THE PHOTOFORMATION OF PEROXIDES OF RUBRENE AND RELATED COMPOUNDS

by

ROBIN M. HOCHSTRASSER

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Introduction:

INTRODUCTION

More than forty years ago the principal constituent of cheropodium oil, ascaridole, was shown to be a naturally occurring stable, liquid peroxide (1). Ascaridole differed from other known peroxides principally in its structure which was found to contain a peroxide bridge across a six membered ring in the 1:4-position. For many years this compound was regarded as an oddity without an analogue in organic chemistry but the study of sterols in more recent times has resulted in the discovery of many other transannular peroxides both liquid and crystalline (2).

The occurrence of such cyclic peroxides is not restricted to alicyclic chemistry. In 1926 was finally proven the existence of a class of organic compounds of comparative simplicity, solutions of which were, on irradiation, capable of combining with molecular oxygen (3). The functional grouping was later found to be a 1:4-dienic system associated with a polycyclic hydrocarbon (4). The product was a colourless transannular peroxide or photo-oxide, which regenerated oxygen and almost pure hydrocarbon on heating.

The readiness with which many of these peroxides are formed under the influence of light and air as well as the ease with which some of them can rearrange into more stable compounds or release oxygen, strongly suggests that they may play an important role in biological oxidation processes. As the investigations, mainly by Moureau and Dufraisse, progressed it became increasingly evident that a more physicochemical study of such aromatic peroxides might prove of fundamental importance in a variety of fields.

The /

The reversible combination of oxygen and haemoglobin in the respiratory system, for example, constitutes an empirical parallel to the reversible photo-oxidation of polycyclic hydrocarbons (5).

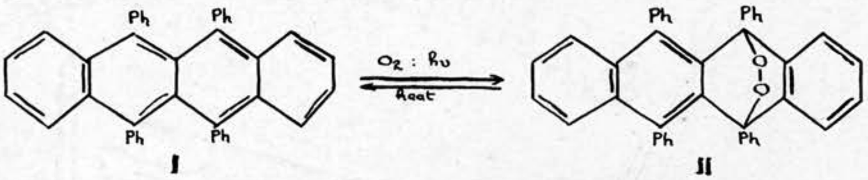
In photosynthesis the presence of a molecule capable of producing oxygen by unimolecular dissociation could result in a great saving of energy over other more involved multimolecular dismutations (6). 'In vitro' experiments on the photosensitisation of related photo-oxidative processes involving chlorophyll have, however, proved unsuccessful (7).

The fading of common dyestuffs in sunlight is a slow and photochemically inefficient process which may involve such peroxidic intermediates (8). In any case as the stage which limits the efficiency is obscure investigations on similar coloured materials, having the property of absorbing oxygen at a measurable rate might prove invaluable.

It was intended in this work to utilise the reversible photo-oxidative properties of the bright red hydrocarbon rubrene, 5:6:11:12-tetraphenyl-naphthacene, and related materials to a lesser degree, to study the general phenomenon of photobleaching in the solid state and to study the properties of the products therefrom.

A study of the photo-oxidation of solutions of this type of hydrocarbon has only illustrated the complexity of the mechanisms involved: the drawbacks in elucidation having been mainly due to an ignorance of the role played by the solvent (9). The oxidations proceed under the influence of natural or artificial light /

light at a rate that depends on the nature of the solvent (10). The maximum quantum efficiencies of oxidation are unity but fall off with concentration of hydrocarbon and oxygen; (11); they are independent of the wavelength of the incident light, over the range 360-550mu for rubrene (12). The overall reaction may be expressed in the form of an equation:



where I signifies rubrene and II the photoxide.

Although the available experimental data does not justify a discussion of complete mechanisms, that a transannular peroxide is formed by a non-chain mechanism remains undisputed.

The increase of potential energy occurring on the absorption of a light quantum results in the formation of an excited molecule which rapidly loses its excess energy as fluorescence or by internal or collisional degredation. It has been suggested that through one of the latter processes the first (forbidden) triplet energy level may be attained (13). It is now easily foreseen how this long-lived metastable molecule may react with oxygen.

Very recently Porter and Windsor have confirmed the existence of the first and second triplet levels in irradiated anthracene and rubrene solutions. These conclusions were reached after the application of the technique of flash spectroscopy to such systems (14). The results from quantum efficiencies of oxidation and of fluorescence and the quenching of the latter lead E.J. Bowen (15, 16) to the conclusion that rubrene molecules in the ground state /

state, after fluorescence but still with vibrational energy, were capable of reaction with oxygen. This postulate explains why the sum of the efficiencies of oxidation and fluorescence is greater than unity at high concentrations.

Three different mechanisms for the photo-oxidation of rubrene in solution have been proposed and they agree only on the following points: the reaction obeys the law of the photochemical equivalent; the reaction is purely photochemical having no temperature coefficient; the intervention of two molecules of rubrene is a necessary step in the reaction (<u>17, 18, 19</u>).

Like triphenylmethyl, rubrene can act as a sensitiser for initiating other oxidations (<u>20</u>) while its own reaction with oxygen is easily inhibited by traces of aniline, nitrobenzene or quinoline (<u>21</u>).

In the case of anthracene the mechanism of the photochemical reaction with oxygen is also obscured by the intervention of solvent molecules although in this case the quantum efficiency is independent of oxygen concentration (<u>22</u>). The photoreactions of anthracene in carbon tetrachloride have, however, provided diagnostic evidence that the excited triplet state of anthracene has a diradical structure (<u>23</u>).

The photoreactions, in solution, of hydrocarbons of this series, containing an anthracene nucleus in the basic resonating system, have been briefly summarised in order to familiarise the reader with the main practical and theoretical concepts which have emerged /

emerged above the complications involved. The intention in this work, however, is to study analogous phenomena in the solid state and as few results concerning the actual oxidation of crystalline hydrocarbons of this type have been reported, it is now purposed to describe the properties associated with crystalline non-ionic substances during irradiation.

The absorption by a crystal of a quantum of radiation of frequency greater than that of the series limit will give rise to a free electron and a free positive hole (24). If a voltage is applied to the crystal these should drift in opposite directions thus contributing to an electric current.

Byck and Borck (25) first observed that anthracene between two charged plates became conducting when illuminated. Bayliss and Riviere (26) have more recently studied the photoconductivity of anthracene but their results have been severely criticised by Vartanyan (27). D.J. Carswell (28) has shown that the photocurrent varies with the wavelength of exciting light in the same manner as the absorption coefficient and also that the current is directly proportional to the light intensity. Further investigations on numerous hydrocarbons including naphthacene have established the above mentioned correllation between photocurrent and light absorption at particular exciting wavelengths (29).

In the case of non-ionic semiconductors the conduction is attributed to the overlap of π-orbitals which form the filled band (30). Eley (31) and Akamuto and Inokuchi (32) have investigated various polycyclic hydrocarbons including some violanthrones /

violanthrones and reached the conclusion that it is unlikely that the semiconductivity in these compounds is due to impurity centres. Chynoweth (33) concludes from the behaviour of the photocurrent at various applied fields and light intensities, in the case of anthracene crystals, that the conventional energy band diagram as used for inorganic substances can be applied to non-ionic organic compounds.

As the process of photoconductivity allows electrons to be transferred through crystals of non-ionic materials it is likely that this mechanism be fundamental in the photochemical reactions of such solids. Indeed recent experimental evidence indicates that the photoconductivity of anthracene and naphthacene is a surface phenomenon, being independent of crystal size up to 99% absorption of incident light (34, 35). There seems little doubt that the energy migrates to the surface as 'excitons' (36).

Closely connected with semiconductivity, in principle, is the phenomenon of photosensitisation. The condition that a light absorber, e.g., a dye, should act as a sensitiser in the presence of a semiconductor is that its excited level should be above the lowest level of the conductor (37). Then each time that a dye molecule absorbs a quantum of radiation it willbe highly probable that an electron be transferred from the absorber to the conduction band of the semiconductor. Such a mechanism has been proposed for the photosensitised oxidation of chlorophyll, at high oxygen pressures, deposited on thallous bromide crystals (38). Chlorophyll itself is known to be a photoconductor (39). In this case the thallous bromide acts as the light absorber although the overall /

overall reaction is simply the production of an excited chlorophyll molecule. In the same manner the spectral sensitivity of some photographic emulsions may be extended to longer wavelengths by the presence of one of the many available blue-green dyestuffs (40).

From this standpoint it was intended to investigate the effect of thallous bromide on the photo-oxidation of rubrene.

The above considerations lead to object of this research. A study has been made of the reactions of rubrene and rubrene peroxide from the general standpoint of solid state kinetics. Previous workers; e.g., G.M. Badger (44), M. Born and Schönberg (45) and C. Dufraisse (46), have stated that solid rubrene, in the absence of solvent, does not photo-oxidise, however, preliminary experiments showed some oxidation under such conditions. It was therefore intended to follow its course by sensitive differential pressure measurements on the oxygen over a thin film of material deposited on a suitable substrate. This technique has been successfully employed in the study of the photo-oxidation of chlorophyll on powdered glass and on thallous bromide; the light absorption of oxygen on titanium dioxide (41); and the photo-reactions of various dyestuffs in the form of solid films (42).

A study has been made of the kinetics and energetics of the decomposition of rubrene peroxide in the form of thin films as well as with ground crystals.

From the starting points of photo-oxidation and decomposition it was intended to investigate the 'dissociation pressure' which has been observed during the photo-oxidation of rubrene in benzene solution (43) and to study generally the effective reversibility of the reaction.

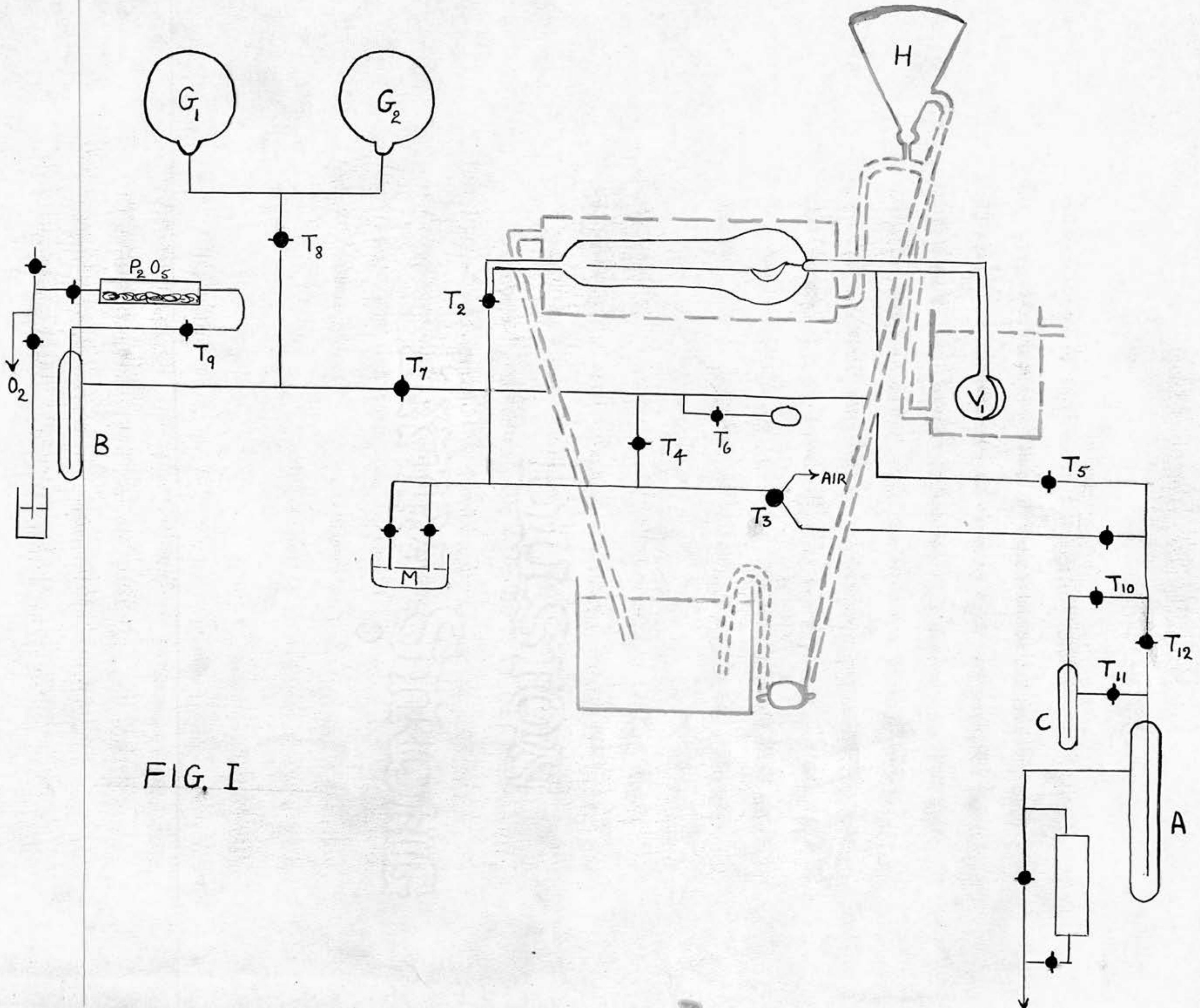


FIG. I

APPARATUS AND EXPERIMENTAL METHODS

The majority of the experiments which will be described in this work involve the measurement of small pressure changes. The apparatus employed for this purpose is represented in Figure (1).

The reaction vessel V is connected through capillary tubing to the sickle side of a Bourdon gauge. Small pressure changes which occurred during reactions were observed through a telescope fitted with a calibrated eyepiece, focussed on a length of thin platinum wire fused to the end of the gauge pointer. The absolute pressure in the apparatus was measured on the mercury manometer M.

The apparatus was constructed almost entirely of soda glass. All 'Quickfit' joints and high vacuum taps were lubricated with Apiezon 'L' grease for normal low temperatures. At higher temperatures Apiezon 'T' high vacuum grease was employed.

An Edwards diffusion pump backed by a Speedivac oil pump was used to evacuate the system to a pressure of less than 0.001mm. mercury. The lower uncondensable gas pressures were measured on a McLeod gauge attached to the apparatus. During evacuation the trap A was surrounded by liquid oxygen.

Temperature Control.

The utilisation of a pressure guage of high sensitivity necessitates accurate temperature control. It is imperative in such a system that not only the reaction vessel and gauge be at the same temperature but that such temperature fluctuations as are unavoidable should apply equally to both. These conditions were achieved /

achieved with a water-circulating divided flow arrangement. Water from a large reservoir was pumped up to constant head device from which it flowed down in two streams, one round the gauge jacket and the other round the reaction vessel. With this system pressure changes due to temperature fluctuations in the thermostat tank were produced on both sides of the gauge and thus tended to cancel out.

The temperature of the thermostat bath was maintained by means of a carbon filament lamp in conjunction with a chloroform-mercury regulator and a Sunvic relay. This water was constantly stirred. The rates of flow of water through the well lagged lines to the gauge and reaction vessel could be controlled by a screw clip at the constant head outlet. Under these conditions the temperature was controlled to within 0.01°C.

While studying reactions at temperatures above 50°C. it was impracticable to employ the above arrangement. Instead of this, the gauge and reaction vessel were thermostated independently by means of a water jacket and furnace respectively. The furnace was cylindrical in shape consisting of two halves which fitted together, with overlapping, round the reaction vessel. By employing a hand rheostat the temperature could be controlled to about 0.5°C. As very low pressures were produced in the reaction vessel in these experiments this degree of temperature control was sufficient.

When studying the photoreactions of solutions it was necessary to control the temperature accurately even at low gas /

gas pressures due to fluctuations in the vapour pressure of the liquid. In such investigations a larger bath was placed round the reaction vessel. The water in this bath was constantly stirred and its temperature controlled to within 0.01°C. of the required value by means of a 15 Watt heater and Sunvic relay. By using liquids whose rate of change of vapour pressure with temperature is small over the working range the experimental error was kept very low.

Calibration of the Gauge

The gauge was calibrated in millimetres of mercury per telescope scale division. This was effected by repeatedly reducing the pressure in the gauge, compensating of the gauge jacket, noting the total number of scale divisions traversed by the gauge pointer and measuring the total pressure change recorded by the mercury manometer.

The apparatus was filled with dry air through tap T_3 to a known pressure as recorded on the manometer M. The gauge and its jacket were then isolated by closing tap T_4. The reaction vessel was then evacuated through T_5 and the compensating evacuation effected through T_3. After an appreciable evacuation the resultant pressure on the manometer was recorded. When this is divided by the total number of scale divisions of the telescope calibrated eyepiece traversed by the gauge pointer the result is the gauge sensitivity in mm./scale division. As the scale could be read to the nearest 1/10 division the true sensitivity is 1/10 of the above value. With one gauge the following results were obtained:-

Number /

	Number of scale divisions moved by the pointer	Manometric pressure change	Sensitivity
	s.d.	mm.Hg	mm./s.d.
1.	433.4	21.8	0.00503
2.	627.4	31.0	0.00494
3.	249.7	12.8	0.00513
4.	288.6	14.5	0.00500
5.	335.2	16.5	0.00492

The above experiments were conducted at 100mm. dry air pressure with the exception of 5. where the pressure was 50mm. During these calibrations the temperature was maintained at 25°C.

The average sensitivity is found to be 0.0050 mm./s.d. subject to a computed experimental error of 3.5%.

C.M.Laurie (38) found that the sensitivity was independent of the temperature although it varied slightly with the absolute pressure in the apparatus. Results from analysis of reacted materials and vapour pressures of liquids have shown that with the gauges employed in this work the variation of sensitivity with absolute pressure is not appreciable and may be neglected.

The Reaction Vessels

These vessels were constructed from either Pyrex or Soda glass according to the experiment. They were spherical in shape and each fitted with a Quickfit A10 socket through which it could be vacuum sealed to the apparatus.

While working with liquids a very much smaller vessel with a flat bottom was employed. This enabled a magnetic stirring element to function more efficiently.

In /

In some experiments a side tube was attached to the reaction vessel by means of Quickfit A7 joints. In this way reactions could be studied in the presence of adsorbents. If two such adsorbents were required either during different stages of the reaction or at the same time a two-way tap arrangement was employed.

Calibration of the Gauge and Reaction Vessel Volumes.

In order to calculate the number of moles of gas reacting in the system it is necessary that the total volume of the reaction vessel gas space be known. In this determination a measured pressure of dry air is allowed to expand into a known volume at temperature. The original volume is calculated from the pressure difference and the known volume by utilising Boyle's Law.

Approximately 200mm. (p_1) of dry air, as recorded on the mercury manometer M, were introduced into the apparatus the taps T_6 and T_7 being closed.

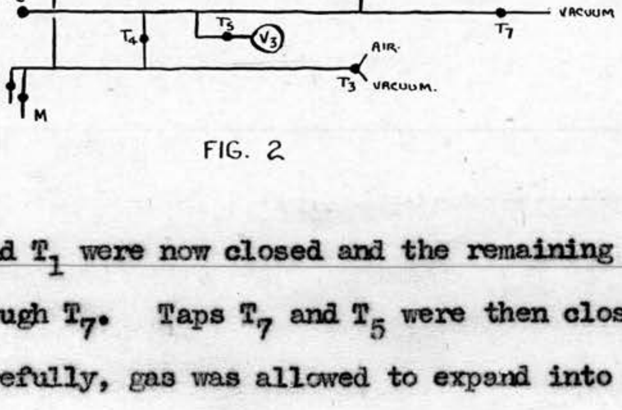


FIG. 2

The taps T_4 and T_1 were now closed and the remaining space evacuated through T_7. Taps T_7 and T_5 were then closed and by opening T_1 carefully, gas was allowed to expand into the volume contained /

contained by $T_4T_5T_6T_7$. During this operation the gauge pointer was balanced by pumping through T_3. When equilibrium was attained and the gauge pointer again at its original position on the telescope scale the new pressure p_2 on the manometer M was recorded. The tap T_5 was now opened and the gas allowed to expand into the volume V_3 the gauge being balanced in the same manner as before. The resultant pressure p_3 was recorded.

If V_1 is the volume of the reaction vessel, capillary and gauge up to T_1 and V_2 the volume between V_1 and V_3 then :

$$(V_1 + V_2 + V_3)p_3 = (V_1 + V_2)p_2 \text{ ------------- } (1)$$

$$\text{thus} \quad (V_1 + V_2) = V_3 \cdot p_3/(p_2 - p_3) \text{ ----------- } (2)$$

$$\text{also} \quad (V_1 + V_2) = V_1 \cdot p_1/p_2 \text{ ----------------- } (3)$$

therefore by combining (2) and (3) we have

$$V_1 = p_2 \cdot p_3 \cdot V_3/p_1 \cdot (p_2 - p_3) \text{ ------ } (4)$$

Thus from a knowledge of the three pressures and the volume V_3 the volume V_1 may be calculated. With one vessel the following results were obtained:

Experiment	1.	2.
V_3 mls.	145.9	145.9
p_1 mm.	106.0	199.5
p_2 mm.	57.5	108.7
p_3 mm.	24.9	47.3
V_1 mls.	60.51	60.55

It can be observed that the accuracy of this determination is less than 0.5%.

The Optical System /

The Optical System

Two radiation sources were used: (1) An Osira mercury vapour lamp, the beam of which, after passage through a water lens, was rich in the Hg^{3650} and Hg^{4658} lines. The input to this 230V/125W. lamp was stabilised by means of a choke and condenser arrangement. (2) An Osram 110V/250W. projector lamp which provided lower energy light but with higher intensity than (1).

In all experiments the light beam was transmitted through at least 6mm. of Soda glass, as well as 1mm. of Pyrex glass when such vessels were employed, and about 25cm. of water. Under these conditions very little light of wavelength less than 3650A° was expected to reach the sample under irradiation.

Whilst irradiating samples at high temperatures the light beam was able to pass through heat resistant 2mm. glass windows attached to the previously described furnace.

Gas Storage and Purification.

Oxygen was introduced into the two litres capacity soft glass bulbs in the following manner.

The bulbs were evacuated for two hours flushed with oxygen a few times and then pumped for 20 hours at 10^{-4}mm. Hg (McLeod). Cylinder oxygen was then introduced through C and after slowly diffusing through phosphoric oxide and the trap B, at liquid oxygen temperature, was allowed to enter the bulbs until the attainment of near atmospheric pressure. The tap T_8 was then closed, trap B warmed up to room temperature and the apparatus pumped out for a further two hours. Tap T_7 was then closed.

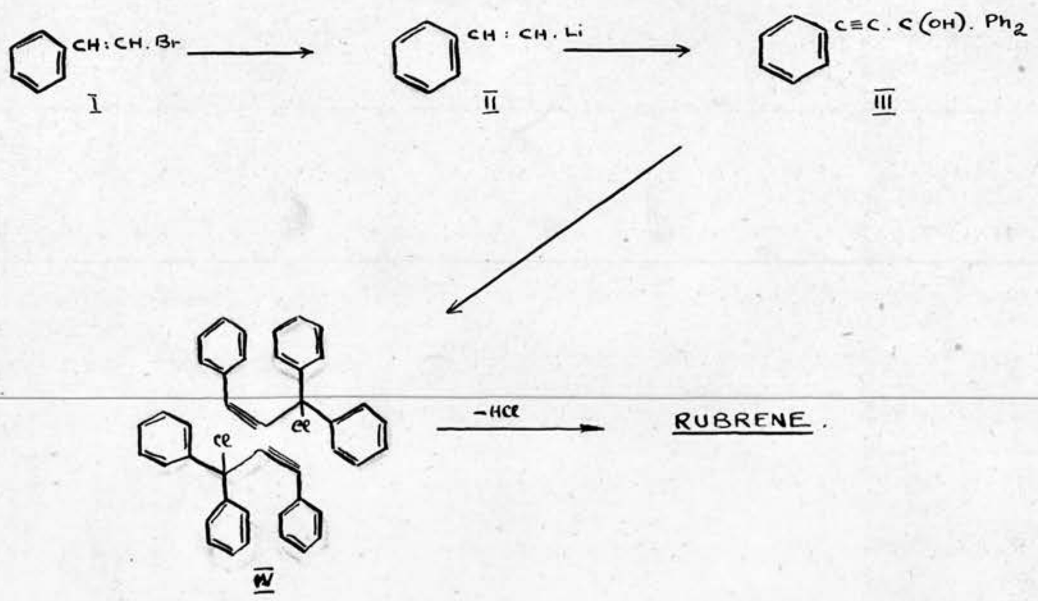
Before /

Before using the purified oxygen for experiment the space $T_7T_8T_9$ was always re-evacuated and liquid oxygen placed round the trap B.

Organic vapours could be admitted to the reaction vessel through T_6 and T_1 the organic liquid having been previously degassed through T_6 with T_1 closed.

Preparation of the Reactants - Rubrene.

Diphenyl-phenylethenyl carbinol was prepared according to the method described by Wittig and Waldi (87). Bromostyrene (I) was treated with phenyllithium in dry ether and under a small nitrogen pressure. The product (II) was condensed with benzophenone to produce the carbinol (III), m.p. 81.5°C. (m.p. 82°C. quoted by the above authors). The carbinol was converted to the chloride (IV) with thionyl chloride at -10°C. which in turn was condensed to rubrene (V) by heating to 120°C. 'in vacuo' in the presence of a trace of quinoline as catalyst (11).



The /

The crude product was washed with ether in the dark and dried 'in vacuo'. Previous workers with rubrene have purified the crude material simply by repeated recrystallisations from benzene-ligroin. As extremely pure samples are required for solid state investigations it was decided to study samples at various stages of purity and ultimately to evolve a method for the purification of rubrene.

Sample A

Obtained after five extractions with acetone, a product melting at 329°C. (previous workers quote melting points of 330 - 332°C. for rubrene).

Sample B

This consisted of sample A twice recrystallised from benzene-high boiling ligroin after distilling off the benzene at room temperature. This sample melted over 0.1°C. at 330°C.

Sample C

The crude product was made into a slurry with acetone and allowed to settle on the top of an alumina column. The operations described below were carried out in the following order -

1. Washed with a large volume of acetone - no elution of rubrene as rubrene is only sparingly soluble in acetone.
2. Further washings with large volume of high boiling ligroin - no elution of rubrene.
3. The top of the column was stirred up slightly after the addition of a little benzene followed by elution with benzene.

4. Recrystallisation from benzene - ligroin as before resulted in the production of rubrene melting at 333°C.

The above operations were carried out in the dark room.

Sample D

As in Sample C but with a newly prepared crude product.

Rubrene Peroxide

In the preparation of the peroxide a concentrated solution of rubrene in benzene was allowed to stand in sunlight until it was completely colourless. Benzene was then allowed to evapourate slowly until such time as crystals of the peroxide separated from the solution. These crystals were dried 'in vacuo' while in total darkness at room temperature.

Standard Solutions of the Peroxide.

Standard solutions of the peroxide were prepared by dissolving a known weight of the rubrene sample in a suitable solvent and exposing the solution to sunlight until such time as the characteristic absorption bands of rubrene could not be detected by the spectrophotometer. The peroxide solution was then made up to a standard volume.

2:3:6:7-dibenzfluoranthene

A sample of this newly synthesised naphthacenic hydrocarbon was kindly supplied by G.V. McHattie.

Absorption Spectrophotometry.

The following table provides the key to the Graphs 1 - 8.

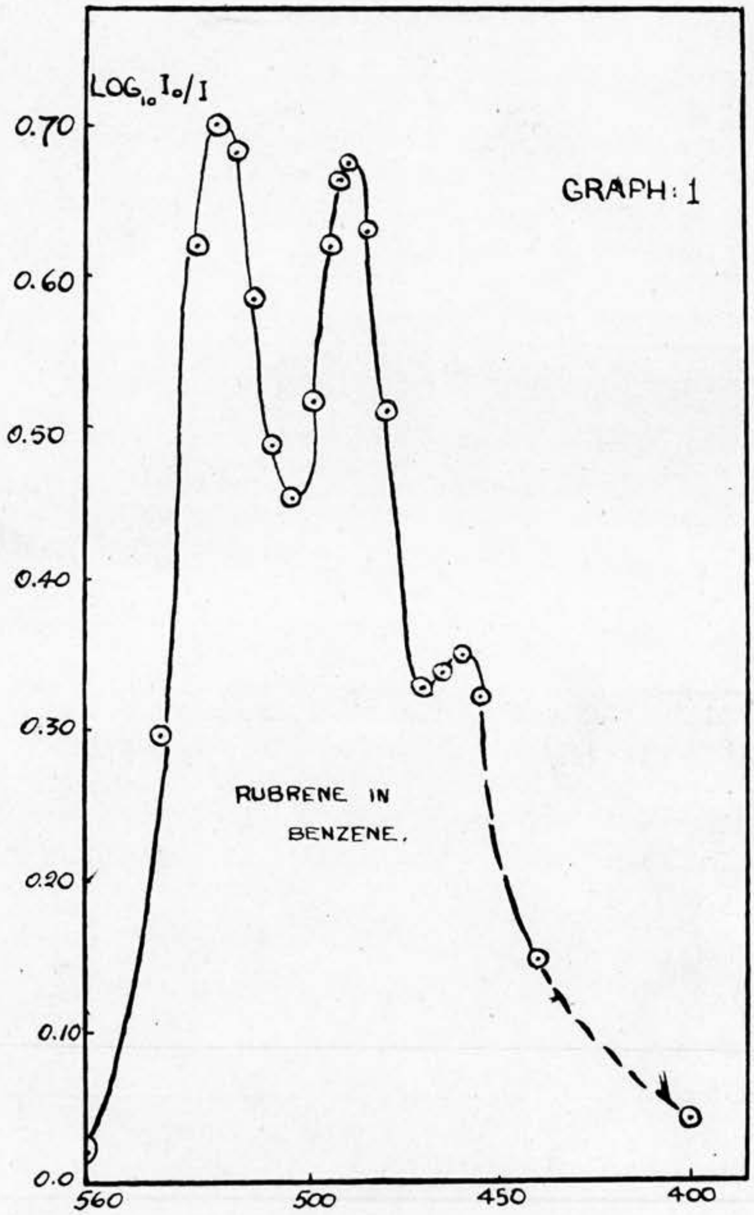
Graph /

Graph	Substance	Concentration mg./Litre	Solvent	Cells
1.	rubrene (C)	32.2	benzene	10mm. glass
2.	rubrene (D)	27.5	benzene	10mm. glass
3.	rubrene (D)	16.5	dioxan	10mm. quartz
4.	rubrene peroxide	109.0	benzene	2mm. quartz
5.	rubrene peroxide	17.5	dioxan	10mm. quartz
6.	rubrene peroxide	21.2	cyclohexane	10mm. quartz
7.	rubrene peroxide	10.45	m-xylene	2mm. quartz
8.	dibenzfluoranthene	23.4	benzene	10mm. glass

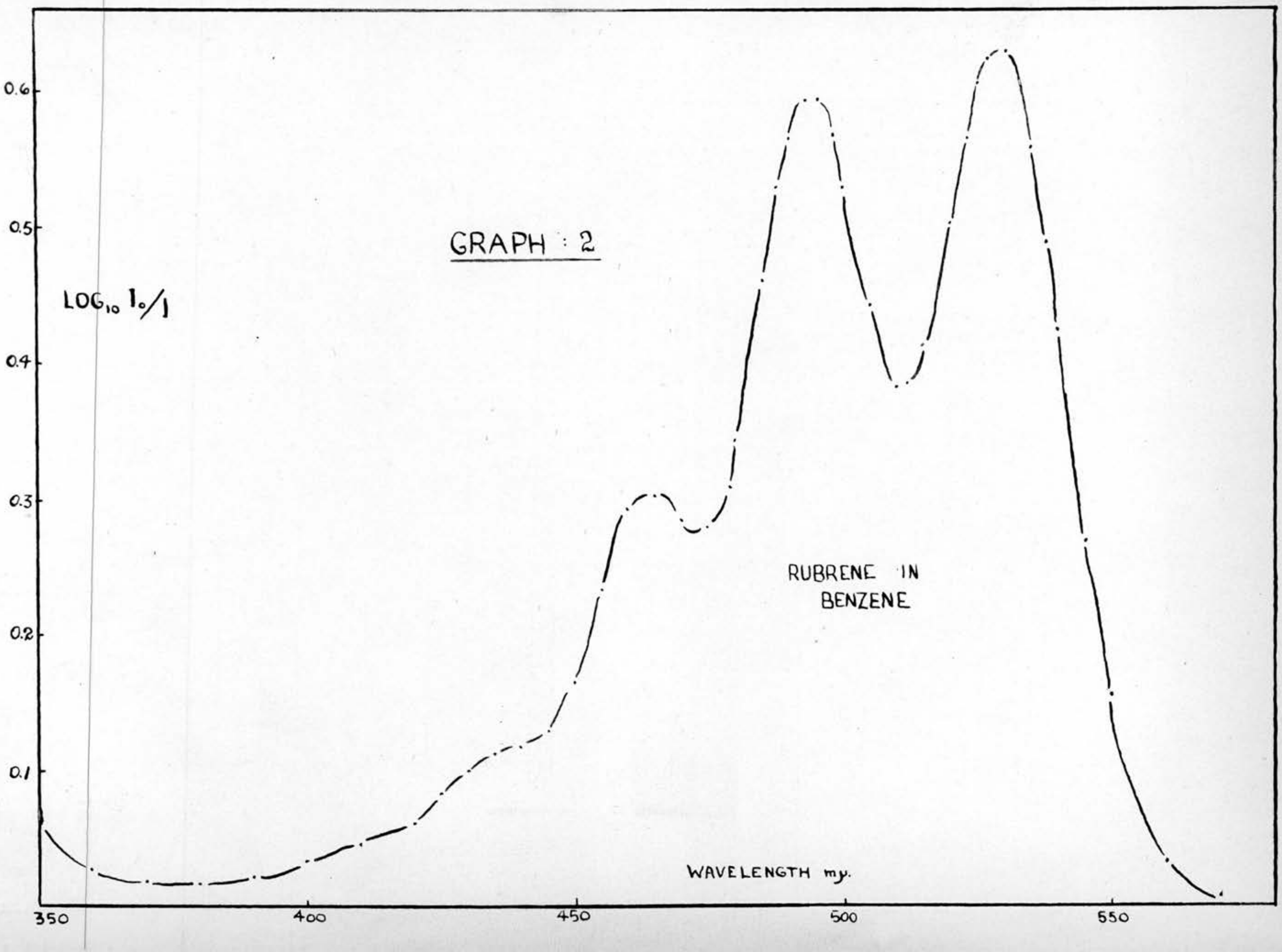
The spectra 1, 2 and 8 were examined on the Unicam (visible) S.P. 600 instrument while the others were examined on the larger Unicam ultra-violet absorption spectrophotometer.

