nitrogen allowed to expand into the whole volume, the resulting pressure being measured on M_1 and M_2. T_1 was again closed, T_3 opened and the apparatus again evacuated to 10^{-6} torr. After closing T_3, T_1 was opened and the process was repeated. By applying Boyle's Law to the data obtained, the volume of the apparatus was found.

5. Vapour Phase Chromatography

Vapour Phase Chromatographic analyses of the gaseous products referred to above were carried out using a Perkin-Elmer "Fraktometer" which employed a thermistor detector. The column consisted of one metre of ¼" copper tubing packed with crushed (30 mesh) Linde molecular sieves (type 5A) which had been activated for 16 hours in a stream of dry nitrogen at 180°C. The column temperature during analyses was 60°C.

Because these gaseous products were non-condensable, the normal technique of injection had to be modified, and the apparatus used is shown in the left-hand side of figure 15. The products of irradiation are introduced via T_2 and T_4 into the bulb of the sampler, X, the tip of which is cooled to -196°C in order to obtain maximum transfer of gases. T_4 is closed and the sampler is then detached from the apparatus and placed in series with the column and a supply of the carrier gas, which in this case is nitrogen. T_6 is opened and the sampler is pressurized with nitrogen, T_5 is then opened and the diluted sample is admitted to the column.

CHAPTER 3

The High-vacuum Photolysis of Polystyrene

1. Introduction

It has already been pointed out that in this investigation of the oxidation of polystyrene, the reactions are photo-initiated by short-wave ultra-violet radiation. Before investigating the oxidation process itself, however, it was decided to examine the photolysis of polystyrene in an attempt to define the action of ultra-violet radiation in promoting oxidation. This can only be achieved if oxygen is rigorously eliminated during irradiation, since the build up of oxygenated structures and their subsequent decomposition would inevitably introduce complicating side-reactions, which could completely alter the course of the reaction. The photolysis was therefore studied under high-vacuum conditions.

2. The photolysis of Polystyrene

The photolysis was carried out in the oxidation apparatus (figure 5) so that any pressure changes arising from the evolution of volatile material during irradiation could be detected and the amounts accurately determined.

A polystyrene film, 0.0044 mm. thick was placed in the oxidation apparatus which was connected to the high vacuum system (figure 7) which was evacuated to 10^{-6} torr, pumping being continued for 24 hours.

The apparatus was then isolated from the vacuum system, the lamp switched on and the progress of the reaction followed by observing pressure changes.

Figure 16 shows the pressure developed in the cell containing the film as a function of time of irradiation. After three hours the reaction was interrupted, stop-cocks, T_1, T_3 and T_4 opened (figure 17) and the gaseous products were expanded from the cell, C_1, into the small calibrated bulb, B, (5 ml.) which had been previously evacuated to 10^{-6} torr.

The pressure of the gas was measured on the manometer, M, the bulb, B, was then immersed in liquid nitrogen (-196°C) and the pressure again measured. The small resultant decrease in pressure was accounted for completely by contraction of a permanent gas by cooling to -196°C. The gaseous products of the photolysis reaction were therefore non-condensable at this temperature.

FIGURE 16.

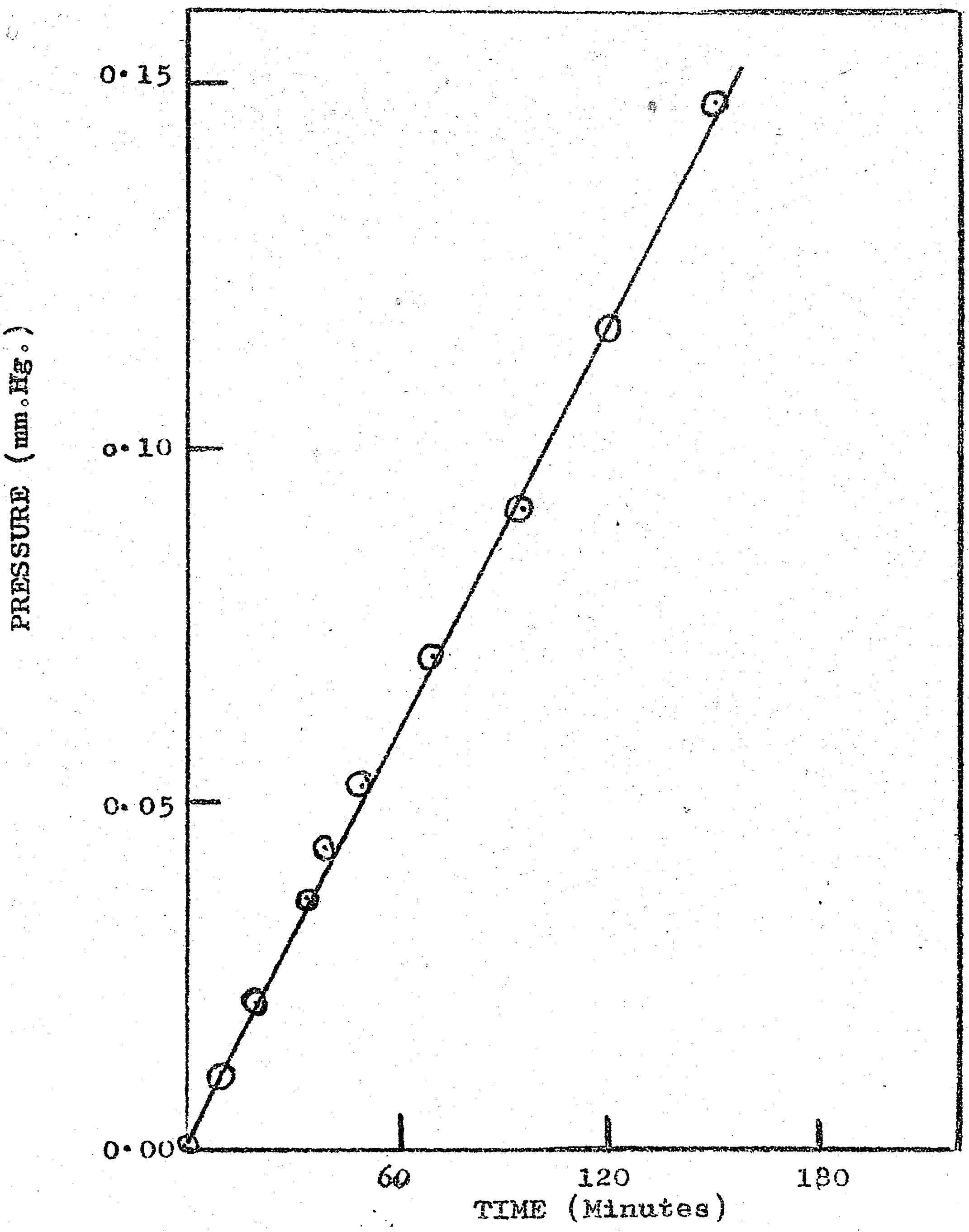
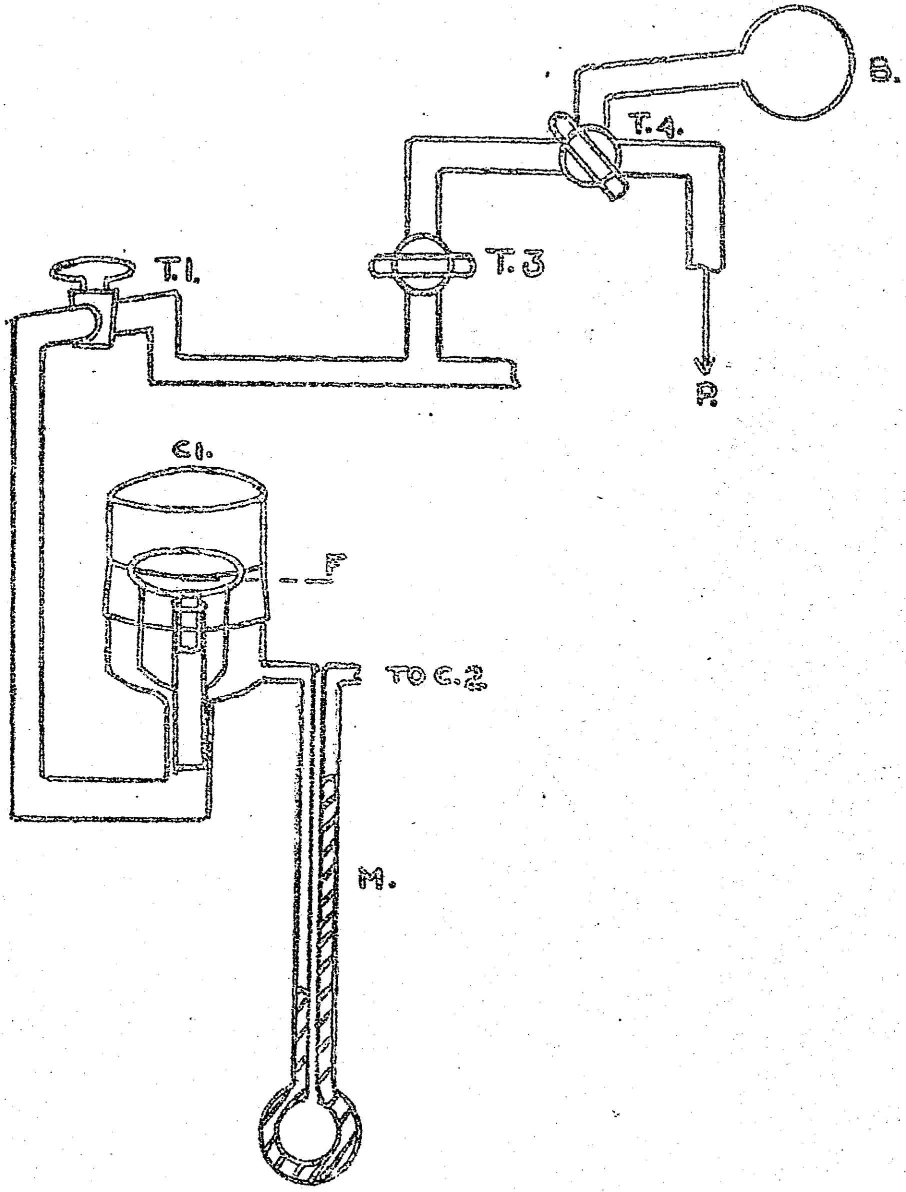


FIGURE 17.



C_1-Cell, F-Film, M-Manometer, T_1, T_3, T_4-Stopcocks, B-Calibrated bulb, P-To vacuum system.

It had to be established, however, that this non-condensable gaseous material was a genuine product of the photolysis of polystyrene, and not, for example, of the photolysis of the manometric fluid. A blank experiment was therefore carried out and no pressure change was observed after twenty-four hours irradiation. It was therefore concluded that the evolution of volatile material was associated with the photolysis of polystyrene.

3. Analysis of the Gaseous Products

Since the gaseous products are non-condensable at -196°C the substances most likely to be present are nitrogen (which could be liberated by the degassing of the film) hydrogen and methane (possible products of photolysis) and carbon monoxide (an oxidation product which might be formed if the film contained residual oxygen).

The analysis was carried out in the apparatus shown in figure 15, the film being irradiated in the silica cell under conditions identical to those described above. The gaseous material was submitted to combustion over copper oxide heated to 300°C ± 3°C, and the products were condensed in the adjacent liquid nitrogen trap. The progress of the combustion was followed by measuring the pressure of the residual non-condensable material using the McLeod gauge.

It was found that after about 100 minutes the pressure in the apparatus had returned to its original value, indicating that there was now no non-combustible material present (figure 18). It is thus extremely unlikely that the mixture contained nitrogen.

If methane and carbon monoxide were present their combustion would lead to the formation of carbon dioxide. This was tested for by measuring the pressure when the liquid nitrogen trap was replaced by one containing solid carbon dioxide (-78°C). No pressure increase was observed, suggesting that carbon dioxide was not present, and thus that the original mixture contained neither carbon monoxide nor methane.

Although these findings strongly suggest that hydrogen is the only product of the photolysis of polystyrene, some independent verification is required. This result was confirmed by the vapour phase chromatographic analysis of the gaseous material. The results are shown in figure 19.

FIGURE 18.

PRESSURE CHANGES DURING COMBUSTION OF THE GASEOUS PRODUCTS.

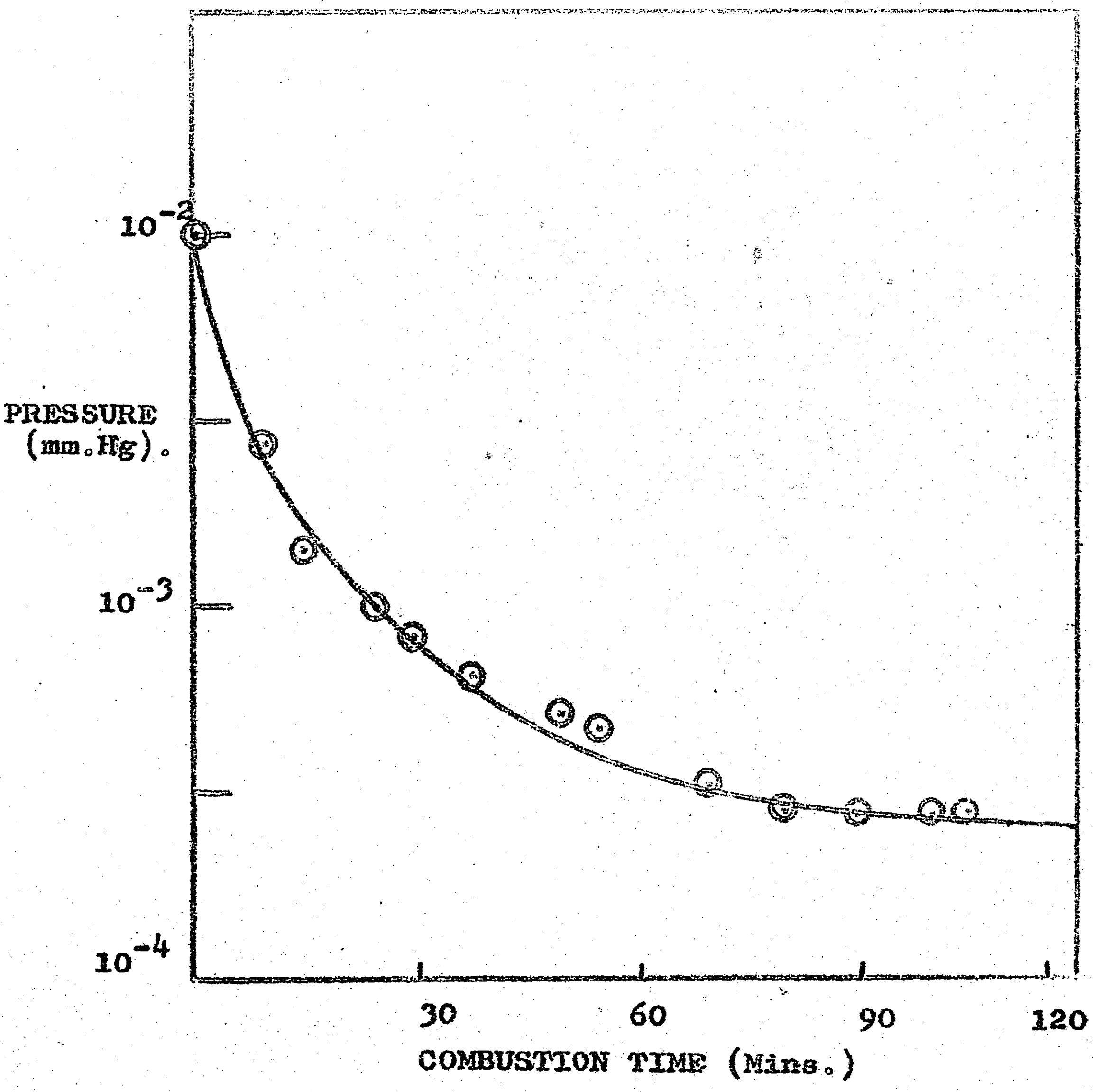
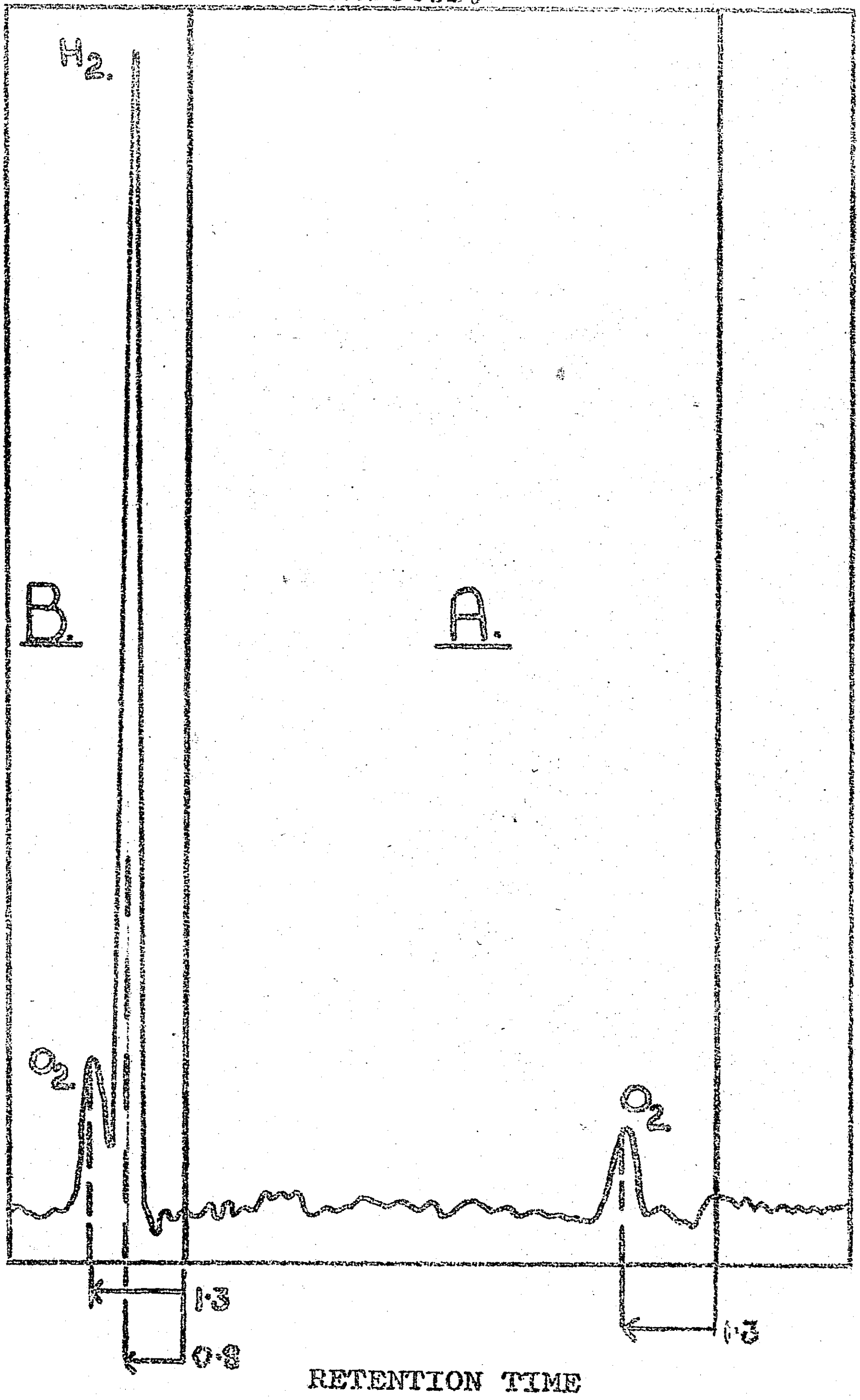


FIGURE 19.

VAPOUR-PHASE CHROMATOGRAPHIC ANALYSIS OF THE PHOTOLYSIS PRODUCTS.



RETENTION TIME

A-Carrier gas alone, B-Carrier gas plus photolysis products.

Two peaks were obtained, one large and the other very small. From the relative retention times (1.3 and 0.8) it was concluded that oxygen and hydrogen were present, the oxygen being present in the smaller amount. A repeat analysis without the photolysis products showed that oxygen was present as an impurity. [redacted] It was thus established that hydrogen was the only gaseous material produced in appreciable amounts on photolysis of polystyrene.

4. Variables affecting the Production of Hydrogen.

Since the effect of such variables as light intensity, temperature, etc. on the rate of oxidation of polystyrene was to be subsequently investigated, it was decided to examine the effect of some of these variables on the rate of production of hydrogen, because the pure photo-reaction would clearly have to be taken into account in photochemically initiated oxidation studies. On account of the high extinction coefficient of polystyrene at 2537Å, this radiation is non-uniformly absorbed throughout the film. Absorbtion is almost complete across a film 0.01 mm. in thickness. It follows then, that the rate of the photo-reaction will also be non-uniform throughout the film, being a maximum at the surface, and extremely small at a depth of 0.01 mm from it.