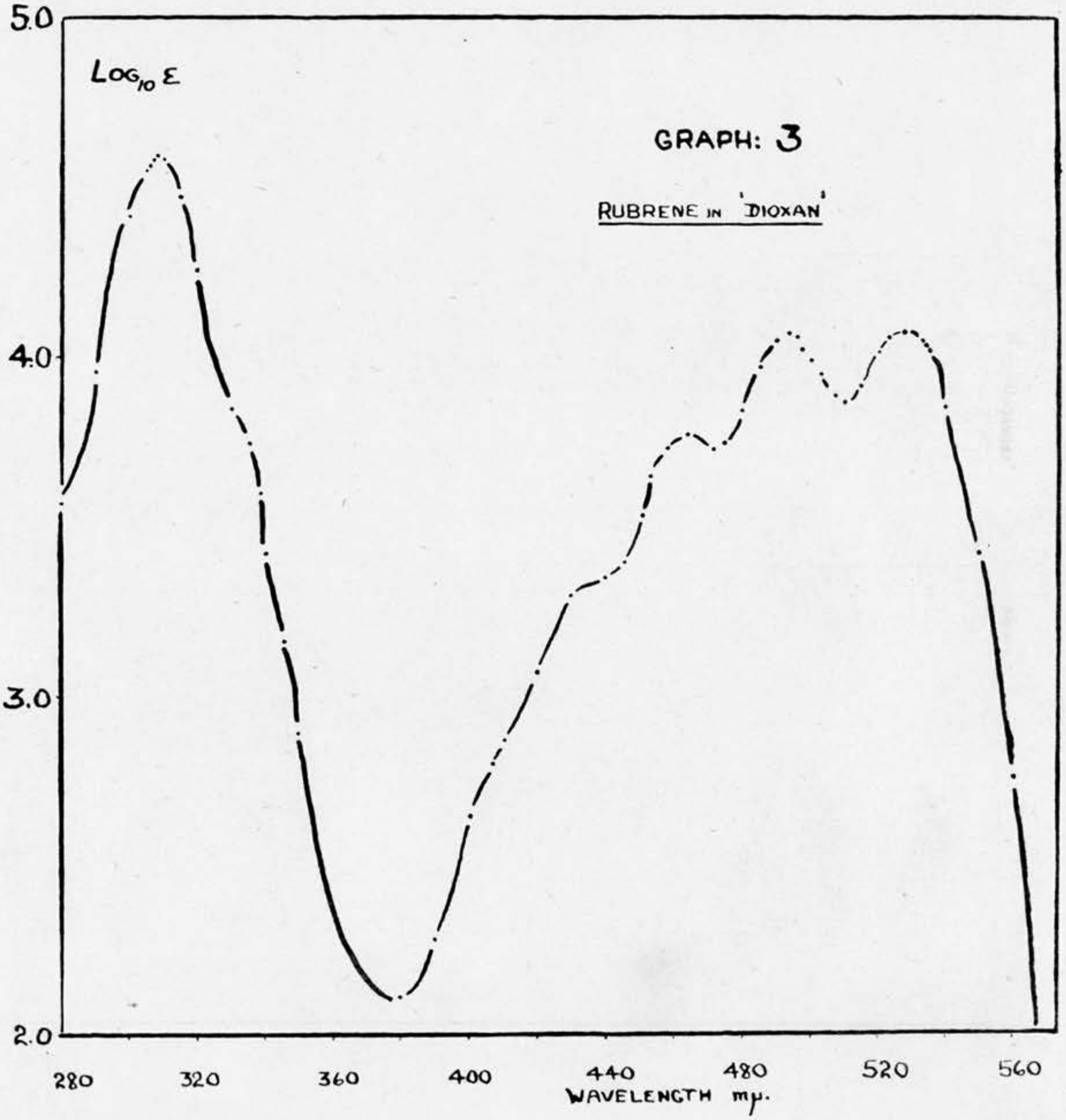
The wavelengths of maximum absorption and the absorption coefficients obtained from the above results on the rubrene and rubrene peroxide spectra are in complete agreement with the values quoted by other workers (47, 48).

The absorption coefficients at the wavelengths of maximum visible absorption were, for example, in the case of rubrene (D) in benzene solution; 530 mu:4.07 (4.08); 495 mu:4.06 (4.07); 465 mu: 3.77 (3.79). The corresponding values computed from the results of G.M. Badger and R.S. Pearce (47) are shown in parenthesis. These authors found that the absorption coefficient as well as the wavelengths of maximum absorption varied with the solvent. Indeed the 'red shift' was formulated as a complex function of the refractive indexes of the numerous solvents employed. The wavelengths /

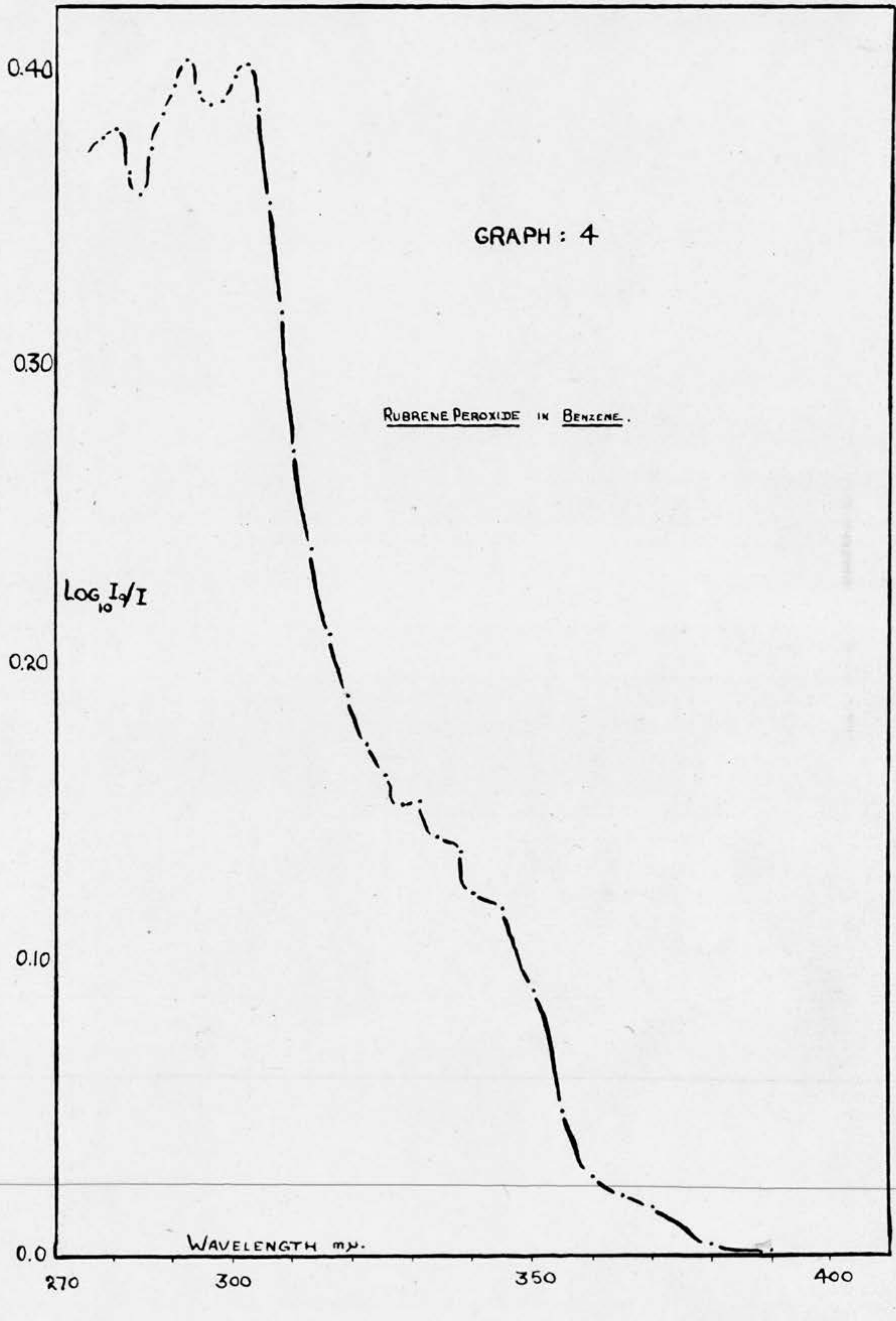
LOG₁₀ I₀/I
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.0
GRAPH: 1
RUBRENE IN BENZENE.
560
500
450
400
λ mμ.

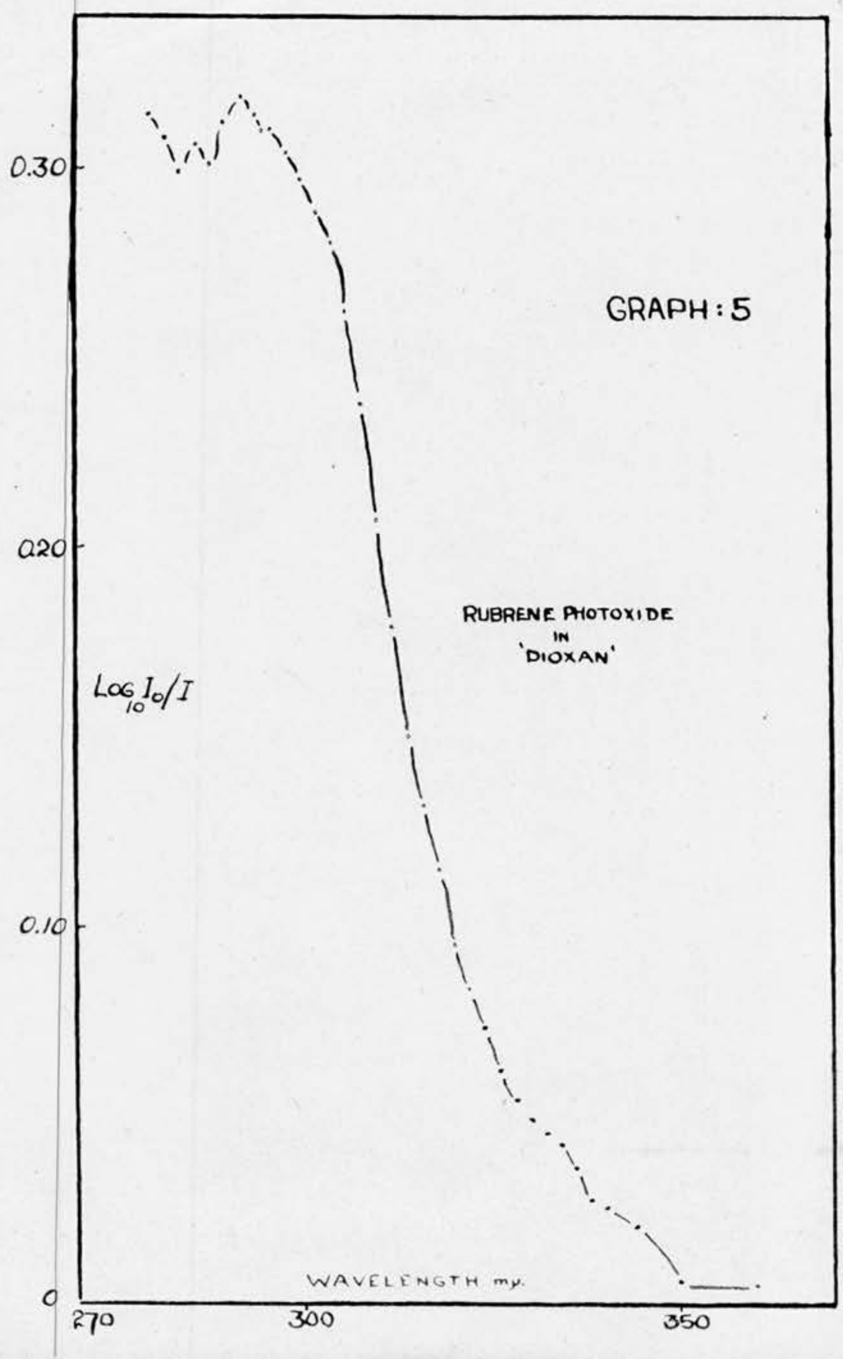
GRAPH : 2


LOG$_{10}$ I$_o$/I
RUBRENE IN BENZENE
WAVELENGTH mμ.
0.6
0.5
0.4
0.3
0.2
0.1
350
400
450
500
550

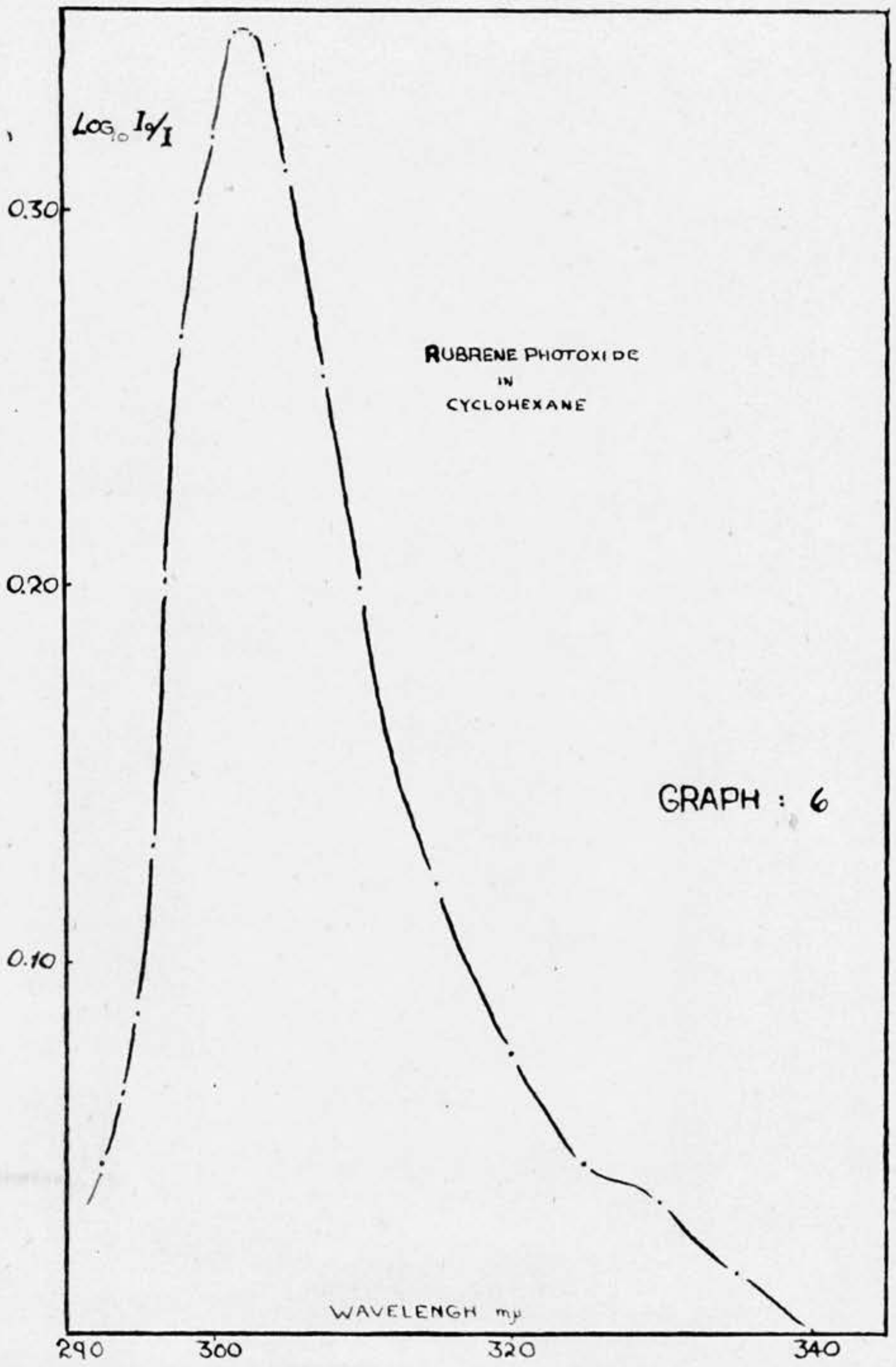

GRAPH: 3

RUBRENE IN 'DIOXAN'

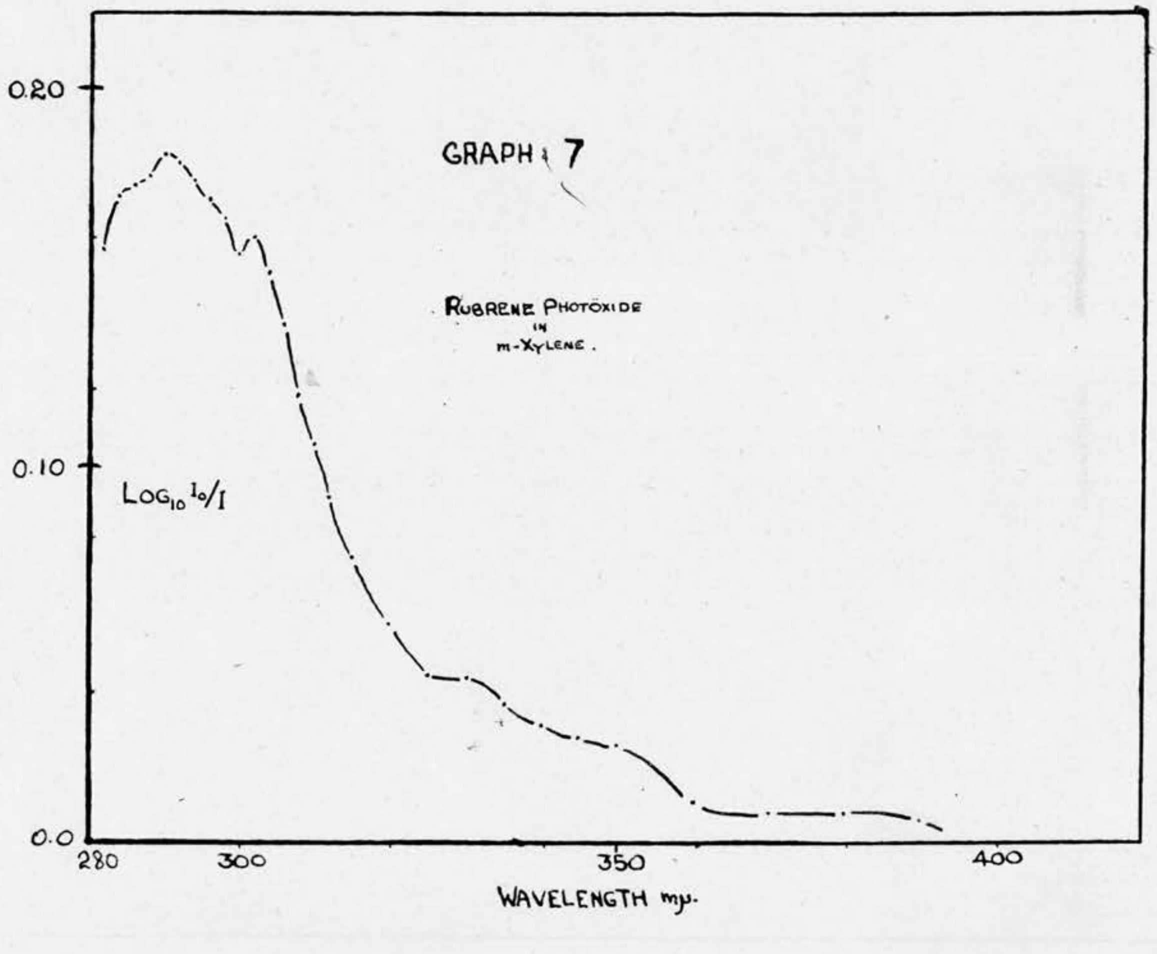

GRAPH : 4
RUBRENE PEROXIDE IN BENZENE.
LOG$_{10}$ I_0/I
0.40
0.30
0.20
0.10
0.0
WAVELENGTH mμ.
270
300
350
400

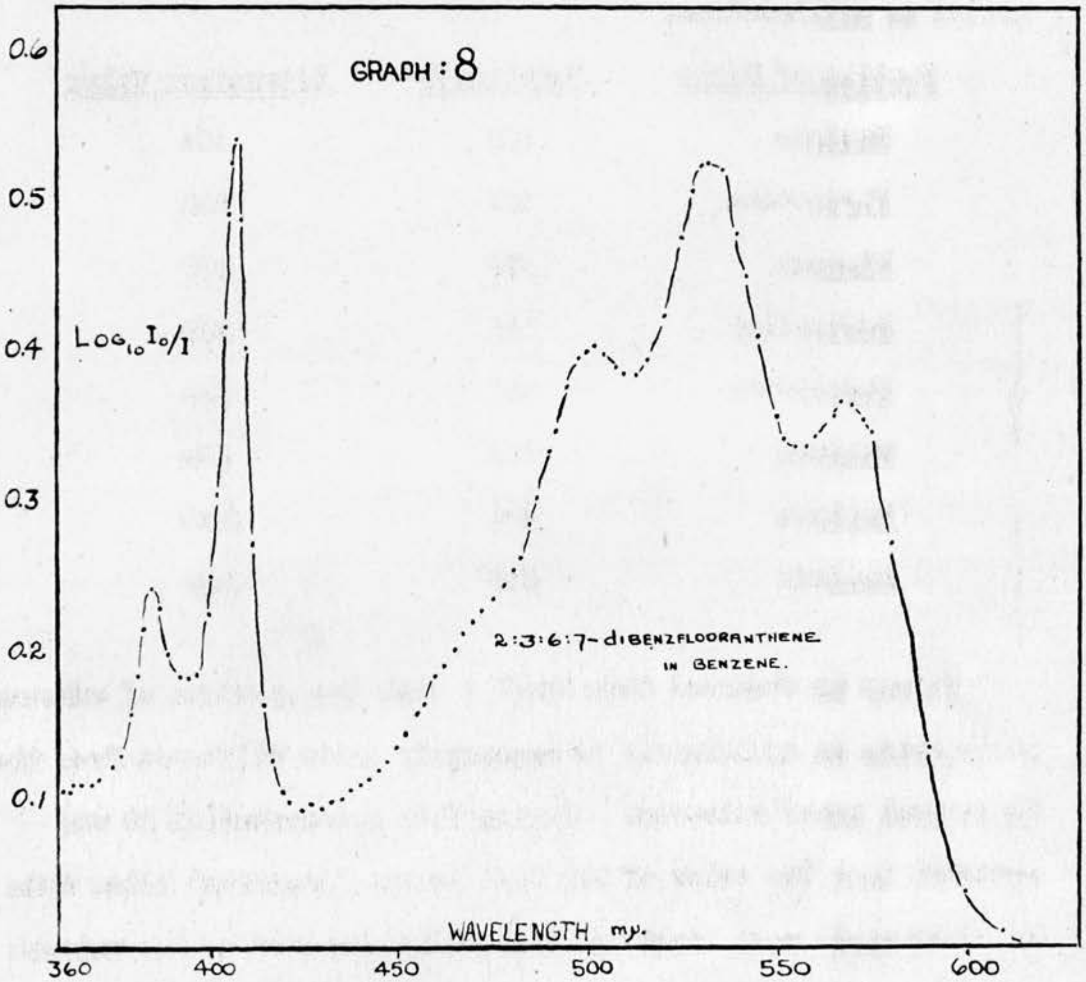


GRAPH : 5



GRAPH : 6


GRAPH 7
RUBRENE PHOTOXIDE
IN
m-XYLENE.
0.20
0.10
0.0
LOG10 I0/I
280
300
350
400
WAVELENGTH mμ.


GRAPH : 8
Log₁₀ I₀/I
2:3:6:7-dibenzfloranthene in benzene.
WAVELENGTH mμ.
0.6
0.5
0.4
0.3
0.2
0.1
360
400
450
500
550
600

wavelengths at which maxima, minima, and points of inflection were detected are compared to the corresponding approximate values as measured by the above authors, in the table below. The values correspond to rubrene in dioxan solution and the wavelengths are quoted as millimictons.

Portion of Curve	Wavelength	Literature Value
Maximum	309	304
Inflection	327	323
Minimum	380	278
Inflection	397	395
Inflection	430	430
Maximum	465	464
Maximum	494	493
Maximum	528	529

It may be observed from Graph 6 that the spectrum of rubrene photo-oxide in cyclohexane is apparently quite different from that in several other solvents. During this determination it was observed that the value of Log Io/I became 'negative' below 290m . In other words more light was apparently absorbed by the solvent alone than by the solution. Such an effect may have been brought about by a process of fluorescence quenching in the solution. Reversing the solutions in the spectrophotometer did not alter the anomaly. The maximum value of Log Io/I, occurring at a wavelength of 305 mu was 3.967 while the corresponding Log Io/I value of rubrene /

rubrene peroxide in benzene at 305 mu. was 3.967.

For the purpose of analysis of rubrene residues calibration curves relating the concentration of rubrene in benzene solution to the amount of light absorbed at a particular wavelength were drawn up. These curves were drawn from the values obtained and recorded in the table below.

Instrument - Unicam SP 600

Cells - 10mm. glass

Solvent - Benzene

Concentration mg./1000mls	530mu.	Log Io/I 495mu.	465mu.
41.1	0.970	0.929	0.476
32.9	0.720	0.688	0.362
20.55	0.461	0.440	0.234
16.44	0.378	0.369	0.194
8.22	0.190	0.185	0.097
4.11	0.091	0.0865	0.0435

The Preparation of the Films

The reactant 'film' normally consisted of a thin layer of the material to be examined, deposited on to a solid substrate. The substrates employed were thallous bromide and Jena glass, both in a thoroughly dried and ground state.

All /

All films were prepared in the dark in the following manner -

A standard weight of the substrate, approximately 0.1, 0.2 or 0.3gm., was carefully placed into the reaction vessel. A measured quantity of the standard solution of the substance to be investigated was then pipetted into the vessel. During this operation the reaction vessel was kept tilted in order that only one side of the vessel be wetted by the solution. The solvent was then carefully removed by evacuating the system, at about 35°C., with a water (filter) pump. When practically all the solvent had been removed the vessel was swirled round a few times in order that the film might be spread evenly over one internal hemispherical surface of the reaction vessel while pumping was continued. After one half hour of further evacuation at the water pump the film containing reaction vessel was ready to be transferred to the apparatus.

Analysis of the Film Residues: Solids

After the completion of a reaction the vessel was removed from the apparatus in darkness and the high vacuum grease removed from the Quickfit joint. The vessel was then filled with benzene and thoroughly shaken. The contents were then filtered through a cotton wool plug and the resulting solution made up to a standard volume with benzene. Spectrographic analysis of these solutions provided Log I_o/I values which were readily convertible to concentrations of rubrene by means of the concentration-absorption coefficient calibration curves.

The Detection of Gaseous Products /

The Detection of Gaseous Products

Condensable Vapours

At the termination of a reaction the taps T_1, T_5, T_{10} and T_{11} were opened and T_{12} closed. The reaction vessel space was then evacuated through the trap C which was surrounded with liquid air. The base of this trap, which was only about 2mm. in diameter, was attached to one junction of a thermocouple, the other junction being kept at 25°C. Thus, on removal of the liquid air container, the temperature of the trap could be measured on a sensitive moving-coil galvonometer connected in the thermocouple circuit. After closing tap T_{11} the trap was allowed to warm up slowly, the temperature being measured on the galvonometer scale. At the same time the vapour pressure of the trap condensate was measured by the gauge pointer deflection.

A plot of 'vapour pressure' against temperature was characteristic for any one vapour.

Acetone

This could be detected by the indigo blue test of Feigl (42). After pumping the vapours through the liquid oxygen trap C the trap was removed from the apparatus. While the contents of the trap were still frozen one ml. of chloroform was added followed by one or two drops of an alkaline solution of o.nitrobenzaldehyde. The whole was then warmed in a water bath. The production of a blue colouration in the chloroform layer indicated the presence of acetone. The sensitivity limit of this test is 100ug.

Oxygen

Illuminated films of titanium dioxide react with oxygen at a

measurable /

measurable rate (<u>50</u>). Experiments have shown that the absorption of oxygen occurs at a finite rate down to pressures less than ultimately measurable by the gauge, while heat reduces the effect of oxygen absorption.

A thin film of titanium dioxide (sample D_2) (<u>50</u>) was prepared in a small flat vessel, 3mm. in diameter, this vessel being in turn attached to the reaction vessel through a Quickfit A7 joint set. A dark cover was fitted round this side tube. When the time arrived to estimate the oxygen this cover was removed and the titanium dioxide film irradiated with the beam from the Osira lamp focussed through a water lens. The resulting decrease in pressure was measured by the gauge pointer deflection. In some experiments a tap was placed between the reaction vessel and the titanium dioxide film to prevent contamination of the film during the reaction.

As may different types of reaction have been studied in this work it has been decided to describe the appropriate experimental procedure at the commencement of each section. Any further unique experimental details, such as apparatus modifications, will also be described in their appropriate section.

EXPERIMENTAL SECTION 1.

The Photo-oxidation of Hydrocarbons on Solid Substrates

Experimental Procedure

The reaction vessel containing the prepared film was attached to the apparatus by means of a Quickfit joint this operation being effected in the dark. The whole system was then evacuated for a standard length of time. Once the water-flow system had commenced and the evacuation completed oxygen was introduced into the apparatus through the tap T_7 (see fig. 1.) to the required pressure as read on the manometer M. The taps T_1, T_2 and T_7 were then closed and the system allowed to reach thermal equilibrium in the dark.

In the study of reactions at low oxygen pressures the tap T_4 was closed and the resultant pressure measured by the gauge pointer deflection.

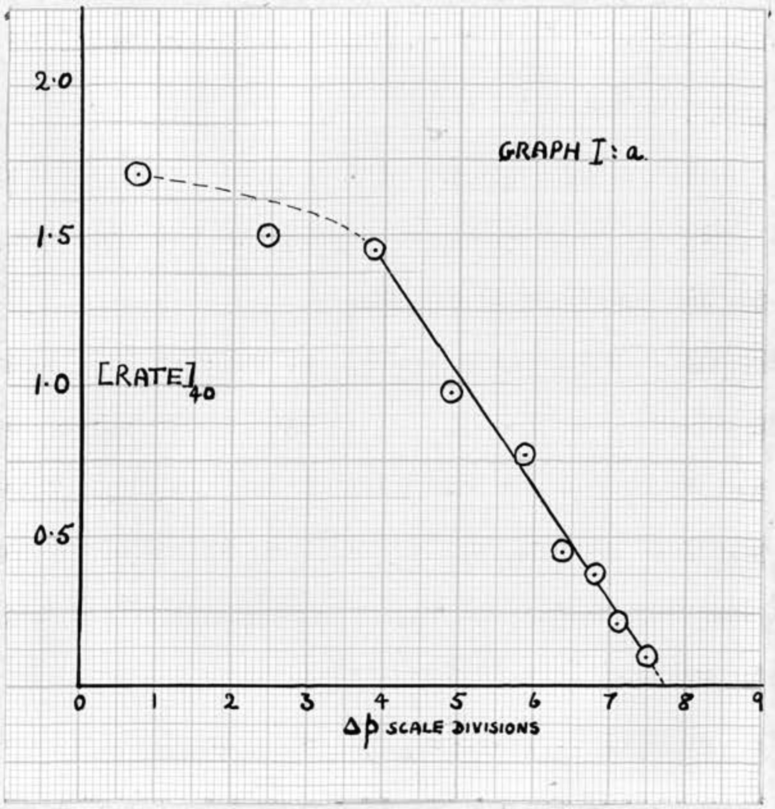
When thermal equilibrium was maintained, observable by a steadiness of the gauge pointer, the film was irradiated and the pressure changes occurring in the reaction vessel were recorded at known time intervals. As the total change of pressure occurring during a typical reaction was less than 1mm. the absolute gas pressure can be assumed to remain constant throughout a reaction for reasonably high initial pressures. The error introduced in the utilisation of this assumption was never greater than 5% depending on the oxygen pressure and the total pressure change.

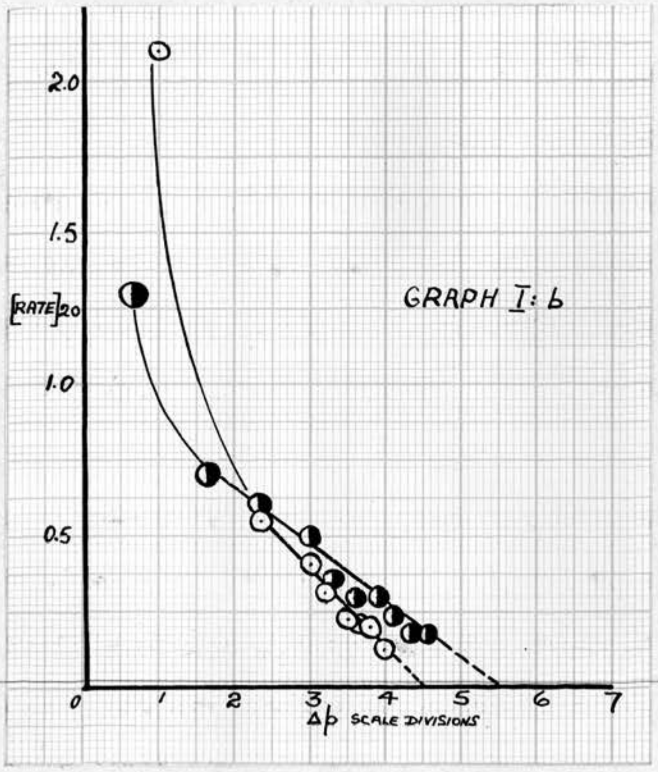
From readings of pressure change at known time intervals the rate of pressure decrease could be calculated and plotted against the pressure decrease resulting in what will be termed a 'rate curve'.

If /

If during a 'run' it was required to alter the absolute pressure of oxygen in the reaction vessel the procedure described below was adopted. The light source aperture was closed and the taps T_1 and T_2 opened. The apparatus was then slowly evacuated through T_3 or oxygen allowed to enter through T_7 according to whether the pressure required to be decreased or increased. The resultant pressure could be measured on the manometer M. After closing the taps T_1 and T_2 the irradiation was continued.

The Photo-oxidation of Rubrene on Thallous Bromide /


GRAPH I: a.
2·0
1·5
1·0
0·5
[RATE]40
0
1
2
3
4
5
6
7
8
9
Δp SCALE DIVISIONS


GRAPH I: b
2.0
1.5
1.0
0.5
[RATE]20
0
1
2
3
4
5
6
7
Δp SCALE DIVISIONS

The Photo-oxidation of Rubrene on Thallous Bromide

Preliminary Experiments

The following experiments were carried out to determine the effect of light on thin films of rubrene on thallous bromide crystals in the presence of oxygen.

In the first experiment 14.1mg. of rubrene (A), deposited from a standard solution of rubrene in acetone on to 0.3gm. of thallous bromide, was evacuated for two hours at 10^{-3}mm. Hg. (McLeod gauge). The film was then irradiated in 100mm. oxygen with the Osira lamp system. The temperature of the reaction was 25°C and the gauge sensitivity was 0.0050mm. / Scale division.

The gauge pointer remained steady in the dark on average although fluctuating around the zero point by not more than 0.5 scale divisions. When the film was irradiated a decrease in pressure was observed and recorded. The rate of decrease in scale divisions / 40 minutes is plotted against the actual decrease of pressure in Graph I:d.

Extrapolation of the curve in Graph I:d suggests the value of 7.7 scale divisions for the total uptake of oxygen at zero rate. This would constitute only about 5% of the possible reaction assuming that unit molar combination of oxygen and all the rubrene occurs.

A series of experiments were then performed at a variety of oxygen pressures, weights of substrate, weights of rubrene and depositing solvents. The percentage reaction occurring was calculated from a knowledge of the extrapolated pressure decrease and the constants of the apparatus. The table below summarises the results.

	I:1.	:2.	:3.	:4.
Weight of rubrene, mg.	14.1(A)	1.83(C)	1.94(C)	1.94(C)
Weight of substrate, gm.	0.3	0.2	0.2	0.2
Depositing solvent	acetone	acetone	benzene	benzene
Oxygen pressure mm.Hg.	100	100	50	50
Time of illumination, mins.	235	600	360	600
Percent reaction	4.6	0	12	0

The results of experiments I:1. - :4. indicate that rubrene samples irradiated in oxygen, show erratic oxygen uptakes and that in any case appreciable pressure decreases under the present experimental conditions are not found.

These small uptakes may be due to many factors and the first one to be investigated was the effect of the substrate. In the next section the non-absorbing substrate, powdered Jena glass, was employed.

The Photo-oxidation of Rubrene on Jena Glass /

The Photo-oxidation of Rubrene on Powdered Jena Glass

In the following experiments the conditions were standardised as now described.

All films were deposited from acetone solution on to 0.2 gm. of Jena glass. The films were evacuated for 2½hours at 10^{-3}mm. mercury (McLeod gauge) and irradiated with the Osira lamp system in a constant pressure (100mm. oxygen) and constant temperature (25°C) system. The gauge sensitivity was 0.0050mm. / scale division.

Degassing was effected 'in situ' by evacuating the vessel in a constant temperature arrangement. This was done to ensure the removal of as much as possible of the physically adsorbed solvent.

I:5. 3.37 mg. rubrene B

:6. 1.84 mg. rubrene C

:7. 5.35 mg. rubrene A : degassed for one hour at 100°C.

:8. 1.35 mg. rubrene B : degassed for one hour at 130°C.

Graph I:b shows the 'rate curves' for the runs 5 and 7 and although these are apparently linear the uptakes are so small that the curves cannot be taken as final evidence of a uni-molecular reaction with oxygen.

The percentage reaction, having the same significance as in the previous section, that occurred in the above experiments are shown in the table below.

No. /

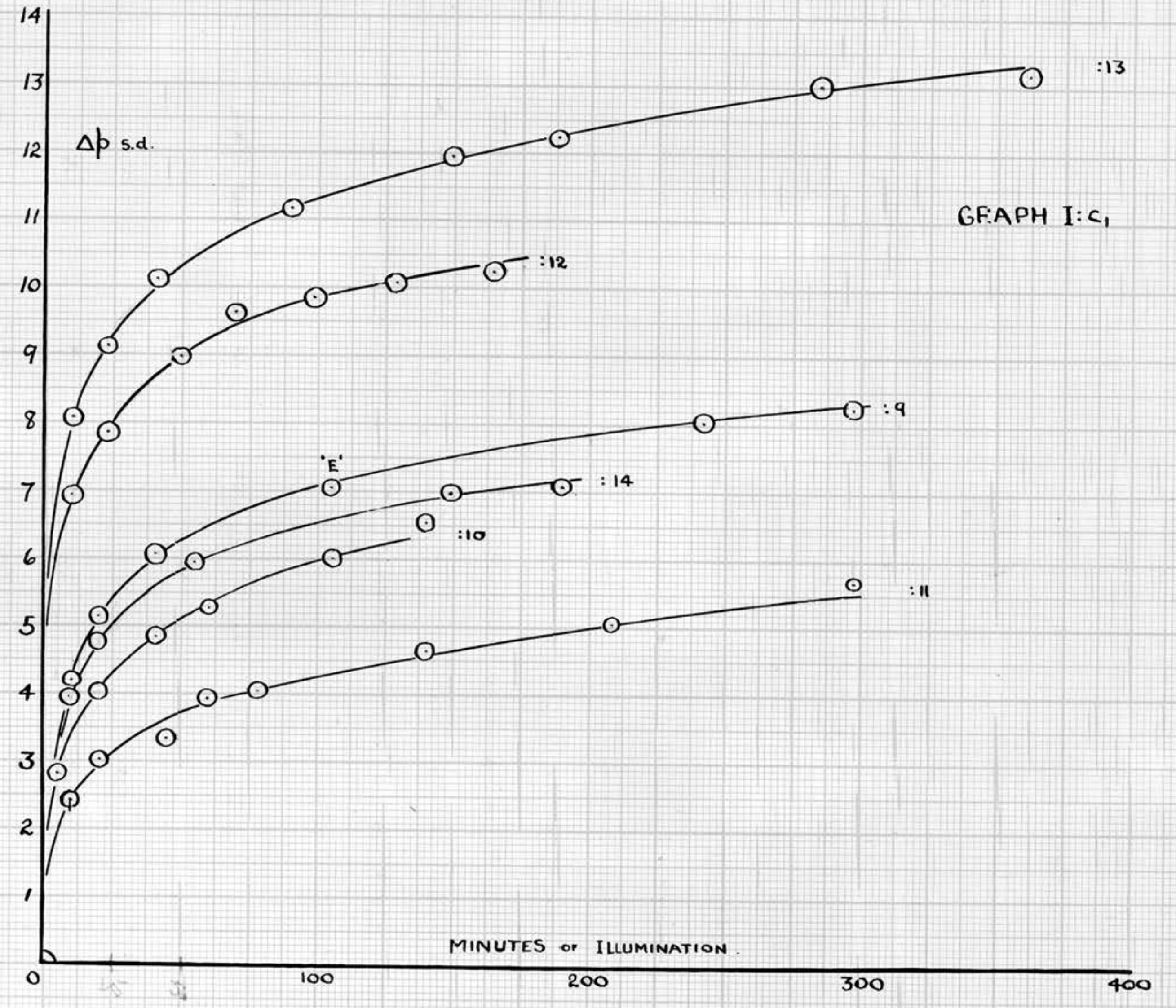
No.	Percent reaction	Time of Illumination (minutes)
I:5.	11	220
:6.	0	600
:7.	9.2	160
:8.	2	200

As the rates and total uptakes on thallous bromide and on Jena glass are not significally different, it seems fairly certain that thallous bromide does not photosensitise the photo-oxidation under the present experimental conditions.

Degassing at higher temperatures does not seem to produce any marked effect. This, combined with the irreproducibility and magnitude of the oxygen uptakes observed, suggests that the surface alone governs any such reaction. In other words either only molecules in the neighbourhood of crystal irregularities or a thin external layer may photo-oxidise under these conditions.

The next surface variable to be investigated was the depositing solvent.

The Photoreactions of Films of Rubrene from Benzene Solution Deposited on Jena glass /


GRAPH I: C₁
Δp s.d.
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
100
200
300
400
MINUTES OF ILLUMINATION.
:13
:12
:9
'E'
:14
:10
:11

The Photo-oxidation of Films from a Benzene Solution of Rubrene Deposited on Jena Glass.

Experimental:

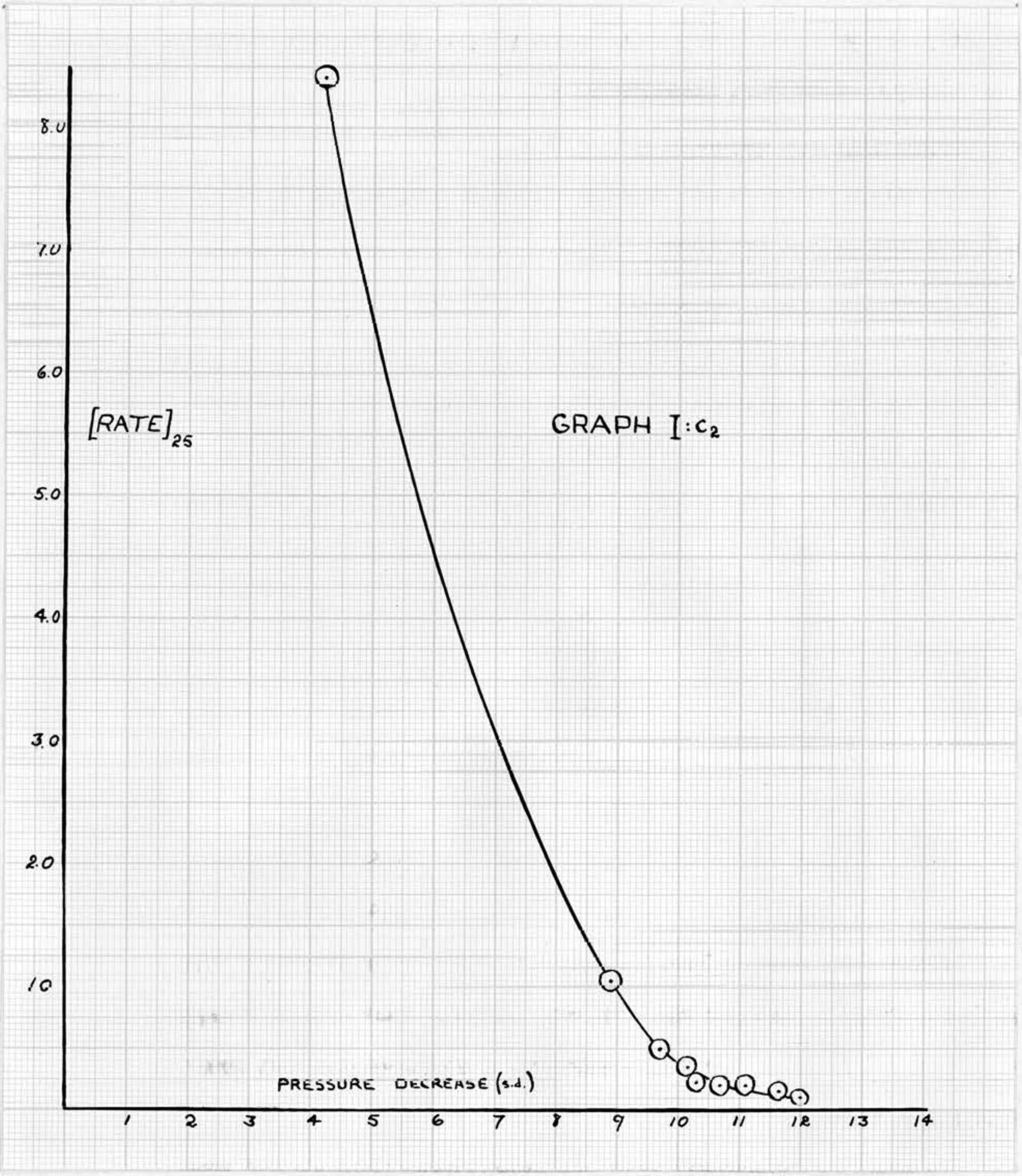
Gauge Sensitivity	: 0.0055mm/sd.
Reaction vessel volume	: 55.7mls.
Oxygen pressure	: 50 mm.
Temperature	: 21.5°C.
Evacuation	: 'Speedivac' oil pump and mercury diffusion pump.
Rubrene	: Sample C. as standard solution of 194.0mg./100mls. redistilled benzene.

After each 'run' the film was spectrographically analysed for rubrene. The results of these analyses will be referred to as percentages of the initial rubrene concentration. The extent of the reaction, as calculated from the analysis, was then compared to the value obtained from a knowledge of the constants of the apparatus and the ultimate total pressure change.

Runs 9. - 14. were performed under the above experimental conditions and the results are outlined in the table below. Graph I:C_1 contains the plots of change in pressure against time for the above experiments.

No.	rubrene mg.	Substrate gm.	% Reaction (calc.)	Analysis
I: 9.	1.94	0.1	42	43
I:10.	1.94	0.3	29 ✓	27
I:11.	1.94	0.3	30 26	28
I:12.	1.94	0.3	18 48?	-
I:13.	1.94	0.3	60	58
I:14.	3.88	0.3	19 16	-

The very good agreement between the spectrographic analysis figures and the extent of the reaction as calculated from the pressure /


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
[RATE]25
GRAPH I: c2
PRESSURE DECREASE (s.d.)
1
2
3
4
5
6
7
8
9
10
11
12
13
14

pressure decrease in the system is in accord with the view that the reaction occurring consists of the combination of one molecule of oxygen with one molecule of rubrene.

In Graph I:C_1 although the experimental points are shown as circles the curves are drawn from values of the pressure change (Δp) calculated from the general equation(1.).

$$\Delta p = A.\log_{10}(B.\ t + 1) \text{ ----------- } (1)$$

A and B are constants for any given film. As can be seen from the table below, A is virtually constant for the given set of experimental conditions while B can be identified with the total uptake of oxygen.

No.	A.	B.
: 9	2.70	2.55
:10	2.55	1.88
:11	2.05	1.33
:12	3.00	18.6
:13	3.24	31.6
:14	3.05	2.2

Graph I:C_2 exemplifies the type of rate curve obtained with such reacting films from which it may be concluded that the oxygen absorption did not proceed according to a unimolecular law over the range studied.

It must be emphasised that the logarithmic plot is not very sensitive to finer deviations. Almost any process which tends to come to a standstill after a while would approximately conform to some sort of logarithmic law. It appears that such a relationship is not necessarily the result of a single uniform process; there are /

are examples available in which the experimentally determined rate law is logarithmic but is actually composed of two or more exponential terms (51, 52). Under these circumstances the deduction of a single comprehensive rate constant becomes impossible. The main trouble in elucidation of these results lies in the fact that the uptakes have been so varied. If the reaction consists of a series of exponentials then under these conditions it becomes difficult to relate one reaction to another: a difficulty which is not lessened when the form of the surface is changing from 'run' to 'run'. It was possible, however, from the curves on Graph I:C_1 to estimate the probable values the 'total oxygen uptake', Δp_{oo}. The factor $(\Delta p_{oo} - \Delta p)$ scale divisions which corresponds to the amount of rubrene available for reaction with oxygen at the time t minutes, is compared to the initial rate, $\left[\text{Rate}_{25}\right]_{0}$, expressed as scale divisions per 25 minutes, in the table below.

No.	$\left[\text{Rate}_{25}\right]_{0} = A$		$(\Delta p_{oo} - \Delta p) = B$		A/B	A/B-2.1
9	8.10	5.45	7.50	5.9	1.08	1.50
10	4.95	4.35	5.70	5.0	0.87	1.38
11	? 5.40	3.10	5.30	4.0	1.02	1.68
12	3.10	8.10	? 4.25	7.0	0.73	1.44
13 ✓	9.40	9.40	8.80	8.03	1.07	1.40
14	5.50	5.05	6.30	5.45	0.88	1.32

The constancy of the rate-concentration ratio in column four strongly indicates that the reaction is unimolecular in the initial stages. If the rates are measured over the whole concentration range /

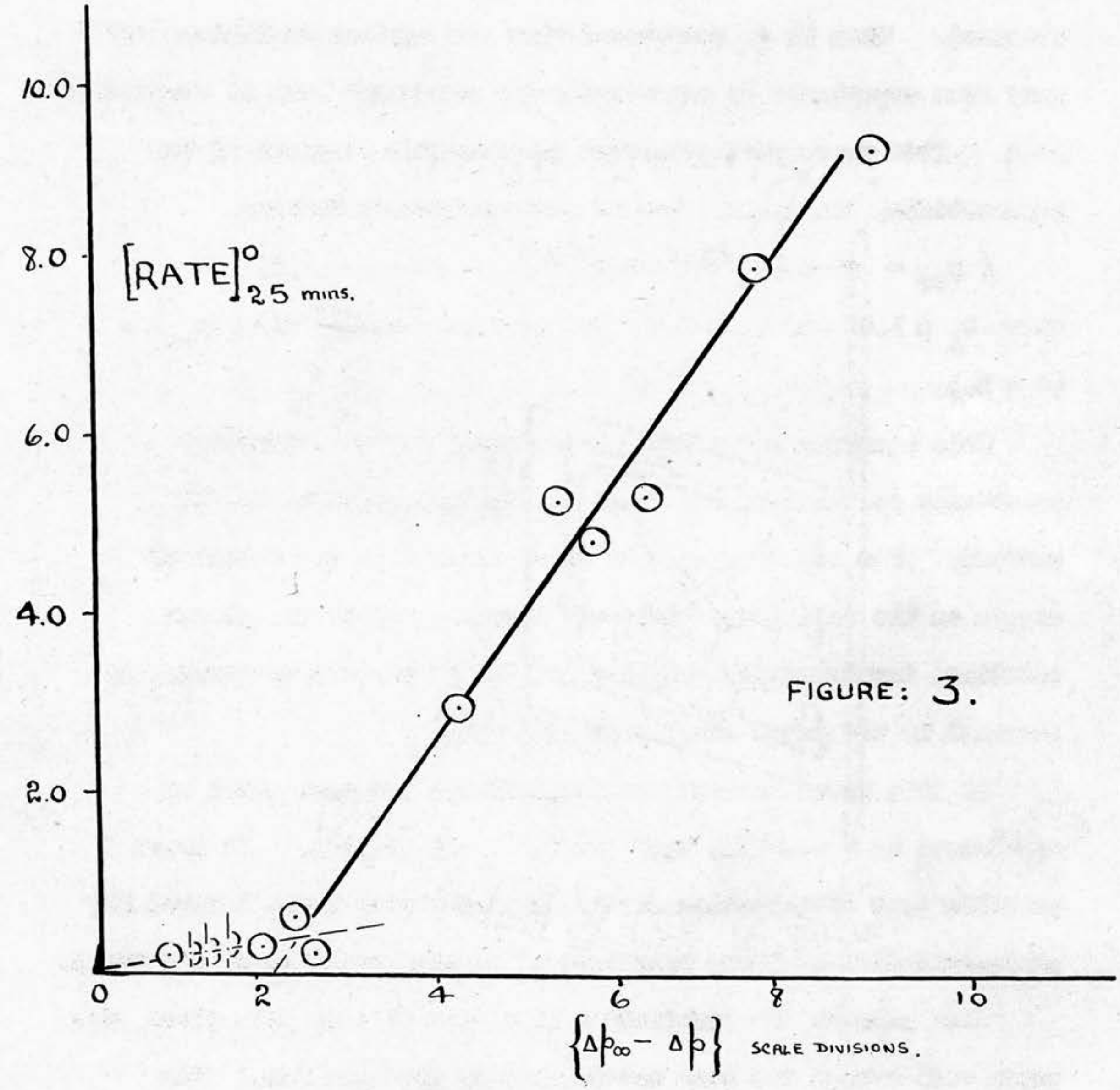

10.0
8.0
6.0
4.0
2.0
0
2
4
6
8
10
$[\text{RATE}]^{0}_{25 \text{ mins.}}$
$\{\Delta p_\infty - \Delta p\}$ SCALE DIVISIONS.

FIGURE: 3.

range and plotted against the rubrene concentration, as measured by pressure change, a curve of the type shown in Figure 3 is obtained. When it is remembered that the surface conditions may vary from experiment to experiment, the agreement here is reasonably good. This curve indicates that the reaction consists of two exponentials, the overall law of photo-oxidation being:-

$$(\Delta p_{\infty} - \Delta p) = A.e^{-k_1.t} + B.e^{-k_2.t} \quad \text{———————} \quad (2)$$

where $k_1 = 1.52$ and $k_2 = 0.15$ (twenty-five mins.)$^{-1}$ and $(\Delta p_{\infty}) = (A + B.)$.

This equation lends theoretical basis to the attractive hypothesis postulating two types of reactive material on the surface. The faster stage may be attributed to the attack of oxygen on the relatively 'unbound' molecules while the slower reaction, involving the oxidation of the crystalline material, is governed by the second term in equation (2).

At this stage however, the logarithmic law must still be considered as a possible explanation of the results. It seems possible that correllation of the constents with those derived for photo-oxidation at lower pressures of oxygen, would be of advantage.

That rubrene, on irradiation of a thin film on Jena glass, does react with oxygen has been established in this section. The uptakes were irreproducible although the pressure-time curves all seemed to follow the same law. The analysis indicated that one molecule of rubrene disappears when one molecule of oxygen is removed from the gas phase. These results also prove that the rubrene sample under consideration contained no appreciable amount of impurity which was oxidisable under the present experimental conditions. /

conditions.

A complete unit molar ratio of oxygen uptake to rubrene concentration could not be approached in any of the experiments. In run 13., for example, 60% of the film reacted in 365 minutes although according to equation 1., this reaction will only proceed to completion in 1.7×10^2 days.

As so far described, the gas in the gas phase has been regarded as oxygen only and the reaction as the simple step:

$$R + O_2 \longrightarrow RO_2$$

where R signifies rubrene and RO_2 the peroxide. The analyses and calculations from pressure decreases have indicated that one molecule of rubrene is used up when a nett loss of one molecule occurs in the gas phase. Such a stipulation does not exclude a reaction of the type:

$$R.B + 2(O_2) \longrightarrow R(O_2)_2 + B$$

where B indicates solvent (benzene) and R.B a rubrene-solvent complex from which the solvent may not be removed by the normal evacuation procedure. Such a reaction would only be in accord with experiment if the adsorption of benzene on the glass surface was negligible. The pressure change results do, however, rule out reactions of the type:

$$R.B + O_2 \longrightarrow RO_2 + B$$

where there is no resultant pressure change.

The Effect of Evacuation in the Dark

When the initial, fast, stage of the reaction had completed in run 9. the film was evacuated for a further 3 hours in darkness (see 'E' in Graph I:C). No change in the general shape of the pressure-time curve was observed when the film was re-irradiated in /

in 50mm. of oxygen. This result suggests that the reaction is not of the simple thermal reversible type.

No simple relationship could be found which included all the experimental points in any one of the above photo-oxidations. For this reason it seemed reasonable to assume that two types of oxidation were occurring simultaneously. At this stage in the work it was considered of prime importance to investigate the effect that occluded or 'chemisorbed' solvent of deposition might have on the photo-oxidation in relation to the total uptake of oxygen.

The Effect of Organic Vapours on the Photo-oxidation /

The Effect of Organic Vapours on the Photo-oxidation : Benzene

Experimental:- Film - 1.94mg. rubrene C. deposited from benzene solution on to 0.1gm. Jena glass.

Evacuation - Oil and mercury diffusion pumps.

The film was evacuated overnight and irradiated in oxygen until the reaction rate became negligibly slow. The illumination was then ceased and the oxygen pumped off. 10mm. of benzene vapour were then introduced into the reaction space and the pressure made up to 60mm. with oxygen. It was found that appreciable dark adsorption of benzene occurred so, 15 hours standing at the reaction temperature was allowed for the system to attain equilibrium.

On further irradiation, first with the Osira and then Osram light sources, no pressure decrease was detected after a period of five hours.

Carbon disulphide

An uncreactive film, prepared as above, was left under 50mm. of carbon disulphide at 20°C. for 24 hours, in complete darkness. The film was then evacuated for about 5 minutes when 50mm. of oxygen were introduced into the system. After 2 hours standing in the dark, by which time the gauge pointer had become steady, the film was re-irradiated. No further reaction could be detected.

Carbon disulphide was chosen because the photo-oxidation of rubrene in this solvent proceeds at a rate nine times greater than in any other solvent (10).

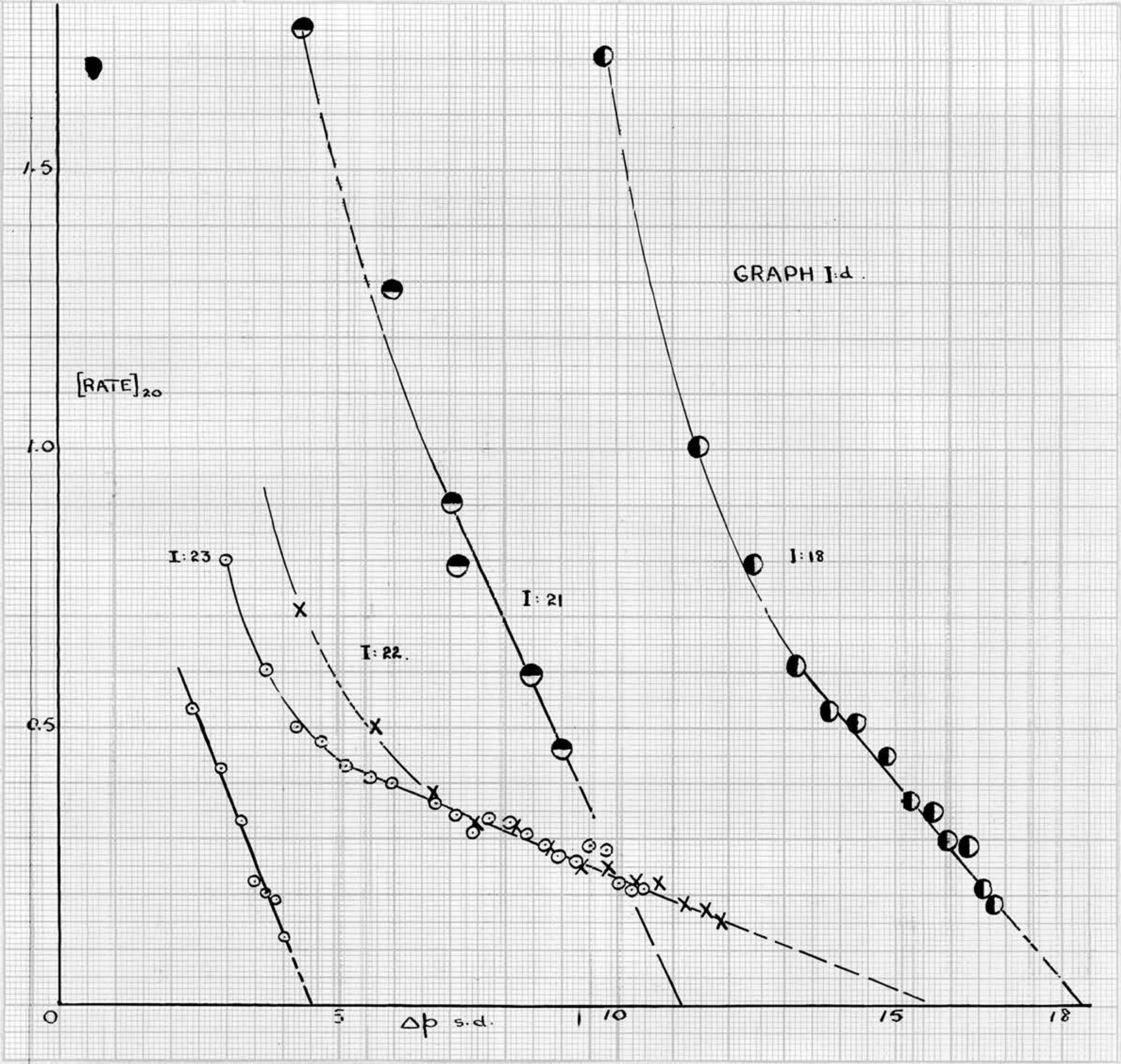
Under /

Under the present experimental conditions the organic vapours investigated have no apparent effect on the photo-oxidation of rubrene in the form of a thin film on Jena glass.

It was suggested in the previous section that two simultaneous reactions occur when films of rubrene, deposited in the described manner, are irradiated. The reproducibility of the curves in every respect except total uptake of oxygen suggest that the final or slow process was common to all the reactions studied. The conjecture is now formed that one of these reactions involves the rapid attack of oxygen on relatively unbound or non-crystalline rubrene while the other constitutes the slow attack on the crystalline material by way of crystal irregularities or faults. The initial step may be visualised as being connected with the method of deposition and the solvent.

In an effort to supress this initial stage it was intended to study the photo-oxidation of films of rubrene prepared 'in situ', on Jena glass, from rubrene peroxide. In this manner it was hoped to remove all traces of solvent and form a film containing only one 'reactive type' of rubrene. It was also hoped that in this way any diffusional process which may be occurring will be accelerated.

The Photo-oxidation of Rubrene prepared 'in situ' from the Peroxide/



GRAPH I:d.

The Photo-oxidation of Rubrene Films
Prepared 'in situ' from the Peroxide

Experimental Procedure

The preparation of the film

After preparing a solution (in acetone) of rubrene peroxide in the standard manner a measured quantity was poured into a reaction vessel which already contained a known weight of Jena glass. The solution was then slowly evaporated to dryness under reduced pressure and at 30°C. In order to form a uniform film, as in the experiments with rubrene, the vessel was gently rotated when only a few drops of acetone remained.

The film was then subjected to simultaneous heating, at 130°C., and pumping with the oil pump over liquid oxygen for a recorded time in the dark. The heating was effected by immersing the vessel in the vapour of boiling chlorobenzene contained in a darkened flask. The flask was fitted with three necks. The first was for a reflux dondenser, the second contained a thermometer and the third the reaction vessel. To the third and largest neck of the flask had been fitted a rubber bung through which the joint of vessel could protrude.

The reaction vessel was then transferred to the apparatus, in darkness, and evacuated for a further three hours. Photo-oxidation was then carried out in the usual manner.

Illumination - Osira lamp system

Oxygen pressure - 100mm.

Temperature - 25°C.

The 'rate curves', which are drawn on Graph I:d, were found to /

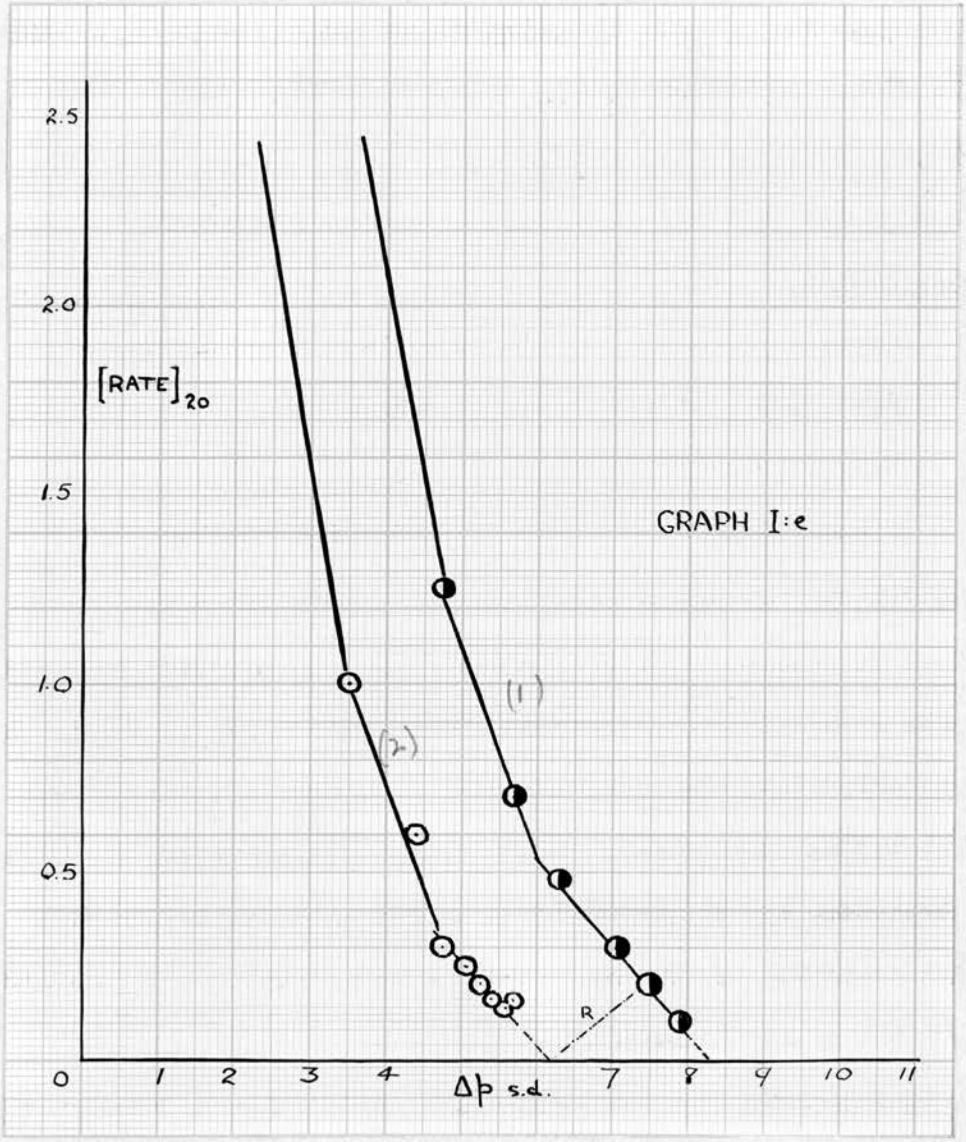
to be linear in the later stages of the reaction thus enabling a value of the ultimate oxygen uptake to be estimated by extrapolation to zero rate. This value is expressed in the table below as a percentage of the total rubrene equivalent of the rubrene peroxide on the film. In the 'runs' where the molar uptake was less than 15% the rate values were not computable owing to the small uptakes involved.

The weights of rubrene peroxide are expressed as rubrene equivalents (R.E.).

No.	Wt. of peroxide mg. R.E.	Wt. of Jena glass gm.	Time of heating (hrs.)	% Reaction. (extrapolated)
I:15.	1.35 B.	0.2	0.5	15
:16.	1.35 B.	0	1	6
:17.	1.35 B.	0.05	1	8
:18.	5.35 A.	0.2	2	9
:19.	1.35 B.	0.2	2	33
:20.	1.35 B.	0.2	2	6
:21.	1.35 B.	0.2	2.5	70
:22.	5.35 A.	0.2	3	24
:23.	No. 21. reheated-------------------		4	99
:24.	1.35 B.	0.2	7	15

No relation between the time of heating and oxygen uptake is apparent from the above experiments.

In 'run' 23. the film previously photo-oxidised in :21. was heated at 130°C. for a further 4 hours and then re-irradiated in oxygen. It was observed that the film was very nearly colourless at the end of the reaction while to begin with, it was a very deep red /



GRAPH I:e

red colour.

The extent of the oxygen uptake in experiments I:21. and :23. indicated that the process of intermittent heating might constitute a simple method of bringing about a change in the deposited rubrene to a variety capable of reversible oxidation. It was with this idea in mind that the following experiment was performed.

Experimental

Rubrene peroxide	-	2.34mg. C (R.E.)
Jena glass	-	0.2gm.
Oxygen pressure	-	50mm.
Illumination	-	Osira lamp system.

The film was heated for 2.5 hours at 130°C. and then irradiated in oxygen. The extrapolated uptake, obtained from the rate curve on Graph I:e:1, was found to be equivalent to 20% of the total vailable material. The oxidised film was then removed and heated at 130°C. for a further five hours. On returning the film to the apparatus and illuminating in oxygen photo-oxidation then proceeded according to the rate curve on Graph I:e:2 to the extent of 15% of the available material.

It is concluded from this experiment that a second heating may not necessarily produce more 'oxidisable material' than is formed during the first heating. In this particular case the amount obtained was less. At the termination of the second photo-oxidation the film was once again heated at 130°C., this time during four hours, and the residue analysed spectrographically for rubrene. The fraction of the peroxide which had decomposed was only /

only 15%. On the assumption that all the rubrene formed by the first heating was photo-oxidised during the first illumination (this is likely as the film became almost colourless), it may be concluded that the cycle of operations performed have reduced the efficiency of the decomposition process.

It is interesting to note that the rate curves on Graph I:e are identical in all respects except for the extrapolated pressure decrease; see dotted line A. Unlike runs I:21 and :23 where the forms of the rate curves were markedly different, in this case the surfaces in the respective experiments must have been nearly identical and possibly the same (fractional) section of the surface has contributed to the oxidation in each case.

The rate curves on Graph I:d, although they are collectively irreproducible, do indicate that the oxidation proceeds with a certain degree of exponential character, particularly in the later stages.

It is apparent that by changing the surface conditions, as in the previous sections, the complete form of the rate curve or 'oxidation law' is also altered.

Now that it has been definitely established that rubrene will photo-oxidise to some extent in the solid state even in the absence of occluded solvent, it is intended to turn attention to oxidations at very low oxygen pressures. An attempt will be made to test the reversibility of the reaction through the detection of a 'dissociation pressure' while the general scheme to elucidate the mechanism of the photo-oxidation will be continued.

The Photo-oxidation of Rubrene at Low Oxygen Pressures /

The Photo-oxidation of Rubrene at Low Oxygen Pressures.

The pressures termed 'low' implies oxygen pressures of the order of one to twenty scale divisions or about 0.05 to 0.10mm. according to the gauge sensitivity.

The absolute oxygen pressure over the film was measured by allowing oxygen to enter only one side of the guage and noting the gauge pointer deflection.

Experimental

Gauge sensitivity	- 0.0055 mm./scale division.
Substrate	- 0.1 gm. Jena glass.
Depositing solvent	- Benzene.
Volume of vessel	- 55.8 mls.
Temperature	- 21.5°C.
Evacuation	- 15 hours with oil and diffusion pumps.

Various films of rubrene sample C. were illuminated in oxygen and the reaction course followed in the usual manner. The oxygen uptakes were small and saturation normally occurred within about 200 minutes depending on the initial pressure. After each low pressure experiment the pressure was raised to 50mm. of oxygen and the film re-illuminated. The resulting pressure decrease was noted. In all the cases investigated an appreciable uptake occurred at the higher pressure indicating that the films still consisted, at least in part, of 'oxidisable' rubrene.