Obviously if the reaction were uniform throughout the film, the rate could be expressed as, for example, moles of hydrogen produced per gm. of polymer, and similarly if the reaction were entirely a surface one, the rate could be expressed as moles of hydrogen produced per unit area of the surface. In this case, however, the reaction is neither, and it was decided to compromise and to express rates as micro-moles of hydrogen per c.c. of polystyrene per sec., the film thickness being kept constant at 0.0044 mm. This is essentially the average rate of hydrogen production throughout the film and it is obtained as follows. The variable measured is the pressure of hydrogen at 28°C in the cell, C_1 which has a volume of 130 c.c. This is then converted to micro-moles of hydrogen per sq. cm. of polymer film, 0.0044 mm. in thickness, i.e. per 0.00044 c.c. The corresponding number of moles per c.c. is then found by proportion.

(a) The Effect of Radiation Intensity

Much information regarding the mechanism of a photochemical reaction can often be obtained from a study of the variation of the rate of the reaction with the intensity of activating radiation.

The intensity of 2537 Å radiation incident on the film was varied both by varying the film-arc distance, the relative intensities being calculated from the inverse square law, and by the use of intensity screens interposed between the film and the arc. These screens consisted of blackened copper gauze of various mesh sizes, the transmissions of which had been accurately determined by actinometry.

Corresponding rates of evolution of hydrogen were obtained by measuring the pressures developed in the cell during irradiation and converting these to the appropriate units. The results are shown in Table 5.

The rates of Hydrogen production were then plotted against various functions of the radiation intensity and a linear relation between the rate and the first power of the intensity was found to obtain (figure 20). The actual value of the intensity exponent derived from figure 21 is 0.978.

(b) Determination of Quantum Yield

The value of the quantum yield for a reaction can often give information about its mechanism. In particular chain reactions often have overall quantum yields greater than unity.

Under these experimental conditions, the rate of hydrogen production per sq. cm. of polymer film 0.0044 mm. in thickness

Table 5. Effect of Radiation Intensity on Rate of Photolysis of Polystyrene (0.0044 mm. film at 28°C)

Experiment No.	Film-arc distance (cm.)	Transmission of screen (%)	Relative intensity (%)	Rate (micro-moles H_2/c.c./sec.)	log Rate	log Intensity
1	7.375	100	100	0.216	-0.665	2.00
2	9.250	100	64.3	0.141	-0.851	1.808
3	11.125	100	43.2	0.0832	-1.0821	1.635
4	13.000	100	32.2	0.0700	-1.155	1.508
5	7.375	21.7	21.7	0.0505	-1.298	1.337
6	7.375	10.1	10.1	0.0230	-1.638	1.004

FIGURE 28.

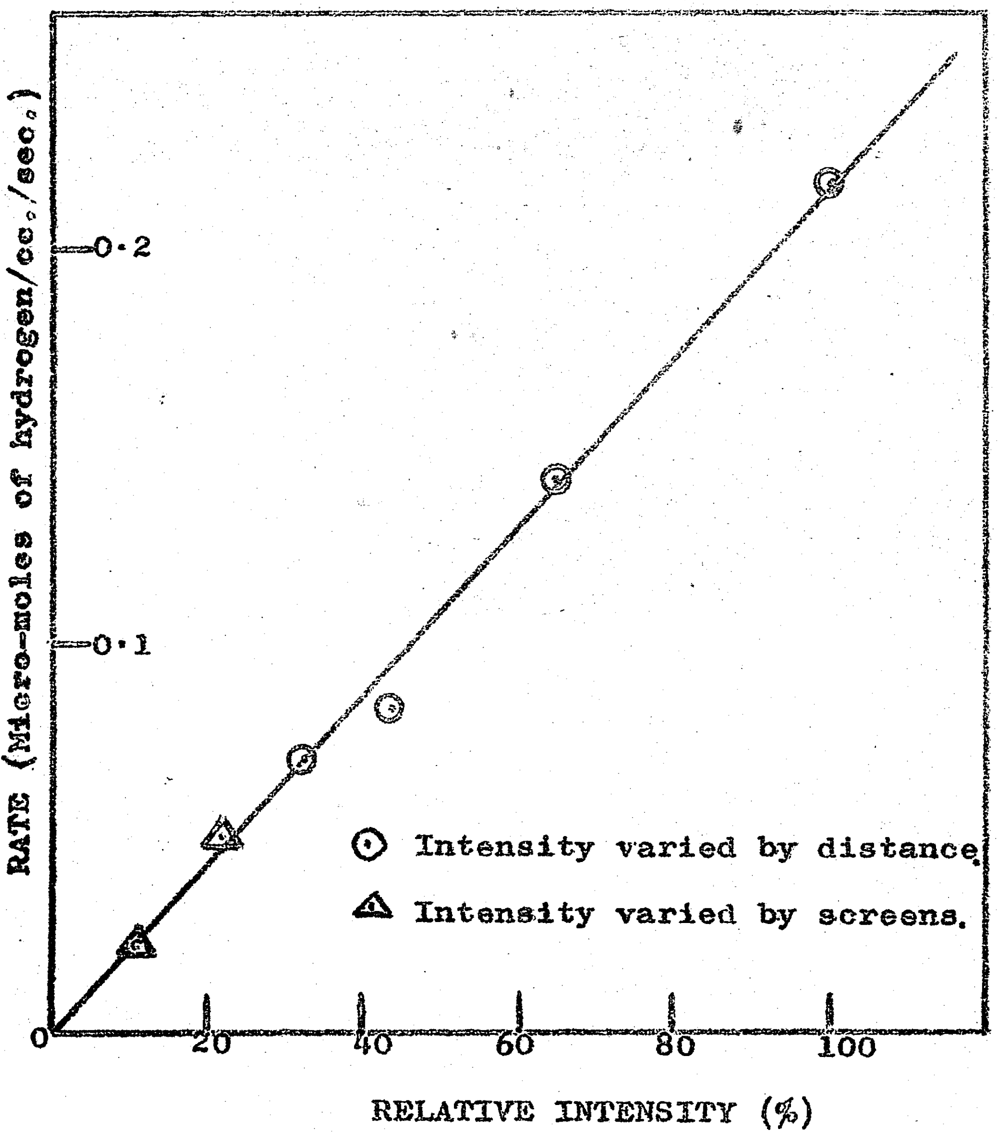
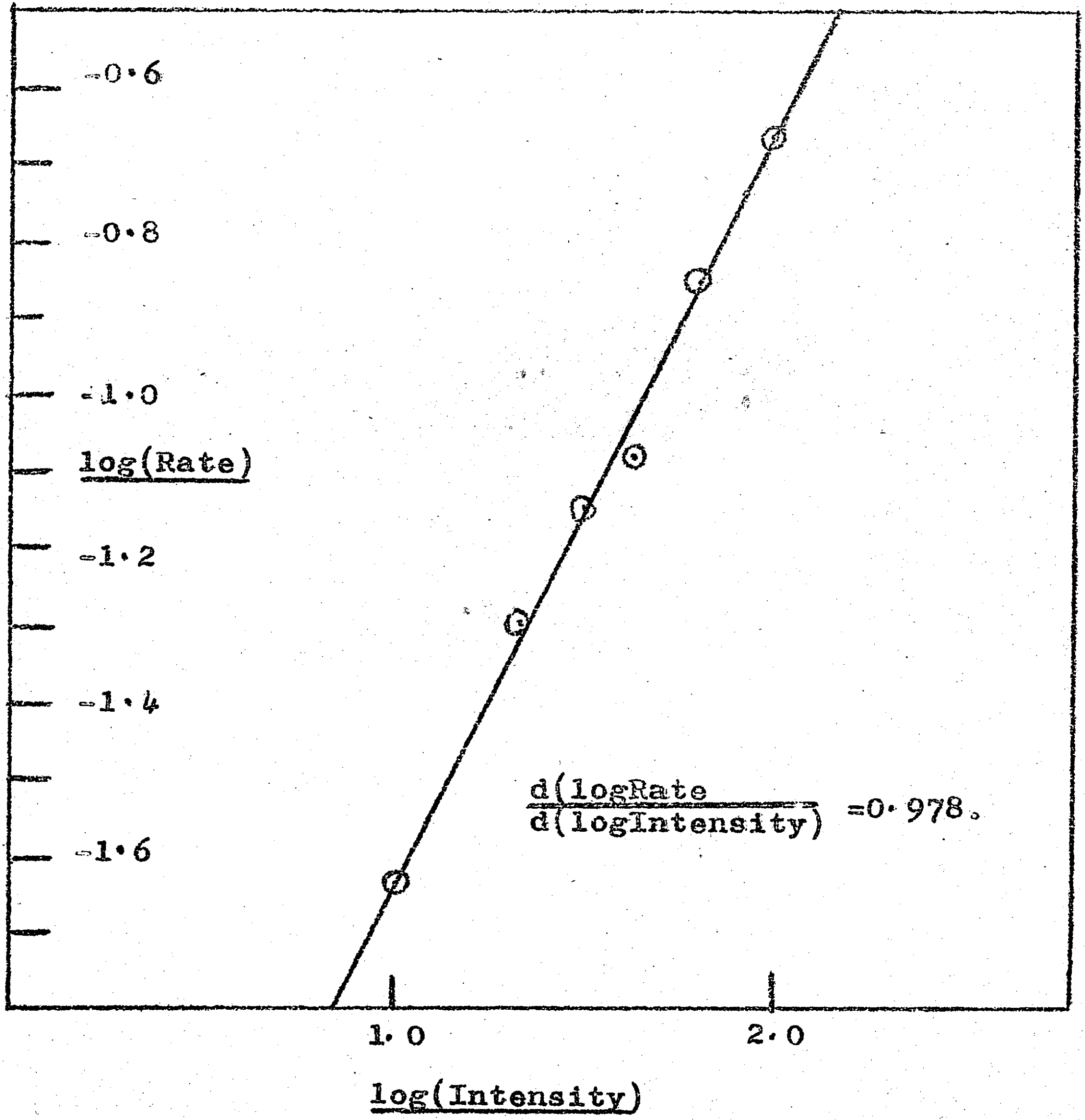

RATE (Micro-moles of hydrogen/cc./sec.)
0·2
0·1
0
20
40
60
80
100
RELATIVE INTENSITY (%)
Intensity varied by distance.
Intensity varied by screens.

FIGURE 21.


-0·6
-0·8
-1·0
log(Rate)
-1·2
-1·4
-1·6
1·0
2·0
log(Intensity)
d(logRate / d(logIntensity) =0·978.

was found to be 9.5×10^{-11} moles per second. This film has an optical density at 2537Å of 0.89, so that 87.2% of the 2537Å quanta incident on the film are absorbed. Now the quantum output of the source at 2537Å is 3.1×10^{-9} einsteins per sq. cm. per second (Table 3). The number of quanta absorbed by this film is therefore 2.71×10^{-9} einsteins per sq. cm. per second. The quantum yield (ϕ) can be defined as:

$$\phi = \frac{\text{Number of moles of hydrogen produced/sq.cm./sec.}}{\text{Number of einsteins of 2537Å quanta absorbed/sq.cm./sec.}}$$

$$\phi = 3.5 \times 10^{-2}$$

The quantum yield being less than unity means that there is no positive evidence that hydrogen is produced in a chain reaction.

(c) Effect of Molecular Weight and the Presence of Initiator Fragments.

It has been suggested in an earlier section that initiator fragments attached to the chains may be photo-active sites. Thus polymers containing those might be expected to have higher rates of photolysis than the thermal polymer. The object of the investigations to be described was therefore two-fold. Firstly, the effect of the presence of different amounts of initiator (2,2'-azoisobutyronitrile) fragments on the rate of hydrogen production was examined, and secondly, and at the same time, the effect of the molecular weight was investigated.

For this a series of polymers was prepared at 60°C using initiator concentrations ranging from 0.001% to 0.4%. Standard films of each were prepared by the method already described, and corresponding rates of hydrogen evolution were obtained. The results are presented in Table 6 and figure 22 from which it can be seen that the measured rates are comparable and probably constant within experimental error. The effect of the molecular weight is isolated by the observations on the thermal polymers S_1 and SG_3.

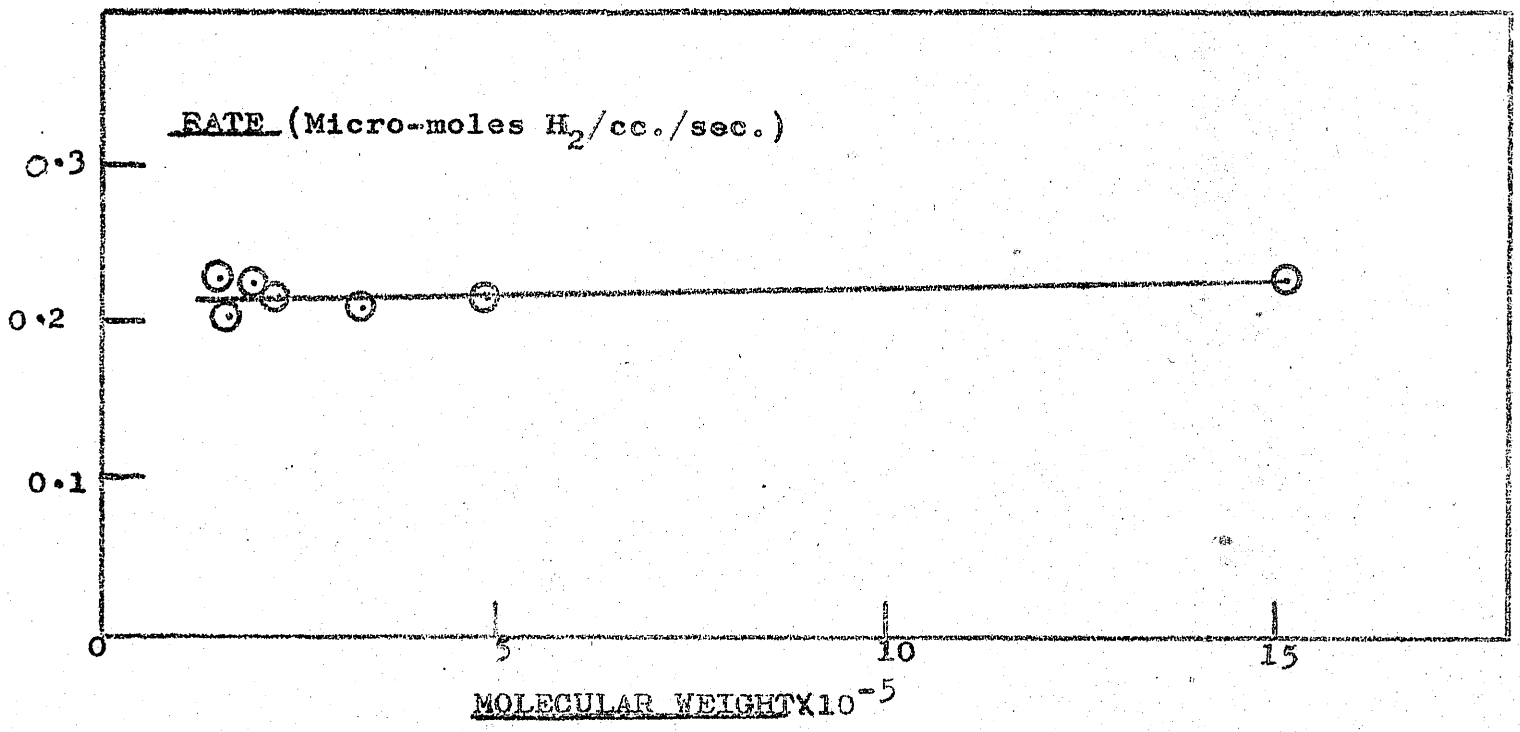
It can therefore be concluded that the rate of hydrogen evolution is independent of the molecular weight in the range of molecular weights examined and it is also independent of the presence of initiator fragments in the concentration range examined. Unfortunately it was not possible to investigate very low molecular weight material prepared using high initiator concentrations, since the resultant films were so brittle that they disintegrated completely before

Table 6. Effect of molecular weight on rate of photolysis of polystyrene (0.0044 mm. films, at 28°C, radiation intensity = 100%).

Polymer	Initiator concentration (%)	Polymerization temperature (°C)	Molecular weight (x 10^{-5})	Rate (micro-moles H_2 per c.c./second)
1	0.001	60	3.31	2.10
2	0.002	60	2.188	2.16
3	0.1	60	1.86	2.25
4	0.2	60	1.59	2.02
5	0.4	60	1.50	2.3
S_1	0	90	4.93	2.16
* SG3	0	60	15.1	2.3

* Prepared by N. Grassie

FIGURE 22.


RATE (Micro-moles H$_2$/cc./sec.)
0·3
0·2
0·1
0
5
10
15
MOLECULAR WEIGHT X10^{-5}

they could be removed from the mercury surface. Pressed films showed similar brittleness. The lower limit of molecular weight which could thus be investigated was approximately 10^5.

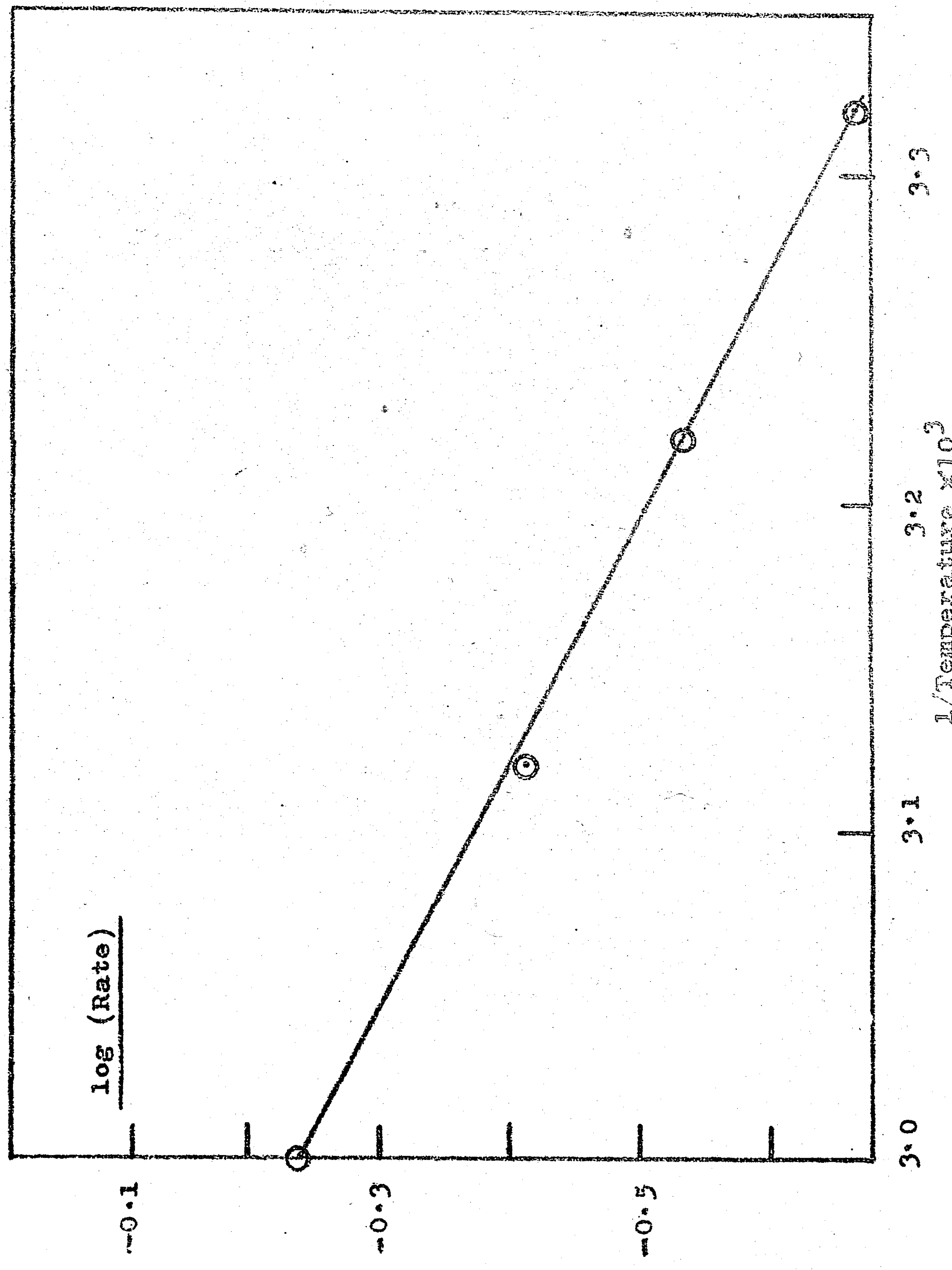
(d) Effect of Temperature

Rates of evolution of hydrogen were obtained under otherwise identical conditions at a number of different temperatures, the results are summarized in table 7.

Table 7. Effect of temperature on rate of hydrogen production (film 0.0044 mm. thick, radiation intensity = 100%)

Temperature (°A)	Rate (micro-moles H_2 per c.c. per sec.)	$\frac{1}{T}$ (x 10^3)	log rate	Activation Energy (k.cal/mole)
301	0.216	3.32	-0.6655	2.9
311	0.292	3.22	-0.5346	
321	0.383	3.12	-0.4175	
333	0.576	3.00	-0.2391	

FIGURE 23.



From the gradient of the graph of log rate versus the reciprocal temperature (figure 23) a value of 2.9 k.cal. per mole is inferred for the activation energy for hydrogen production. This small temperature dependence is what would reasonably be expected in a photochemical reaction.