At the termination of each experiment the film residues were analysed, spectrographically, for rubrene. The amount of rubrene which reacted with oxygen during the irradiations was calculated from the total pressure decrease on the assumption $R + O_2 = RO_2$ was the only reaction, and /

and the constants of the apparatus and this value compared to the analysis figure.

In order to investigate reactions at extremely low pressures, of the order of 0.08mm., a sickle guage of sensitivity 0.0040 mm./s.d. was employed. The experimental variables and the analysis results are reproduced in the table below.

No.	Oxygen Pressure mm. Hg.	Weight of Rubrene mg.	% Reaction calc.	Analysis %	
I:25.	0.545	1.94	22	24	bsram
:26.	0.825	1.94	29	27	bsr
:27.	0.825	3.88	32	33	bsira
:28.	1.10	1.94	27.5	27	bi
:29.	0.196	4.11	31	29	bsr
:30.	0.080	4.11	20	-	bsr
:31.	0.556	1.53	77	78	bi
:32.	1.183	4.11	65	65	bi

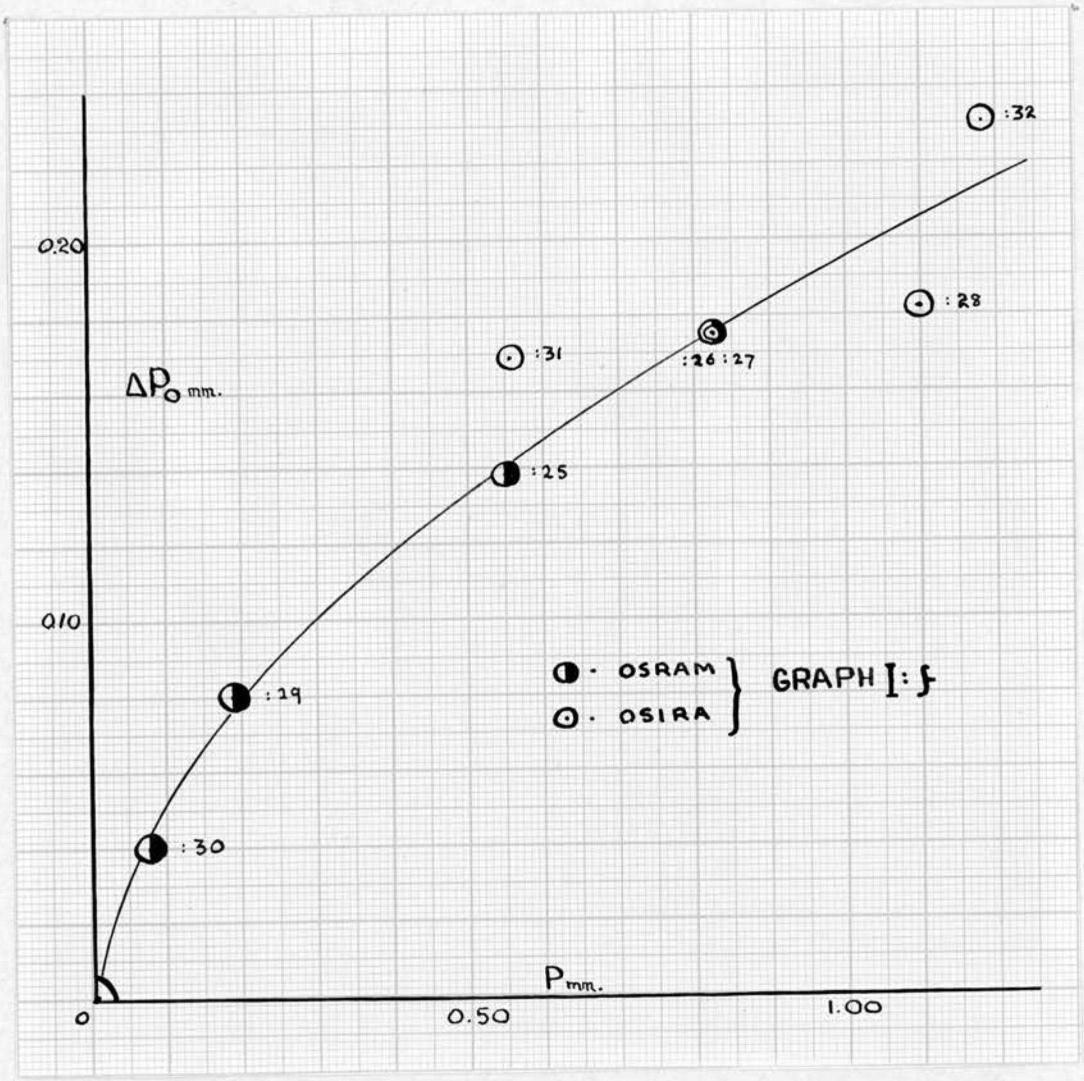
The symbols which will be employed to signify the appropriate experimental variables are listed below:

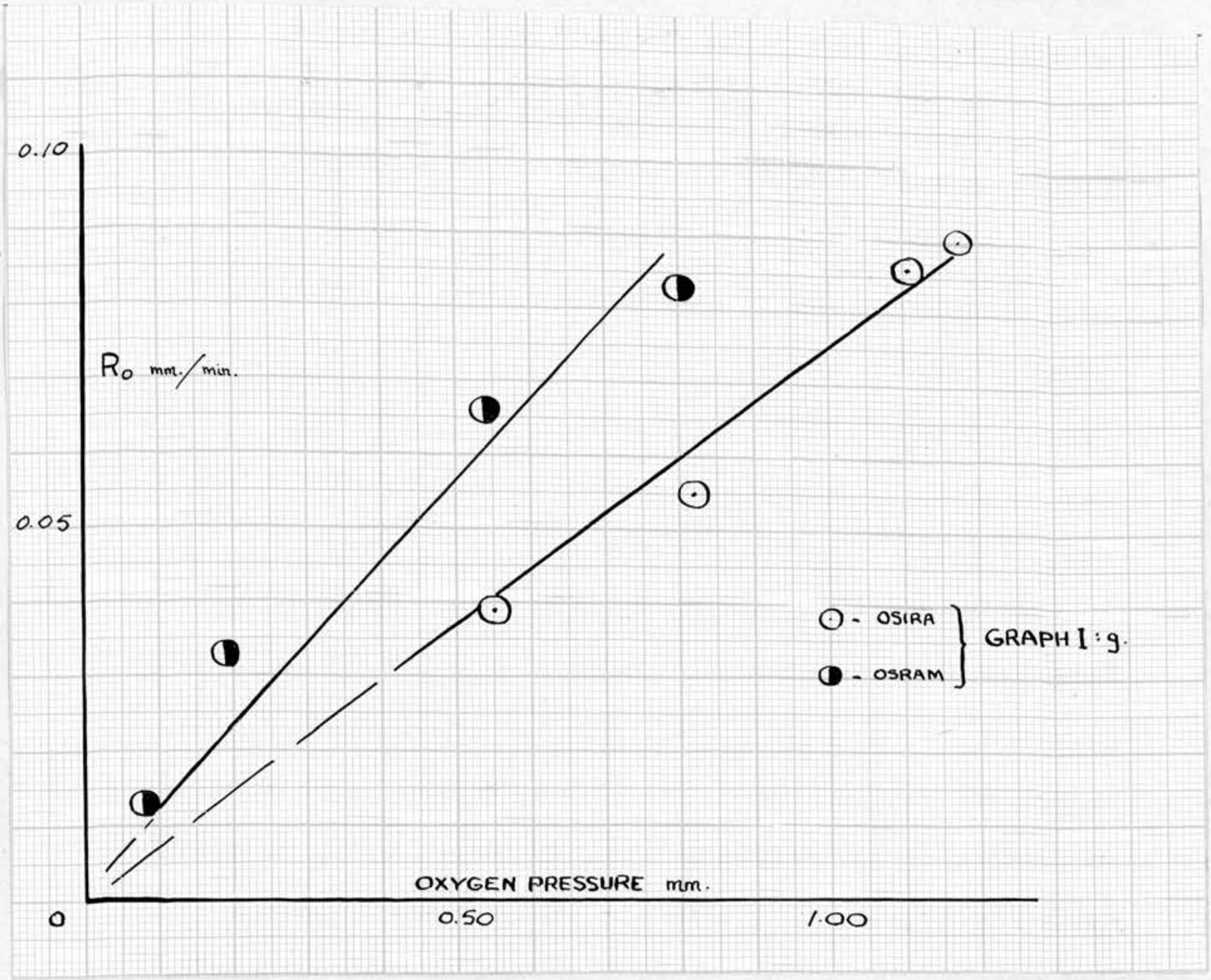
P - The initial pressure of oxygen in millimetres of mercury.

ΔP_o - The total pressure decrease which occurred when a film was illuminated at the initial pressure P until the rate became immeasurably slow. This time was normally about 300 minutes.

R_o - The initial rate of oxygen uptake, expressed in millimetres per minute, calculated from the guage pointer deflection during the first 12.5 minutes of the reaction. The rate per 12.5 minutes was chosen after trial and error plots of the rate/n minutes, where n ranged from 5 to 50 minutes. Below 12.5 the form of this curve was not affected by the rate time increment.

The /


:32
0.20
:28
:31
:26 :27
ΔP₀ mm.
:25
0.10
◑ · OSRAM
⊙ · OSIRA
GRAPH I : f
:29
:30
Pmm.
0
0.50
1.00


0.10
0.05
0
R_o mm./min.
OXYGEN PRESSURE mm.
0.50
1.00
⊙ - OSIRA
◐ - OSRAM
GRAPH I : g.

The actual values of P, ΔP_o and R_o are given in the succeeding table along with the type of illuminating system employed.

No.	P mm.	ΔP_o mm.	R_o mm./min.	Light Source
I:25.	0.545	0.138	0.066	Osram
:26.	0.825	0.176	0.080	Osram
:27.	0.825	0.176	0.0545	Osira
:28.	1.100	0.182	0.0875	Osira
:29.	0.196	0.08	0.033	Osram
:30.	0.08	0.04	0.012	Osram
:31.	0.556	0.169	0.0393	Osira
:32.	1.183	0.231	0.088	Osira

Graph I:f shows the plot of P against ΔP_o and Graph I:g, that of P against R_o. The most obvious conclusion from these results was the apparent non-existence of a finite pressure below which no photo-oxidation was occurring. All the drawn curves appeared to include the origin. If a dissociation pressure of photo-oxidation does exist it is certainly less than 0.04 mm. at 21.5°C. with either light source.

Graph I:g indicates that the rate is a linear function of the initial oxygen pressure which in turn governs the total uptake. The constant of proportionality in the former case depends on the light intensity. The light intensity of the beam from the Osram lamp was approximately 4.2 times that from the Osira as measured by an oside coated photocell arrangement.

The spectral distribution of the light emitted from the Osram lamp is indicated in the table below:

Wavelength A° /

Wavelength A°	Relative intensity %
4000	10
5000	30
6000	60

No light above a wavelength of about 5600A° is effective in bringing about photo-oxidation, thus, only 40% of the incident light could possible contribute to the photo-oxidative process in the absence of sensitisors. If it is assumed that all this light is absorbed by the rubrene on the film and all the incident light from the Osira lamp is also absorbed by the film, then the effective intensity ratio becomes 1.9:1 (Osram:Osira).

The slopes of the two curves in Graph I:g are in the ratio of 1.4:1, indicating that the rate of photo-oxidation is probably a linear function of the light intensity. The absolute values of the rate are difficult to assess owing to the dependence of this function on the available rubrene concentration. From the present experimental results, however, it is impossible to determine which one of these variables is independent.

It can be observed from the table above that the ratio $R_o/\Delta P_o$ is approximately constant even for a tenfold variation in ΔP_o, and as such, is independent of the initial pressure of oxygen.

Each film after reaction at low pressure was photo-oxidised further at 50mm. and each film took up more oxygen: thus it cannot be assumed at this point that ΔP_o has any more significance than an uptake value after a standard time interval. If, for example, ΔP_o was also some function of a surface variable, such as the formation o of mechanical imperfections, surface film formation or the revertion /

revertion to a slow diffusional process, then $R_o/\Delta P_o$ would not depict a true rate constant.

When the oxygen pressure is increased, after saturation at a lower value a further uptake of oxygen occurred. This suggested a type of equilibrium; if for example the oxygen concentration in a solid solution on the surface was the controlling factor in the reaction such a state of affairs might result. The other theory which may explain these results would involve a reaction of very high order with respect to oxygen concentration.

Experiments were carried out in which the reaction course was followed first at a low pressure then at a slightly higher pressure and finally at 50mm. of oxygen. In all cases more oxygen reacted at the higher pressure after saturation at the lower value. The rate at which oxygen was taken up by the film after elevation of the pressure was lower than during the first illumination. This effect was probably due to the effective change in concentration of the solid phase.

In an actual experiment the pressure was raised to 0.392mm. from an initial value of 0.196mm. after an uptake of 0.08mm. of oxygen at this pressure. During the second illumination the pressure decrease observed was 0.04mm.. The value of ΔP_o at 0.392mm. may be estimated from Graph I:f as 0.115mm.. The sum of the ΔP_o values at the two pressures was 0.12mm., indicating that the 'proportionality' between P and ΔP_o still exists if the past history of the film is taken into account.

In /

In the table below, which summarises the results of similar experiments, (ΔP_o)calc. symbolises the value of ΔP_o at the higher pressure which was obtained from Graph I:f.

No.	Lower Pressure		Higher Pressure		$\{(\Delta P_o)$low + (ΔP_o)high$\}$	(ΔP_o)calc.
	P	ΔP_o	P	ΔP_o		
I:33.	0.08	0.04	0.804	0.100	0.14	0.19
:34.	0.196	0.08	0.392	0.04	0.12	0.115
:35.	0.545	0.138	0.688	0.011	0.149	0.16

The mathematical form of the individual curves at low pressures could not be deduced owing to the low magnitudes of the pressure decreases involved.

It is difficult to visualise the mechanism which will explain all the experimental data without introducing the concept of a diffusional process. The values of P, ΔP_o and R_o have, however, provided a useful basis for a mechanism for the solid state photo-oxidation of rubrene under these conditions.

In one experiment the pressure was lowered after reaction at 0.825mm.. No further uptake of oxygen was observed over a period of 200 minutes; neither was an decrease of pressure observed.

It was now intended to investigate more fully the effect of changing oxygen pressure on the oxidation at higher absolute oxygen pressures in the range 5 - 100mm.. It was also hoped to gain competent evidence which will settle whether or not either whole or part of the reaction rate is determined by a diffusional process.

The Effect of Varying Oxygen Pressure on the Photo-oxidation of Rubrene /

The Effect of Varying Oxygen Pressure on the Photo-oxidation of Rubrene

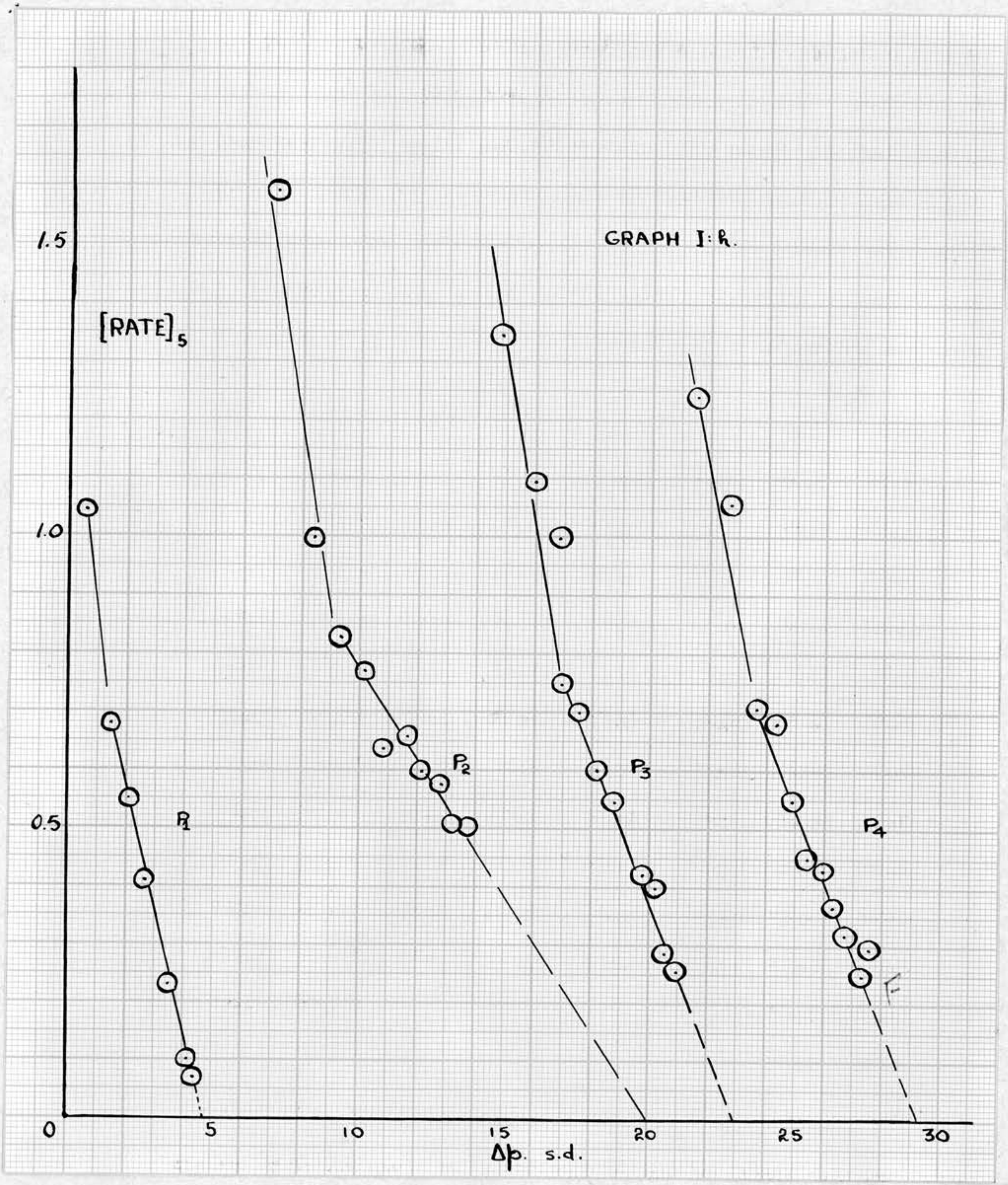
The observation, made at low pressures, that the amount of reaction which occurs and hence the rate of oxidation, depends directly on the oxygen pressure, allowed many possible conclusions and attracted divers propositions. It was now intended to discover whether or not this effect continued to operate at high oxygen pressures.

Experimental

Films of rubrene on Jena glass were prepared in the usual manner and after transference to the apparatus, were evacuated for a standard time. A known pressure of oxygen was then allowed into the reaction space. The pressure changes were recorded at known intervals until a substantial portion of a rate curve could be drawn. The light beam was now interrupted and the oxygen pressure altered through the tap T_1. After the attainment of thermal equilibrium the film was again irradiated. This operation could be carried out three or four times during one 'run'. It was particularly desired to study the initial rapid stage of the reaction, so gauge pointer readings were recorded as often as was practicable over the first twenty minutes of the experiment.

Gauge Sensitivity - 0.055mm./s.d.
Vessel Volume - 55.8 mls.
Illumination - Osira lamp system.

A film of 4.11mg. rubrene, which was deposited on to 0.2gm. of Jena glass from a benzene solution, was first illuminated at 1.18mm. (P_1) oxygen pressure. After 65 minutes the pressure was raised /

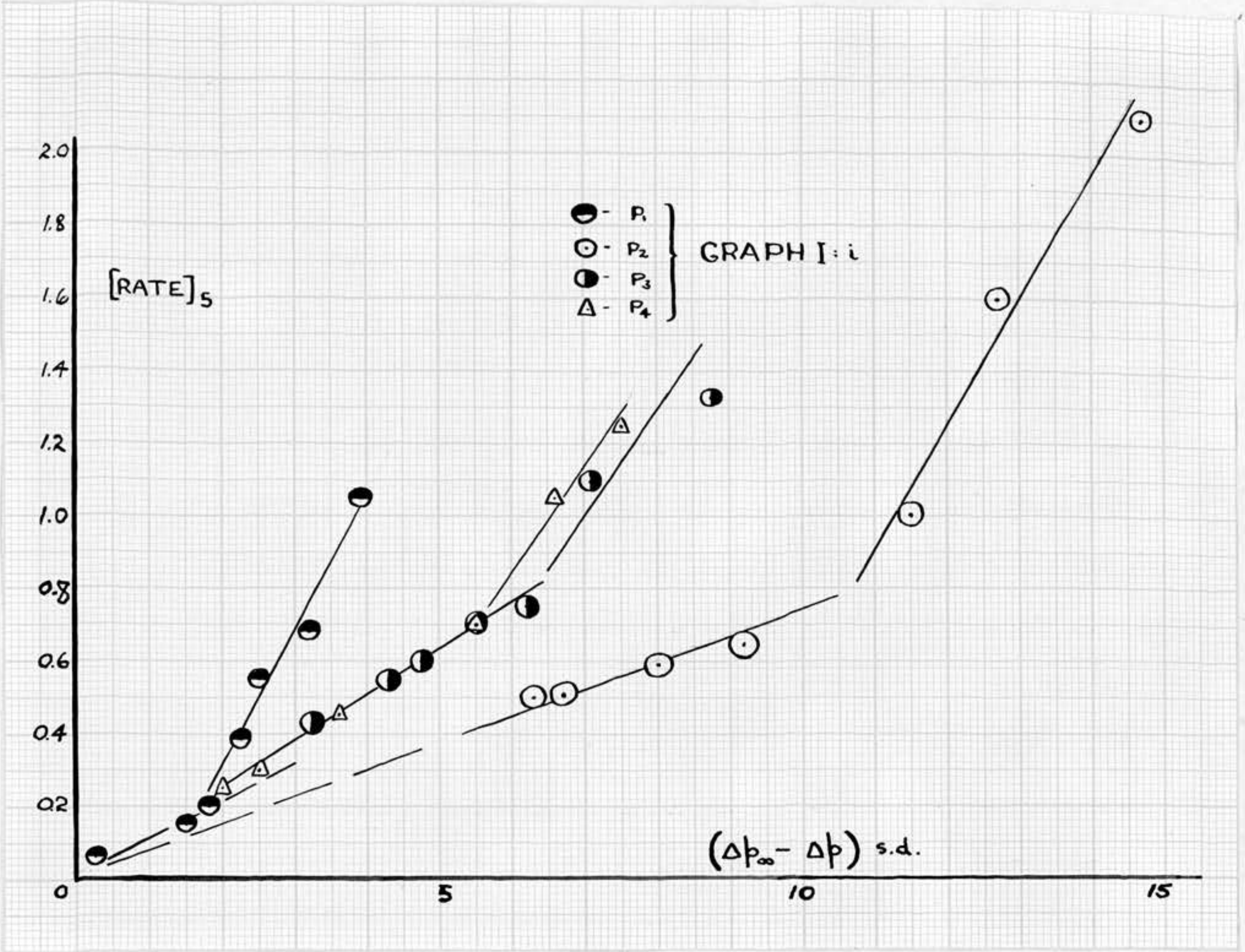


GRAPH I: h.

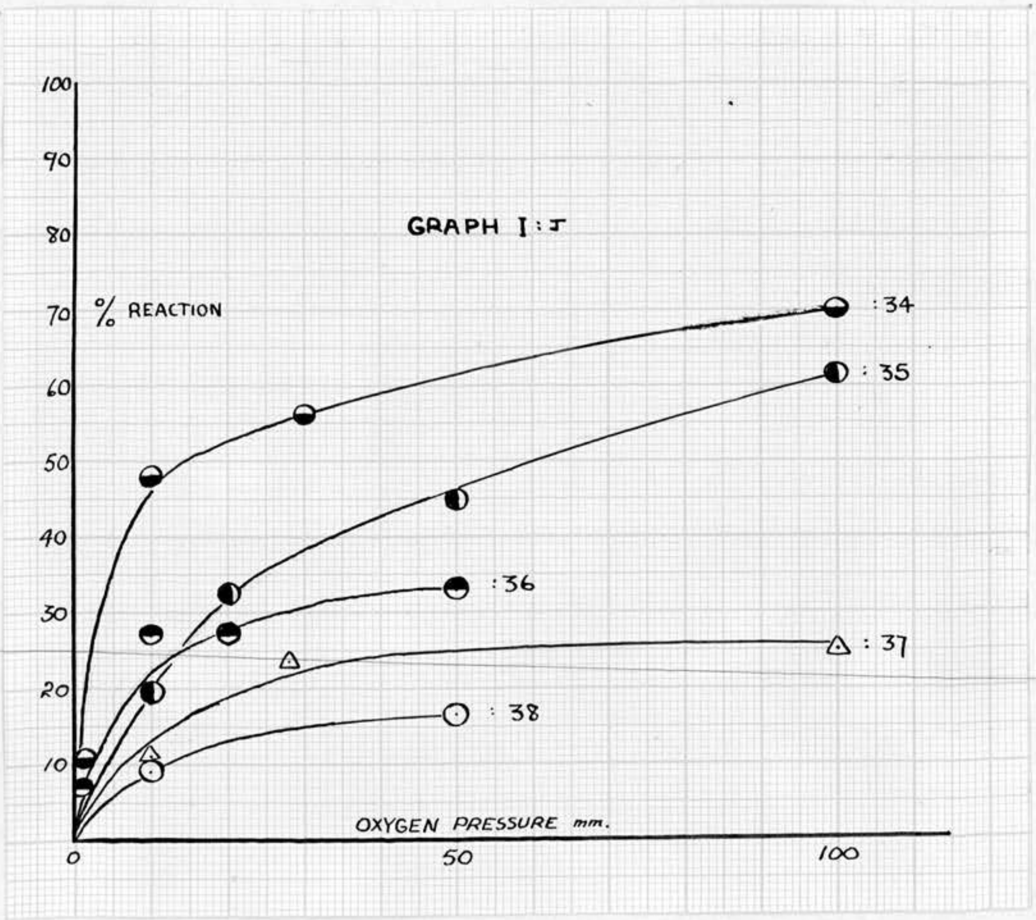
raised to 9.5mm. (P_2) and the film re-irradiated for a further 55 minutes. The pressure was subsequently raised and the film illuminated at 30 mm. (P_3) and at 100 mm. (P_4). The rate curves which were obtained at the various pressures are drawn in Graph I:h. The actual values of the rate, expressed as scale divisions per 5 minutes (R_5), at particular stages of the reaction as measured by the total pressure change (Δp), are given below:

P_1		P_2		P_3		P_4	
Δp	R_5	Δp	R_5	Δp	R_5	Δp	R_5
0.58	1.05	5.25	2.10	14.70	1.35	21.53	1.25
1.39	0.68	7.10	1.60	15.90	1.10	22.68	1.06
2.01	0.55	8.40	1.00	16.83	0.75	23.56	0.71
2.48	0.41	9.32	0.83	17.55	0.70	24.26	0.68
2.84	0.31	10.12	0.77	18.20	0.60	24.88	0.55
3.14	0.28	10.82	0.64	18.78	0.55	25.38	0.45
3.40	0.23	11.47	0.66	19.32	0.53	25.82	0.43
3.61	0.19	12.10	0.60	19.79	0.42	26.22	0.37
3.80	0.20	12.69	0.58	20.20	0.40	26.56	0.32
3.96	0.12	13.23	0.51	20.55	0.29	27.04	0.33
4.07	0.10	13.74	0.50	20.82	0.26	27.17	0.25
4.17	0.09					27.45	0.30
4.25	0.07						

It is concluded from Graph I:h that the rate curves are at least partly linear within the limits of the experimental error. At 'F' the film was removed from the apparatus and analysed for rubrene. The amount of rubrene that had reacted was 65% of the total concentration while the value calculated from the total pressure /



GRAPH I : i
◓ - P_1
⊙ - P_2
◑ - P_3
Δ - P_4
[RATE]$_5$
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
5
10
15
$(\Delta p_\infty - \Delta p)$ s.d.



GRAPH I : J
% REACTION
100
90
80
70
60
50
40
30
20
10
0
50
100
OXYGEN PRESSURE mm.
: 34
: 35
: 36
: 37
: 38

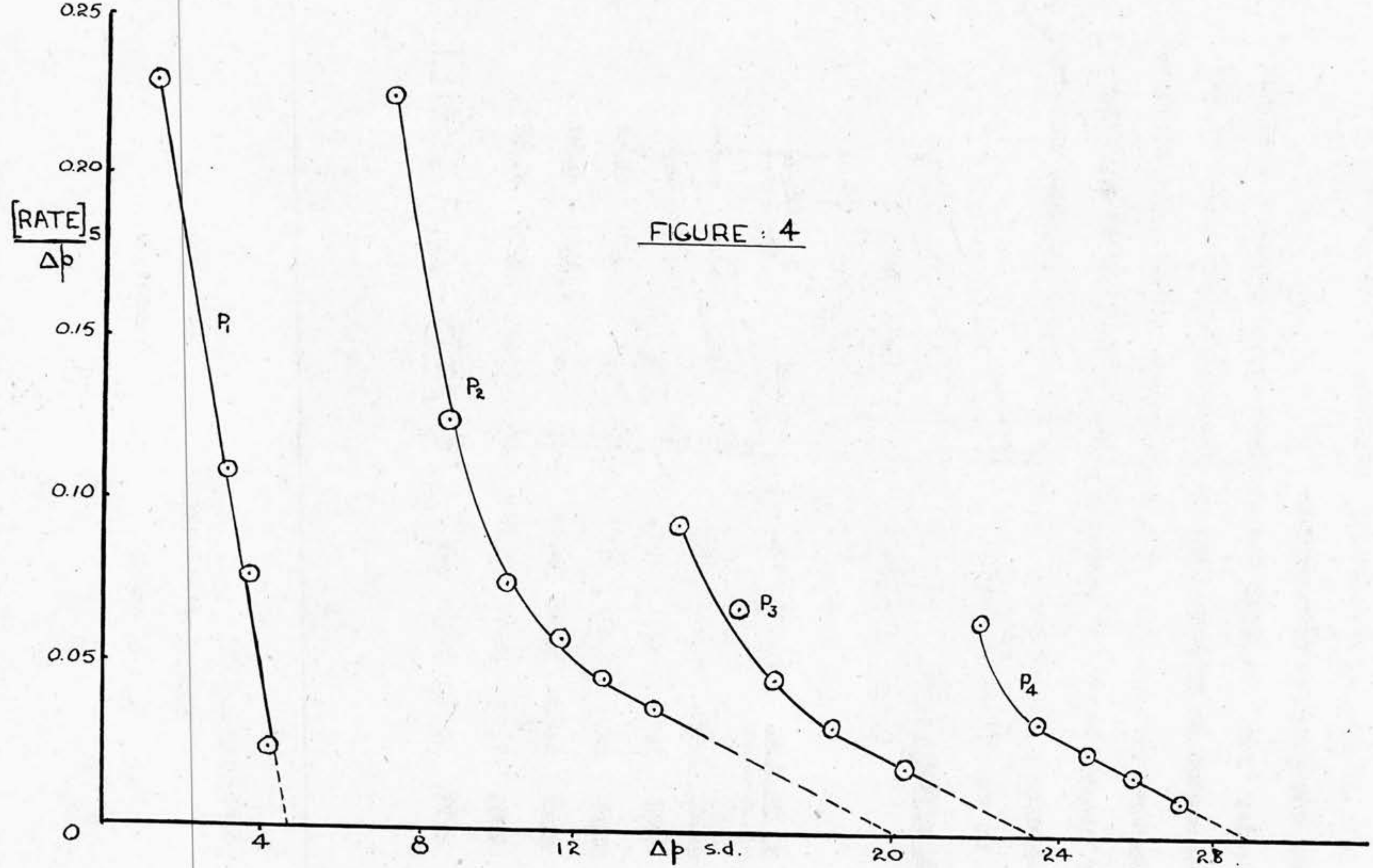
pressure decrease and the constants of the apparatus was 65.5% on the assumption of a unit molar uptake. It can therefore be concluded that one mole of oxygen has combined with one mole of rubrene during the reaction.

As they stand the rate curves in Graph I:h are not easily compared with one another. If the reaction (corresponding to the final portions of the rate curves) is truly unimolecular then the rate will depend on the concentration of reactive material on the surface and this factor has been varied from one pressure to another. The plot of $(\Delta p_{\infty} - \Delta p)$ against the rate, where Δp_{∞} is the extrapolated uptake of oxygen at zero rate at a particular pressure, should result in the oxygen pressure being the only variable. Such a plot is shown on Graph I:i.

Again the reaction appears to be two stage and apparently neither of the rate constants are markedly pressure dependent. The rate constant for the reaction at the lowest oxygen pressure seems to exceed that at 10 mm. This observation is puzzling but may be due to only the faster stage occurring at the lower pressure. This postulate would necessitate the rate being limited by the surface concentration of oxygen.

One other method of clarifying the relation between the rate and the oxygen pressure is depicted on Figure 4., where the 'rate per molecule of reactant', or $R_{\sigma}/\Delta p$, is plotted against Δp. This method eliminates the assumption of an extrapolated uptake. It can be observed from this curve that the reaction proceeds in an identical manner regardless of the pressure, apart from the fact that the respective rate curves are displaced along the p-axis. The /

FIGURE : 4


0.25
0.20
0.15
0.10
0.05
0
$\frac{[\text{RATE}]_S}{\Delta p}$
P_1
P_2
P_3
P_4
4
8
12
20
24
28
Δp s.d.

The results have indicated therefore that an increase of pressure over a film of rubrene effectively increases the amount of rubrene available for reaction with oxygen.

Similar 'runs' in which the absolute oxygen pressure over the film was varied in different graded steps during the course of the reaction were carried out. The rates, expressed as scale divisions per 'n' minutes where 'n' depended on the reactivity of the film under examination, are quoted at their respective pressure decrease values in the following tables.

Experiment I:35.

Weight of rubrene	1.94 mg.
Vessel volume	55.8 mls.

P_1 10.5mm.		P_2 19.9mm.		P_3 50 mm.		P_4 100mm.	
Δp	R_2	Δp	R_2	Δp	R_2	Δp	R_2
0.88	1.75	4.35	0.71	7.19	0.78	10.06	0.32
2.17	0.83	5.11	0.75	7.85	0.53	11.54	0.12
2.86	0.56	5.73	0.54	8.36	0.49	12.16	0.09
2.34	0.41	6.40	0.39	8.88	0.45	12.50	0.07
2.70	0.30	6.54	0.30	9.22	0.34		
				9.50	0.22		
				9.70	0.18		
				9.84	0.10		

Experiment I:36.

Weight of rubrene	4.11 mg.
Vessel volume	84.0 mls.

P_2 /

P_2 (10mm.)		P_3(50mm.)	
Δp	R_{20}	Δp	R_{20}
4.20	2.60	11.0	0.50
6.10	1.20	11.55	0.35
7.15	0.90	12.00	0.40
7.90	0.59	12.35	0.30
8.40	0.42	12.65	0.29
8.81	0.40	12.90	0.22
9.20	0.38		
9.54	0.31		

P_1:0.40 mm.

The small uptake combined with the very low value of the rate only allowed an estimation of the total uptake and not a reproduction of the pressure-time curve.

Experiment I:37.

Weight of rubrene 4.11 mg.

Volume of vessel 84.0 mls.

P_1 (10mm.)		P_2 (28mm.)	
Δp	R_{20}	Δp	R_{20}
2.60	5.19	10.75	0.90
5.80	1.81	11.55	0.70
7.55	1.10	12.20	0.60
8.54	0.88	12.73	0.45
9.29	0.62	13.18	0.45
9.80	0.41	13.10	0.40
10.16	0.29	13.82	0.25
		14.25	0.20

P_3 (100mm.)

The small uptake combined with thermostatic fluctuations only allowed an estimation of the total uptake and not a reproduction of the pressure-time curve, at 100 mm.

Experiment I:38.

Weight of rubrene 4.11 mg.

Vessel volume 55.8 mls.

(10mm.) P_1 /

(10mm.) P_1		P_2 (50mm.)	
Δp	R_{1o}	Δp	R_{1o}
0.58	1.13	4.40	0.60
1.52	0.78	4.90	0.39
2.12	0.43	5.24	0.31
2.52	0.35	5.55	0.31
2.84	0.31	6.15	0.28
3.12	0.23	6.20	0.22
3.32	0.18	6.35	0.77
3.49	0.16	6.56	0.17
3.64	0.13	0.73	0.16
3.75	0.09	6.90	0.18
3.83	0.09		
3.91	0.06		
3.97	0.05		

The analysis results and the extrapolated uptakes from the above experiments are listed in the table below

Graph /

Graph IJ %	Reaction(calc.)	Analysis%	Oxygen Pressure mm.	Extrapolated Uptake %
34			1.18	10.7
			10	48
			30	56
	65	65.5	100	70
35			10	19.8
			20	32.7
			50	45.0
	58	54	100	61.6
36			0.4	7
			10	27
	31	30	50	33
37			10	11
			28	23.5
	25	27	100	25
38			10	9.0
	15.2	14.8	50	16.8

The variation of the extrapolated uptakes, expressed as percentages of the total surface concentration, with the absolute oxygen pressure is indicated in Graph I:j. It has been observed throughout this work that although a film may react to the extent of say 60 - 70%, another, apparently prepared in exactly the same manner with the same sample of rubrene and substrate, might react to only 15%. As a consequence of this inherent irreproducibility no importance has been attached to actual weight of rubrene deposited on to the film. In other words the amount of oxidisable material on the surface is purely determined by that specific surface.

In /

In 'runs' I:37 and :38 where the films were relatively uncreactive the plot of the extrapolated uptake against oxygen pressure indicated that these factors might be related by the equation:

$$\% \text{ Reaction} = a.P/1 + b.P \text{ -------------(3)}$$

where a and b are constants for a particular film. The rate curves for these reactions were exactly linear over the complete range.

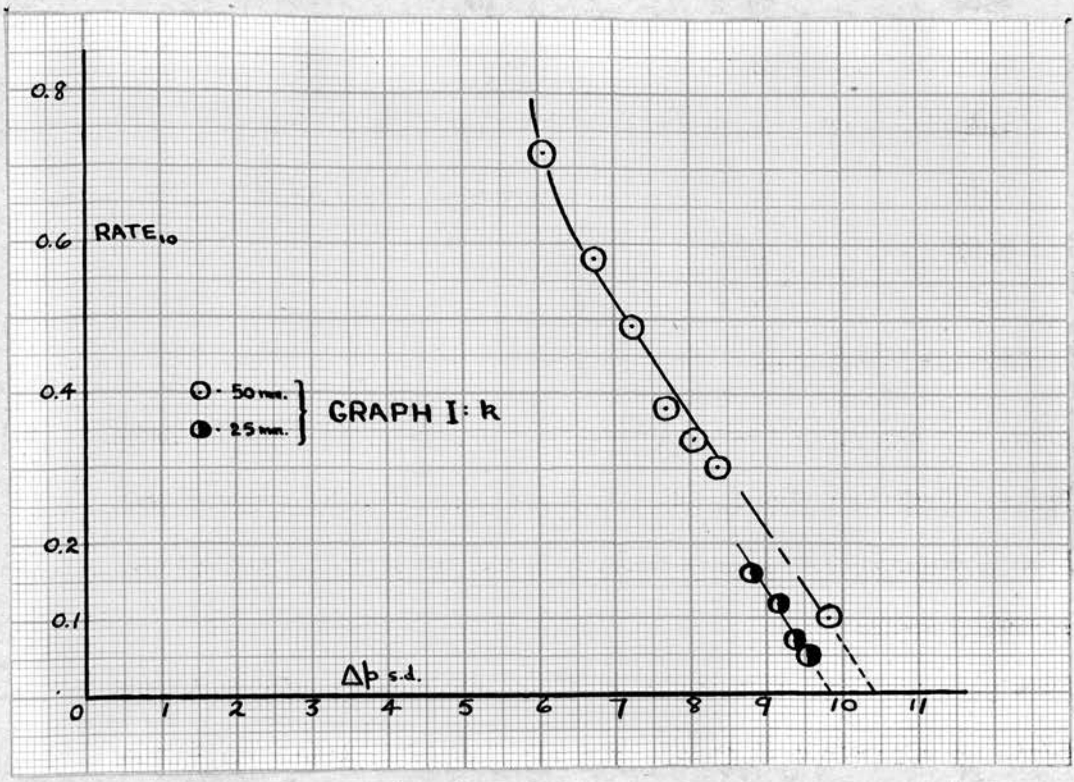
The effect of increasing the oxygen pressure during a reaction has now been investigated but prior to theorising further on the results, it was decided to investigate the reverse effect, i.e., to study the variations in rate which might occur when the oxygen pressure be reduced during the course of a reaction.

Experimental:

Gauge sensitivity	0.055 mm./ s.d.
Vessel volume	55.8 mls.
Weight of rubrene	4.11 mg.
Substrate	Jena glass, 0.2gm.

A film was prepered and evacuated for 15 hours with the oil and diffusion pumps. The photo-oxidation was carried out in 50mm. of oxygen until the rate of uptake of oxygen dropped to about 0.5 scale divisions per 10 minutes. At this stage the light was extinguished and the pressure reduced to 25mm. by evacuation. Illumination was then continued until enough reaction had occurred to enable a portion of the rate curve at this pressure to be drawn. The final stage, therefore, before the analysis, consisted of re-illuminating the 50mm. oxygen for a short time.

The /


0.8
0.6
RATE10
0.4
⊙ - 50 mm.
◐ - 25 mm.
GRAPH I: k
0.2
0.1
Δp s.d.
0
1
2
3
4
5
6
7
8
9
10
11

The actual results as plotted on Graph I:k are given below.

Δp s.d.	Rate/10mins.	Δp s.d.	Rate/10mins.
2.5	4.50	8.80	0.16
5.1	1.20	9.15	0.12
6.06	0.72	9.38	0.07
6.71	0.58	9.53	0.05
7.24	0.49	Increased to 50 mm.	
7.67	0.38	9.80	0.10
8.03	0.34		
8.35	0.30		

Reduced to 25 mm.

Once the oxidation has apparently commenced to tend towards a definite limit and the absolute oxygen pressure is reduced and the film instantly re-illuminated, the reaction still occurs at a measurable rate.

The rate and the extrapolated limit thus falls off at lower pressures as expected, although the extrapolated value at 25 mm. was not, under these conditions, markedly different from that at 50mm.

The Variation of the Rate of Photo-oxidation of Rubrene /

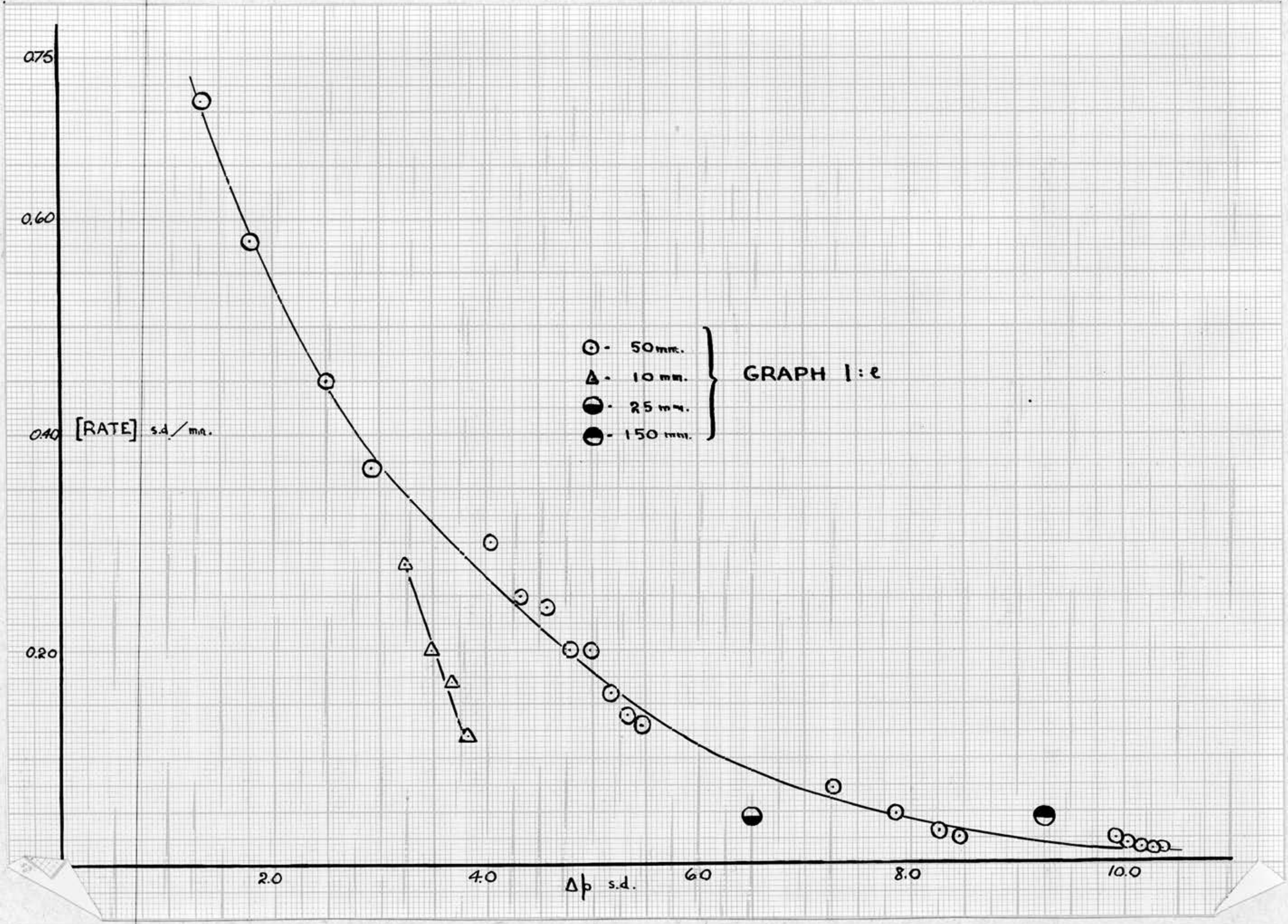
The Variation of the Rate of Photo-oxidation of Rubrene with the Absolute Pressure of Oxygen.

The experiments described in this section were conceived as a result of the series of observations which have been made throughout this section. One of the main difficulties in the interpretation of the past results has been the inability to determine accurately the true form of the rate curve. This difficulty has been due, in the main, to the difference in the order of the rate of uptake of oxygen in the initial and final stages of the reaction. The following method was unambiguous and independent of the law or laws governing the photo-oxidation.

Experimental:

Gauge sensitivity	0.0038 mm./s.d.
Vessel volume	85.7 mls.
Temperature	21.5°C.
Weight of rubrene	4.11 mg.
Substrate	0.2 gm.

The film was evacuated for 15 hours and illuminated in an oxygen pressure of 50mm. of mercury. Readings of the gauge pointer deflection were recorded every minute until a few points on the rate curve were obtained. The pressure was then reduced to 10mm. and further readings taken every minute. At this stage the pressure was again raised to 50mm. and the original curve continued. By now, the rate of pressure change was rather slow but in order to counteract this effect the 'rate interval' was proportionately increased during subsequent illuminations. Various pressure reductions and increases were effected although after each change the pressure was brought back to 50mm. and the standard curve continued. /


GRAPH 1:2
⊙ - 50 mm.
△ - 10 mm.
◒ - 25 mm.
◓ - 150 mm.
[RATE] s.d./mn.
0.75
0.60
0.40
0.20
2.0
4.0
6.0
8.0
10.0
Δp s.d.

continued. As little as possible of the reaction was carried out at any pressure other than 50mm. The plot of the rate, expressed in scale divisions per minute, against the total change in pressure that occurred up to that point is shown in Graph I:ℓ. The actual results obtained in one experiment were as follows:

Δp	Rate	Δp	Rate
0.50	0.99	7.26	0.072
1.54	0.71	7.86	0.048
1.79	0.58	8.26	0.032
2.50	0.45	8.45	0.026
2.92	0.37		(e)
	(a)	9.25	0.045
3.24	0.28		(f)
3.48	0.20	9.92	0.025
3.67	0.17	10.03	0.015
3.81	0.12	10.16	0.011
	(b)	10.26	0.010
4.05	0.30	10.36	0.009
4.32	0.25		
4.57	0.24		
4.79	0.20		
4.99	0.20		
5.17	0.16		
5.32	0.14		
5.45	0.13		
	(c)		
6.50	0.045		
	(d)		

(a) Decreased pressure to 10mm.

(b) Increased pressure to 50mm.

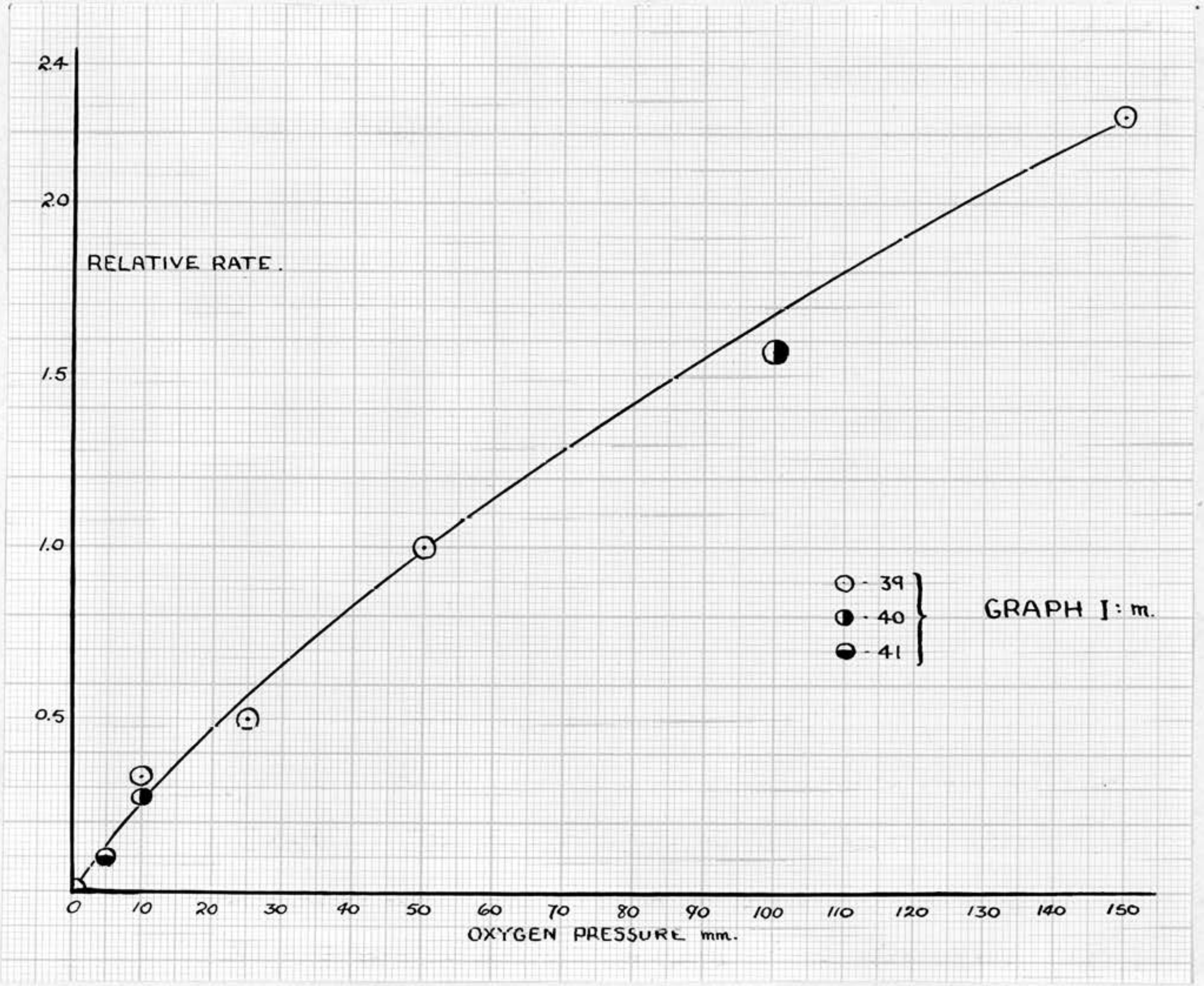
(c) Decreased pressure to 25mm.

(d) Increased pressure to 50mm.

(e) Increased pressure to 150mm.

(f) Decreased pressure to 50mm.

A /


RELATIVE RATE.
2.4
2.0
1.5
1.0
0.5
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
OXYGEN PRESSURE mm.
⊙ - 39
◐ - 40
◒ - 41

GRAPH I: m.

A detailed examination of the rate curve on Graph I:l yielded values for the rates, at the various pressures, relative to the rate at 50mm. on the same concentration co-ordinate. Similar experiments were carried out under the same conditions but at different pressures. Graph I:m shows a plot of relative rate against oxygen pressure while the final results are tabulated below:

No.	Relative rate	Oxygen Pressure (mm.)
39	0.327	10
	0.50	25
	2.25	150
40	0.266	10
	1.57	100
41	0.1	5

The curve on Graph I:m is drawn from the equation:

$$\text{(Relative) Rate of Reaction} = 2.4 \times 10^{-2}\, P_{O_2}/1 + 4.0 \times 10^{-3} P_{O_2} \quad \text{--(4)}$$

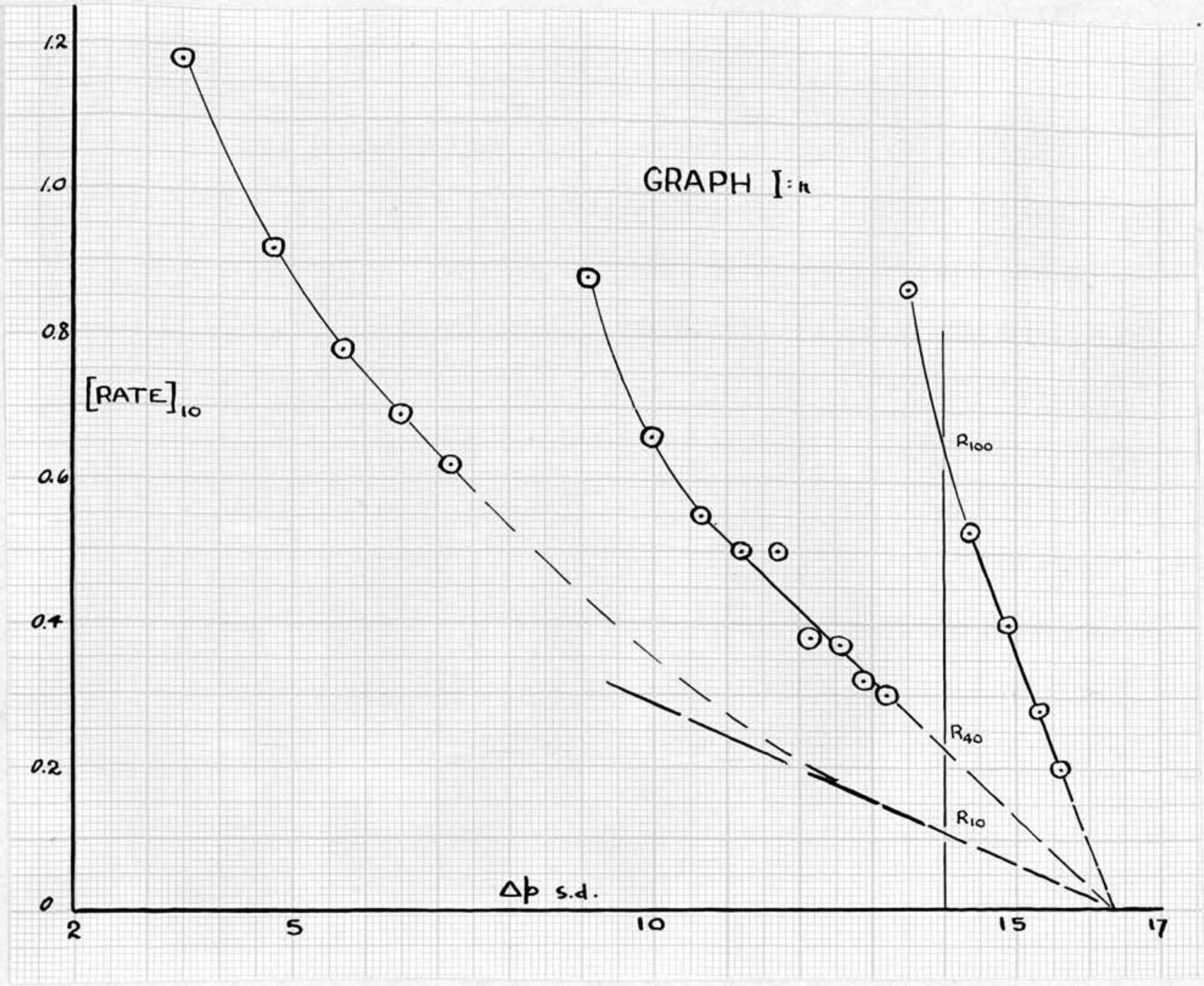
where P_{O_2} is the pressure (mm.) of oxygen over the film. When P_{O_2} is small the rate is proportional to the pressure. The theoretical ?, continuous (straight) line is drawn in the diagram. It can be seen that the rate is virtually proportional to the pressure below 25mm.

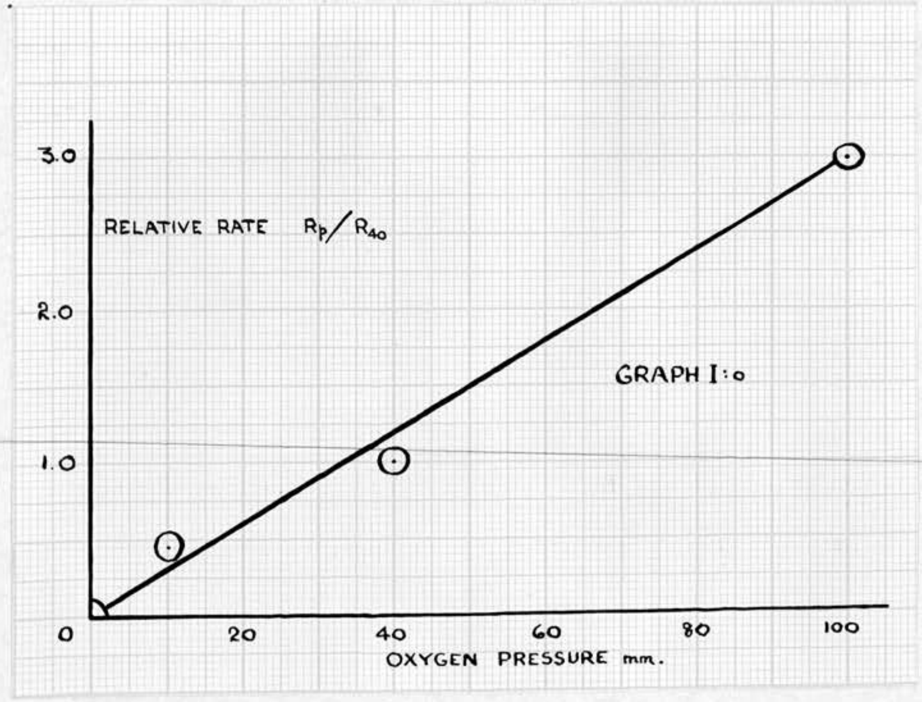
Typifying the unpredictability of the type of surface involved in this series of experiments was the following fortuitous result:

Experimental:

Weight of Rubrene	4.11 mg.
Vessel volume	84 mls.
Weight of substrate	0.2 gm.
Illumination	Osira light system.

The /


1.2
1.0
0.8
0.6
0.4
0.2
0
GRAPH I:n
[RATE]$_{10}$
R_{100}
R_{40}
R_{10}
Δp s.d.
2
5
10
15
17


3.0
2.0
1.0
0
RELATIVE RATE R_p/R_{40}
GRAPH I:o
20
40
60
80
100
OXYGEN PRESSURE mm.

The film was first illuminated at 10mm. oxygen pressure for one hour after which the pressure was raised to 40mm. The plot of the rate, expressed as scale divisions per 10 minutes, against the pressure change is shown in Graph I:n and the actual results are tabulated below. After 100 minutes the pressure was raised to 100mm. and the film illuminated for a further 75 minutes. At this stage the film was left in darkness in 100mm. of oxygen and then re-illuminated. No further pressure decreased was observed. The film was then analysed for rubrene and 37.5% of the initial amount was found to have disappeared. The extent of the reaction as calculated from the pressure decreased was 35%.

P_1 (10mm.)		P_2 (40mm.)		P_3 (100mm.)	
Δp	R_{10}	Δp	R_{10}	Δp	R_{10}
3.50	1.18	7.80	1.31	13.50	0.87
4.75	0.92	9.10	0.88	14.35	0.53
5.70	0.78	9.99	0.66	14.90	0.40
6.50	0.69	10.65	0.55	15.30	0.28
7.20	0.62	11.20	0.50	15.60	0.20
		11.70	0.50		
		12.15	0.38		
		12.55	0.37		
		12.89	0.32		
		13.20	0.30		

It is apparent from the rate curves that the extrapolated uptakes at 100mm. and 40mm. are identical; and the results at 10mm., where /

where extrapolation is uncertain, are not in opposition to this conclusion. The plot of the relative rate of reaction at the three pressures, as extracted from this Graph by calculating the ratios R_{100}/R_{40}, R_{40}/R_{40} (and R_{10}/R_{40}) along the ordinate A, is shown in Graph I:o. This curve indicates that the relative rate in this case was virtually proportional to the oxygen pressure over the examined range. Another example of this type was never encountered during the course of the work.

Investigations on the Thermal and Photochemical Reversibility /

Investigations on the Thermal and Photochemical Reversibility of the Oxidation at Room Temperature.

Many experiments were carried out in which the illumination was interrupted and the film evacuated at 10^{-4} mm. Hg. (McLeod) for varying times up to 30 hours. It was hoped to detect thermal reversibility by noticing an increased rate of photo-oxidation when the film was re-irradiated in oxygen. No such increase was apparent.

Similar experiments were attempted where during the course of a photo-oxidation at 50mm. oxygen the film was evacuated while the illumination was continued. In this way it was hoped to determine whether or not the reaction was photochemically reversible by observing any change in rate which might occur when the film was re-illuminated in oxygen. No change in rate could be detected.

In one experiment a film was allowed to react in oxygen until the rate became immeasurably slow. The film was then evacuated at 10^{-4} mm. Hg. for 60 hours whilst being constantly illuminated. On introducing 50mm. of oxygen no further reaction was detected. The resulting analysis of the film residue provided a value for the percent reaction which was in agreement with the value calculated from the original pressure change.

It was by no means impossible that, under the conditions of the experiments described in this section, the peroxide product itself might be attacked by oxygen or might rearrange in the presence of oxygen. In order to clear up this point a film of the pure peroxide was irradiated in 50mm. of oxygen. No resultant pressure /

pressure change was observed over a period of 150 minutes. No change of colour was detected in the film residue.

Before completing this work on the photo-oxidation of rubrene an attempt was made to oxidise a sample of pure crystalline rubrene, deposited in the form of a film, not from a solution but as a slurry in a very small amount of solvent.

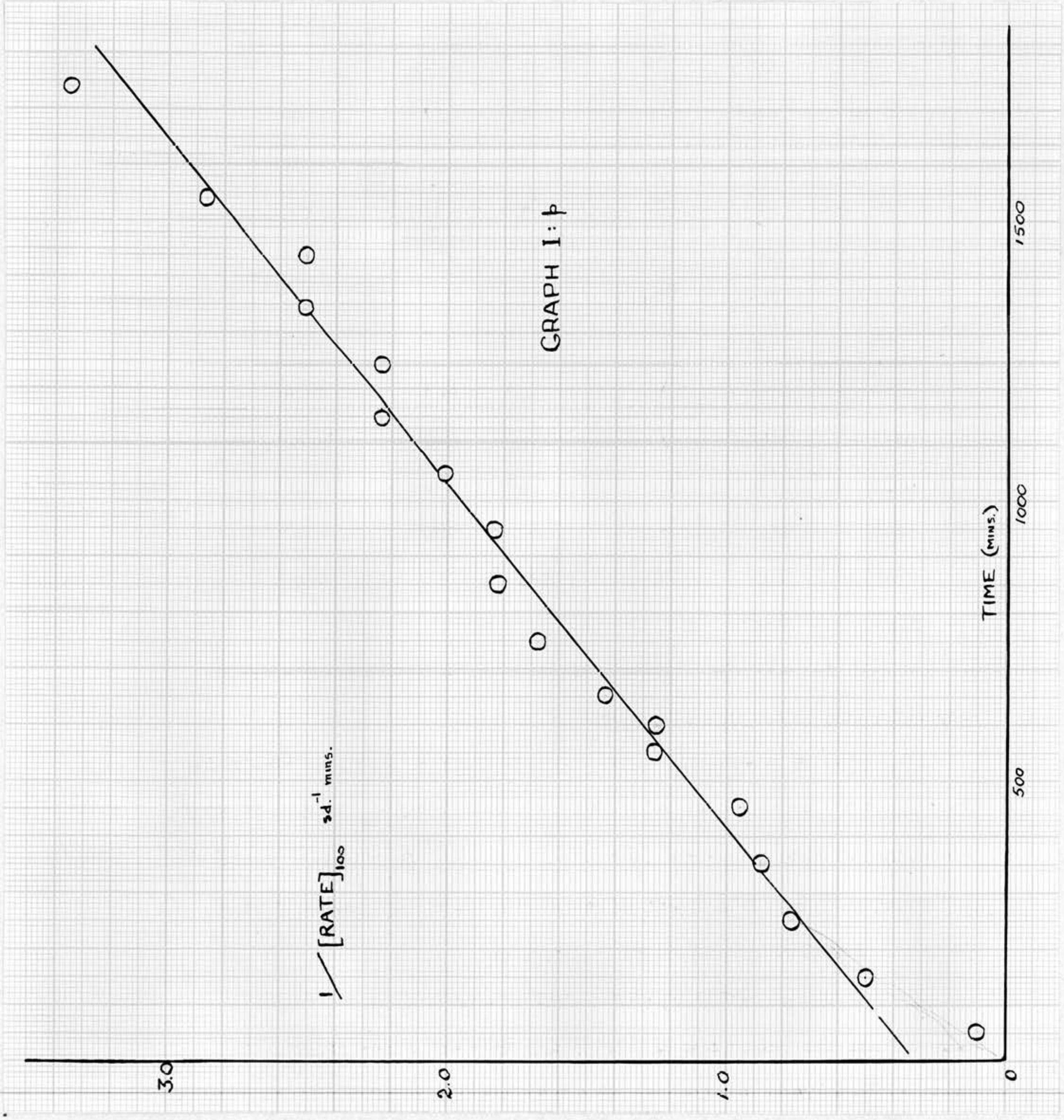
Experimental:

Weight of Rubrene	11.92 mg.
Weight of Jena glass	0.1 gm.
Gauge Sensitivity	0.004 mm./s.d.
Vessel Volume	51.0 mls.
Oxygen Pressure	49.0 mm.
Temperature	21.5°C.

The film was prepared by adding 2 mls. of distilled benzene to the vessel containing an intimate mixture of rubrene crystals and Jena glass and rotating the whole gently while pumping off the benzene at 40°C. The vessel was then transferred to the apparatus in darkness and after evacuating the system for 15 hours at 10^{-4}mm. was illuminated with the Osira lamp set up.

The value of the pressure decrease at various times is given in the following table as Δp scale divisions:

Time /


GRAPH I: b
1/[RATE]₁₀₀ sd.⁻¹ mins.
TIME (MINS.)
0
500
1000
1500
1.0
2.0
3.0

Time (Mins.)	Δp	Time (Mins.)	Δp	Time (Mins.)	Δp
0	0	1	1.7	2	2.5
3.5	2.9	5	3.7	7.5	4.5
10.5	4.8	14	5.4	20	6.0
25	6.7	30	6.9	36	7.6
40	7.8	45	7.9	50	8.2
55	8.6	62.5	8.7	67	8.8
71.5	8.9	78.5	9.5	85	9.7
90	9.8	102	10.1	140	11.1
183	11.8	200	11.8	214	11.9
260	12.7	320	13.0	400	13.9 (A)
422	14.1	465	14.8	565	15.7
605	16.0	650	16.9	700	17.1
765	17.7	1770	22.0	2040	22.1
2160	22.8				

At (A) the film was left in darkness and in 50mm. of oxygen overnight and then reilluminated.

The plot of reciprocal rate against time is shown in Graph I:p from which it may be concluded that the experimental values of time and pressure change are related by an equation of the type shown in Equation (1). The total pressure decrease corresponded to a 13% utilisation of the available rubrene.

p31

It was not possible to fit a double exponential to these results but the log plots of functions involving the estimated value of the final uptake Δp_{∞} did not exclude a multistage process. The rate of the initial stage was, however, too fast compated with the final stage to enable the constants to be calculated accurately.

Throughout /

Throughout this section the importance of the solvent and the mode of deposition of the rubrene film have been emphasised. Rubrene crystals, dried and ground, when placed in an oxygen atmosphere in the reaction vessel produced no pressure decrease on illumination. On adding a little solvent to wet the crystals intimately mixed with Jena glass and subsequently drying the crystals 'in vacuo' and in the dark resulted in the formation of a photo-oxidisable film. Solvent is thus necessary to bring about the photo-oxidation.

The exact role of the solvent is not clear but experiments on films degassed at 130°C. have indicated that solvent is probably not involved in the oxidation stage. In the presence of Jena glass the rubrene film may be deposited in such a manner, i.e., as a solid solution or part crystal with many surface irregularities, as to render it oxidisable.

Slow Gaseous diffusion as a Rate Controlling Factor /

Slow Gaseous diffusion as a Rate Controlling Factor

A series of experiments were carried out in which the film was left in an oxygen atmosphere for long periods of time before being illuminated. This operation did not result in any marked change in the form of the pressure-time curve. Some films were 'soaked' in oxygen after or during the reaction and no apparent change in the form of the rate curve was observed on re-illumination. It would therefore follow that a slow gas diffusion process was not a rate determining factor in the reaction. The possibility exists, however, that diffusional channels may only be produced on irradiation of the film in which case these experiments could not be expected to detect any change.

Similar experiments to the ones described above but employing air were performed. Again no dark reaction was detected.

The Photo-oxidation of Rubrene

Discussion of the Results

Absorption spectra and melting point determinations have indicated that apart from samples A and B, which were not chromatographed, the rubrene samples employed were not demonstratively impure. Repeated analyses of the film residues served to prove that the samples under question contained no appreciable impurity which was oxidisable under the experimental conditions. Owing to the relative solubilities of the peroxide and the hydrocarbon in the crystallising solvent it is doubtful whether the process of recrystallisation removed peroxide impurity from the rubrene (53). Experiments indicated, however, that no pressure decrease occurs when a film of the peroxide is illuminated in oxygen. Thus small quantities of the peroxide, i.e., 1 - 2%, as impurity in the rubrene samples would not affect the final result of the photo-oxidation.