(e) Effect of Wavelength

Several films were irradiated with a similar (to the 2537Å) intensity of 3650Å radiation and the reactions investigated in the usual manner. No hydrogen was detected after long periods (100 hours) of irradiation. It seems likely that the threshold energy required for the production of hydrogen is in excess of that associated with the 3650Å radiation (77.8 k.cal per mole). If this energy were indeed sufficient to break the C-H bonds, a constant rate of hydrogen production of approximately 1/80 that of the rate of hydrogen production on irradiation with 2537Å quanta would be expected, since the ratio of absorbtion of 2537Å quanta to the absorbtion of 3650Å quanta is 80:1; assuming of course, that the transfer of absorbed energy to the dissociating bonds is equally efficient in both cases.

CHAPTER 4

Discussion of the Photolysis Process

1. Origin of the Hydrogen

(a) Primary Processes

The primary step in the production of hydrogen during the irradiation of polystyrene with 2537Å quanta must involve the fission of C–H bonds to form hydrogen atoms. This, however, cannot be brought about by the direct interaction of the C–H bonds with the radiation, since only quanta of shorter wavelengths (about 1600Å) are absorbed by such bonds. The 2537Å quanta are, however, absorbed strongly by the benzene rings and the dissociation of the C–H bonds will result from the transfer of the radiation energy acquired by the absorbing centres to these dissociating bonds.

In polystyrene there are three different types of C–H bonds which could conceivably be broken. These are tertiary and secondary C–H bonds in the backbone of the polymer and the C–H bonds of the benzene rings. These bonds are not all equivalent and their order of breaking will be determined principally by two factors, bond dissociation energy and resonance stabilization.

(a) Bond Dissociation Energy

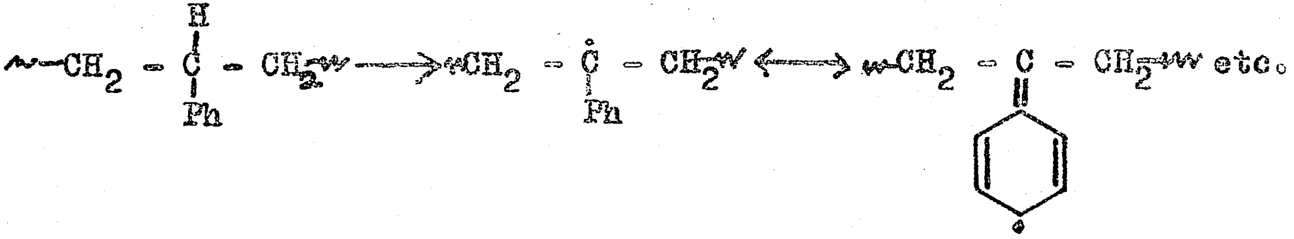
The dissociation energies of the three bonds in question are as follows,(71)

C-H (benzene ring)	104 k cal./mole
C-H (secondary)	76 k cal./mole
C-H (tertiary)	71 k cal./mole

It follows then that the tertiary bond will be the most readily broken.

(b) Resonance Stabilization

If fission of the tertiary bond occurs the resulting radical will have resonance stabilization,



No comparable resonance stabilization would be available to the radicals resulting from the fission of the other two C-H bonds.

It would thus appear that the most energetically favourable initial step in the production of hydrogen is the fission of the tertiary C-H bonds. In practice, however, the situation is likely to be more complex, since the energy associated with 2537Å radiation (112 k cal/mole) is sufficient to break all of these bonds, provided of course, it can be effectively transmitted from the benzene rings, and hydrogen atoms are probably obtained by the fission of all three bonds.

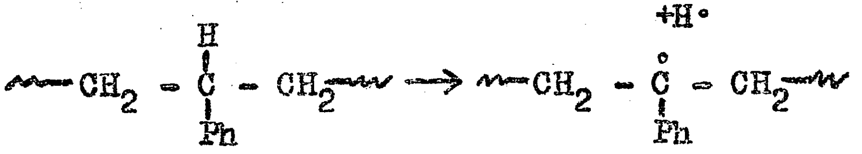
Although the energy transfer to the C-H bonds would in this case be expected to be a reasonably efficient process, the low quantum yield (10^{-2}) for hydrogen production indicates that the dissociation of C-H bonds affords only a minute dispersion route for the absorbed energy. No evidence for C-C bond fission was obtained either from product analysis or from molecular weight measurements, and it is unlikely that this process would account for the discrepancy. It is much more likely, especially since the reaction takes place in the condensed phase, that the absorbed energy is dissipated through such quenching reactions as recombination and collisional deactivation.

(b) Secondary Processes

Although several secondary reactions are possible, the present data permits the evaluation of only one, namely the production of hydrogen molecules from the hydrogen atoms produced in the primary process.

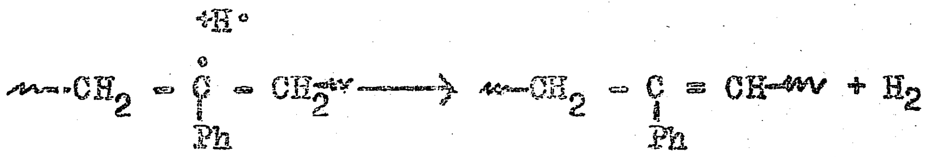
The most obvious route to molecular hydrogen is through the bimolecular combination of two hydrogen atoms. This process, however, takes place only in presence of a third body, or on the walls of the containing vessel and only these hydrogen atoms produced on the surface and within a few atomic diameters of it will escape and participate in such a reaction. Hydrogen atoms produced at lower levels in the film will abstract further hydrogen atoms from the polymer and the resulting molecules will then diffuse out of the polymer. In both of these reactions two chain radicals are formed for each molecule of hydrogen evolved, and although their mobilities are low it is unlikely that bimolecular combination will be completely precluded, cross-linking will therefore be concomitant with hydrogen production.

Another energetically favourable reaction leading to hydrogen evolution is the abstraction of a hydrogen atom from the carbon atom adjacent to the radical centre produced in the primary process by the hydrogen atom produced in the primary process thus,



$$\sim CH_2 - \overset{H}{\underset{Ph}{C}} - CH_2 \sim \longrightarrow \sim CH_2 - \overset{+H\cdot}{\overset{\circ}{\underset{Ph}{C}}} - CH_2 \sim$$

(Primary process)



$$\sim CH_2 - \underset{Ph}{\overset{+H\cdot}{\dot{C}}} - CH_2\sim \longrightarrow \sim CH_2 - \underset{Ph}{C} = CH\sim + H_2$$

This reaction also involves the formation of double bonds in the chain.

2. The Kinetics of Photolysis of Polystyrene

These reactions can be formulated in the following scheme, in which RH represents the polymer and R, the chain radical.

Primary Process

(1) $RH \xrightarrow{h\nu} R\cdot + H\cdot \quad r_i$

Secondary Processes

(2) $H\cdot + RH \longrightarrow H_2 + R\cdot$

(3) $H\cdot + R\cdot \longrightarrow H_2 + U$

(4) $H\cdot + H\cdot + M \text{ or } S \longrightarrow H_2 + M \text{ or } S$

(5) $R\cdot + R\cdot \longrightarrow R - R$

M is a third body, S a surface, U and R-R are non-radical products (U being unsaturated). Since the overall rate of hydrogen production depends on the rate of production of hydrogen atoms and since the reaction is not a chain process, the rate expression for hydrogen production is,

$$\frac{d(H_2)}{dt} = kr_i$$

$$\text{i.e.} \quad \frac{d(H_2)}{dt} = kk_1\,(RH)\,I$$

where I is the intensity of radiation.

Evidence for the Proposed Mechanism of Hydrogen Formation

1. Kinetic Evidence

The rate expression derived above on the basis of the proposed reaction scheme predicts that hydrogen will be produced at a constant rate and that the intensity exponent for the process will be unity. An analysis of the experimental data leads to similar conclusions, and it can therefore be inferred that, at least kinetically, the mechanism is plausible.

2. Cross-linking

The mechanism also predicts that cross-linking of the polymer chains will be concurrent with hydrogen evolution. Although no systematic study was made of molecular weight changes occurring during photolysis, it was established that cross-linking did indeed occur, a rapid insolubilization and embrittlement of the polymer becoming obvious after short periods of irradiation.

3. Spectroscopic Evidence

In addition to hydrogen production, one of the reactions also yields unsaturated compounds ($R\cdot + H\cdot \rightarrow H_2 + U$), the double bonds being formed in the polymer backbone. Spectroscopic investigations did indeed reveal the presence of such unsaturation.

(a) Infra-red Spectra

Infra-red spectra of the polystyrene films undergoing photolysis were obtained at intervals during the irradiation. A shoulder appeared at 825 $cm.^{-1}$ on the band at 840 $cm.^{-1}$ after about ten hours (figure 24). Absorbtion in this region has been attributed to the out of plane vibration of the C-H bond in a tri-substituted ethylene,(72)

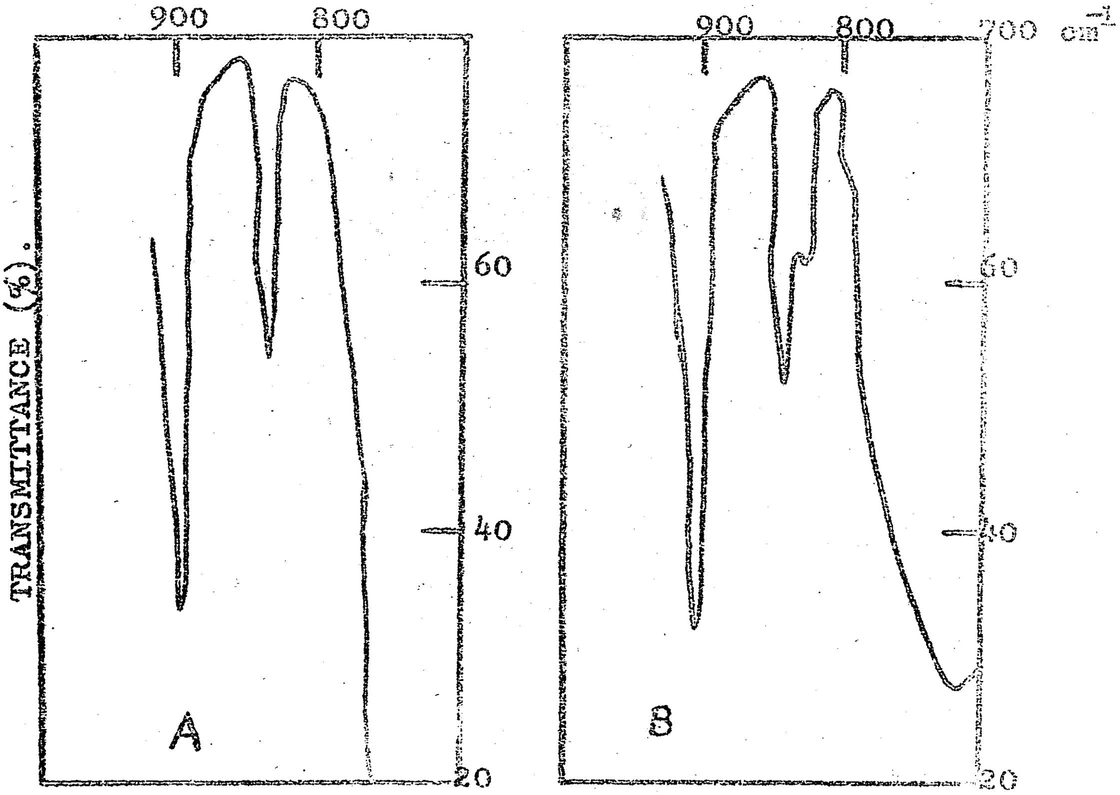
$$R_1R_2C = CHR_3$$

The structure expected from the reaction just mentioned would, in fact, be a tri-substituted ethylene,

$$\sim CH_2 - \underset{\displaystyle Ph}{\overset{}{C}}=CH - CH_2 \sim$$

Quantitative interpretation of the formation of this compound in terms of its infra-red absorption, however, is extremely

FIGURE 24.



The infra-red spectrum of polystyrene in the 800 cm^{-1} region.

A, no irradiation.

B, vacuum irradiation for 10 hours.

difficult, since the new band overlaps an existing band. The corresponding ultra-violet spectra do not suffer from this disadvantage and as such are more amenable to interpretation.

(b) Ultra-violet Spectra

Ultra-violet absorbtion spectra of the polystyrene films were also obtained during their irradiation, a general increase in absorbtion throughout the 2300Å to 3500Å region being observed. Rates of increase in absorbtion in the 2400Å and 2900-3000Å regions, however, were appreciably greater than those in the 2500Å to 2800Å region (figure 25).

Absorbtion in the 2400Å region is characteristic of compounds having a carbon-carbon double bond in conjugation with a benzene ring: styrene, for example, has a maximum in its absorbtion spectrum at 2440Å.(73)

Table 8. Optical Density changes on Irradiation (0.0044 mm. film, at 28°C, intensity - 100%).

Time (mins.)	Optical Density at 2400Å	Increase in Optical density
0	4.90	0
15	5.15	0.25
30	5.45	0.55
45	5.70	0.80
60	6.00	1.10
75	6.200	1.30
90	6.42	1.52
105	6.70	1.80
120	6.84	1.94

FIGURE 25

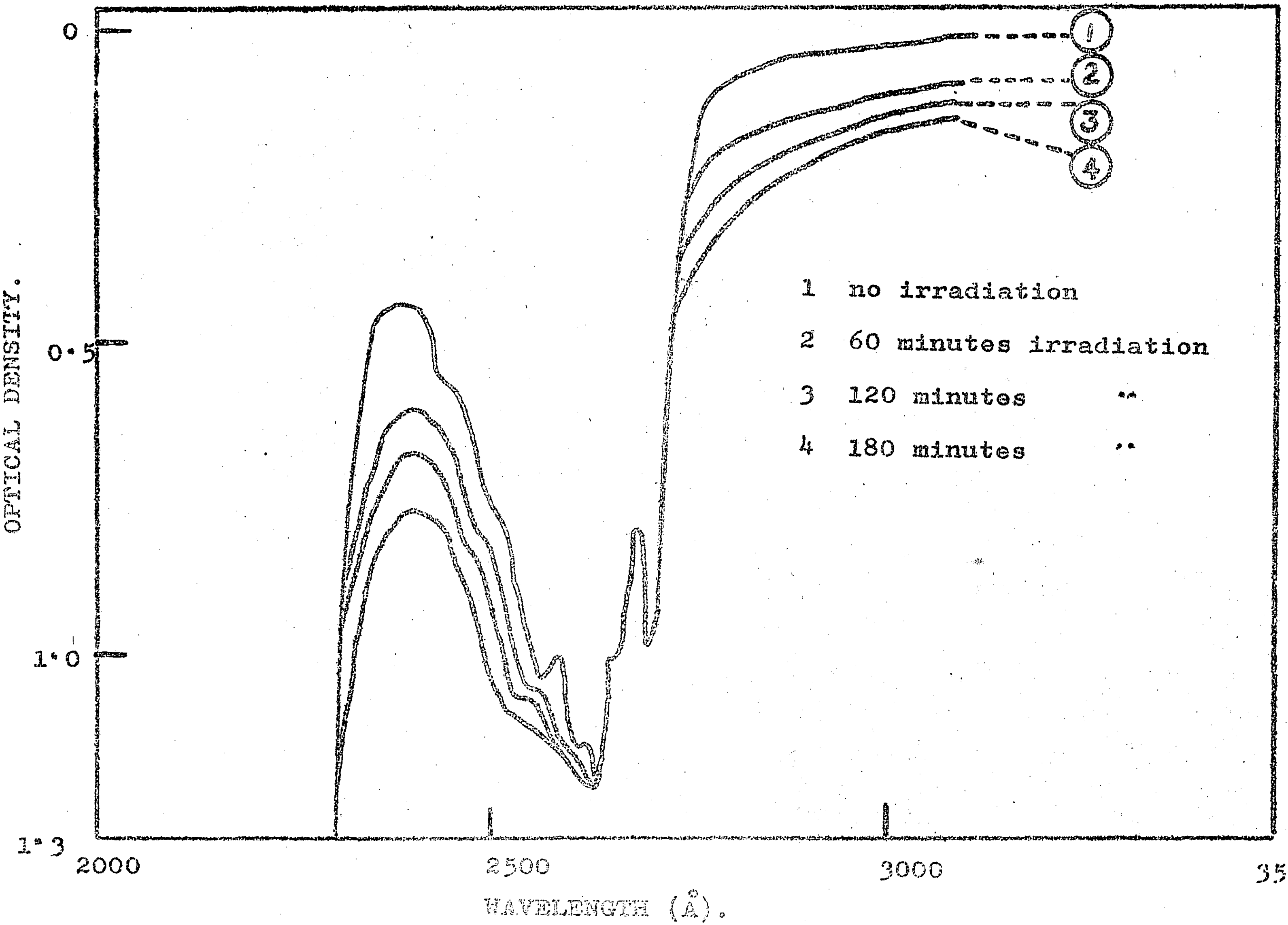

OPTICAL DENSITY.
0
0·5
1·0
1·3
2000
2500
3000
3500
WAVELENGTH (Å).
1 no irradiation
2 60 minutes irradiation
3 120 minutes "
4 180 minutes "
1
2
3
4

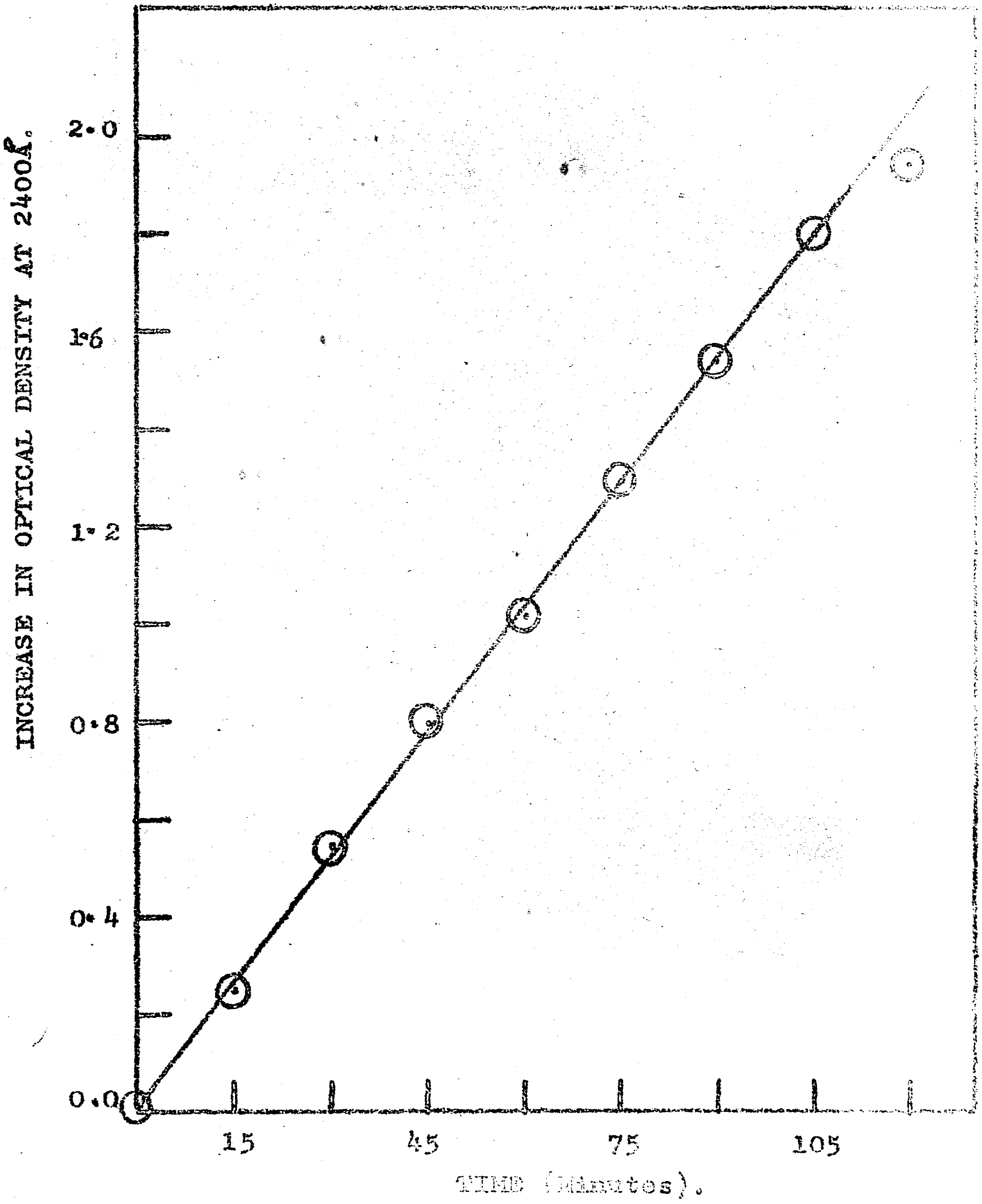
Figure 26 shows the optical density increase at 2400Å as a function of time of irradiation. It can be seen that the amount of unsaturation, in common with the amount of hydrogen formed increases linearly with the time of irradiation, indicating that double bond formation is concomitant with hydrogen formation.