The magnitudes of the total oxygen uptakes by rubrene on thallous bromide crystals never approached the values obtained using a Jena glass substrate. This was the case regardless of the nature of the depositing solvent. It would appear that thallous bromide in this form did not photo-sensitise the oxidation of rubrene either at low or at high oxygen pressures. It is possible that the organic depositing solvents had some effect on the crystalline properties of the thallous bromide or alternatively that the thallous bromide crystals affected the precipitation of 'photo-oxidisable' rubrene. On the other hand there is no evidence to show that the relative energies of the excited and conductance bands /

bands of the adsorbate and substrate should permit electron transfer in this case.

When Jena glass was the substrate the initial experiments, in which acetone was used as the depositing solvent, the oxygen uptakes were small. With benzene as solvent, however, the uptakes were larger although irreproducible. It is not thought that this fact has any more significance than that the more polar acetone molecule will be much more strongly bound than benzene to the surface of the glass and to rubrene. The acetone will thus contaminate the surface to a greater extent or simply tend to deposit the rubrene in a manner which renders it less accessible to the oxygen.

The magnitudes of the oxygen uptakes have been very erratic, varying from 10 - 65% of the total available rubrene on the surface, suggesting that the form of the surface was quite irreproducible and that mechanical imperfections might have played a big part in determining the rate and amount of oxygen uptaken.

The experimental observations that the pressure change over a film of rubrene varies with time according to the equation:

$$\Delta p = A.\mathrm{Log}_{10}\,(Bt + 1) \text{ ------------ } I:(1)$$

or

$$\frac{dp}{dt} = \mathrm{Constant}\ e^{-A.\,\Delta p} \text{ ------------ } I:(2)$$

may be explained on the basis of film formation on the surface. Such a law has been found to govern the oxidation of a few metals and the theories that have been evolved are based on the concept of pores, cracks and blisters of the oxide on the metal surface (54, 66). The appropriate relationship may be arrived at by assuming that blisters, which are impermeable to oxygen molecules, are /

are formed on the surface and that the free surface area available for the trapping of oxygen molecules is greatly reduced as a consequence of the inability of ions to diffuse across the internal blister space. In such a process the rate of film thickening is necessarily determined by the rate of diffusion of ions through the oxide layer and is further limited by the area of metal-oxide contact.

It is difficult to visualise how a similar mechanism be applicable to the oxidation of non-ionic organic crystals, as, in this case it is unlikely that the 'normal' molecules in the crystal lattice would be subject to this type of mobility. It is more likely in the case of rubrene films on Jena glass that the oxidation of the surface layers produces a thin film of peroxide which is impermeable to oxygen and which protects the lower layers from oxidation. In this way the rate of formation of the surface film will be the competing step and thus cause sudden saturation of the pressure-time curves.

If the only rate determining stage in the oxidation is a solid diffusional process then the rate of the reaction will be independent of the surface oxygen concentration when the number of oxygen molecules on the surface is large compated to the number of reactive sites at any time. It would be expected that this condition would be in operation down to quite low pressures, say 1 - 5 mm..

The experimental results indicate that the rate of the reaction is proportional to the surface concentration of oxygen, $[O_2]_{ADS.}$, where this factor is given by the equation:

$$[O_2]_{ads.} = a.P/1 + b.P \text{ -------------------- } (1)\ \mathrm{DI}$$

where P is the oxygen pressure over the film and a and b are constants. This is in accordance with the Langmuir 'isotherm'. In one or two other experiments, however, the rate of reaction, i.e. the rate of uptake of oxygen, appeared to be independent of the oxygen pressure over the film, a fact that would indicate that all film preparations did not oxidise in the same manner or follow the same law. Owing to the uncertain manner of film preparation it is not unlikely that mechanical imperfections may have only been formed in isolated cases. The only alternative oxidation law which will fit the experimental results is that involving a multi-exponential process, i.e., two or more unimolecular reactions occurring simultaneously at different specific rates. Such is the case, of course, at high oxygen pressures when the oxygen pressure does not change appreciably during a reaction.

If the rate of the reaction is proportional to the concentration of adsorbed oxygen then the migration of oxygen to reactive positions must be a controlling factor. The other factor which determines the rate at any time is the concentration of available reactive rubrene on the surface at any time, which is governed by the light intensity.

Although the reaction consists of a series of simultaneous stages, if they are all unimolecular, the actual process of photo-oxidation may be treated as a pseudo-unimolecular reation; the separate rate constants being attributed to various distinct surface properties. These properties are randomly determined by the /

the method of deposition.

Thus it is possible to write:

$$\text{Rate} = k_1 . \left[O_2\right]_{ads.} \text{ ---------------- D.I:(2)}$$

where $$k_1 = k_1^1 . k_2 . \phi \text{ ----------------D.I: (3)}$$

where ϕ is the amount of light absorbed. By analogy with previous work in solution (21) this factor will be taken as being proportional to the first power of the rubrene concentration; i.e.,

$$k_2 . \phi = k_2^1 . \left[\text{rubrene}\right] \text{ -------------- D.I:(4)}$$

The combination of the above equations and substitution from equation (1) D.I: yields:

$$\text{Rate} = a . k_1^1 . k_2^1 . [R]\ P_{o2}\ /1 + b.\ P_{o2} \text{ ----- D.I:(5)}$$

The analysis figures indicate that the factor $[R]$; the rubrene concentration, may be considered as equivalent to $(\Delta p_{oo} - \Delta p)$ at any time, where Δp_{oo} and Δp have the significance described in the text. It may therefore be concluded that:

$$-\frac{dp}{dt} = A . (\Delta p_{oo} - \Delta p) .\ P_{o2}\ /\ 1 + b.\ P_{o2} \text{---D.I:(6)}$$

where the constant A is surface dependent and has two or more discrete values for any one film.

The surface sensitivity of the reaction provides a useful basis for the elucidation of the mechanism of the photo-oxidation as the proposed scheme will have to explain this fact above any other.

The absorption of light by a crystal of the rubrene type will result in the formation of an electron and a positive hole which in the absence of trapping impurities will drift to the surface as an 'exciton'. This energy may be utilised by the surface molecules in /

in a variety of ways.

The primary stage is effectively the absorption of light to produce an excited (singlet) molecule R^{*} on the surface:

$$R + h.v \longrightarrow R^{*} \text{ ------------ } (a)$$

This molecule may lose its excess energy as light (singlet-singlet fluorescence, b.) or by internal degradation (c).

$$R^{*} \longrightarrow R + h.v \text{ ------------ } (b)$$

$$R^{*} \longrightarrow R \text{ ------------ } (c)$$

On the other hand this molecule may lose part of its excess energy resulting in the attainment of the triplet state of the molecule. This process may be visualised as occurring in various ways; the first is shown in equation (d) where collision between excited and unexcited molecules results in the optimum conversion:

$$R^{*} + R \longrightarrow R^{1} + R + \text{light or heat ------- } (d)$$

where R^{1} depicts the long-lived triplet state of rubrene. At this stage the molecule must undergo radical changes in spatial configuration and as such a conversion may be strongly opposed by neighbouring molecules immediate deactivation (e) will be probable:

$$R^{1} \longrightarrow R \text{ --------------- } (e)$$

The next stage is postulated to involve the reversible combination of this long-lived diradical with oxygen to form an unstable peroxide RO_2^{*} (f):

$$R^{1} + O_2 \rightleftharpoons RO_2^{*} \text{ ------------ } (f) \text{ and } (g)$$

It is conjected ured that the unstable peroxide may still contain the spatial configuration of diradical and thus may decompose readily into oxygen and rubrene, the reaction (g), requiring a very low activation /

activation energy. Finally, irreversible stabilisation may occur as indicated by equation (h):

$$RO_2^{*} \longrightarrow RO_2 + \text{energy} \text{ ------------- (h)}$$

If the stage (h) is very rapid, at no time should a very large concentration of RO_2^{*} be allowed to build up. Further, the dissociation pressure of oxygen will be determined by the equilibrium constant of the reaction (h), if the solid phases are not in unit activity states.

An examination of this mechanism under steady state conditions results in the following equation for the rate of decrease of oxygen pressure:

$$-\frac{d\,O_2}{dt} = \frac{\Phi.a.b.[R]}{1 + a.[R]} \cdot \frac{[O_2] - [O_2]_e}{1 + [O_2].c} \text{ ---------- D.I: (7)}$$

where $[O_2]$ is the gas pressure of oxygen and $[O_2]_e$ the dissociation pressure of oxygen. The constants have the following values:-

$$a = k/k_b + k_c$$

$$b = k_f.k_e$$

$$c = k_f.k_g/k_e(k_g + k_h)$$

Although it would not be possible to detect the reversible oxidation stage by pressure measurement, over the non-pure crystalline deposit, a study of the photoconductivity of anthracene has provided useful evidence in favour of such a scheme.

The photoconductivity in the surface layers of anthracene crystals has been found to increase considerably over its vacuum level when it is measured in the presence of air or oxygen (<u>55</u>). The increased photocurrent is attributed to the photo-oxidation of the surface, both light and air being necessary to produce the effect /

effect. The results could only be explained by postulating a two stage process for the formation of the surface oxide. The intermediate step involved a highly unstable peroxide while the product was believed to be the transanmular peroxide. These authors (55) consider that this stable peroxide may slowly dissociate into oxygen and the parent hydrocarbon, which seems, to the writer, to be an invalid assumption quite contrary to the results of Dufraisse on the decomposition of anthracene photo-oxide (56). It also seems remarkable that the destruction of the conjugated double bond system in anthracene should result in an increase in the mobility of the current carriers.

Several workers have reported that oxygen quenches the fluorescence of anthracene and other hydrocarbons but that the fluorescence returns when the oxygen is pumped out of the system or replaced by nitrogen. As this effect is not caused by dark oxygen absorption it is believed that an unstable peroxide is formed (57.58)

As far as the effects of variations of oxygen pressure and probably absorbed light intensity, experimentally measured as pressure change, are concerned the deduced formula is in accord with experiment; on the assumption that the reaction is unimolecular. The factor $a.R/1 + aR$, however, presents a problem. In order that this cancel out of the kinetic equation the ratio $k_d/k_b + k_c$ must be large in comparison with unity. The majority of the molecules which absorb light must then eventually arrive in the triplet energy state; they may subsequently react with oxygen or degrade to normal rubrene. In other words the efficiency of fluorescence, in the oxidisable material, must be very low, the fluorescence /

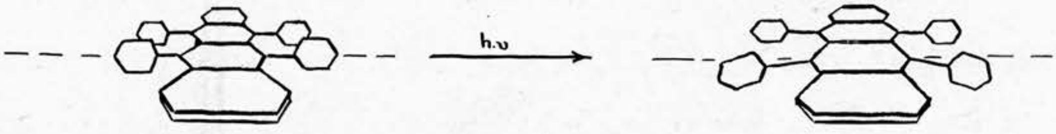
fluorescence being 'quenched' by frequent collisions of excited with unexcited molecules or with oxygen.

It is now considered opportune to mention the result of some visual observations on reacted and unreacted films. After reaction with oxygen, when only un~~c~~reactive rubrene remained, the films were yellow in colour until solvent was added to the film residue when the red colour of unreacted rubrene was again evident. Before reaction the films appeared red in varying degrees. The 'redness' of the surface enabled an approximate value of the oxygen uptake to be estimated; a very red film reacted to a greater extent than a slightly red film. Very often films were prepared which only reacted to about 5% and such films appeared yellow. As the colour of the fluorescence of rubrene is yellow it seems reasonable to conclude from the above observations that highly fluorescent rubrene was not capable of reaction with oxygen under the experimental conditions. It is suggested that the yellow parts of the film constituted the pure crystalline material while the red areas consisted of rubrene deposited by the solvent in a manner which rendered it reactive. The rubrene in the latter state was probably in solid solution.

The fluorescence of many adsorbed dyestuffs is quenched by oxygen at low pressure (59). Such a process may be occurring in this case although it is unlikely that it will affect the actual photo-oxidation rate. No general simple relation between the quenching efficiency of oxygen and rate of photo-oxidation exists and the quenching process probably only involves the formation of unstable intermediates which are able to convert the electronic energy by internal conversion into thermal energy (60).

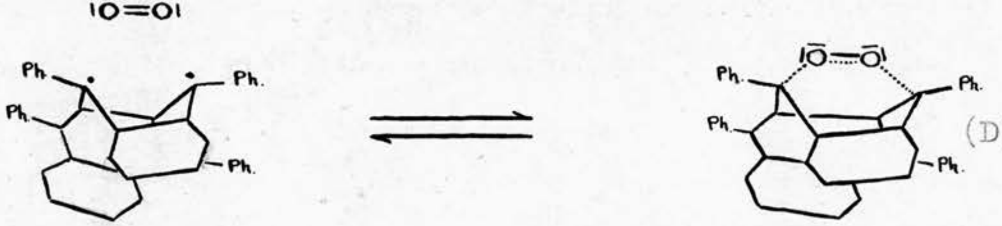
It /

It is now the intention to represent the photo-oxidation of rubrene in a pictorial manner in order to lend some significance to the postulated intermediates. Rubrene (A) absorbs a light quantum to produce the molecule (B) which is capable of fluorescence. This molecule will have a lifetime of about 10^{-8} seconds and will be slightly distorted.



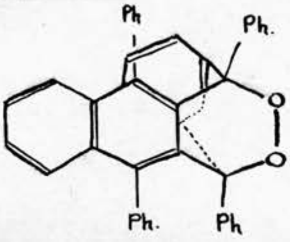
(A) (B)

Within its lifetime (B) will collide with a neighbouring molecule resulting in the formation of the diradical with a corresponding loss in energy. This energy loss is accompanied by a configurational change and the molecule (C) results. (C) may degrade to rubrene or combine with oxygen to form the unstable peroxide (D) which is pictorially represented below.



(C) (D)

The unstable (D) rapidly reverts into the stable oxide (E), this process involving a further change in the spatial arrangement of the atoms. This change is permanent and the peroxide (E) is probably stabilised by the surface.



(E)

This mechanism emphasises one of the main features of polynuclear hydrocarbon oxidation; i.e., the necessity for a strongly mesomeric structure which can still exist, after bond rupture, by virtue of its resonance energy (61).

How does the mechanism, as just described, fit in with the results at low oxygen pressures? No pressure below which oxidation would not occur was detected. The high instability of the peroxide intermediate combined with its ease of stabilisation in the direction of configuration rather than decomposition and the very slight difference in structure between the diradical and the excited peroxide would suggest that the activation energies of the forward and reverse stages (k_g and k_h) be markedly different, in which case the standard free energy of formation of oxygen from the peroxide will be large. Assuming this is about 10Kg.cals./mole at 25°C., for example, then the corresponding equilibrium pressure of oxygen would be:

$$\left[O_2\right]_e = 760.e^{-10,000/R.T} = 3.4 \times 10^{-5} \text{ mm. Hg.}$$

Such a dissociation pressure would not be detectable with the apparatus employed.

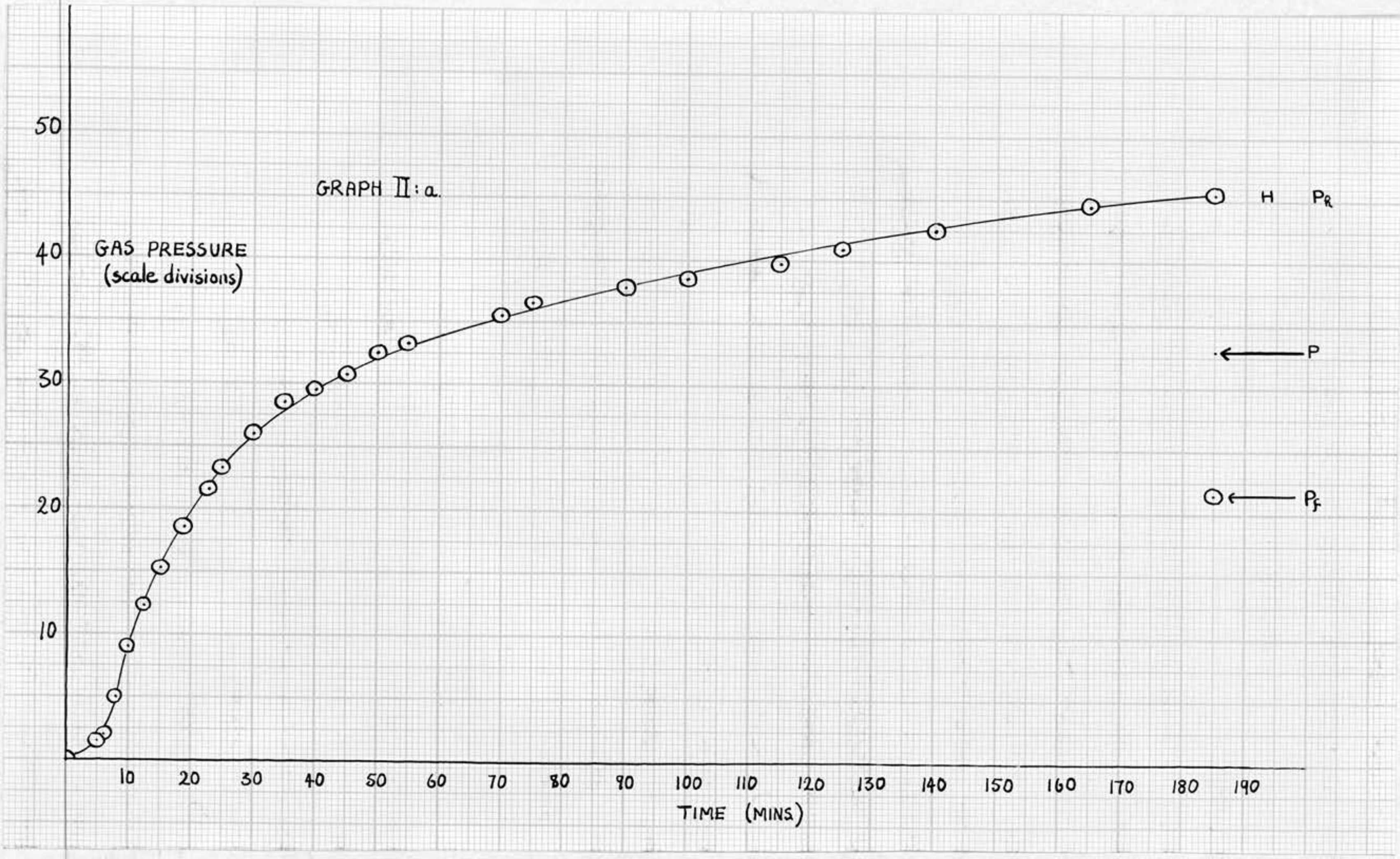
On the other hand if the rubrene is in solid solution the rate expression would become complicated with terms involving the molar fractions of the solid phases.

Again on the basis of a solid solution the variations of total uptake of oxygen with absolute oxygen pressure might be explained. At the lowest pressure oxygen dissolves in the solution until the attainment of solution equilibrium, in the dark. The film is then illuminated and the oxidation proceeds until chemical equilibrium is /

is reached; the position of the chemical equilibrium is governed by the concentration of oxygen in the solution which is in turn determined by the gas pressure. On increasing the pressure the oxygen concentration and hence the position of equilibrium is altered thus more reaction occurs. The position of the photochemical equilibrium will depend on other factors including the light intensity, which is in accord with experiment. The fact that little variation in rate, apart from that casued by the 'change' in concentration of reactive material, brought about by changes in oxygen pressure, was observed when the pressure was less than 1 mm. suggests that the rate of dissolution of oxygen in the solid solution might here have been a determining stage. At higher pressures, when the solution is saturated with oxygen, no such effect should be detectable.

A reduction of the oxygen pressure after a period of oxidation at a particular pressure did not cause any pressure increase on irradiation at the new pressure. This fact supports the contention of a two stage process involving a stable and an unstable peroxide being responsible for the apparent absence of reversibility.

The mechanism of the photo-oxidation of rubrene will be discussed further at the end of Section IV following a knowledge of the energetics of the decomposition of the peroxide.


GRAPH II: a.
GAS PRESSURE
(scale divisions)
50
40
30
20
10
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
TIME (MINS)
H
P_R
P
P_f

EXPERIMENTAL SECTION II.

The Thermal Decomposition of Thin Films of Rubrene Peroxide on Jena Glass,

'In vacuo'.

Experimental Procedure

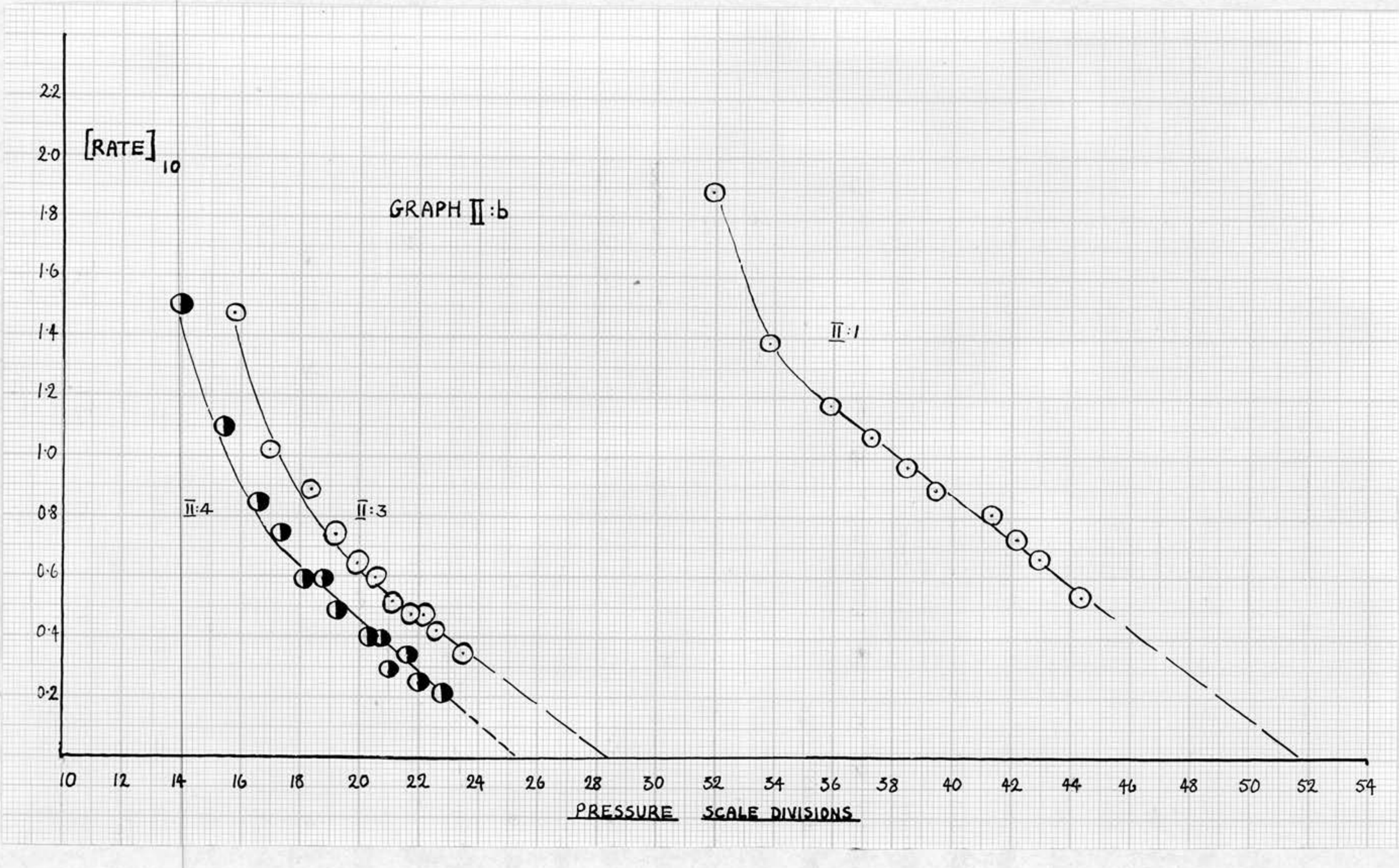
The films were prepared by evaporating a measured quantity of a standard solution of the peroxide on to a known weight of Jena glass. The amount of glass was chosen in order that the conditions would be comparable with photo formation experiments. The vessel, containing the film on one internal hemispherical surface, was then transferred to the apparatus and pumped for a standard time (15 hours) at 10^{-4} mm. Hg. (McLeod gauge) at normal temperature. The furnace was arranged round the reaction vessel as described on page . The initial setting of the furnace rheostat determined the ultimate temperature of the reaction vessel.

After closing the gauge taps the furnace was switched on and the position of the gauge pointer on the scale recorded after known time intervals. A description of a typical experiment is given below.

Reaction vessel volume	- 47.0 mls.
Gauge sensitivity	- 0.16 mm./s.d.
Weight of Jena glass	- 0.1 gm.
Weight of rubrene peroxide (R.E.)	- 3.8 mg.
Ultimate temperature	- 130°C.

The manner in which the pressure increased with time is

× depicted in Graph II (a). At T the temperature reached 130°C. At 'H' the furnace was turned off and the vessel allowed to cool down to room temperature. The ultimate gas pressure in the vessel after the attainment of room temperature, is shown as a dotted line in /


[RATE]10
GRAPH II:b
II:1
II:3
II:4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
PRESSURE SCALE DIVISIONS

in the graph and denoted as P_f. The gas pressure at 'H' will be denoted by P_h. If P_h scale divisions of gas are cooled from 130°C. to 20°C. in a constant volume system the resultant pressure P should be given by (i):

$P = P_h . 293/403 = 33$ s.d. -------------------- (i)

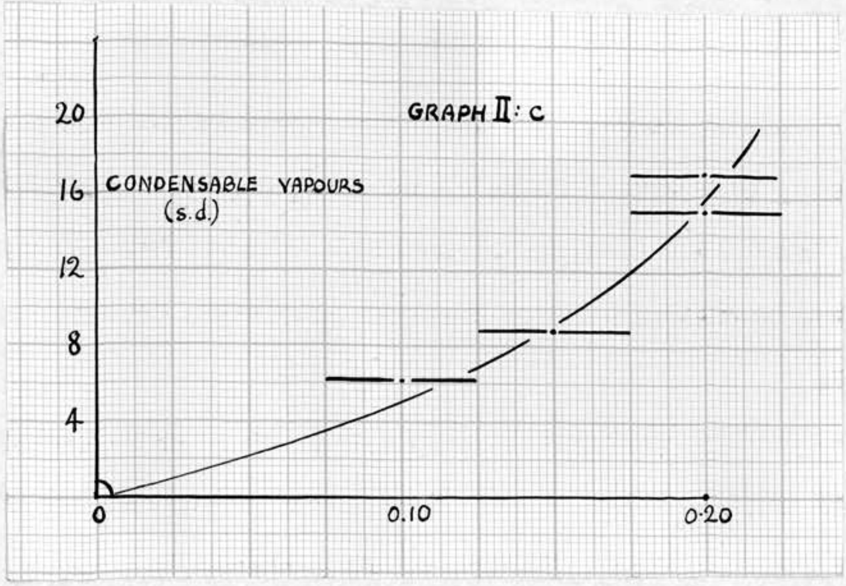
The value of P_f was 20.7 divisions at 20°C. There was thus a discrepancy between P and P_f of 12.3 divisions at 20°C.

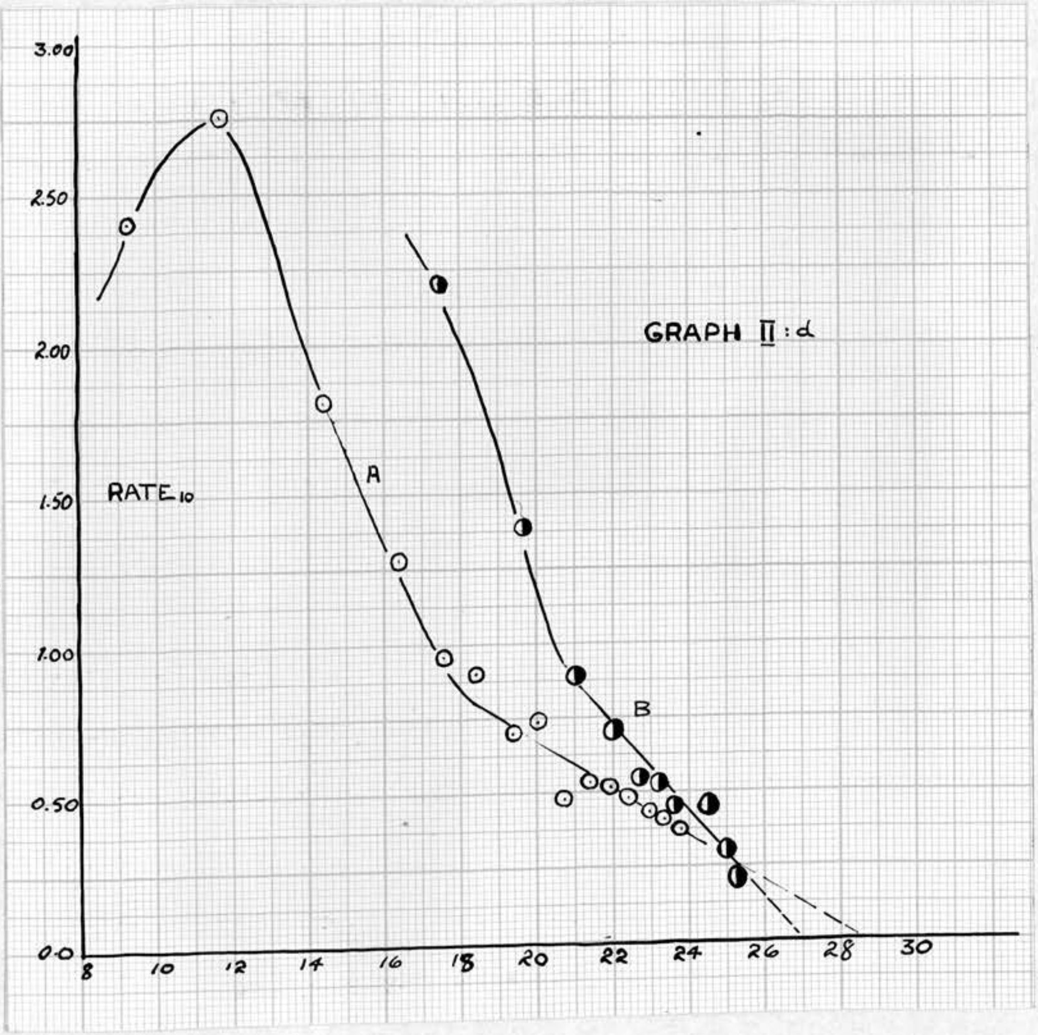
The contraction on cooling was greater than expected on a purely temperature effect as calculated for a permanent gas and part of the gas phase products must have been adsorbed on the film and substrate on cooling.

The table below has been drawn up in order to summarise the results of a series of experiments performed in the same manner as the one described above. 'Condensable vapour' implies the material which readsorbed on the surface on cooling and the 'extrapolated uptake', obtained from the rate curves shown on Graph II (b), is quoted as the value before correction for these adsorbed vapours. The molar ratios, expressed as moles of gas produced per mole of peroxide in the film, were calculated from the constants of the apparatus and the corrected extrapolated pressure limit.

No.	II 1.	II 2.	II 3.	II 4.
Peroxide (R.E.) mg.	2.7 B	3.8	2.7 B	2.34 C
Substrate gm.	0.2	0.1	0.15	0.2
Acetone vol. mls.	20	1.2	20	10
Scale Divisions -				
Total gas evolution	52.0	23.4	25.8	28.4
Cond. gases ($P - P_f$)	17.2	1.3	8. 8	15.2
Molar ratio	2.05	0.95	0.99	0.96
T°C.	130	130	112	115

The /


GRAPH II: c
20
16
12
8
4
CONDENSABLE VAPOURS
(s.d.)
0
0.10
0·20


GRAPH II : d
3.00
2.50
2.00
1.50
1.00
0.50
0.0
RATE10
A
B
8
10
12
14
16
18
20
22
24
26
28
30

The volumes of acetone quoted in the table correspond to the number of mls. of standard peroxide solution used to deposit the film. In 'run' II:2 a sample of powdered rubrene peroxide was employed thus rendering a large quantity of binding solvent unnecessary.

The gases which readsorbed, on cooling, were approximately proportional to the weight of substrate used. Graph II (c) illustrates this relationship. It then seems probable that these gases originated from the adsorbed layer on the substrate.

As far as can be ascertained at this stage, considerable gases may have been evolved by the peroxide and subsequently adsorbed on the Jena glass in amount proportional to the weight of substrate. However, as a unit molar amount of gas is left in the system on cooling, after practically all the experiments, the suggestion that the condensable gases originated from the Jena glass surface appears sound.

These results besides illustrating the unimolecular nature of the decomposition taking place, indicate that the system, rubrene peroxide deposited from an acetone solution on to a Jena glass substrate, produces, above 110°C., a gas and/or vapours in amount molarly equivalent to the initial concentration of rubrene peroxide.

The molar ratio of 2.05 (see run II:1) was obtained from an experiment conducted in an exactly similar manner to the other runs of this section. The film residue was not analysed for rubrene and the result could never be checked by duplication.

The rate curves were quite similar in slope ($k_{130} = 8.5 \times 10^{-3}$ mins.$^{-1}$) while indicating a small temperature coefficient.

The /

The Effect of cooling and reheating Expt.II:5.

Gauge Sensitivity	- 0.16 mm./s.d.
Vessel Volume	- 47.0 mls.
Ultimate Temperature	- 115°C.
Weight of peroxide	- 2.34 mg. (R.E.)

The film was heated for about 200 minutes when the total gas evolution was 24.2 scale divisions. The temperature was then lowered to 20°C. and the new steady pressure measured and found to be 8.0 scale divisions. The temperature of the vessel was then raised to 115°C. again and the pressure changes recorded at known times. After 300 minutes, when the total gas pressure was 25.4 divisions the temperature was lowered to 20°C. and the equilibrium pressure at this temperature measured (10.4 divisions). The rate curves for the first (A) and the second (B) heating periods are shown on Graph II:d from which the extrapolated pressure values could be estimated.

Although at first sight, it would seem that the extent of the decomposition was not the same in both parts of this experiment, after correction for readsorbed vapours it was found that 15.2 divisions (A) and 15.6 (B) of 'non-adsorbing' gas were produced under these conditions. The average value corresponds to a molar ratio of 1.09 of vapour to rubrene peroxide.

This experiment constitutes further evidence that the Jena glass surface is associated with quantities of adsorbed vapour which may be desorbed or re-adsorbed by the surface by appropriate temperature changes.

The Analysis of the Vapours Produced during the Decomposition /

The Analysis of the Vapours Produced during the Decomposition.

In the following experiments sample C. rubrene peroxide was deposited from an acetone solution on 0.1 gm. Jena glass, unless otherwise stated, and the weights of peroxide quoted are as rubrene equivalents. All films were pumped overnight at 10^{-5} mm. Hg. (McLeod gauge).

Gauge sensitivity - 0.084 mm./s.d.
Vessel volume - 52.8 mls.
Ultimate temperature - 128°C.

In this 'run' (II:6) a three way tap connected the reaction vessel to two small side tubes. One contained soda lime and the other was packed with phosphoric oxide. In this manner either one or both of the adsorbents could be exposed to the reaction system. The films and adsorbents were evacuated overnight after which the side tubes were isolated from the system, the gauge taps closed and the heating of the film commenced. When the reaction was nearing completion, as judged by the rate of pressure increase, the system was exposed to soda lime. An instantaneous pressure decrease occurred which corresponded to 91% of the total vapours present. The residual gases were pumped off and the film allowed to reach room temperature when it was pumped for a further 10 hours. On raising the temperature to 128°C. again, the system still being exposed to soda lime, only a very small pressure increase was observed over a period of 5 hours.

The molar decomposition of the film obtained by spectrographic analysis was 16%, a value which agreed with that calculated from the /

the constants of the apparatus and the residual gas pressure.

The next experiment (II:7) differed from the previous one in only the nature of the adsorbent. In this case phosphoric oxide was employed. The film was heated for 220 minutes after which the vapours were exposed to the adsorbent by opening the three way tap. After 5 minutes 95% of the product vapours were adsorbed on the phosphoric oxide as detected by the reduction in pressure. The film was heated for a further three hours with the adsorbent in the system and the pressure in the vessel did not increase appreciably.

The results from the two experiments described above indicated that the main gaseous product of the decomposition was not oxygen and the next series of investigations were designed in an attempt to define the nature of these products.

Spot Analysis of the Vapour Products of the Decomposition/

Spot Analysis of the Vapour Products of the Decomposition.

Experiment II:8 - 2.34 mg. of the peroxide (R.E.) were deposited on the plane glass surface of the reaction vessel by slowly pumping off the acetone with a water pump. The film was evacuated overnight at room temperature and then heated for 400 minutes at 130°C. The vapours were then pumped through the trap C, and the trap condensate tested for acetone (as described on page 22). Result - negative, no blue colouration of indigo being observed.

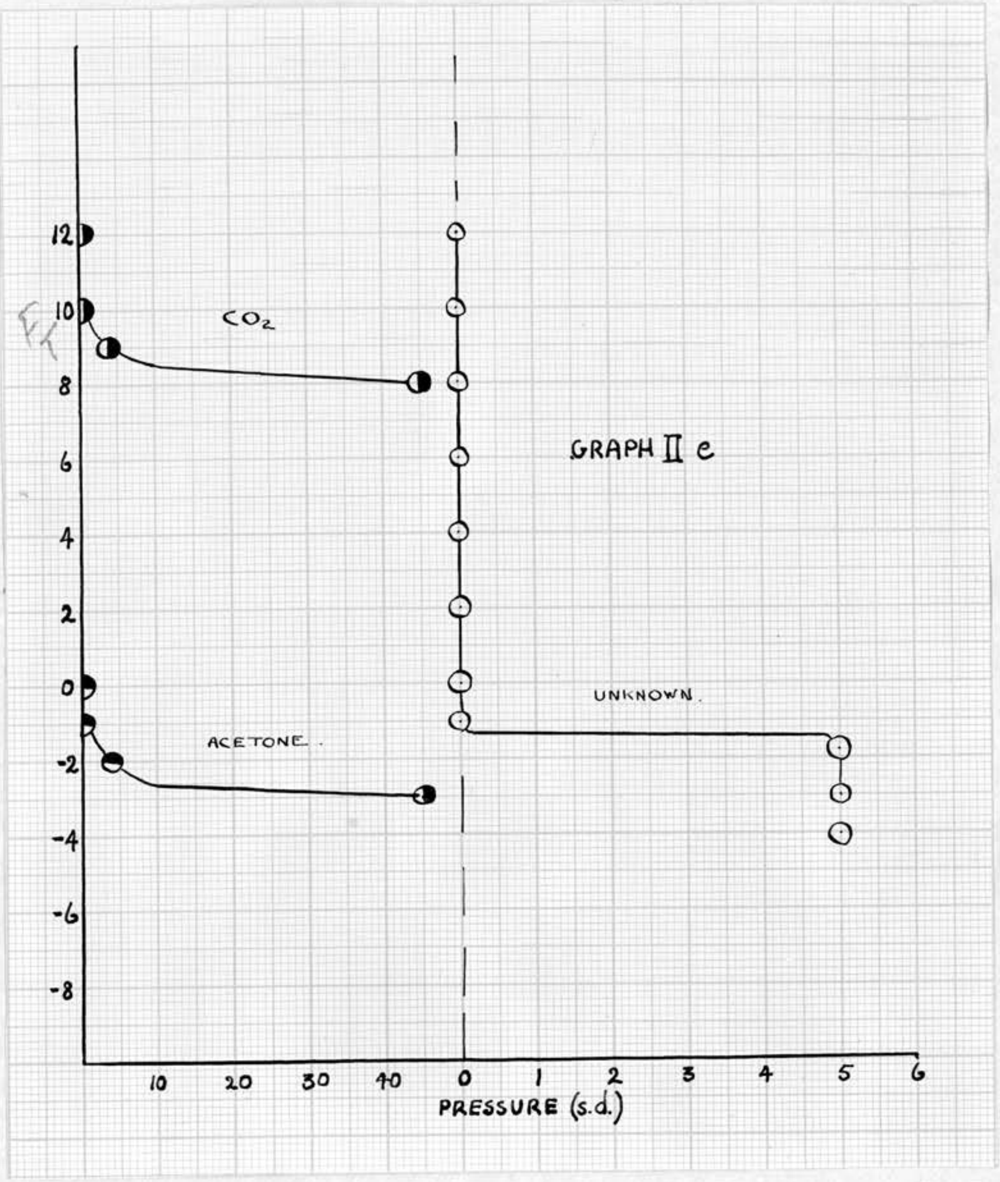
Experiment II:9 - This consisted of a repeat of II:8. In this case however, the spot test was positive for acetone, the blue indigo colour being clearly observed in the chloroform layer. This film was heated for 460 minutes at 130°C. The rate curve for the decomposition was of the same type as shown in Graph II:b and indicated that the reaction conformed to a unimolecular law under the present experimental conditions. The total extrapolated pressure of vapour produced corresponded to 0.73 moles of gas per one mole of peroxide on the film. No rubrene was detected on the film residue after this time.

Experiment II:10 - 2.34 mg. of the peroxide (R.E.) were deposited from acetone solution on 0.1 gm. Jena glass and after the usual evacuation the film was heated at 129°C. for 575 minutes. The reaction vapours when pumped through the liquid oxygen trap produced a condensate which gave a positive reaction for acetone with o-nitrobenzaldehyde.

It /

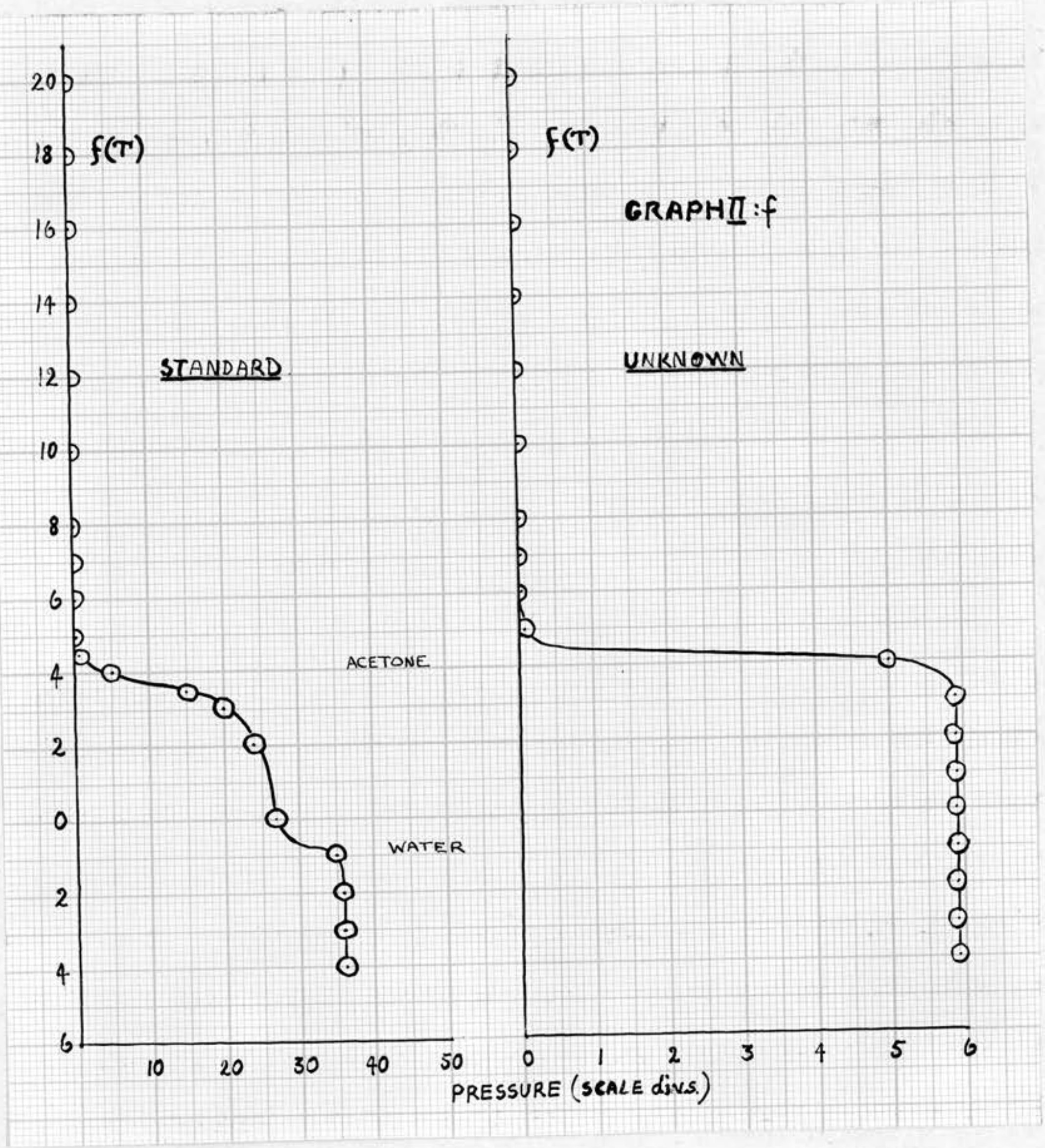
It has now been qualitatively determined that acetone, the solvent used in preparing the film, is produced during the decomposition. The next step was the quantitative analysis of the reaction vapours using the technique of microdistillation as described on page 22.

The Microdistillation of the Product Vapours /



GRAPH II e

12
10
8
6
4
2
0
-2
-4
-6
-8
CO_2
ACETONE
UNKNOWN
10
20
30
40
0
1
2
3
4
5
6
PRESSURE (s.d.)


GRAPH II : f
f(T)
f(T)
STANDARD
UNKNOWN
ACETONE
WATER
20
18
16
14
12
10
8
6
4
2
0
2
4
6
10
20
30
40
50
0
1
2
3
4
5
6
PRESSURE (SCALE divs.)

The Microdistillation of the Product Vapours

Standardisation

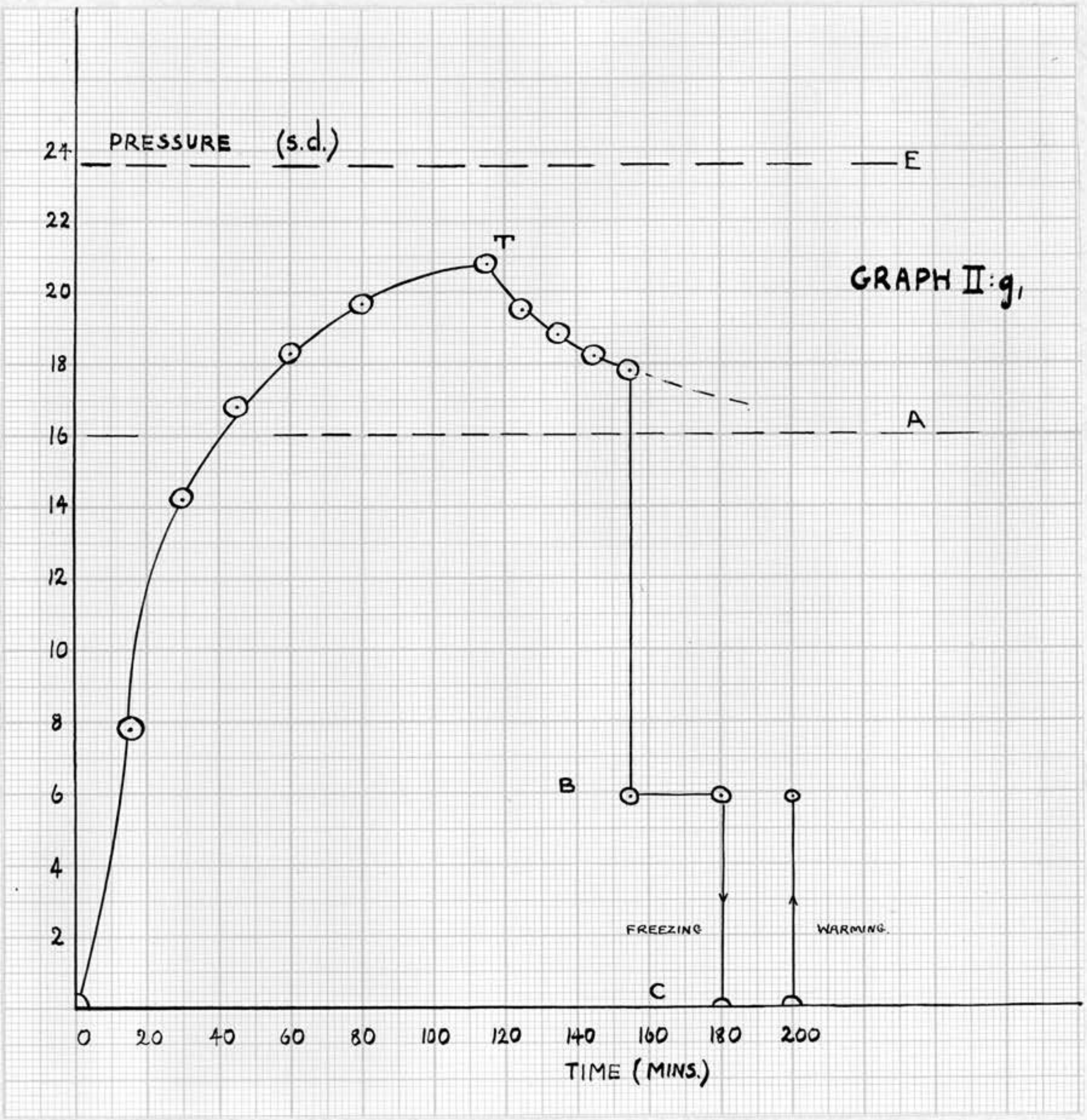
Small quantities of either carbon dioxide, water or acetone were placed in the trap C and frozen with liquid oxygen. The apparatus was then evacuated and the trap allowed to warm up slowly to room temperature. The gauge pointer reading p was plotted against the galvonometer deflection f (T) resulting in a standard curve for each vapour. As the values of f (T) were purely relative and were only reproducible over two successive experiments, standard 'runs' were perfomed directly after each actual experiment, after thoroughly degassing the trap.

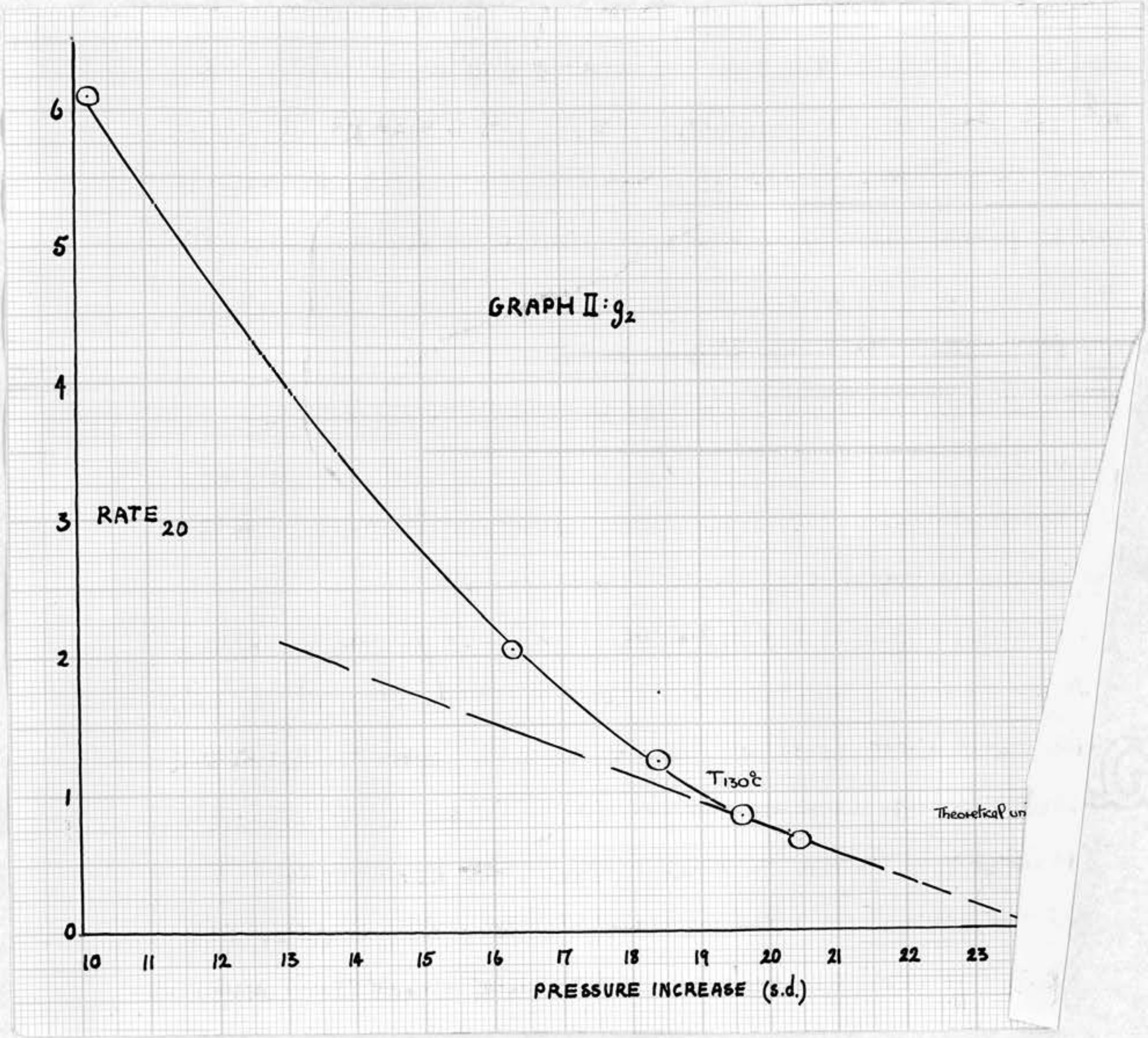
Experiment II:11 - The Vapours from the Jena Glass.

In this experiment 0.1 gm. of Jena glass was made into a film by employing 10 mls. of acetone as the binding solvent this being evaporated off at the water pump. The film was evacuated overnight and heated at 120°C. for 350 minutes after which the product vapours were condensed in the trap C. The distillation curve obtained, on warming the trap, is shown in Graph II:e. A comparison with the standard acetone curve indicates the presence of this vapour. No other vapour was detected. Taking into account in the calculation, the volume of the distillation apparatus, the total amount of distillate was accounted for as acetone.

Experiment II:12.

2.34 mg. of the peroxide (R.E.) was made into a film on the plane glass surface of the reaction vessel (volume = 55.8 mls.). The film was evacuated for 15 hours and heated for 115 minutes at 125°C. The progress of the experiment may be followed by inspection of the pressure-time curve in Graph II:g. After this time /


GRAPH II:g,
PRESSURE (s.d.)
24
22
20
18
16
14
12
10
8
6
4
2
E
T
A
B
C
FREEZING
WARMING
0
20
40
60
80
100
120
140
160
180
200
TIME (MINS.)


GRAPH II: g_2
RATE$_{20}$
6
5
4
3
2
1
0
10
11
12
13
14
15
16
17
18
19
20
21
22
23
PRESSURE INCREASE (s.d.)
T130°C
Theoretical un

time (T) the pressure in the reaction vessel system was 20.8 scale divisions. On cooling the vessel to room temperature the pressure dropped to 15.8 divisions (the dotted line A) and on expanding the cooled vapours into the trap the resulting pressure on the gauge was 5.9 divisions (the dotted line B). After freezing out for 3 hours the pressure dropped to zero (C) and on warming the trap a vapour pressure-temperature curve of the form shown in Graph II:f was obtained. The amount of vapour recovered from the trap was 5.9 divisions. This was identified as acetone by a comparison with the standard curve. The dotted line 'E' indicates the theoretical pressure increase corresponding to a unit molar ratio of vapour (vessel volume - 54.5 mls.) to which this curve and the rate curve in Graph II:g_3 may be extrapolated.

The results have indicated that the main reactions occurring were the release of acetone molecules from the surface of the Jena glass (first order velocity constant 7.3×10^{-3} mins.$^{-1}$; Exp.II:11) and also from the peroxide-solvent complex (first order velocity constant 12×10^{-3} mins.$^{-1}$; Exp. II:12). The specific rate of removal of solvent from the substrate was thus only slightly less than that for the decomposition of the peroxide complex although definite molar quantities of acetone were produced in the latter case.

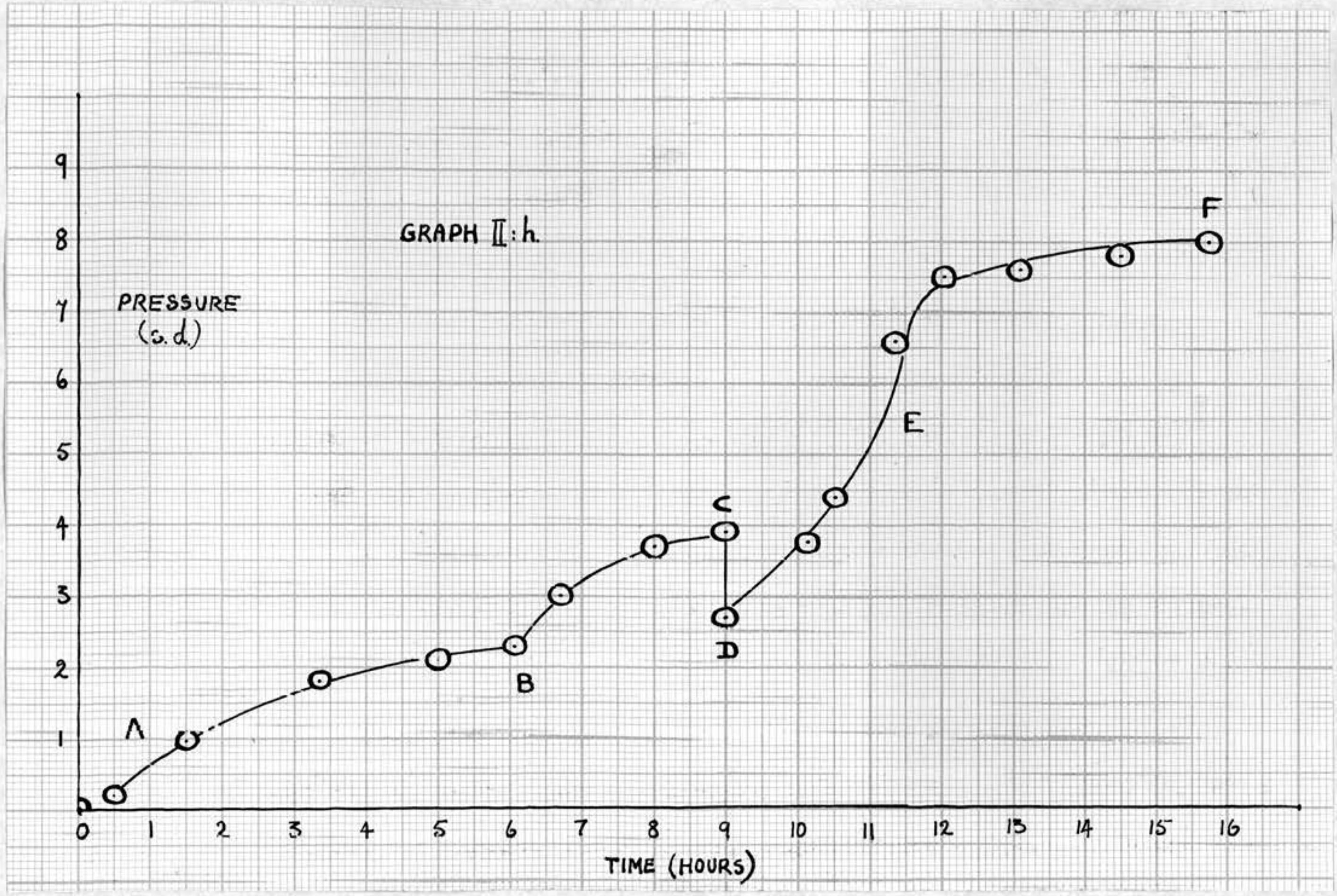
There now seems little doubt that the rubrene peroxide was associated with one molecule of acetone of crystallisation which was not removable by prolonged evacuation at room temperature.

The /

The experiments with soda lime and phosphoric oxide have indicated that only traces of a permanent gas were evolved under these conditions, while in the experiments involving distillation all the produced gases were invariably recovered as condensable vapours.

On exposing 25 scale divisions of acetone vapour to phosphoric-oxide contained in a side tube the pressure dropped instantly to 0.3 divisions and subsequently became less than o.1 divisions. This direct experimental observation that phosphoric oxide readily and completely adsorbs acetone vapour under the prescribed conditions provided the starting point for the next series of experiments, the study of the kinetics of the decomposition of rubrene peroxide 'in vacuo', in the presence of phosphoric oxide.

The Decomposition of Rubrene Peroxide in the Presence of Adsorbents /


GRAPH II: h.
PRESSURE
(s.d.)
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
TIME (HOURS)
A
B
C
D
E
F

The Decomposition of Rubrene Peroxide in the Presence of Adsorbents.

In order to have some idea of the magnitude and rate of the release of the gases which are not adsorbed on the phosphoric oxide, the preliminary experiments II:13 and :14 were carried out.

Experiment II:13

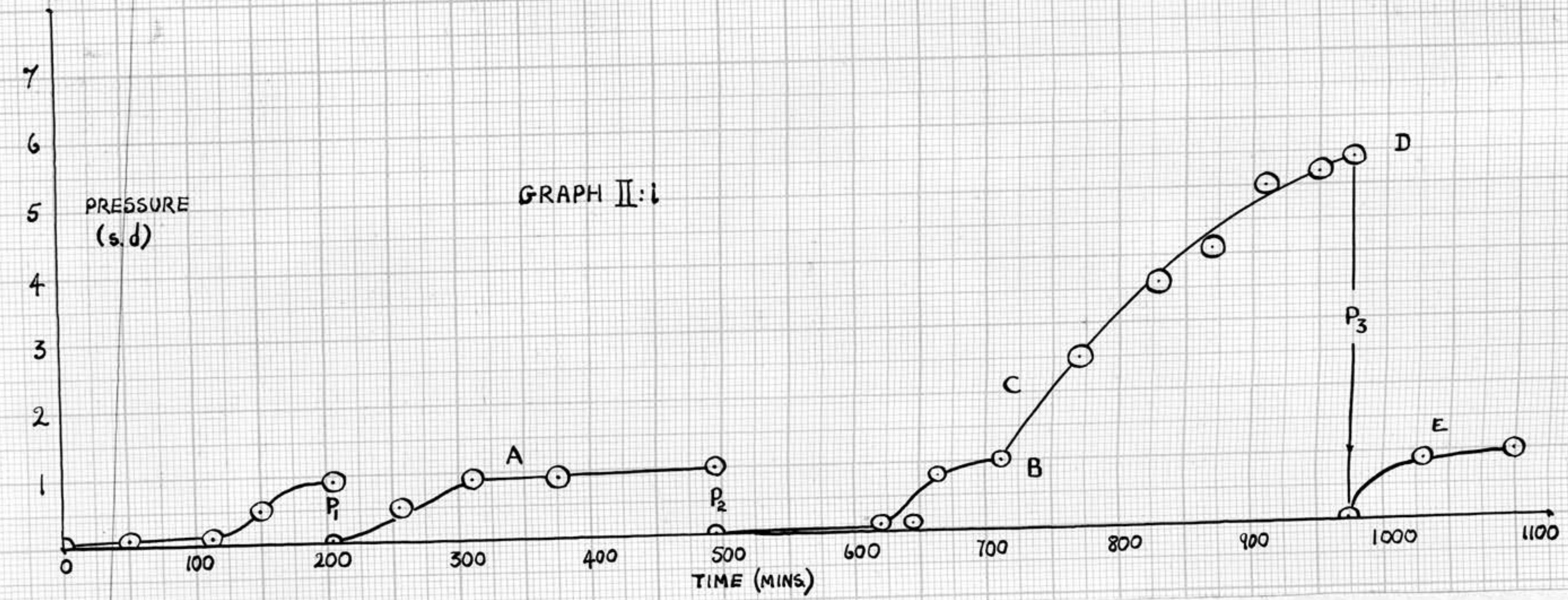
4.68 mg. of rubrene peroxide (R.E.) was deposited from acetone solution on 0.2 gm. Jena glass and the resulting film evacuated for 5 hours with the oil and diffusion pumps. The residual pressure was less than 10^{-4} mm. of mercury (McLeod gauge).

Gauge sensitivity - 0.16 mm./s.d.

Vessel volume - 50.0 mls.

The reaction vessel was fitted with a small side arm to which was attached, by means of a Quickfit A7 joint, a small tube containing about 0.5 gm. of phosphoric oxide. The variation of pressure in the reaction vessel with time is illustrated in Graph II:h.

At 'A' the temperature reached 120°C. where it was kept constant until 'B'. At 'B' the temperature was raised to 130°C., this operation taking only a few minutes, for a further 3 hours. After a total of 9 hours, 'C', the vessel was cooled to room temperature when the pressure dropped to 0.755 of the value at 130°C. (the ratio of 293/403 is 0.729). The cooled film was then slowly heated to 150°C. this temperature being attained at 'E'. Between 'E' and 'F' the temperature was raised from 150° - 160°C. The reaction had virtually ceased at 'F' when 8 scale divisions of a permanent gas in the presence of P_2O_5 had been evolved. This gas evolution /



GRAPH II:1

PRESSURE
(s.d)
7
6
5
4
3
2
1
0
100
200
300
400
500
600
700
800
900
1000
1100
TIME (MINS)
P_1
A
P_2
B
C
D
P_3
E

evolution corresponded to a decomposition of 28.6%, calculated from the original concentration of the peroxide assuming a unit molecular ratio.

In order that the pressure changes at slightly lower temperatures might be followed a similar experiment to the above was carried out using a much more sensitive gauge.

Experiment II:14

2.34 mg. of rubrene peroxide (R.E.) was deposited from acetone solution on 0.1 gm. Jena glass and the resulting film evacuated for 5 hours. A side tube containing about 0.5 gm. of phosphoric oxide was attached to the reaction vessel.

Gauge sensitivity - 0.031 mm./s.d.
Vessel volume - 63.5 mls.

The variation with time of the pressure developed in the reaction system is illustrated in Graph II:i.

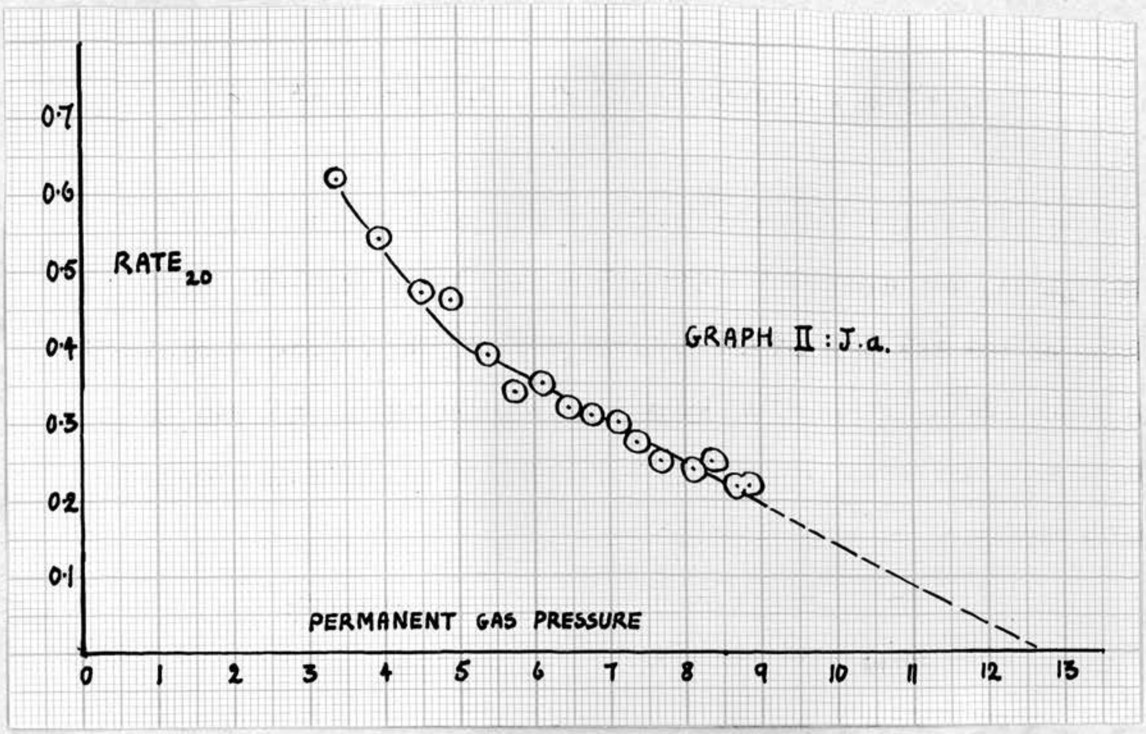
The temperature was slowly raised to 84°C. and it was observed by pressure measurement, that no appreciable decomposition occurred below 60°C. After 200 minutes the vessel was cooled and evacuated for 1 hour (P_1) when, after re-isolation of the system, the temperature was again raised to 84°C. until 'A' when it was elevated to 100°C. At P_2 the vessel was cooled and evacuated for 3 hours and the film then reheated to 100°C. The pressure changes now occurring were very slow so the temperature was raised first to 109°C (B) and finally to 130°C (C) where it remained constant until 'D'. At 'D' the vessel was cooled and the vapours were pumped off (P_3) until the pressure in the vessel was apparently zero (limited by /

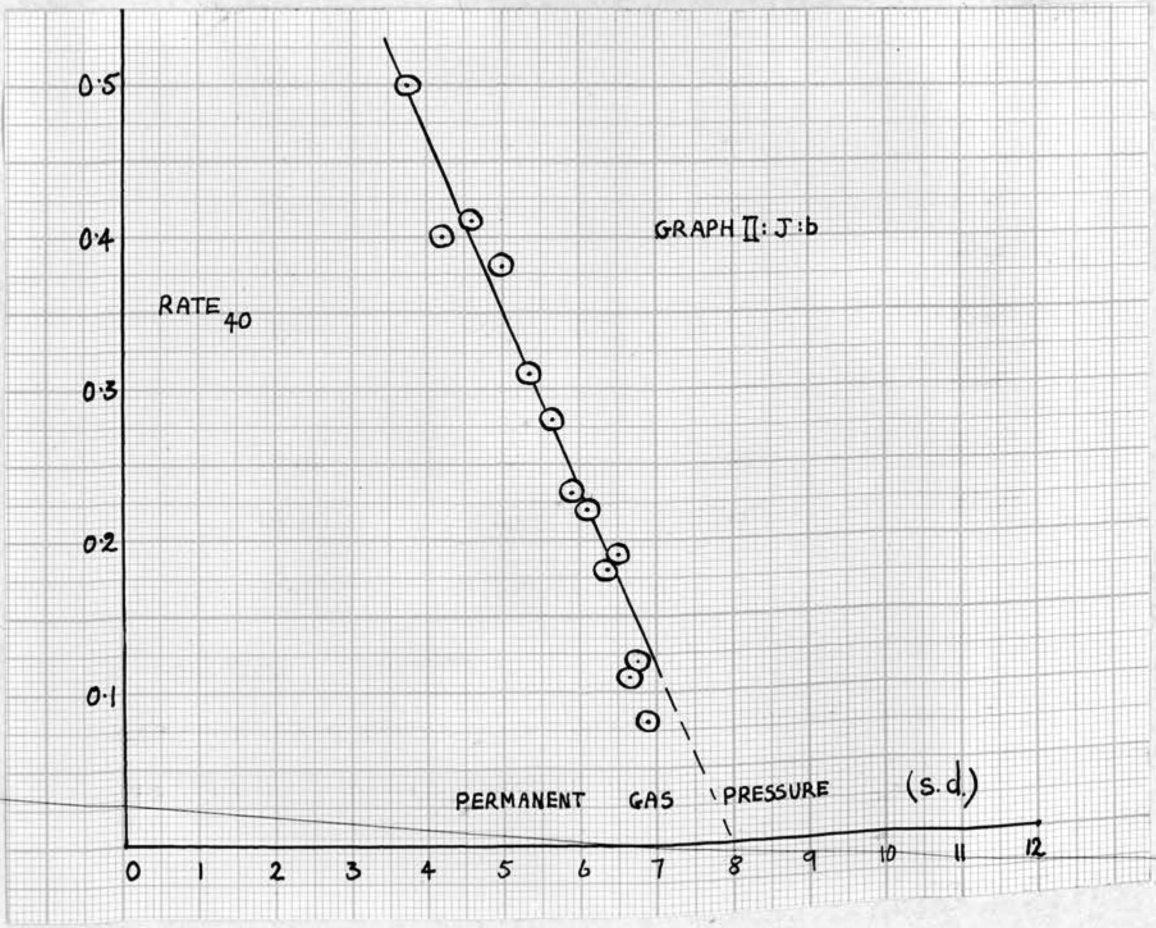
by the gauge sensitivity). The temperature was again raised to 130°C (E) when further increases of pressure became negligible.