Vacuum irradiation was also accompanied by a yellowish discolouration of the polymer. This could be attributed to the build-up of conjugated double bonds in the polymer backbone, the method of their formation being analogous to that described above. The absorbtion in the 3000Å region could also be accounted for in terms of such a conjugated structure This and other aspects of colouration are discussed in detail in a subsequent chapter.

4. Irradiation in Nitrogen

All the proposed hydrogen-producing reactions depend on the mobility of the hydrogen atoms. Reaction (4), for example, would be depressed if the mobility were decreased, since the escape of atoms from the surface would be rendered more difficult. Reactions (2), (3) and the reverse of (1) would, on the other hand, be facilitated by limitations on mobility, since the atoms would tend to react in the immediate

FIGURE 26.


INCREASE IN OPTICAL DENSITY AT 2400Å.
2·0
1·6
1·2
0·8
0·4
0.0
15
45
75
105
TIME (Minutes).

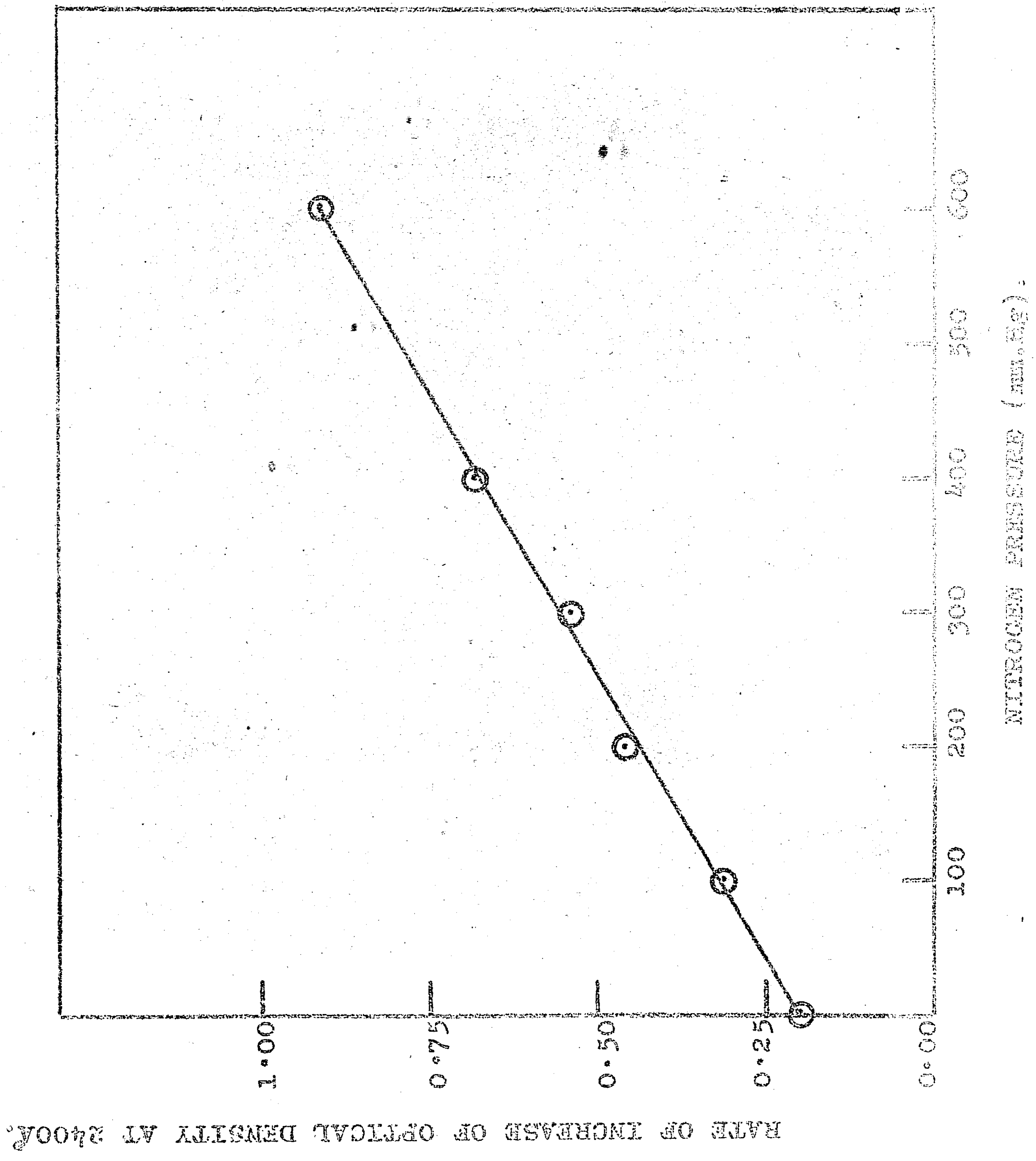
vicinity of their formation. The higher probability of reaction (3) under these conditions should be reflected in the ultra-violet spectra of the polymer films undergoing irradiation.

To test this hypothesis, films were irradiated in presence of various pressures of nitrogen. Under these conditions the mobility of the atoms is reduced, yet the nitrogen is sufficiently inert not to participate in the photolytic reactions. Rates of increase of optical density at 2400Å were obtained at each nitrogen pressure, and these are shown in Table 9.

Table 9. Effect of Nitrogen on the Optical Density Increases (0.0044 mm. film, T = 28°C, Intensity = 100%).

Rate of Increase of Optical Density at 2400Å	Nitrogen Pressure (mm. Hg.)
0.200	0
0.310	100
0.460	200
0.538	300
0.681	400
0.909	600

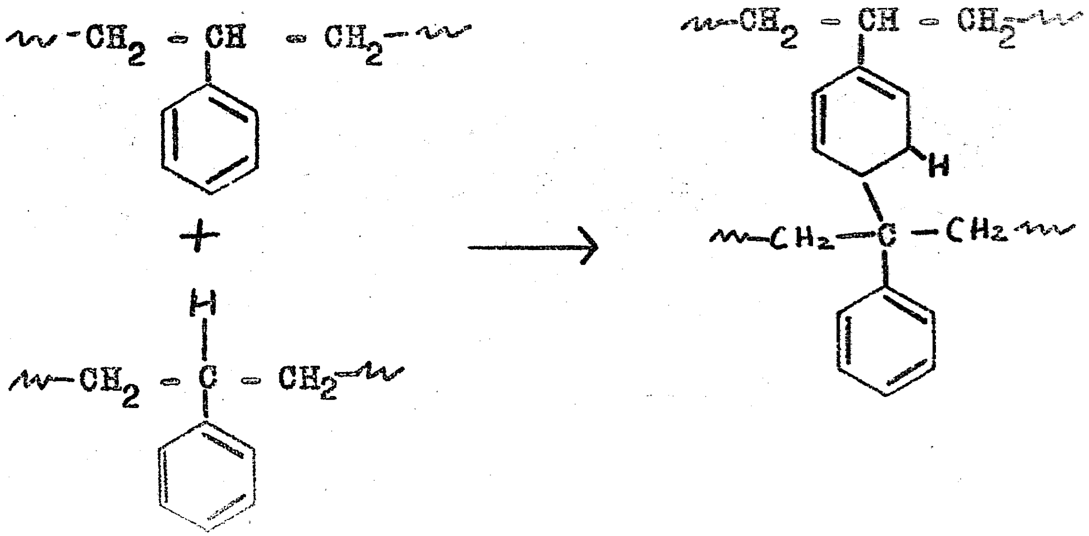
FIGURE 27.



1·00
0·75
0·50
0·25
0·00
100
200
300
400
500
600
NITROGEN PRESSURE (mm.Hg).
RATE OF INCREASE OF OPTICAL DENSITY AT 2400Å.

Figure 27 shows the effect of nitrogen pressure, and hence mobility of hydrogen atoms on the production of unsaturation in the polymer. It can be seen that the decreased mobility of the atomic hydrogen leads to an increase in the rate of formation of double bonds in the polymer. It can thus be seen that the suggested mechanism, does indeed account for the more important observed features of the reaction.

Wall,[57] on the basis of results obtained from the γ-radiolysis of polystyrene, suggested an alternative mechanism of cross-linking. According to this a hydrogen atom produced by the fission of a C-H bond in the polymer backbone adds to the double bond of a neighbouring benzeme ring to form a cyclohexadienyl radical which combines with the other polymer radical to form a cross-link.



The overall reaction would be kinetically indistinguishable from reactions (2) and (5) above, and since the cyclohexadiene ring contains a tri-substituted ethylene group, this structure would account for the absorbtion at 825 cm.$^{-1}$ The cis di-substituted olefin also appearing in the ring, however, should show an absorbance in the 675 cm.$^{-1}$ to 728 cm.$^{-1}$ region[72]. Despite the fact that there is an intense absorbtion in this region by the polystyrene itself, Kargin et al[74] have observed a shoulder at 625 cm.$^{-1}$ on the 700 cm.$^{-1}$ peak following the bombardment of polystyrene with high speed electrons, and this has been attributed to the cis olefin shown above. No such absorbtion was observed in this investigation. There is also a serious objection to the application to the theory of Wall on the basis of ultra-violet spectra. The cyclohexadiene is essentially a substituted butadiene and it is extremely unlikely that even the high degree of substitution would be sufficient to account for the very large bathochromic shift observed, the spectrum of the irradiated polymer showing high absorbance in the 2400Å to 3500Å region (butadiene has a maximum absorbance at 2170Å). It thus appears that this reaction, although possibly contributing to the cross-linking process, is of much less importance in the photolysis than in the radiolysis and electron irradiation of polystyrene.

CHAPTER 5

Oxidation of Polystyrene

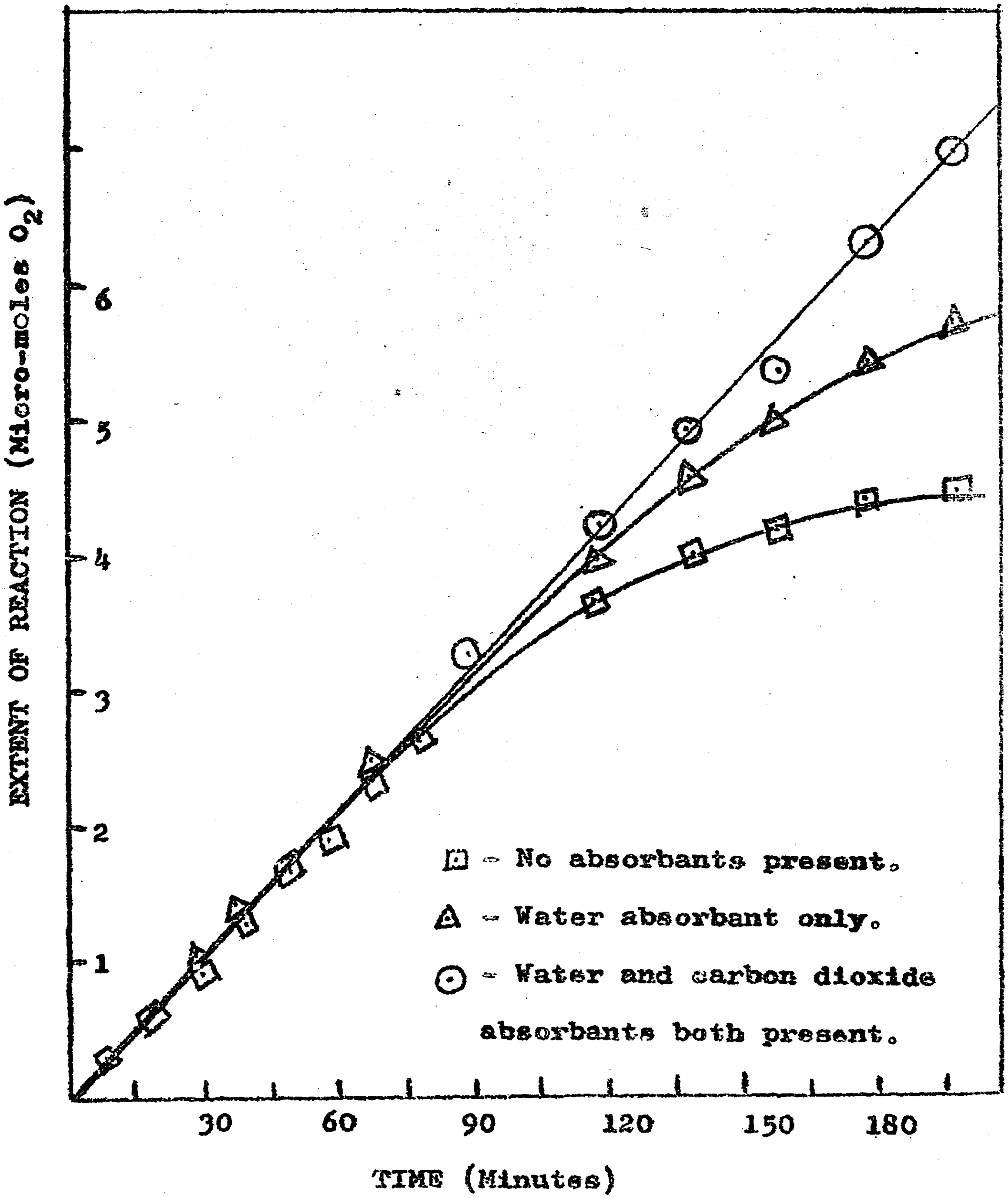
Measurement of Rate

Polystyrene films, 0.0044 mm in thickness, were oxidised in the apparatus described in Chapter 2, the progress of the reactions being followed by measuring the amounts of oxygen absorbed. Results of a typical run are given in Table 10 and shown in figure 28 (bottom curve).

Table 10. Oxidation of polystyrene film (0.0044 mm thick, oxygen pressure = 600 mm Hg, intensity = 100%, temperature = 28°C)

Time (mins.)	Extent of Reaction (micro-moles of O_2 absorbed)	Time (mins.)	Extent of Reaction (micro-moles O_2)
0	0.0	80	2.544
10	0.324	90	2.982
20	0.678	100	3.254
30	0.919	120	3.633
40	1.30	140	4.03
50	1.72	160	4.22
60	1.88	180	4.43
70	2.3	200	4.48

FIGURE 28.


EXTENT OF REACTION (Micro-moles O_2)
1
2
3
4
5
6
30
60
90
120
150
180
TIME (Minutes)
⊡ - No absorbants present.
△ - Water absorbant only.
⊙ - Water and carbon dioxide absorbants both present.

It can be seen from figure 28 that after an initial rapid absorbtion of oxygen the rate of oxidation decreases, the rate after three hours being about one fifth of the initial rate. Since this occurs at a minute extent of oxidation, it is unlikely that the deceleration of the reaction rate will be caused by the depletion of the polymer through oxidation, and an alternative explanation must be sought. This behaviour may be due to one or more of the following factors.

(a) <u>Diffusion</u>

It is possible that the initial fast reaction represents the oxidation of the surface layer of the polymer and that the deceleration in rate is due to the oxidation of lower layers becoming dependent on the diffusion of oxygen through the polymer, in other words, after the polymer surface, which is in direct contact with oxygen, has reacted the reaction becomes diffusion-controlled. This conclusion is, however, incompatible with the findings of Barrer[61] and Stannett[62] whose data predicts that the rate of diffusion of oxygen into these films would be several times greater than the observed rate of oxidation.

A more likely explanation is that the rate of diffusion decreases with the crosslinking which accompanies oxidation. As the surface and layers immediately below it become crosslinked, the rate of oxidation at lower levels within the film becomes less on account of the decreased permeability of the crosslinked matrix which separates them from the oxygen supply. Sobolev et al[75] have found that the rate of diffusion of oxygen through the crosslinked polyethylene is less than one half that through normal polyethylene.

(b) Reduction of Light Intensity

It has been shown[46] that carbonyl and other unsaturated chromophores are formed on the chains during the oxidation of polystyrene. Since these compounds have high extinction coefficients for 2537Å radiation, a build up of these on the surface would result in a considerably attenuated intensity of radiation reaching the bulk of the polymer. Thus the surface layer containing these highly absorbing groups would act as an internal filter, protecting the bulk of the polymer from the activating radiation, and this would be reflected in a diminished rate of oxidation.

(c) Formation of Inhibitors

Jellinek[42] has shown that inhibitors, like benzaldehyde, formed during the oxidation of polystyrene, can suppress the chain scission which occurs during oxidation. It is conceivable that such compounds can also retard the oxidation process itself.

(d) The Reaction Mechanism

It has been observed[76] that in the later stages of the oxidation of cumene the oxygen absorbtion ceases, the predominant reaction being the bimolecular combination of two peroxy radicals to yield an oxygen molecule and a non-radical product. It is possible that this effect may also operate in polystyrene oxidation. It is unlikely, however, especially since the extent of oxidation is extremely low, that this effect alone could account for the observed facts.

(e) Formation of Volatile Products

The reaction was followed by measuring the decrease in the volume of oxygen in the cell, due to absorbtion by the polymer. It follows then, that if some gaseous products are formed in the cell during oxidation, their volume would compensate or partially compensate for the volume of oxygen lost by polymer absorbtion, and the result of this would be an apparent deceleration in the rate of oxygen uptake.

If these products were capable of absorbing the 2537Å radiation, (benzaldehyde for example, has a high extinction coefficient for this radiation) however, a genuine reduction in the rate of oxidation would result, on account of the decreased intensity of this reaching the polymer.

Since the effect (e) was the most amenable to study it was decided to investigate the production of gaseous material during oxidation. Although Wall has shown that there is a fairly large number of different species formed, most of them can be selectively removed by the introduction of an appropriate absorbent into the oxidation cell.

The oxidation was repeated in presence of 5 gm. anhydrous magnesium perchlorate (M.A.R. grade), this being contained in the glass cup attached to the glass support for the film (figure 6). Magnesium perchlorate removes water to the level of 1 part in 10^4. As before, amounts of oxygen absorbed were obtained as a function of time. The results are shown in Table 11 and figure 28 (middle curve). It can be seen that although the overall characteristics are similar to those when absorbant material is not present, the apparent amount of oxygen absorbed is greater. This suggests that water is formed on oxidation and is being absorbed by the magnesium perchlorate. The result also suggests, however, that water may not be the only gaseous material being produced.

The experiment was repeated in presence of equal amounts of magnesium perchlorate and "carbosorb" (M.A.R. grade), the purpose of the latter being to remove any carbon dioxide formed during oxidation. Results of this experiment are also given in table 11 and figure 28 (top graph). It can be seen that the measured rate is constant and that the apparent deceleration in rate can be entirely accounted for in terms of the production of carbon dioxide and water.

This finding does not exclude the possibility of participation by some of the other factors mentioned above. It is difficult, however, to reconcile the above finding with any significant participation in the initial stages of the oxidation by these other factors, and it is likely that each will become increasingly important in the later stages of the reaction.

Table 11

Oxidation in presence of water absorber.		Oxidation in presence of water & carbon dioxide absorbers	
Time (mins.)	Extent of Reaction (micro-moles O_2 absorbed)	Time (mins.)	Extent of Reaction (micro-moles O_2 absorbed)
0	0.0	0	0
10	0.357	10	0.388
20	0.68	20	0.712
30	1.01	30	1.013
40	1.312	40	1.53
50	1.748	50	1.79
60	2.03	60	2.144
70	2.42	70	7.56
80	2.82	80	2.98
90	2.98	90	3.24
100	3.40	100	3.44
120	3.92	120	4.12
140	4.54	140	4.85
160	4.90	160	5.21
180	5.38	180	6.22
200	5.66	200	6.87

It seems reasonable to assume, however, that the constant rate measured in presence of carbon dioxide and water absorbants is a true measure of the rate of oxygen uptake by the polymer; all measurements quoted hereafter in this thesis have been measured in this way.

CHAPTER 6

Oxidation of Polystyrene - Effect of Variables on rate.

The effects of several variables on the rate of oxidation of polystyrene were investigated. The standard conditions of the reaction are radiation intensity 100% (as defined in chapter 3), oxygen pressure 600 mg Hg, film thickness 0.0044 mm and temperature 28°C. Rates of oxidation are quoted as micro-moles of oxygen absorbed per second per cc of polymer.

(a) Effect of Radiation Intensity

The intensity of 2537Å radiation incident on the polymer films was varied both by varying the arc-film distance and by interposing actinometrically calibrated intensity screens between the arc and the film. Corresponding rates of absorbtion of oxygen were obtained and these are shown in Table 12. The results are also presented in figure 29 from which it is clear that the rate of oxidation of polystyrene is proportional to the first power of radiation intensity. The actual value of the intensity exponent obtained from the plot of log rate versus log intensity (figure 30) is 1.098. This value, being close to unity,

FIGURE 30.

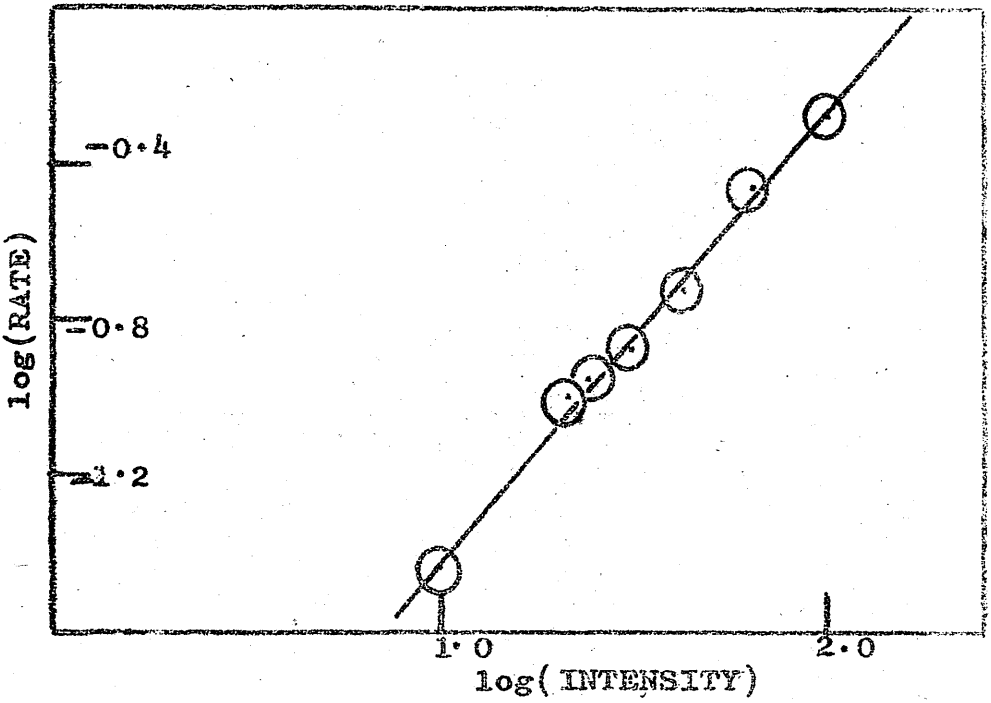
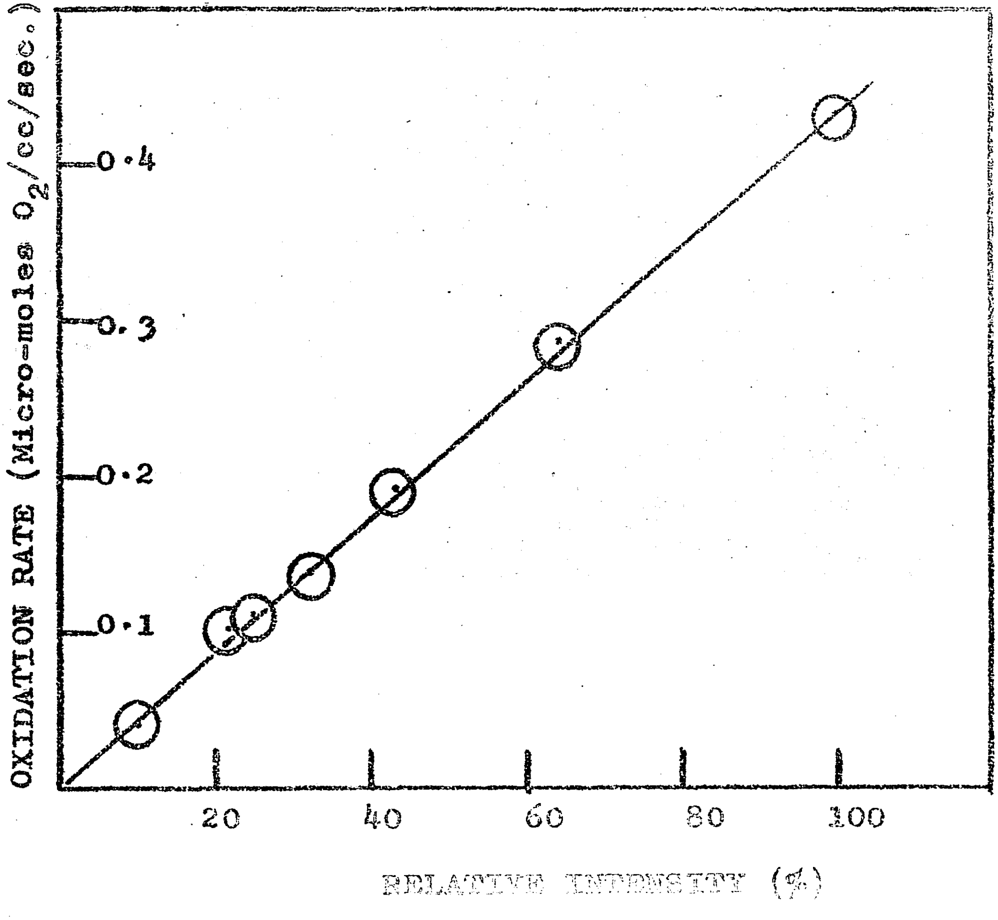


FIGURE 29.



suggests that bimolecular combination of radicals is not an important step in the reaction, a situation which would be expected from the very limited mobility of radicals in the condensed phase at the temperature of these experiments.

Table 12

Distance (cm.)	Transmission (%)	Relative Intensity (%)	log Intensity	Oxidation rate (micro moles O_2/cc/sec)	log Rate
7.375	100	100	2.000	0.434	−0.3625
9.250	100	64.3	1.808	0.289	−0.5391
13.000	100	32.2	1.508	0.136	−0.8665
14.800	100	24.8	1.3945	0.112	−0.9508
7.375	43.1	43.1	1.6345	0.191	−0.7190
7.375	21.7	21.7	1.337	0.102	−0.9914
7.375	10.1	10.1	1.004	0.0365	−1.4377

(b) The Quantum Yield

The quantum yield, ϕ, for this reaction can be conveniently defined by

$$\phi = \frac{\text{Number of moles of } O_2 \text{ absorbed per unit area of film per sec.}}{\text{Number of einsteins of 2537Å quanta absorbed per unit area per second.}}$$

The rate of oxidation of a 0.0044 mm film under standard conditions is 1.93×10^{-10} moles/sq.cm./sec. and the corresponding rate of absorbtion of 2537 Å quanta is 2.71×10^{-9}. A value of 7.12×10^{-2} can thus be inferred for the quantum yield for the oxidation process. This low value (<1) probably indicates that the oxidation of polystyrene does not proceed by a chain reaction.

(c) Effect of Oxygen Pressure

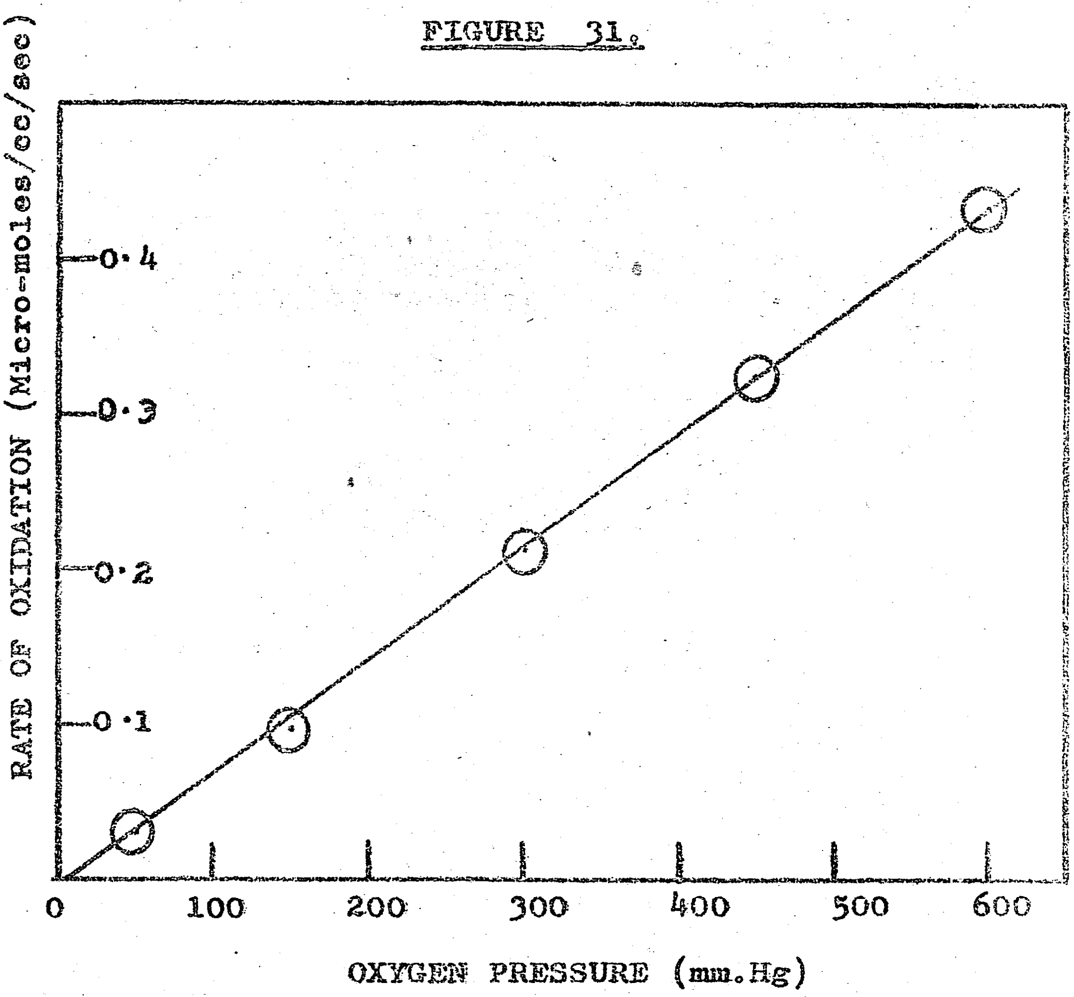
The pressure of oxygen in the apparatus was varied and corresponding oxidation rates were obtained. Table 13 and figure 31 summarize the data.

Table 13

Rate of Oxidation (micro-moles O_2/cc/sec)	Oxygen Pressure (mm Hg)
0.434	600
0.325	450
0.214	300
0.0982	153
0.0311	50

It is clear that the rate of oxidation is directly proportional to the oxygen pressure in the pressure range studied. This result is in complete disagreement with the

FIGURE 31.


RATE OF OXIDATION (Micro-moles/cc/sec)
0·4
0·3
0·2
0·1
0
100
200
300
400
500
600
OXYGEN PRESSURE (mm.Hg)

observations of Bolland[21] and Bateman[22] who concluded that in general the more difficultly oxidised substances showed little if any pressure dependence above a few mm. Hg of oxygen. It was therefore suspected that the effect might be an artefact of the system, possibly associated with the rate of diffusion of oxygen or of products within the polymer, and not a genuine characteristic of the reaction. The experiment was repeated, the oxygen pressure being varied, but the total pressure in the apparatus being kept constant at 600 mm Hg by the addition of the appropriate amount of nitrogen. These results are presented in Table 14 and figure 32. It can be seen that the results are almost identical to those obtained in the previous investigation, the rate of oxidation is thus dependent on oxygen pressure in the range of pressures examined.

Table 14

Rate of oxidation (micro-moles O_2/cc/sec)	Oxygen pressure (mm Hg)	Nitrogen pressure (mm Hg)	Total pressure
0.434	600	0	600
0.334	450	150	600
0.2265	300	300	600
0.124	150	450	600
0.039	50	550	600

FIGURE 32.

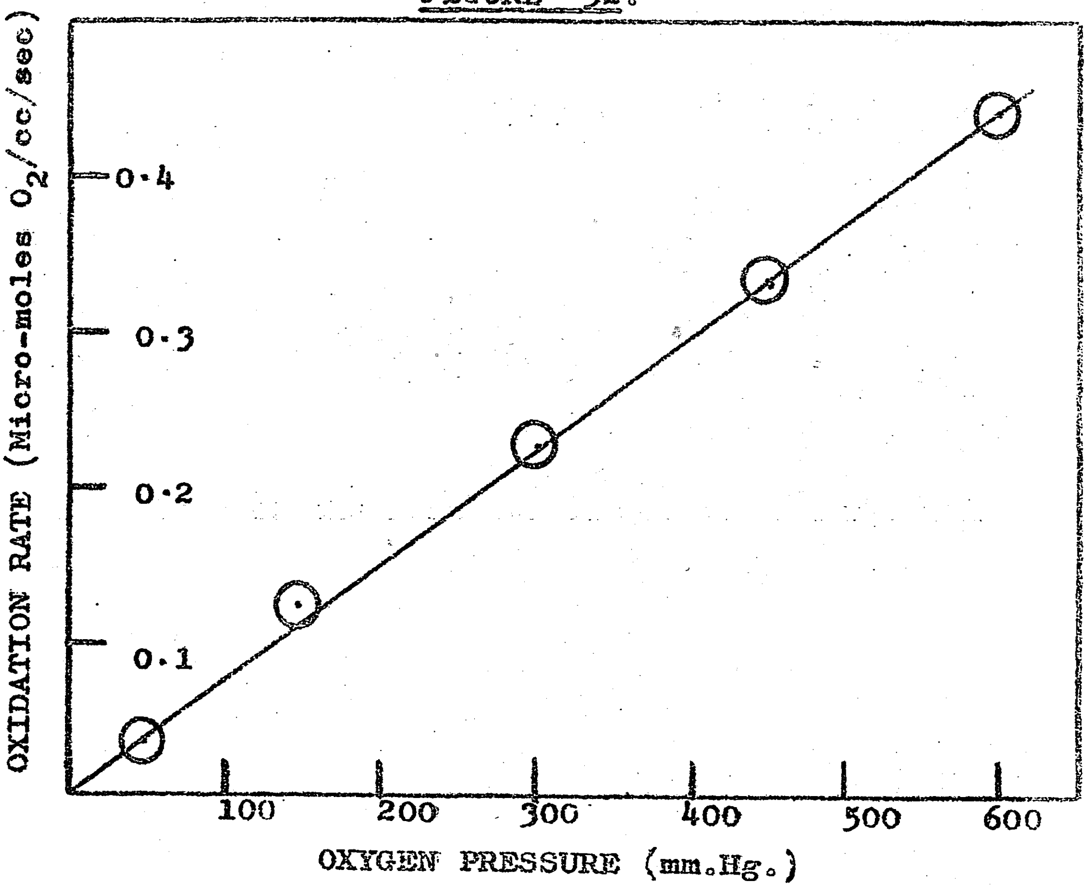
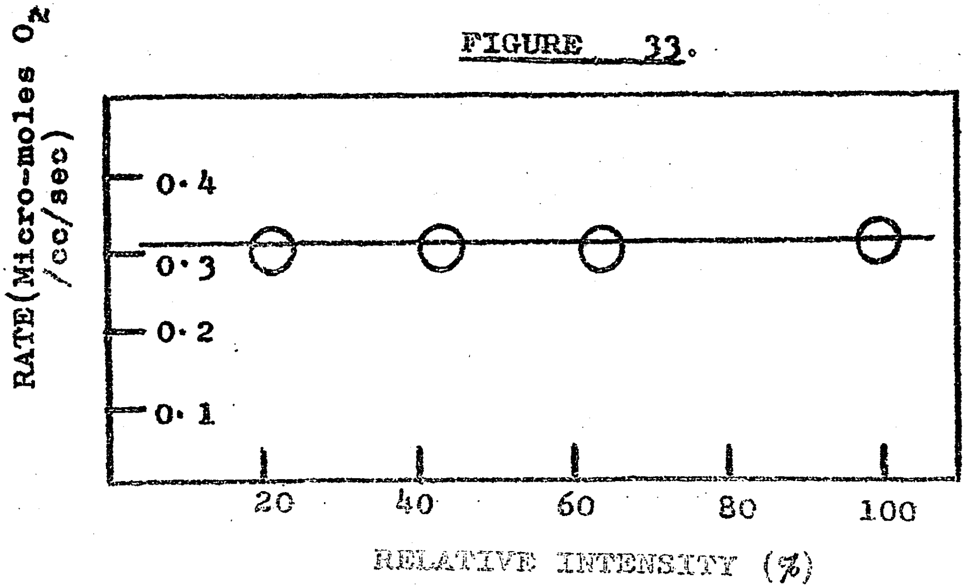


FIGURE 33.



(d) Effect of Light Intensity at Low Oxygen Pressure

It has been shown that at 600 mm Hg of oxygen, the intensity exponent for the reaction is unity. In some oxidation reactions, however, the mechanism changes at low pressures of oxygen, and it is sometimes possible to diagnose this by investigating the intensity exponent at low pressures.

Rates of oxidation corresponding to varying intensities of 2537 Å radiation were obtained, the oxygen pressure in the apparatus being 20 mm Hg. Table 15 and figure 33 show the effect of intensity on the rate at low oxygen pressure.

Table 15

Rate of oxidation (micro-moles O_2/cc/sec.)	Relative intensity (%)
0.313	100
0.307	64.3
0.307	43.2
0.306	21.7

It appears that at low oxygen pressure the rate of oxidation is independent of intensity in the range of intensities studied (10% to 100%), that is the intensity exponent has a value close to zero. This finding suggests that there is a high rate of production of radicals, and that the rate of oxidation is determined by the rate of interaction of oxygen with these.

(e) Effect of Molecular Weight and Initiator Fragments

The effect of the presence of varying amounts of initiator fragments in the chains on the rate of oxidation of polystyrene was investigated by obtaining rates of oxidation of polymers prepared using varying amounts of 2,2'-azoisobutyronitrile. Information regarding the effect of molecular weight on oxidisibility was obtained from a similar study of thermal polymers. The results are collected in Table 16.

Table 16

Rate of oxidation (micro-moles O_2/cc/sec)	Polymer	Polymerization Temperature	Initiator concentr. (%)	Mol.Wt. x 10^{-5}
0.434	1	60	0.001	3.31
0.439	2	60	0.002	2.188
0.454	3	60	0.10	1.86
0.415	4	60	0.20	1.59
0.430	5	60	0.40	1.50
0.434	S1	90	none	4.93
0.443	SG3	60	none	15.1

FIGURE 35.

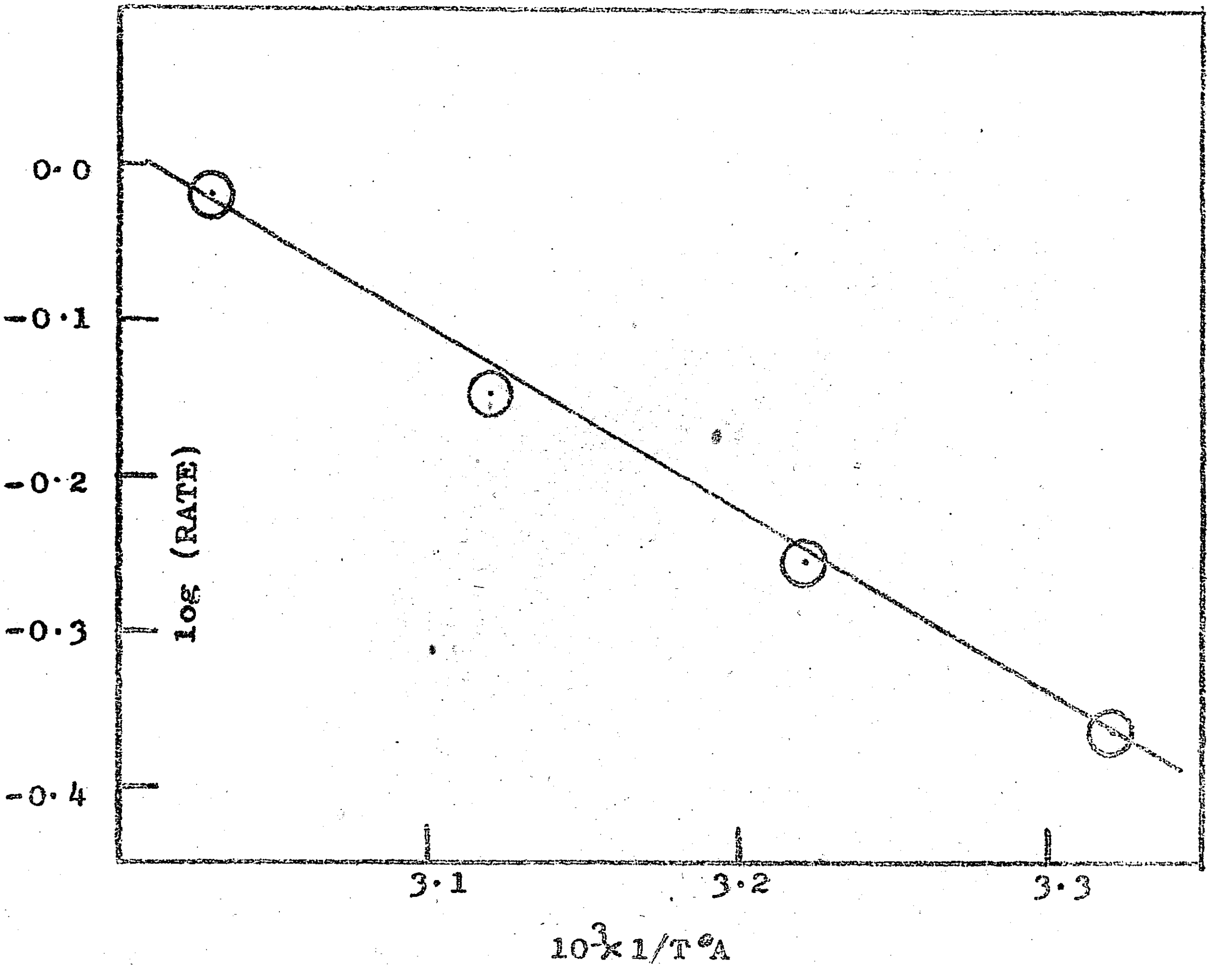


FIGURE 36.

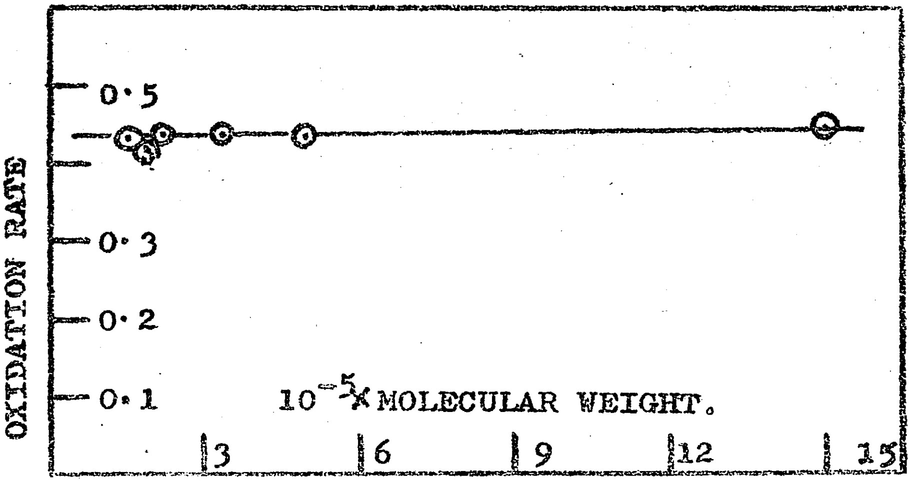


Figure 34 shows the effect of these variables on the rate of oxidation. Rates of oxidation are very similar and it thus seems unlikely that within the ranges of these variables investigated that either the molecular weight or the presence of catalyst fragments has a profound effect on the oxidation reaction, a finding which is compatible with a random addition of oxygen to the polymer. It was not possible to investigate the effect of very low molecular weights on the rate of oxidation on account of the difficulty of obtaining films from these materials.

(f) Effect of Temperature

Rates of oxidation were obtained at a series of temperatures, these are shown in Table 17.

Table 17

Rate of oxidation (micro-moles O_2/cc/sec.)	log Rate	Temperature (Å)	$10^3(\frac{1}{T})$	Activation energy (k cal/mole)
0.434	-0.3625	301	3.321	6.0
0.556	-0.2549	310	3.222	
0.712	-0.1475	320	3.120	
0.951	-0.0218	330	3.03	

The value of the energy of activation derived from the graph of log rate versus reciprocal temperature (figure 35) is 6 k.cal per mole, a low value, characteristic of many photochemical reactions.

(g) Effect of Film Thickness

It has already been pointed out that because of the non-uniform absorbtion of 2537 Å radiation throughout polystyrene films the rate of oxidation is also non-uniform throughout the films. It was therefore decided to investigate the relation between rate and film thickness in an attempt to define the actual way in which the rate varies across a film. A series of polymer films of varying thicknesses was prepared, the thicknesses being calculated from optical density data at 2537 Å. Corresponding rates of oxidation were found for these films; these are expressed as micro-moles of oxygen absorbed per sq.cm. of film and are summarized in Table 18. The variation of rate with film thickness can be explained in the following way. If I' is the number of quanta absorbed in a layer $d\ell$ cm. thick with a unit cross-section at a depth ℓ cm. from the surface on which the radiation is incident, and I_0 is the number of quanta entering the system

Table 18

Rate of oxidation (micro-moles O_2/ cm^2/sec.) $\times 10^4$	Thickness (ℓ) (cm) $\times 10^4$	$a\ell$	$e^{-a\ell}$	$1-e^{-a\ell}$
1.42	2.2	0.926	0.3968	0.6032
1.735	2.94	1.240	0.2894	0.7106
1.991	3.76	1.582	0.2050	0.7950
2.184	4.4	1.852	0.1575	0.8425
2.361	5.13	2.260	0.1043	0.8957
2.59	6.6	2.78	0.0620	0.9380

$$I' = d[I_o(1-e^{-a\ell})]/d\ell$$

$$= aI_o\, e^{-a\ell}$$

where a is the extinction coefficient.

But the rate of oxidation is proportional to the intensity of radiation

i.e. Rate = kI in which k is a constant

So local rate = r_ℓ

$$r_\ell = k\ \alpha\ I_o\ e^{-a\ell}$$

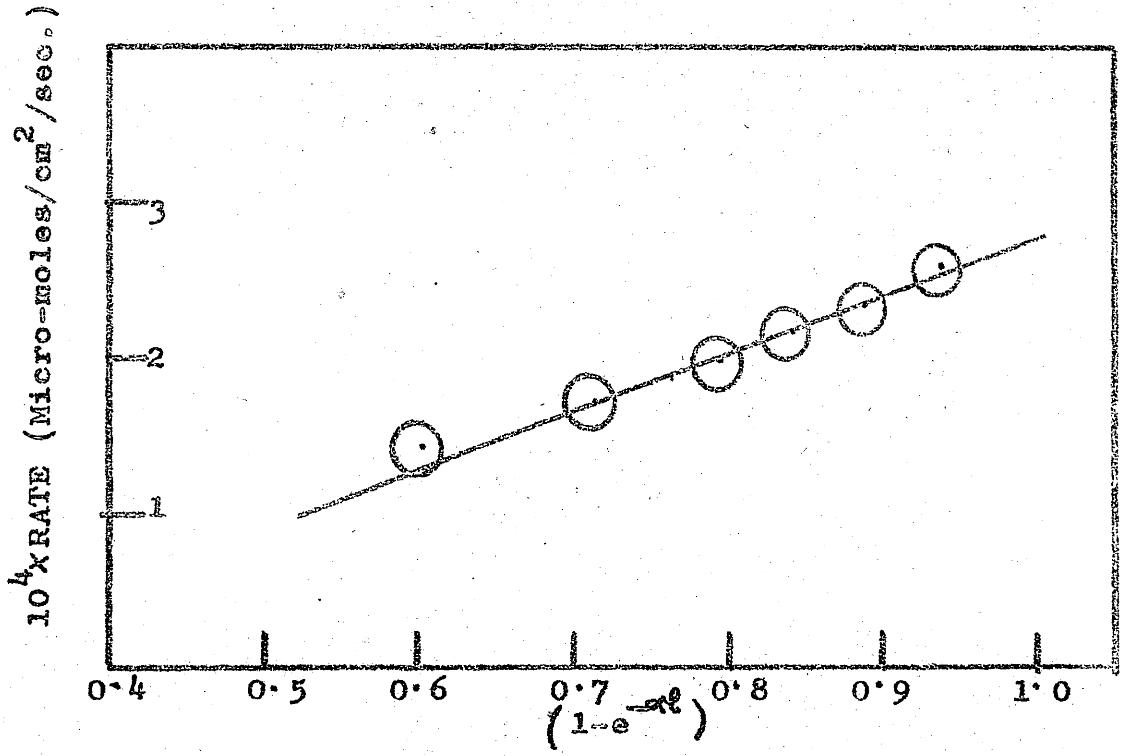
Total rate of oxidation, R, in a film ℓ cm. thick, is given by the equation,

$$R = \int_0^{\ell} k\,\alpha I_0 e^{-\alpha \ell}\, d\ell$$

$$= kI_0(1-e^{-\alpha \ell})$$

The rate is thus proportional to $(1-e^{-\alpha \ell})$. It has been shown that the value of the extinction coefficient, μ at 2537 Å derived from the equation $\log_{10} \frac{I_o}{I} = \mu \ell$, is 1825 (cm. units). It follows then that the value of α derived from the equation $\log_e \frac{I_o}{I} = \alpha \ell$ will be 2.303 x 1825 i.e. 4210 (cm. units). Figure 36 shows the relation between rate and $1-e^{-\alpha \ell}$. It can be seen that over the greater part of the film thicknesses examined there is a good agreement between these two quantities, showing that in common with the radiation intensity the oxidation rate is exponentially attenuated across the film. Because of the very high extinction coefficient at 2537 Å, absorbtion of the incident radiation is almost complete across a film 0.01 mm thick. It follows then that the greater part of the photo-oxidation will take place in a 0.01 mm layer of polystyrene adjacent to the illuminated surface, the bulk of the polymer being relatively unaffected.

FIGURE 36.


$10^4 \times$ RATE (Micro-moles/cm^2/sec.)
1
2
3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
$(1-e^{-\alpha l})$

The range of film thicknesses investigated was of necessity comparatively narrow. Complications due to diffusion of oxygen into the polymer would have been introduced in film thicknesses greater than 0.01 mm and films thinner than 0.002 mm. do not have sufficient mechanical strength.

(h) Effect of Wavelength

Films were irradiated with a similar (to 2537 Å) intensity of 3650 Å radiation. Figure 35 is a typical reaction curve, the amount of oxygen absorbed by a standard film being shown as a function of reaction (data in Table 19). The characteristics of oxygen absorbtion are fundamentally different from those observed in oxidations photo-initiated with 2537 Å radiation. It can be seen that after a long induction period of 90 hours the reaction proceeds at a constant rate of one fortieth that of the reaction initiated by 2537 Å quanta, suggesting that the initiation steps in the two reactions are different. This subject is discussed in detail in the following chapter.

FIGURE 37.

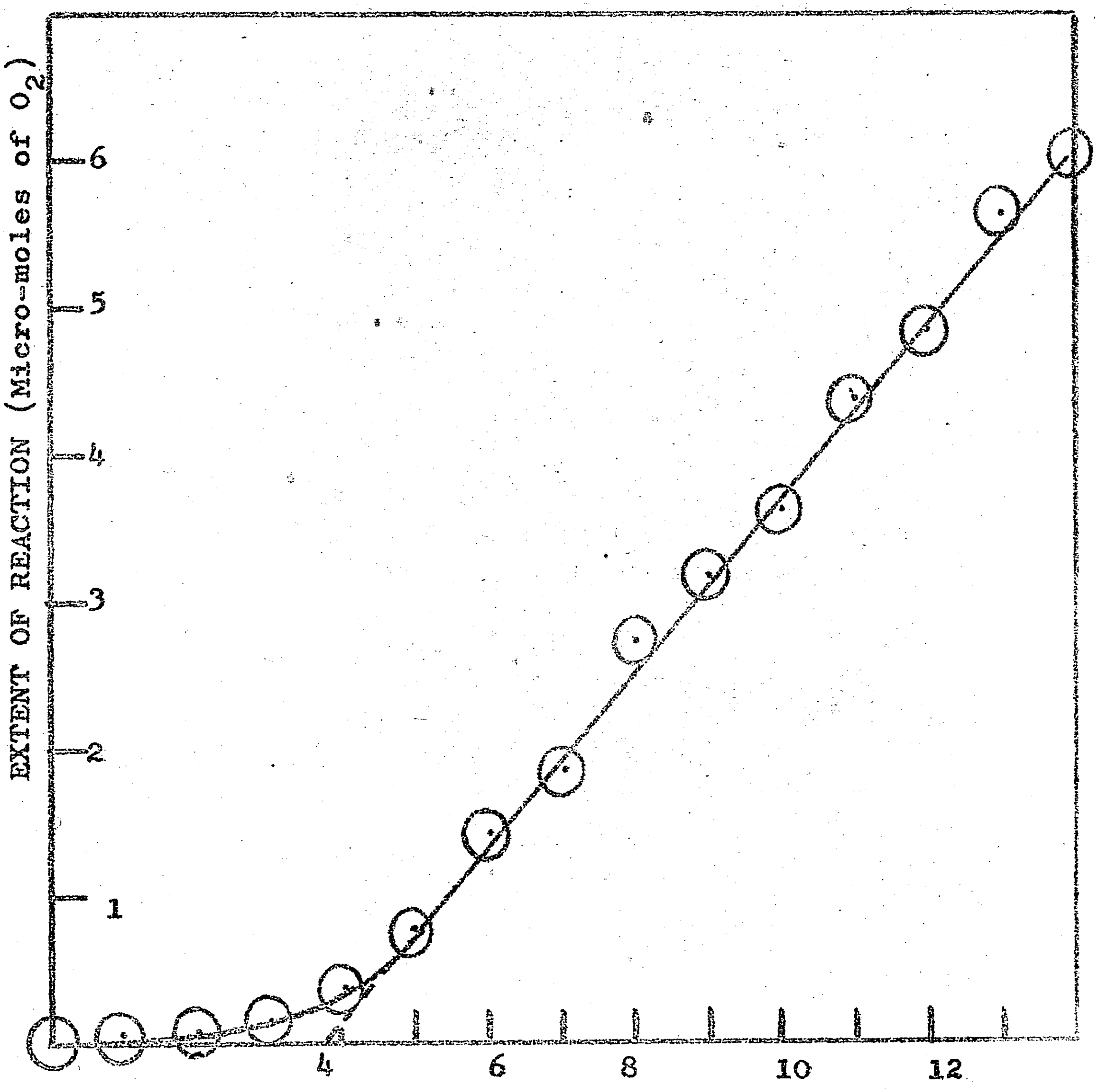

EXTENT OF REACTION (Micro-moles of O_2)
1
2
3
4
5
6
4
6
8
10
12
TIME (Days).

Table 19

Time (days)	Extent of Reaction micro-moles of O_2	Time (days)	Extent of Reaction micro-moles of O_2
0	0	8	2.72
1	0.052	9	3.17
2	0.080	10	3.63
3	0.151	11	4.38
4	0.378	12	4.84
5	0.755	13	5.62
6	1.44	14	6.04
7	1.82		

(i) Effect of Free Radical Inhibitors

Bolland[25] has shown that the presence of small amounts of free radical inhibitors, like aromatic phenols and amines leads to induction periods in oxidation reactions, the inhibitors stabilizing peroxy radicals by transferring hydrogen atoms to them. Although many of these compounds have been used commercially to stabilize polymer systems, information regarding their ability to suppress photo-oxidations is limited, and the purpose of this investigation was to assess the effect of free radical inhibitors on the photo-oxidation of polystyrene.

The choice of inhibitor was determined by two factors,
(1) absorbtion of 2537 Å radiation and
(2) compatability with the polymer.

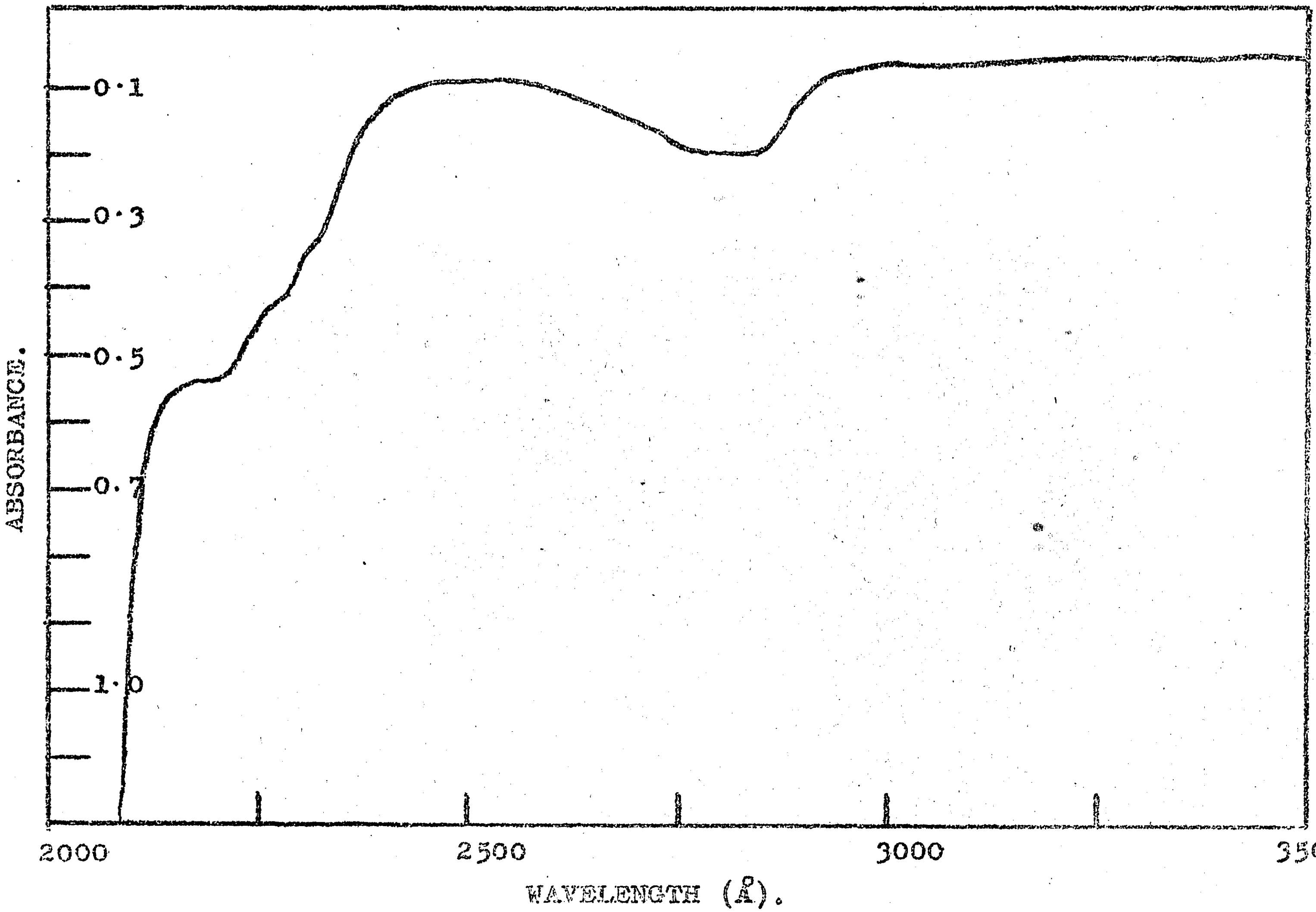
(1) Absorbtion of 2537 Å radiation: It would have been extremely difficult to assess the effect of an inhibitor which also showed high absorbtion at 2537 Å since it could inhibit the reaction by reducing the intensity of the activating radiation, or perhaps even act as a photosensitizer.

(2) Compatibility with the polymer: The inhibitor must be compatible with the polymer both in solution and in the form of a film in order that it can be uniformly incorporated in the film.

Butylated hydroxy toluene (2:6 di *tert* butyl, 4 methyl phenol) has both of these desirable properties, the ultraviolet spectrum of a cyclohexane solution is shown in figure 38. That it was indeed an effective free radical inhibitor was demonstrated by carrying out a polymerization of styrene at 60°C in presence of 0.1% of this compound; an induction period characteristic of the presence of free radical inhibitors

FIGURE 38.

ULTRA-VIOLET SPECTRUM OF B.H.T. (Butylated hydroxy toluene) Concentration =7·7mgs./100ml. cyclohexane, Path length =2mm.



was observed. Since very small amounts of inhibitor were required to be incorporated into the films, and since it was observed that incorporation was not complete, i.e. some crystallization of the inhibitor occurred on the mercury surface, a sensitive method of determining the amounts of inhibitor actually present in the films was required. This was achieved by measuring optical densities at 2800 Å of films containing inhibitor, the extinction coefficient of butylated hydroxy toluene (B.H.T.) at 2800 Å (λ_{max}) having been previously determined. The concentration of the inhibitor was found from the equation,

$$D = \ell(\alpha + \beta c)$$

where D is the optical density at 2800 Å ℓ is the film thickness, c is the concentration of inhibitor in the film, and α and β are the extinction coefficients of polystyrene and B.H.T. respectively at 2800 Å.

The inhibitor was introduced into the films during their formation from chloroform solution, 1 c.c. of stock solution of inhibitor in chloroform being added to the polymer solution on the mercury surface. Rates of oxidation of these films are shown in Table 20 and figure 39.

FIGURE 39

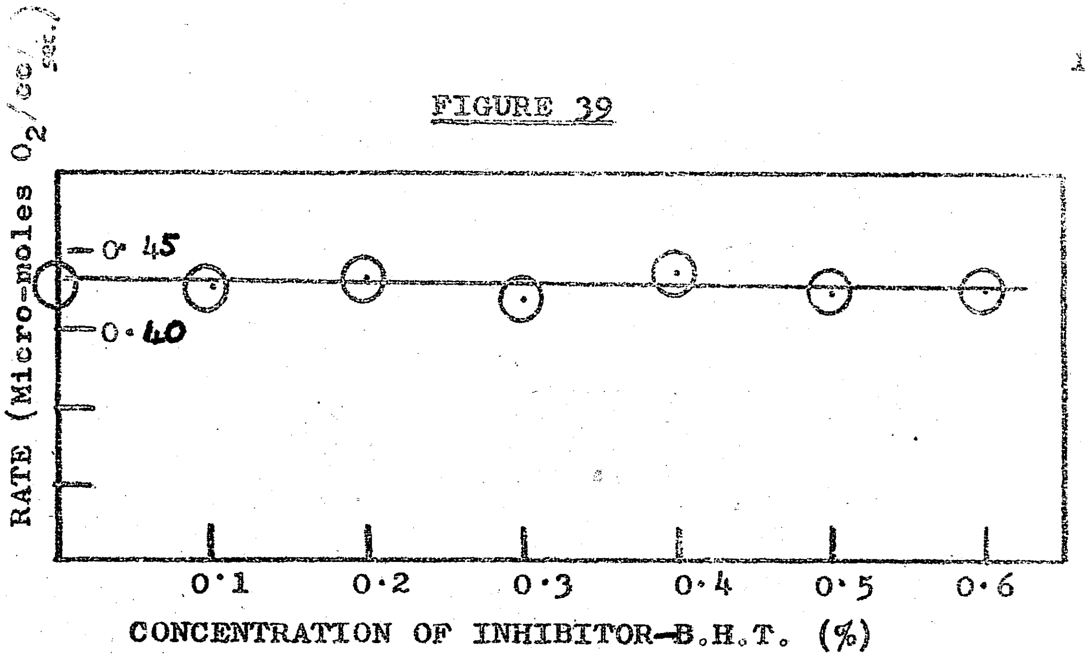


FIGURE 41.

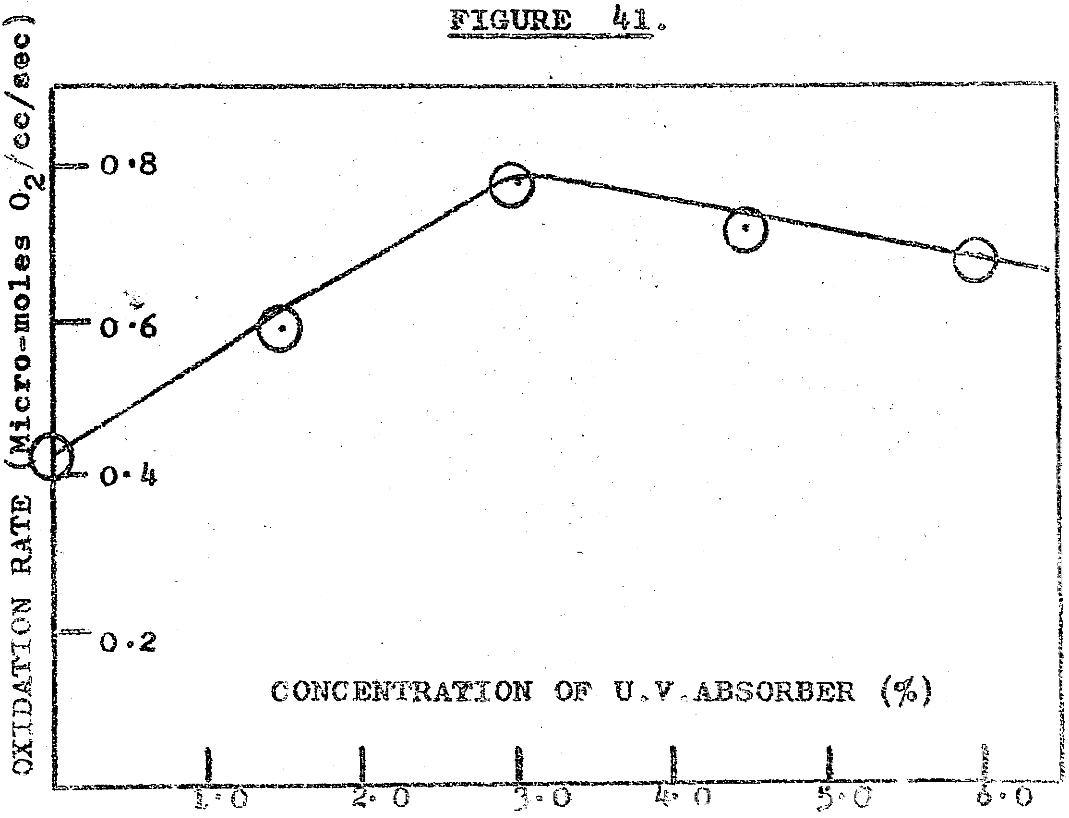


Table 20

Rate of oxidation (micro-moles O_2/cc/sec.)	Concentration of butylated hydroxy toluene (%)
0.434	0.0
0.429	0.1
0.434	0.2
0.420	0.3
0.439	0.4
0.425	0.5
0.429	0.6

The rates of oxidation in presence of varying amounts of the free radical inhibitor are comparable and are almost identical with the rate of oxidation of the polymer containing no inhibitors. In addition, the characteristics of oxygen uptake in presence of the inhibitor are identical with those of the pure polymer, no induction periods being observed.

The failure of free radical inhibitors to stop the reaction must be largely a consequence of the limited interaction of the inhibitor molecules with the radicals produced in the reaction, resulting from their lack of mobility in the condensed phase.

(j) Oxidation in Presence of Light Absorbers

It has been found that certain compounds, in particular 2-hydroxy benzophenone are effective inhibitors of photo-chemical reactions by virtue of their ability to absorb the activating radiation in preference to the substrate;(77) these are commonly termed ultra-violet absorbers. All these compounds contain the o-hydroxy phenyl keto-group and it is believed that the conjugate hydrogen bond chelate group formed is responsible for the strong absorbtion of short-wave radiation. The grouping also appears to confer stability to ultra-violet radiation.(78)

The compound chosen for this investigation was 2-hydroxy 4-methoxy benzophenone, on account of its compatibility with the polymer. The salient features of the molecule are shown by the formula, and the ultra-violet spectrum is shown in figure 40.

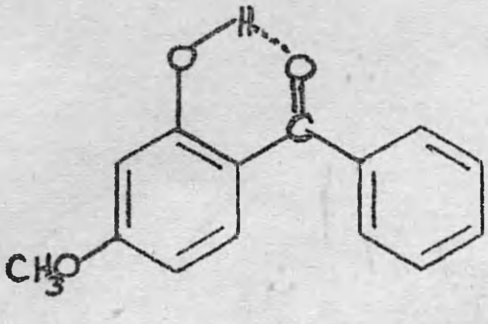
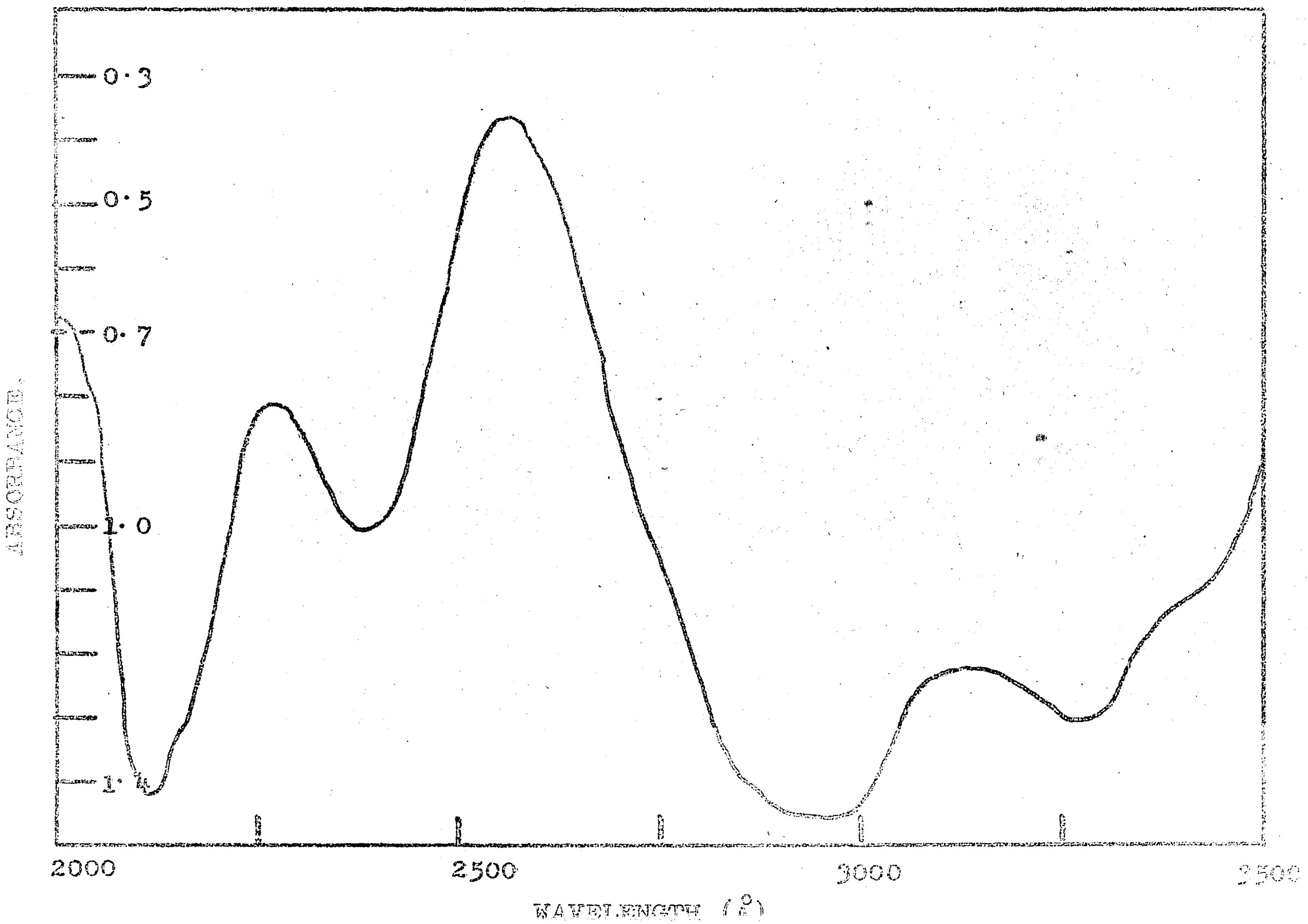


FIGURE 40.

ULTRA-VIOLET SPECTRUM OF 2-HYDROXY 4-METHOXY BENZOPHENONE, Concentration = 3·75mgs./100ml. Hexane, Path length = 2mm.



It was introduced into the films in chloroform solution during the casting process, concentrations present in the films being determined from optical density data at 2900 Å. The concentration range investigated was from zero to 6%, since it appears that the optimum concentration is between 2 and 5%$^{(79)}$. Rates of oxidation of films containing varying amounts of U.V. absorber are shown in table 21.

Table 21

Rate of oxidation (micro-moles O_2/cc/sec.)	Concentration of 2-hydroxy 4-methoxy benzophenone (%)
0.434	0
0.592	1.5
0.779	3.0
0.720	4.5
0.680	6.0

Figure 41 shows the variation of rate with U.V. absorber concentration; two features are immediately apparent. The rate of oxidation in presence of absorber is greater than that of the pure polymer throughout the concentration range investigated, and in addition the rate of oxidation passes through a maximum (about 3% U.V. absorber).

From the first of these observations it would seem that either the U.V. absorber is acting as a photosensitizer for the polystyrene oxidation, or it is itself being oxidised. The work of Kasha(80) suggests that this is not so, since it is possible for these molecules to lose their excess electronic energy as thermal energy before reacting, that is,

$$AH^* \longrightarrow (AH) + kT$$
$$(AH) \longrightarrow AH + h\nu$$

in which AH* is the excited U.V. absorber molecule, (AH) is not sufficiently energetic to participate in photosensitizing reactions, and AH is the ground state of the molecule. These observations are, however, in turn incompatible with the recent findings of Hirt and Schmitt(81) who showed that the high vacuum irradiation of U.V. absorbers, with 2537 Å quanta resulted in appreciable photolysis of these compounds. Photo-sensitization of polystyrene oxidation and oxidation of the absorbers themselves are thus quite feasible. The quantum yield for photolysis being low, however, means that a large part of the acquired energy is being degraded to thermal energy.

The second observation can be explained as follows. Because of the very high extinction coefficient of the light absorber at 2537 Å, the intensity of this radiation penetrating the bulk of the polymer and hence the rate of oxidation of the polymer will decrease rapidly (exponentially) with increasing absorber concentration. In other words, progressively more of the activating radiation is being absorbed by the absorber in the surface layers so that the amount of polymer capable of being oxidised rapidly decreases with increasing absorber concentration. Since more of the energy acquired by the absorber is converted to thermal energy than is used in the photolysis process, the increasing absorbtion of 2537 Å radiation by the absorber in preference to the polymer will not be matched by a corresponding increase in photosensitization and self-oxidation by the absorber; the overall rate of oxidation will thus decrease with increasing absorber concentration. It is significant to note that whereas concentrations of 2 to 5% of U.V. absorber are used and recommended commercially, concentrations of about 10% would be required to decrease the overall rate of oxidation to a value less than that of the pure polymer. The effect of the U.V. absorber then is to protect the bulk of the polymer from photo-oxidation, the surface and layers immediately below it being sacrificed in the process.

CHAPTER 7

The Mechanism of the Oxidation Reaction

(1) Primary Processes

It has already been shown in Chapter 3 that the high-vacuum irradiation of polystyrene with 2537 Å quanta leads to the fission of C-H bonds with the production of hydrogen atoms and long chain radicals, that is $RH \rightleftharpoons R^{\circ} + H^{\circ}$. Since this is purely a photochemical process, resulting from the absorbtion of 2537 Å quanta, it is unlikely that the presence of oxygen molecules, which do not absorb these quanta and are thus in no way modified by them, will alter it fundamentally. The mobility of the hydrogen atoms will, however, be reduced by the presence of oxygen, and there is likely to be appreciable recombination as represented by the reverse process in the above equation. The initiaton step in the photo-oxidation of polystyrene thus involves the production hydrogen atoms and chain radicals.

(2) Secondary Processes

Although a very large number of secondary reactions involving these radicals is possible, it is fairly certain that on account of the oxygen molecule being itself a diradical, the initiation step will be followed by a rapid combination of these radicals with oxygen molecules to form the corresponding peroxy radicals

$$H\cdot + O_2 \longrightarrow HO_2\cdot$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

It is not possible to state unequivocally the point of attack of the oxygen on the polymer molecule, since all three types of chain radical (the radicals formed by breaking secondary, tertiary and benzene ring C-H bonds) will be present simultaneously. It can be predicted on the basis of the following information, however, that attack of oxygen will be predominantly on the tertiary substituted carbon atom. Firstly, the tertiary chain radical and the resulting peroxy radical are considerably more resonance stabilized than are the other chain and peroxy radicals, thus the production of tertiary radicals will be favoured. Secondly, no evidence for attack of oxygen at the secondary carbon atom or at any of the benzene ring carbon atoms yet exists, whereas a large volume of evidence for attack at the tertiary carbon atom in not only polystyrene, but also in its model compound, cumene, has already accrued. For example, production of benzaldehyde during oxidation of polystyrene can only be rationalized in terms of attack of oxygen at the tertiary position.

The peroxy radicals will then, by analogy with the Bolland mechanism, abstract hydrogen atoms from the polymer to form hydroperoxides, and at the same time chain radicals will be regenerated according to the equation, $RO_2\cdot + RH \longrightarrow RO_2H + R\cdot$. It has been shown that in the oxidation of olefins, this, the vital step in the chain reaction is very largely influenced by steric factors, for example, small kinetic chain lengths for oxidation are associated with systems in which hydrogen abstraction by the peroxy radicals is sterically difficult. It is obvious that the corresponding step in polystyrene is going to be sterically unfavourable on account of the bulk and lack of mobility of the large radicals. It follows then, that the kinetic chain length is going to be correspondingly short. In fact, no positive evidence has been obtained to suggest that the oxidation of polystyrene is a chain reaction, and this is presumably a direct result of the characteristics of the radicals involved. Evidence exists, however, for the formation of the tertiary hydroperoxide, although existing analytical methods have so far failed to detect it. It is likely, however, that small amounts of hydroperoxides are formed by the above mechanism, but being both thermo- and photo-labile they will be decomposed almost as quickly as they are produced; thus the stationary concentration will be sufficiently low to preclude their detection by conventional analyses. Hydroperoxide decomposition has been found to lead to autocatalysis in olefin oxidation. Autocatalysis, however, was not observed in polystyrene oxidation; thus it appears that no appreciable amounts of hydroperoxide are formed. The yield of hydrogen peroxide will no doubt exceed that of the polymer hydroperoxide on account of the greater mobility of the small hydroperoxy radical, and being volatile and thus decomposed predominantly in the gas-phase, it is unlikely that the hydrogen peroxide will play any major part in the oxidation of the polymer.

It has been observed that cross-linking of the polymer is concomitant with its oxidation. This can be readily explained in terms of bimolecular combination of chain radicals, there being three types, R°, RO_2° and RO° (from the decomposition of the tertiary hydroperoxide) present. Both combination of like and different radicals can lead to cross-linking, for example,

$$2R \longrightarrow R - R$$

$$R + RO_2 \longrightarrow RO_2R$$

$$RO + RO_2 \longrightarrow ROR + O_2$$

Partial cross-linking will, however, lead to a further immobilization of the chain radicals, thus mutual destruction will be inhibited to a certain extent and the oxidised polymer will contain residual radicals. That this is so has been demonstrated by paramagnetic resonance studies(82) and chemical studies.(83)

(3) The Kinetics of Oxidation

The reactions discussed above can be summarized as follows

$$(1)\ RH \overset{h\nu}{\rightleftharpoons} R\cdot + H\cdot \quad \text{Initiation, } r_I$$

$$(2)\ R\cdot + O_2 \longrightarrow RO_2\cdot \quad k_2(R\cdot)(O_2)$$

$$(3)\ H\cdot + O_2 \longrightarrow HO_2\cdot \quad k_3(H\cdot)(O_2)$$

$$(4)\ RO_2\cdot + RH \longrightarrow RO_2H \longrightarrow RO\cdot + OH\cdot$$

$$(5)\ HO_2\cdot + RH \longrightarrow H_2O_2 \longrightarrow 2OH(?)$$

$$\left.\begin{array}{r} 2R \longrightarrow \\ 2RO_2 \longrightarrow \\ 2RO \longrightarrow \\ R + RO_2 \longrightarrow \end{array}\right\} \quad \text{Cross linking reactions}$$

etc.

Since this is not a chain reaction the overall rate will be determined by the rate of initiation, thus

$$\text{Rate} = \frac{-d(O_2)}{dt} = K(RH)I$$

in which K is a constant and I is the intensity of 2537 Å radiation. A first order dependence of rate on radiation intensity has indeed been observed. It has also been observed, however, that the rate is a function of the oxygen pressure, which means that addition of oxygen must also be a rate determining step. This situation would arise of the rate of production of radicals was greater than the rate of their reaction with oxygen, that is, if the concentration of R° and H° radicals exceeded those of the HO_2° and RO_2° radicals. It is likely then, that since the reaction is photo-initiated, the rate of initiation is high; the overall rate will then also be determined by the rate of interaction of the oxygen with the initially formed radicals; in other words, the rate of oxidation will be a function of oxygen pressure.

If the rate of initiation is high compared with the rate of addition of oxygen, that is, if $r_I > k_2(R^\circ)(O_2) + k_3(H)(O_2)$ the overall rate would be expected to be independent of r_I; in other words, the value of the intensity exponent would approach zero. Such a situation would arise at low oxygen pressures. This has indeed been observed, the rate of oxidation being independent of radiation intensity at 20 mm. Hg oxygen. When the rate of initiation is comparable with that of oxygen addition, that is,

when $r_I \overset{\frown}{=} k_2(O_2)(R) + k_3(R)(O_2)$

tha rate will be dependent on both oxygen pressure and radiation intensity, as has been found. Thus two rate expressions can be distinguished,

(a) at low oxygen pressures,

$$\frac{-d(O_2)}{dt} = k_L(RH)(O_2)$$

and (b) at high oxygen pressures,

$$\frac{-d(O_2)}{dt} = k_H(RH)I(O_2)$$

in which k_L and k_H are the respective constants of proportionality. It could be argued, that if the reaction is diffusion-controlled, the rate will be a function of oxygen pressure and that at low oxygen pressures the rate will be independent of the radiation intensity. It is unlikely that the reaction is diffusion-controlled, however, since Barrer's data predicts that the rate of diffusion of oxygen into films 0.0044 mm in thickness will be several times greater than their oxidation rates. Moreover, if the reaction were diffusion controlled, the rate would be independent of film thickness, since effectively the same thickness of polymer is being oxidised each time on account of the shape of the oxygen concentration profile throughout the films. No such relation between rate and thickness has been observed; the rate of oxidation is proportional (exponentially) to the film thickness.

It has been shown that the characteristics of the reaction are different when radiation with a wavelength of 3650 Å is used. Since the ratio of absorbance of 2537 Å to 3650 Å quanta is 80:1, it would be anticipated that the rate of an oxidation reaction initiated by 3650 Å radiation would be 1/80 that of the corresponding reaction initiated by a similar intensity of 2537 Å radiation, provided that the initiation steps and the quantum yields for initiation are identical. There is no evidence of this, instead an induction period is observed, suggesting that the initial steps differ.

An examination of the dissociation energies of the C-H bonds in the molecule reveals that whereas the 2537 Å radiation has associated with it sufficient energy (112.8 k.cal/mole) to break all three types of C-H bond, the energy associated with 3650 Å radiation (78 k cal/mole) is only slightly in excess of that required to rupture the secondary and tertiary C-H bonds, assuming that the values of the dissociation energies of these bonds in polystyrene are similar to those for the corresponding bonds in model compounds (76 and 71 k.cal/mole) Although this predicts a decrease in the rate of initiation and hence in rate of oxidation when the activating radiation has a wave-length of 3650 Å, it does not explain the induction period. It is likely therefore that the secondary and tertiary C-H bond dissociation energies are in excess of that associated with the 3650 Å radiation (78 k.cal/mole) and that the initiation step does not involve fission of C-H bonds. This can be interpreted in terms of a partial loss of resonance stabilization in the tertiary radical due to the geometry of the macromolecule. As evidence of this theory, no hydrogen was detected during the high-vacuum photolysis of the polymer with 3650 Å quanta.

It seems possible that the initiation step involved reaction of oxygen with residual radicals from the polymerization process to form hydroperoxides and eventually ketones, both of which will yield radicals on photolysis by 3650 Å radiation. The induction period can thus be associated with the building up of a concentration of such radicals which are capable of initiating further oxidation.

CHAPTER 8

The Colouration of Polystyrene

Although the investigation of colouration of polystyrene was not the object of this work, polystyrene colouration has been encountered during its high-vacuum irradiation, irradiation in nitrogen and its oxidation, and this chapter deals briefly with some aspects of colouration.

An explanation must be sought for not only the origin of the colour, but also for the fact that under all the conditions mentioned above the actual colour produced is yellow, no bathochromic shift in visible absorbtion being produced on continued irradiation or oxidation.

The characteristics of colouration of standard films under different conditions are shown in figure 42 in which colouration, expressed as an increase in optical density at 4400 Å, is shown as a function of reaction time. It can be seen that colouration of polystyrene films under all conditions increases linearly with time of exposure to the activating radiation, the rate of colouration in presence of nitrogen being greater than that in presence of a similar pressure of oxygen. Table 22 summarizes relevant data for irradiation in vacuum, 600 mm. Hg nitrogen and 600 mm. Hg oxygen.

FIGURE 42.

COLOURATION OF POLYSTYRENE.

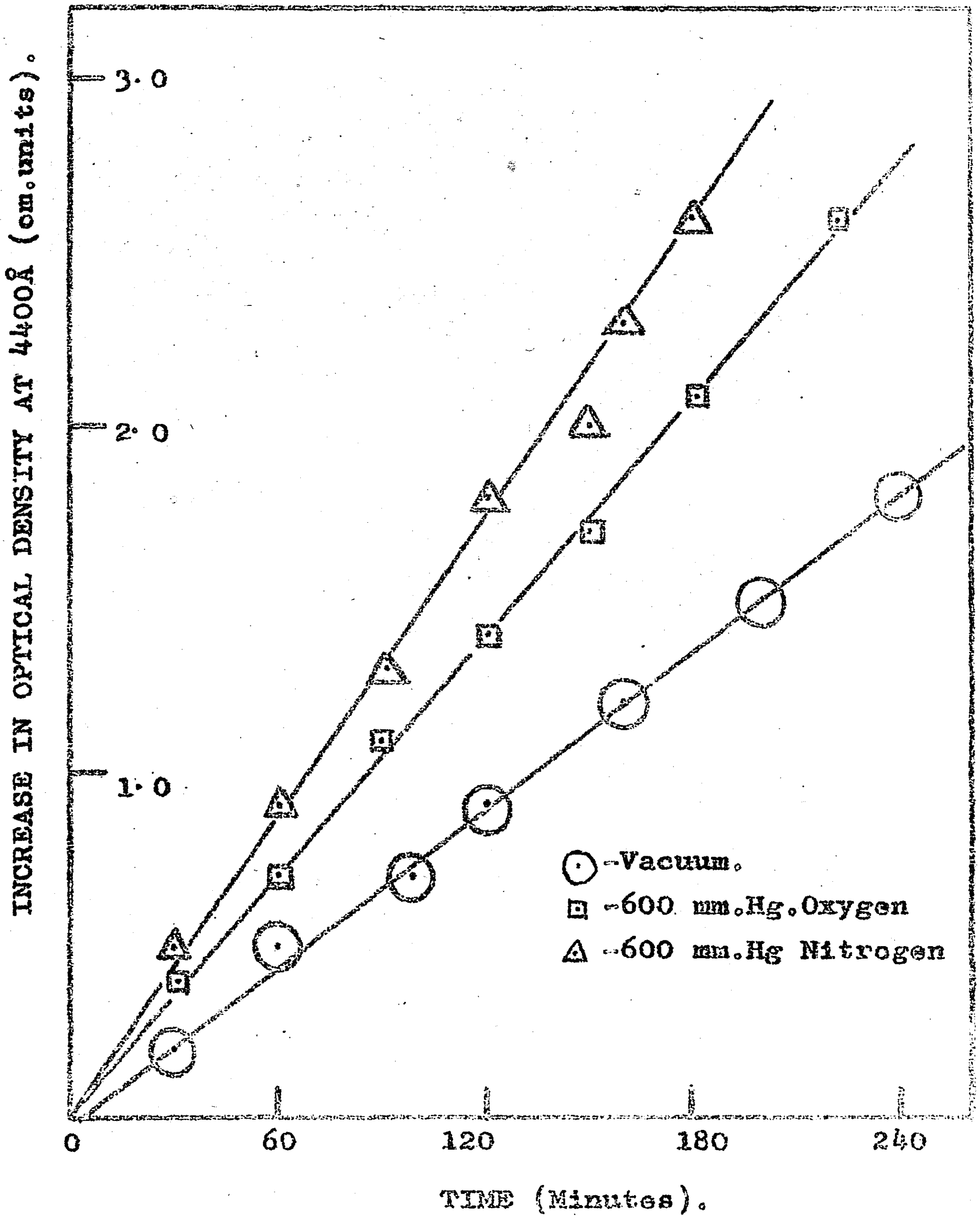


Table 22

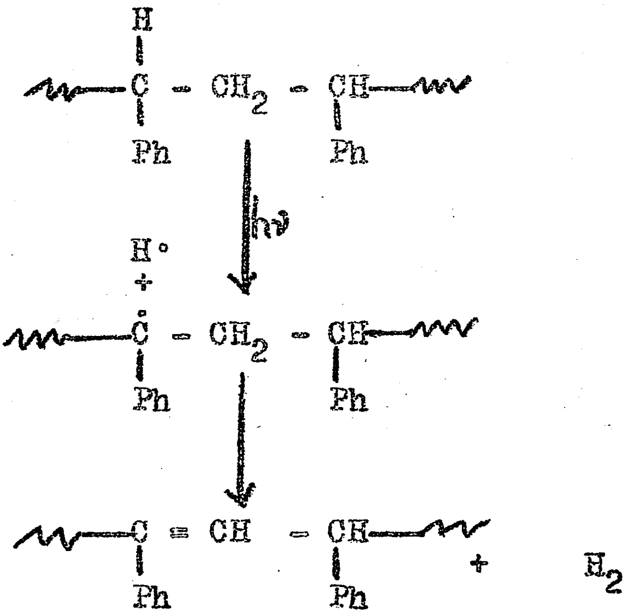
	Increase in optical density at 4400 A		
Time (mins.)	Vacuum	600mm. Hg Nitrogen	600mm. Hg Oxygen
0	0	0	0
30	0.2	0.5	0.4
60	0.5	0.9	6.7
90	-	1.3	1.1
100	0.7	-	-
120	0.9	1.8	1.4
150	-	2.0	1.7
160	1.2	-	-
180	-	2.6	2.1
200	1.5	-	-
220	-	3.2	2.6
240	1.8	-	-

Origin of Colour during High Vacuum Irradiation

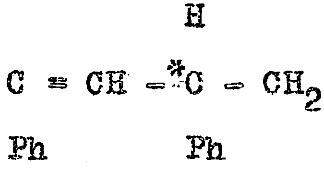
It was seen in Chapter 4 that whereas hydrogen atoms produced on the surface of the film and within a few atomic diameters of it combined to form molecules on the walls of the cell or in presence of a third body, hydrogen was formed in the bulk of the film by the interaction of hydrogen atoms with the polymer, i.e.

$$H\cdot + RH \longrightarrow H_2 + R\cdot$$

Abstraction of hydrogen from the carbon atom adjacent to the one at which the initial bond fission occurs could also lead to the formation of a double bond between the two atoms in question, that is

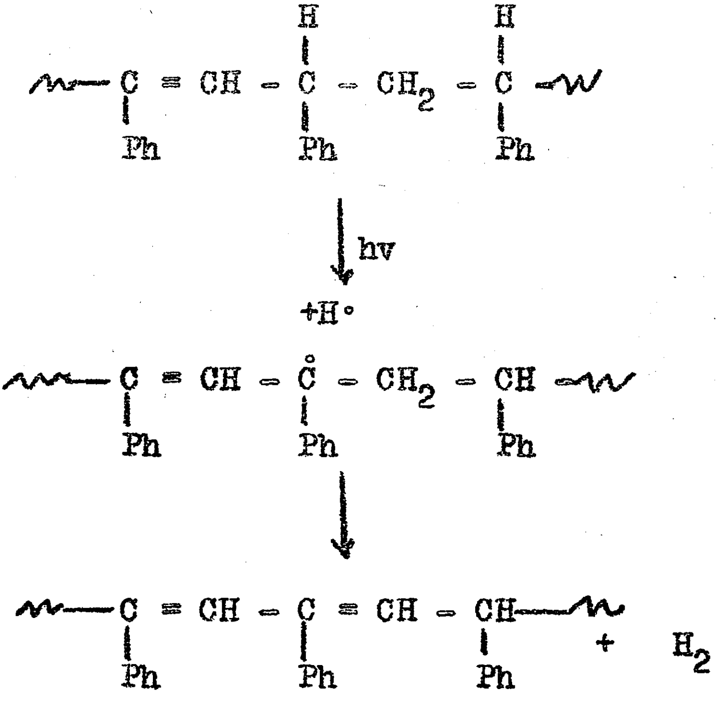


The presence of the double bond renders the hydrogen on the carbon atom in the α-position (tertiary carbon atom) more labile by lowering the dissociation energy of the tertiary C-H (*) bond.



$$\underset{Ph}{C} = CH - \overset{H}{\underset{Ph}{\overset{*}{C}}} - CH_2$$

Although the photolytic production of hydrogen from a polystyrene chain is a random process by virtue of the random nature of the absorbtion of quanta by the polymer, the probability of breaking a tertiary C-H(*) bond which is activated by a double bond in addition to the benzene ring will be greater than that of normal tertiary bond fission. It is conceivable, then that this bond will break preferentially and if the hydrogen abstraction process mentioned above is repeated, two conjugated double bonds will be formed, that is,



Although the presence of such structures would account readily for the observed infrared and ultraviolet absorbtion characteristics of vacuum irradiated polystyrene, it is difficult to reconcile absorbtion in the visible region with such limited conjugation. If, however, three conjugated double bonds are introduced into such a structure, that is,

$$\sim\!\!\sim C(Ph) = CH - C(Ph) = CH - C(Ph) = CH \sim\!\!\sim$$

visible absorbtion will be conferred on the molecule.(84) It is possible that the colouration of polystyrene on irradiation in high vacuum is associated with the production of conjugated double bonds in the backbone of the molecule in this way, these being formed by hydrogen abstraction from carbon atoms in the β-position. The production of the visible chromophore shown above requires hydrogen abstraction to occur at three consecutive monomer units and although the presence of one or perhaps two double bonds will, to some extent, direct the abstraction of a third hydrogen atom, the probability of forming three or more conjugated double bonds will not be very great. Hence a possible explanation for the observation that no bathochromic shift in visible absorbtion is produced. Even if it were possible to produce large sequences of conjugated double bonds it is unlikely that they would exist permanently. This is clear when the geometry of a large conjugated structure is considered. On constructing models it is found that the conjugated centres are coplanar only if there are three or less double bonds; it is impossible to retain even an approximately coplanar configuration when a further conjugated double bond is added, since two benzene rings coincide. If more than three conjugated double bonds are formed in the chain, the molecule will rearrange, thus the coplanarity of the unsaturated system necessary for resonance and the associated visible absorbtion will be destroyed. Hence it would be impossible to produce a bathochromic shift in visible absorption and the colouration will be associated with the three conjugated double bond system shown.

Colouration in Nitrogen

If this mechanism of colour production is correct, then since the presence of an atmosphere of nitrogen imposes a restriction on the mobility of hydrogen atoms, the probability of hydrogen abstraction from adjacent carbon atoms, and hence the rate of colouration will increase. Moreover, there should be a correlation between nitrogen pressure and rate of colouration, since the mobility of hydrogen atoms is inversely proportional to the nitrogen pressure.

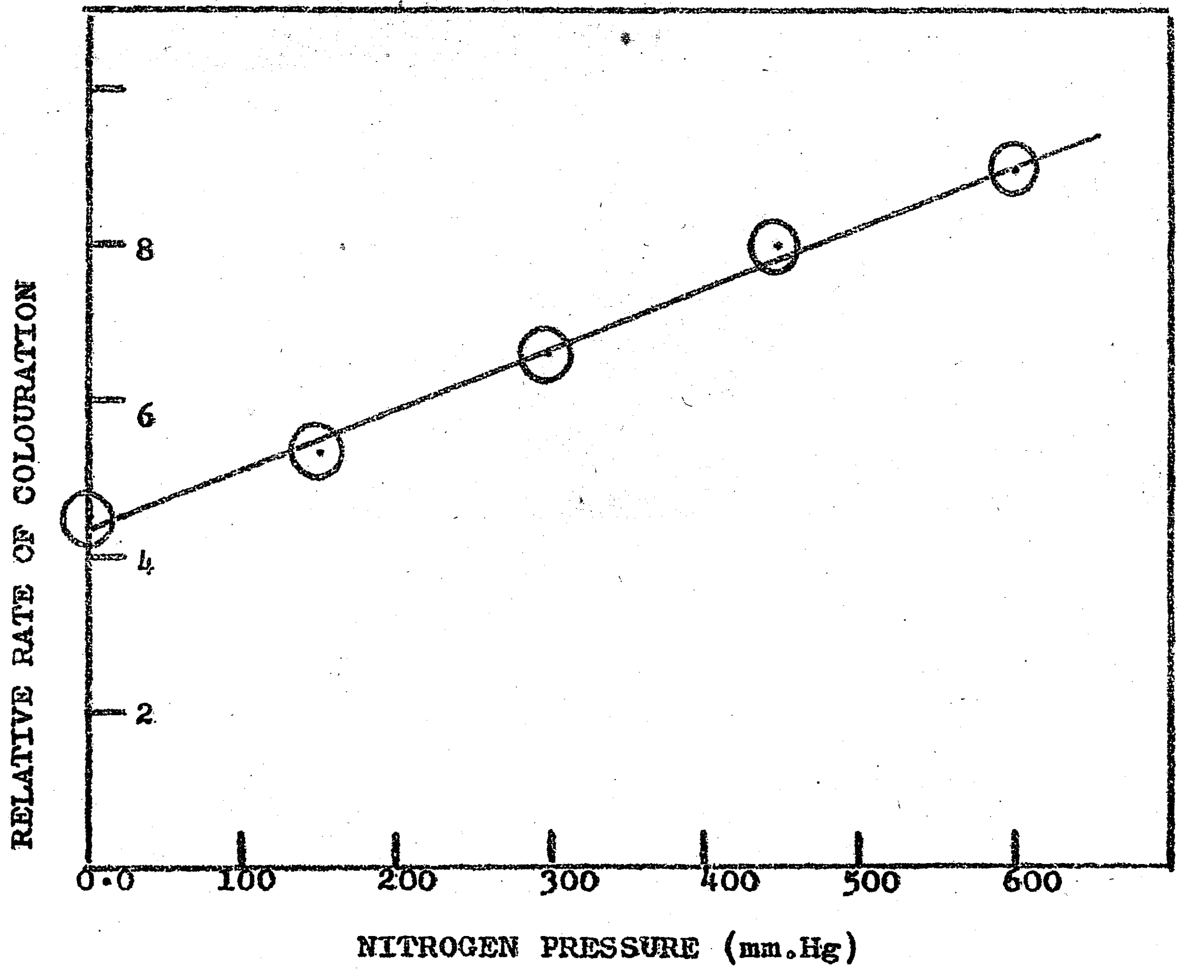
The effect of varying pressures of nitrogen on colouration rates of polystyrene on irradiation was examined. The results are given in Table 23 and figure 43.

Table 23

Rate of increase of optical density at 4400 Å	Nitrogen pressure (mm. Hg)
0.05	0
0.535	150
0.65	300
0.800	450
0.900	600

It can be seen that the rate of colouration is directly proportional to the nitrogen pressure, a result which would be predicted by the mechanism of colouration suggested above. It can also be predicted that the more facile elimination of hydrogen associated

FIGURE 43.



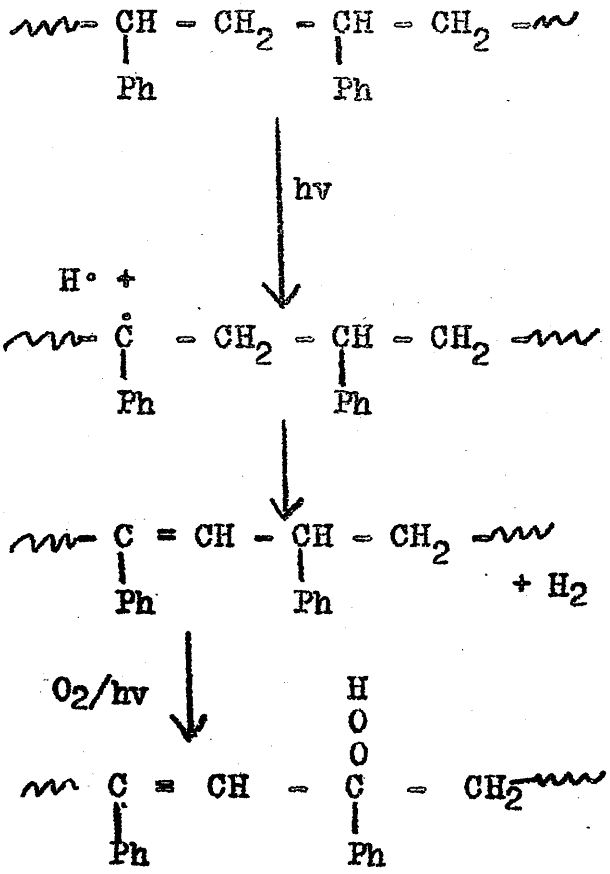
RELATIVE RATE OF COLOURATION
8
6
4
2
0·0
100
200
300
400
500
600
NITROGEN PRESSURE (mm.Hg)

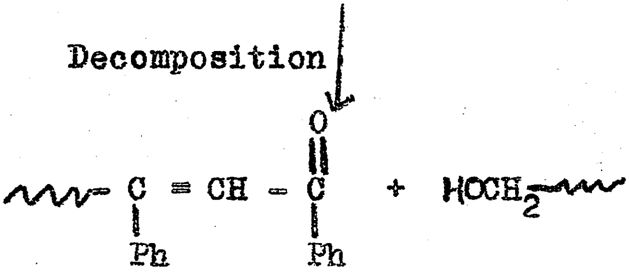
with irradiation in nitrogen will result in the formation of extended conjugated structures. Thus if the absence of a bathochromic shift in visible absorbtion is associated with a limited degree of conjugation alone, and not with the geometry of the molecule, irradiation in nitrogen should be accompanied by a bathochromic shift. No such changes in spectra were, however, detected and it thus appears that the geometrical factor is of greater importance in defining the extent of conjugation, and hence the actual visible absorbtion pattern, the intensity of the particular colour produced, is however, largely determined by the extent of hydrogen abstraction.

Colouration in Oxygen

It was seen in Chapter 1 that the development of colour in polystyrene during oxidation was attributed to the formation of either substituted quinomethanes or to substituted benzal-acetophenones. Although present evidence favours the latter hypothesis, Wall, its originator, was not able to provide a mechanism whereby carbon-carbon double bonds could be formed. In other words, the formation of the carbonyl group could be explained in terms of hydroperoxide decomposition but the origin of the carbon-carbon double bond in conjugation with it was unknown.

It is conceivable that hydrogen abstraction occurs to a minor extent in the presence of oxygen, that is, a hydrogen atom might occasionally abstract a further hydrogen atom as in vacuum irradiation instead of reacting with oxygen; a double bond would thus be formed as before. If oxidation and hydroperoxide formation accompanied this process, the chromophore suggested by Wall would result, that is,





$$\sim\underset{\mathrm{Ph}}{\mathrm{C}} = \mathrm{CH} - \underset{\mathrm{Ph}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}} + \mathrm{HOCH_2}\sim$$

(benzalacetophenone)

If this were true, hydrogen would be formed during oxidation of polystyrene. Wall (49,50) has established by mass-spectrometric measurements that hydrogen is indeed formed, thus there is some evidence for the suggestion.

Again no bathochromic shift in the visible spectrum was observed on continued oxidation. This may be a result of the geometry of the molecule, but the chromophore being a potential photolyte, it appears that photo-oxidation will occur before appreciable conjugation can be built up. This is also very probably the explanation of the observation that the rate of colouration in presence of oxygen is less than the corresponding rate in presence of an equal pressure of nitrogen.

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