Although the results of the above experiments may not have much quantitative basis, owing to the duration of the 'runs', they have indicated that oxygen (it will be assumed for the present - see later; p. - that oxygen is the residual gas) is not produced in amounts even approaching a 100% decomposition of the peroxide under these conditions. A 100% decomposition at 130°C. would produce a gas pressure of 56.2 scale divisions in this system. Appreciable gas pressure increases were detectable only above 100°C. After pumping, the pressure apparently increased to the same value as before the evacuation at the same temperature. This was only true, however, at the lower temperatures investigated.

It was now hoped to investigate any equilibrium pressure effect which may be a controlling factor. The method of tackling this problem will consist of heating films at constant temperature and estimating the total amount of gas evolved at particular temperatures.

The Decomposition of Rubrene Peroxide at 120°C. /


0·7
0·6
0·5
0·4
0·3
0·2
0·1
RATE$_{20}$
GRAPH II : J.a.
PERMANENT GAS PRESSURE
0
1
2
3
4
5
6
7
8
9
10
11
12
13


0·5
0·4
0·3
0·2
0·1
RATE$_{40}$
GRAPH II : J:b
PERMANENT GAS PRESSURE (s.d.)
0
1
2
3
4
5
6
7
8
9
10
11
12

The Decomposition of Rubrene Peroxide at 120°C.

The films were prepared in the usual manner on 0.1 gm. of Jena glass, and evacuated overnight before being reacted. The rheostat was set in a position which enabled the furnace temperature to reach 120°C. in about 30 minutes. Approximately 0.5 gm. of phosphoric oxide was contained in the side tube, a fresh sample being employed for each experiment.

Gauge sensitivity - 0.051 mm./s.d.
Weight of peroxide - 2.34 mg.
Vessel volume - 63.5 mls.

The results of experiment II:15 were as follows:-

Pressure (s.d.)	Rate/20mins.	Pressure	Rate/20mins.
3.41	0.62	6.74	0.31
3.99	0.54	7.05	0.30
4.50	0.47	7.34	0.27
4.96	0.46	7.69	0.25
5.39	0.39	7.85	0.27
5.75	0.34	8.11	0.24
6.10	0.35	8.35	0.25
6.43	0.32	8.59	0.22
		8.81	0.22

Extrapolated pressure increase :12.2 divisions 0.38 mm.

The rate curve for this experiment is shown in Graph II:j_a and indicates the unimolecular nature of the decomposition in the later stages.

Experiment II:16.

Gauge sensitivity - 0.048 mm./s.d.
Weight of peroxide - 2.34 mg.
Temperature /

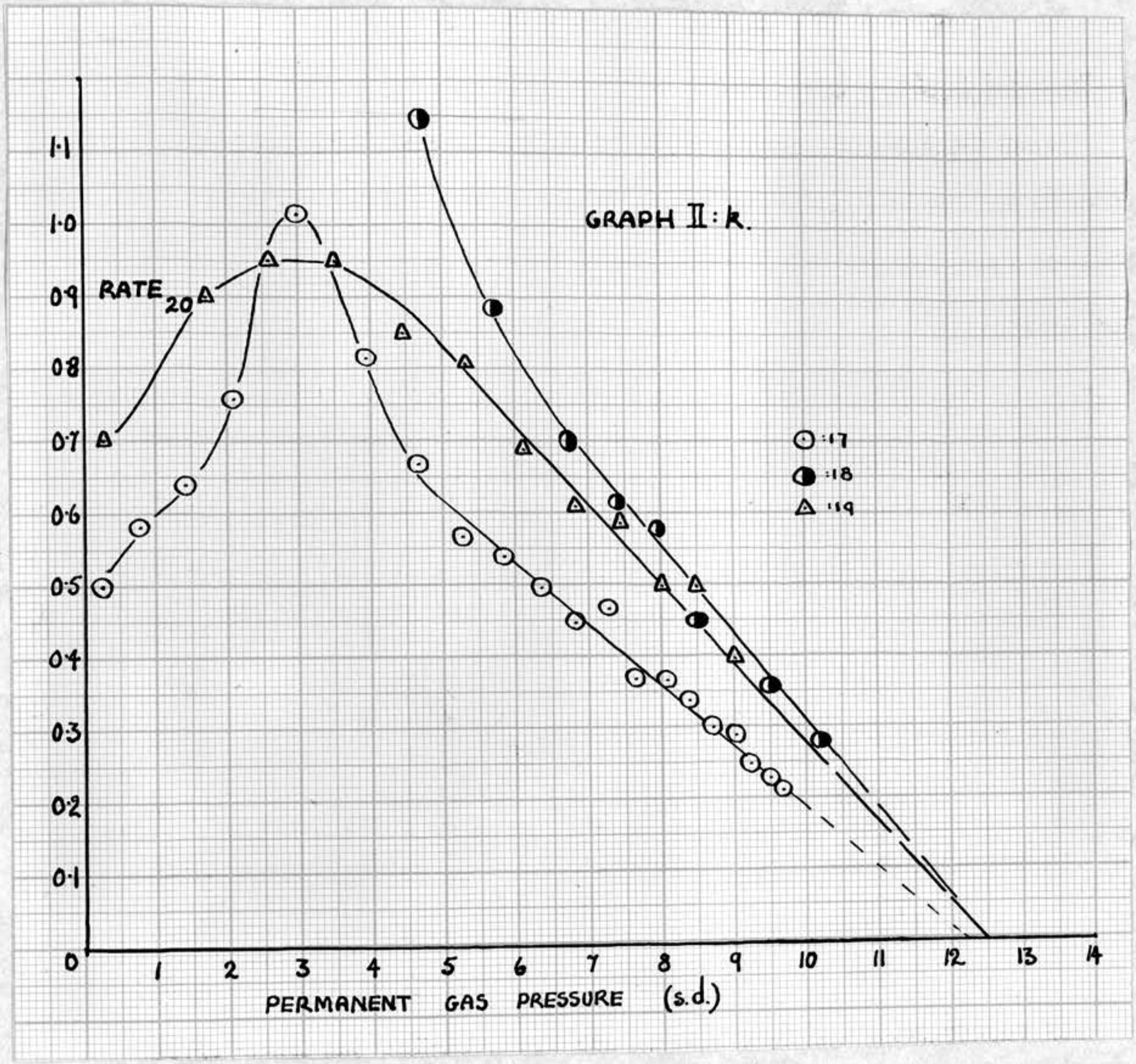
Temperature - 120°C.

Vessel volume - 55.3 mls.

This reaction proceeded similarly to II:15 and the rate curve is also shown in Graph II:j_b. The extrapolated pressure increase was in this case, 7.9 divisions which corresponded to 0.38 mm.

Although different reaction vessel volumes were employed in the above 'runs' the same pressure of gas was produced. A degree of saturation was observed at higher pressures in 'run' II:16, the rate falling off to zero rather rapidly. The main part of the rate curve was linear and the extrapolation considered valid. The cause of this was possibly due to one of a variety of surface effects and was only a rate determining factor towards the end of the reaction. These effects will be discussed in a later section.

The Decomposition of Rubrene Peroxide at 130°C. /


GRAPH II: k.
RATE$_{20}$
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
PERMANENT GAS PRESSURE (s.d.)
⊙ :17
◐ :18
△ :19

The Decomposition of Rubrene Peroxide at 130°C.

Gauge sensitivity - 0.048 mm./s.d.

Weight of peroxide - 2.34 mg.

Esperiments II:17 - 19.

These experiments were carried out in the standard manner. The rate curves are drawn in Graph II:k and the actual results obtained from one experiment are shown below.

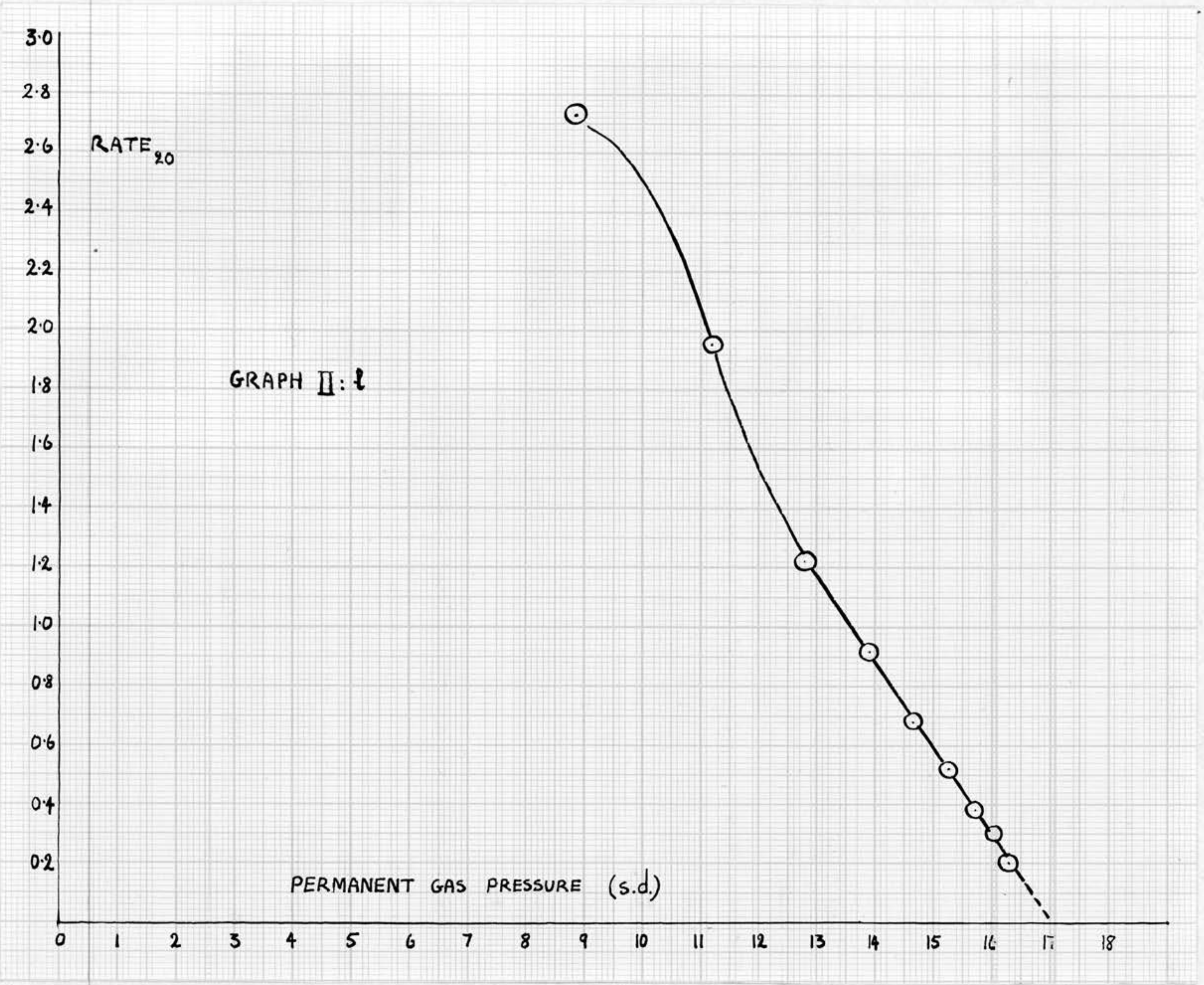
Experiment II:17

	Pressure (s.d.)	Rate/20mins.	Pressure (s.d.)	Rate/20mins.
	0.25	0.50	6.82	0.45
	0.79	0.58	7.27	0.47
	1.40	0.64	7.67	0.36
	2.10	0.76	8.04	0.37
	2.99	1.02	8.39	0.34
130°C attained -	3.91	0.82	8.71	0.30
	4.68	0.67	9.01	0.29
	5.27	0.57	9.27	0.25
	5.83	0.54	9.52	0.23
	6.35	0.50	9.73	0.21

All experiments carried out at 130°C. provided the same value for the extrapolated pressure, viz., 0.59 mm. ± 0.01 mm.

A further experiment (II:20) was designed to determine the effect of the initial peroxide concentration on the total gas evolution at constant temperature. 4.68 mg. of the peroxide was deposited on 0.1 gm. of Jena glass and the resulting film reacted in the usual way. An extrapolation of the rate curve from this reaction provided the value of 0.59 mm. for the ultimate pressure at zero rate.

The /



GRAPH II : 1

RATE$_{20}$
3·0
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
PERMANENT GAS PRESSURE (s.d.)

The reproducibility of the results at this stage suggests that the measured pressures at zero rate are 'dissociation pressures' of gas. Further evidence for this is the fact that the ultimate pressure is independent of the initial peroxide concentration.

The Decomposition of Rubrene Peroxide at 145°C.

Experiment II:21.

Gauge sensitivity	- 0.048 mm./s.d.
Weight of peroxide	- 2.34 mg.
Weight of Jena glass	- 0.1 gm.

This film was reacted in the usual manner and the rate curve II:1, drawn from the experimental results quoted below.

Pressure (s.d.)	Rate/20 mins.	Pressure (s.d.)	Rate/20 mins.
8.87	2.73	15.26	0.52
11.21	1.95	15.71	0.38
12.79	1.22	16.05	0.30
13.86	0.92	16.30	0.20
14.66	0.69		

Extrapolated gas evolution 17.0 divisions 0.82 mm.

The following table summarises the final results of this series of experiments.

P(extrap.)	T°C	1/T°K.	Log_{10} P(extrap.)
0.39	120	2.548	1.5911
0.59	130	2.485	1.771
0.82	145	2.395	1.914

Energy considerations involved in the Decomposition /

Energy Considerations Involved in the Decomposition

On the assumption that the evolution of oxygen was a stage in the reversible reaction whose equilibrium constant is given by the oxygen pressure at zero rate, it was possible to calculate a value for the heat of dissociation of the peroxide. The appropriate plot of Log_{10} (extrapolated-pressure increase) against the reciprocal temperature for experiments II:15 - 20 is shown in Graph II:m_1. The slope of the best straight line was -2.20×10^3 which is equivalent to a heat of dissociation of + 10 Kg.cals/mole.

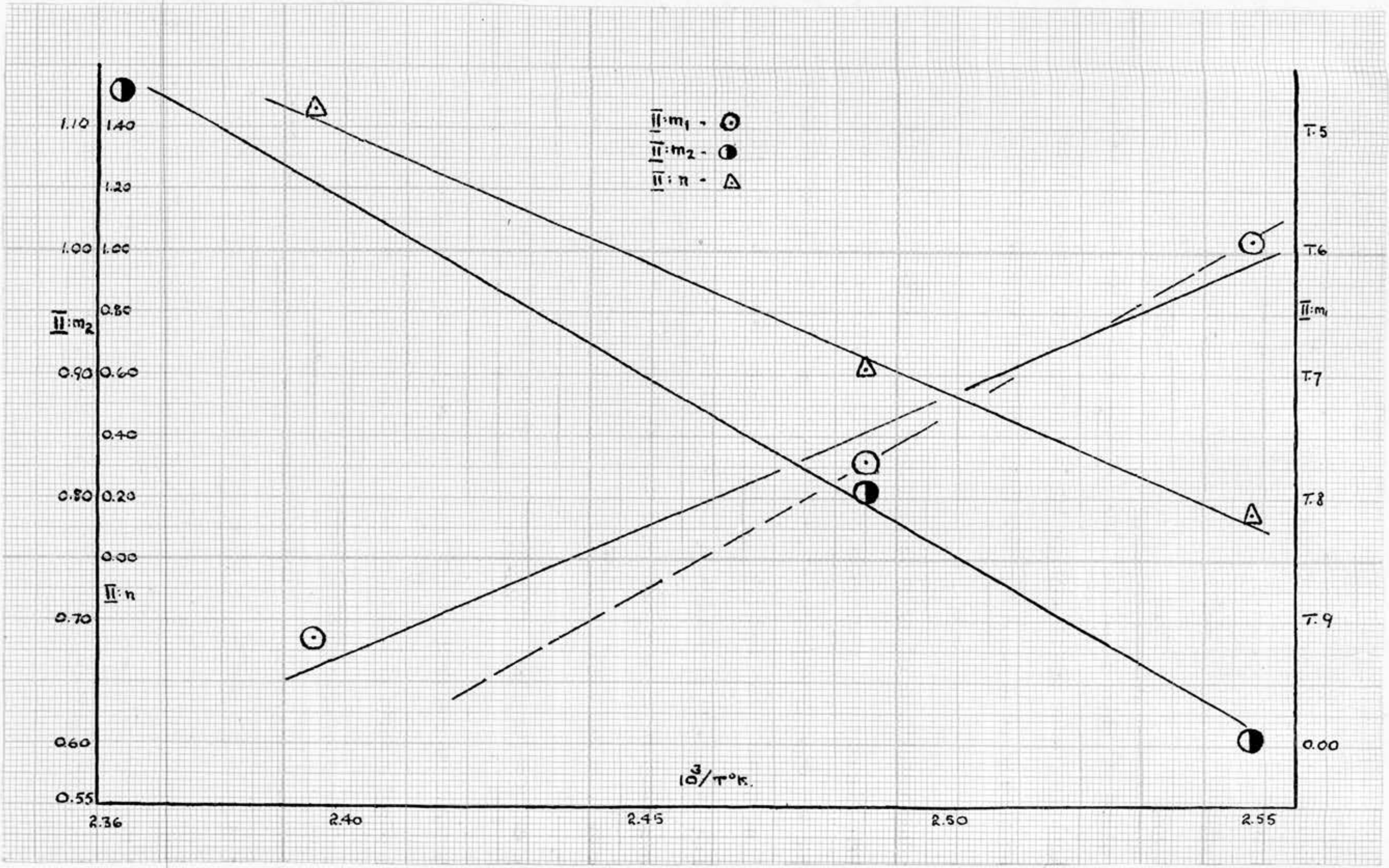
A similar plot of the extrapolated pressure values from one 'run', i.e., II:15, is indicated on Graph II:m_2 while the computed values are given in the table below.

$1/T^\circ K$	Extrapolated Pressure (mm.)	$\mathrm{Log}_{10}\ P_{\mathrm{Extrap.}}$
2.548	0.40	0.602
2.485	0.64	0.806
2.364	1.34	1.127

The value of -2.86×10^3 for the slope of this somewhat more satisfactory straight line corresponds to a heat of dissociation of + 12.9 kg.cals/mole.

From the slopes of the rate curves in this series of experiments it was possible to estimate average values of the rate constants for the decomposition at the various temperatures; these values are indicated in the table below, while the results are plotted in Graph II:n.

$1/T^\circ K$ /


$\underline{II}:m_1$ - ⊙
$\underline{II}:m_2$ - ◐
$\underline{II}:n$ - △
$\underline{II}:m_2$
1.10
1.00
0.90
0.80
0.70
0.60
0.55
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
$\underline{II}:n$
$\bar{1}.5$
$\bar{1}.6$
$\underline{II}:m_1$
$\bar{1}.7$
$\bar{1}.8$
$\bar{1}.9$
0.00
$10^3/T°K.$
2.36
2.40
2.45
2.50
2.55

$1/T^{\circ}K$	$k \times 10^{2}$ mins.$^{-1}$	$\log_{10}(k \times 10^{2})$
2.548	1.4	0.155
2.485	4.1	0.613
2.395	25.5	1.406

The slope of this straight line corresponds to an energy value of + 40 Kg.cals./mole which may be identifiable with the apparent activation energy of a stage in the decomposition of rubrene peroxide.

The decomposition of rubrene peroxide appeared to take place in a reversible manner, analogous to the decomposition of calcium carbonate, the equilibrium constant being given by the 'dissociation pressure' of gas. The results to date indicate that there are three types of reaction occurring on the surface although it is not certain whether or not they are independent.

1. $\underset{(s)}{\text{Glass}} - \text{Solvent} \xrightarrow[\text{vacuum}]{\text{heat}} \underset{(s)}{\text{Glass}} + \underset{(g)}{\text{Solvent}}$
2. $\underset{(s)}{\text{Peroxide}} - \text{Solvent} \xrightarrow[\text{vacuum}]{\text{heat}} \underset{(s)}{\text{Peroxide}} + \underset{(g)}{\text{Solvent}}$
3. $\text{Peroxide or complex} \xrightarrow[\text{vacuum}]{P_2O_5} \text{Permanent gas + Residue.}$

The third reaction only occured to the extent of about 28% at 130°C. It is probable that the third reaction is reversible as the pressure of gas produced was independent of the initial solid phase concentration. It may be of importance to note that very little decomposition occurred when the solvent pressure was allowed to build up over the film. The 'equilibrium pressure' may also be due to a balance between the rate of emission of acetone and the rate /

rate of adsorption on the P_2O_5. This mechanism, however, is deemed unlikely unless gaseous products from the oxidation of acetone by phosphoric oxide provided the gas phase in the equilibrium.

Analysis of the film residues for rubrene were not always carried out in this series of 'runs'; however, when a film was spectrographically analysed the per cent decomposition agreed on every occasion with the value obtained from the constants of the apparatus and the total pressure change.

The Effect of the Substrate on the Decomposition of the Peroxide /

The Effect of the Substrate on the Decomposition of the Peroxide

Experiments II:22 and 23.

The conditions in the present 'runs' were as in the previous experiments excepting that 0.2 gm. of Jena glass was employed as substrate. The temperature of the dissociation was 130°C;

Gauge sensitivity - 0.048 mm./s.d.

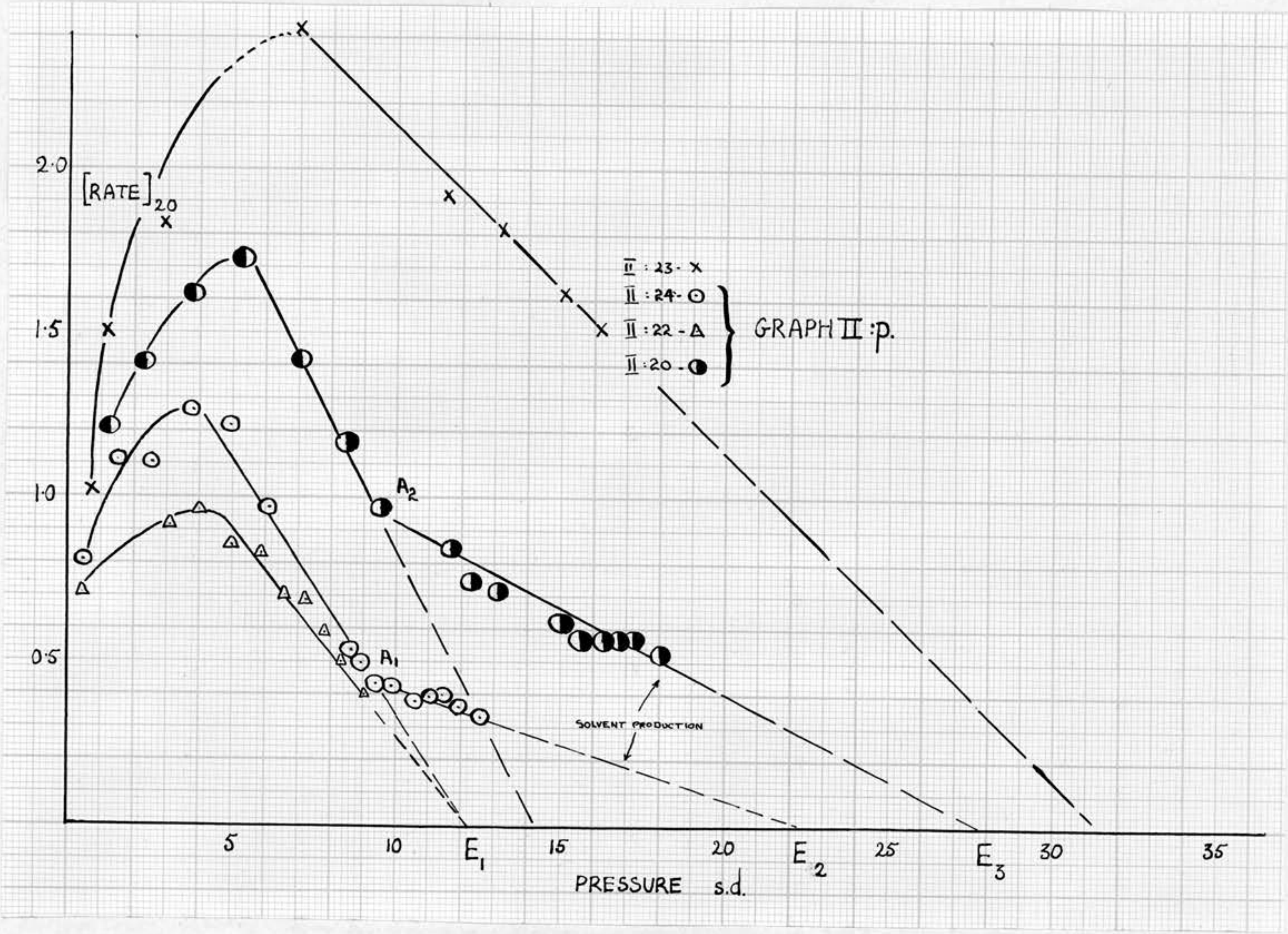
Weight of Peroxide - 4.68 mg. (R.E.)

The rate curves for these experiments are shown in Graph II:p where it may be observed that the 'normal' dissociation pressure was well exceeded. The extrapolated pressures were 27.6 and 31.6 scale divisions as opposed to 12.2 divisions when the film was prepared on 0.1 gm. of Jena glass.

An experiment was now carried out in which 2.34 mg. of peroxide was deposited on 0.2 gm. of glass. Extrapolation of the rate curve provided a value of only 6.2 divisions for the equilibrium pressure.

It was now apparent that the reaction was markedly surface dependent. The series of experiments II:15 - 21 were carried out over a short period of time and in a highly standardised manner and for this reason, combined with the reproducibility of the results of these 'runs', it will be assumed, in future arguments, that the temperature alone governs the ultimate pressure of gas produced by a film under such standardised conditions.

A duplication of the last experiment in fact resulted in the 'normal' dissociation pressure, after extrapolation of the linear


[RATE]$_{20}$
2·0
1·5
1·0
0·5
5
10
15
20
25
30
35
PRESSURE s.d.
E_1
E_2
E_3
A_1
A_2
SOLVENT PRODUCTION
II : 23 - ×
II : 24 - ⊙
II : 22 - △
II : 20 - ◐
GRAPH II : p.

rate curve. The irreproducibility of the above results II:22 and :23, could not be explained although the rapid rate of pressure increase in such 'runs' may signify that the solvent, from the increased amount of substrate, was not completely removed from the system because of a surface layer or other obstruction on the adsorbent. The same effect would be observed if the P_2O_5 became exhausted by the increased amount of acetone. This suggestion was validated by a chance experiment involving the decomposition of 4.68 mg. of the peroxide on 0.1 gm. of glass.

Experiment II:24.

Gauge sensitivity - 0.048 mm./s.d.
Weight of peroxide - 4.68 mg.
Weight of substrate - 0.1 gm.

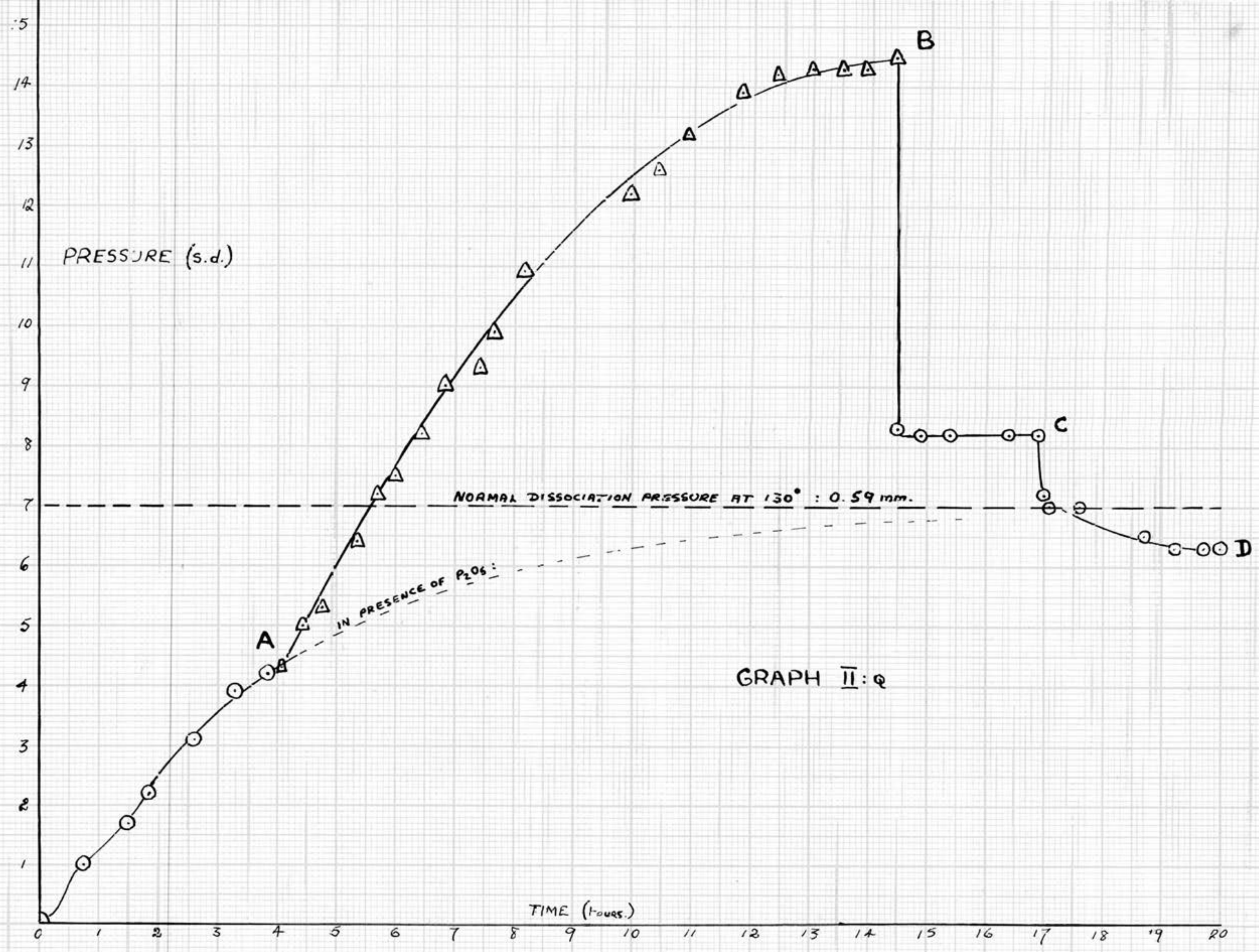
The rate curve for this 'run' is drawn in Graph II:p. 'Runs' II:20 and :22 are drawn on the same Graph for purposes of comparison. In the 'normal' reaction, II:20, the decomposition is unimolecular from the maximum rate (the approximate point of the film attaining 130°C.) until the dissociation pressure E_1 is reached at zero rate. In II:24 however, the 'normal' course was interrupted at A_1 and the rate of pressure increase fell off more slowly while gradually approaching the equilibrium value E2. The same process may be visualised as having occurred in run II:22 where the extrapolated pressure increase is denoted by E_3. The similarity of these curves supports the contention that the rate of adsorption of acetone on the phosphoric oxide had suddenly become a rate determining factor at A_1 and A_2.

Film /

Film formation on the surface of the adsorbent is one of the various possible explanations for this saturation effect. It is also apparent from this graph that the relative rate of approach to equilibrium in 'run' II:22, where 0.2 gm. of Jena glass was employed, was very much greater than the rates using the smaller amounts of substrate.

The thermal decomposition of rubrene peroxide (2.34 mg.) deposited from acetone solution on the plane glass surface of the reaction vessel was effected in the presence of phosphoric oxide. The decomposition proceeded very slowly, as recorded by pressure change; 9 hours at 190°C. only bringing about 13% decomposition. This constituted about one half of the previous equilibrium pressures at much lower temperatures. Analysis of this film residue provided a figure of 12.5% for the amount decomposed.

The Effect of Acetone Vapour on the Thermal Decomposition/



GRAPH II: Q

PRESSURE (s.d.)
TIME (hours.)
NORMAL DISSOCIATION PRESSURE AT 130° : 0.59 mm.
IN PRESENCE OF P_2O_5:
A
B
C
D
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

The Effect of Acetone Vapour on the Thermal Decomposition

Experiment II:25.

Gauge sensitivity - 0.084 mm./s.d.
Weight of peroxide - 4.68 mg. (R.E.)
Weight of substrate - 0.1 gm.

The vessel was connected via a side arm through a three way tap to two adsorbent tubes. One contained phosphoric oxide and the other soda lime. The pressure was allowed to approach the equilibrium value, in the presence of phosphoric oxide, until it was apparent that the rate curve would extrapolate to the 'normal' dissociation pressure for this temperature. At this stage (at 'A' on the pressure-time curve drawn in Graph II:q) the phosphoric oxide was excluded from the system thus permitting the solvent pressure to build up in the reaction vessel. When the acetone pressure had slowly increased over a period of 11 hours the vapour was again exposed to the phosphoric oxide (at 'B'). After 2 hours the pressure had dropped to 'C' at which stage the soda lime tube was opened to the reaction system. A further pressure decrease occurred under these conditions. The final gas pressure in the vessel is indicated by the point 'D' after a 5% correction for volume change. The horizontal line at 0.59 mm. indicates the true dissociation pressure at 130°C. The dotted line signifies the theoretical pressure-time curve for this film in the presence of phosphoric oxide.

The /

The composition of the peroxide has proceeded normally while the pressure of solvent was building up in the vessel. At 'B' 85% of the vapours were adsorbed on the phosphoric oxide and the remaining 15% was probably carbon dioxide produced through the thermal degradation of rubrene peroxide. This would indicate that about 3% of the peroxide degraded on heating for 20 hours. It can now be concluded that solvent vapour has little, if any, effect on the thermal decomposition of the peroxide under the present experimental conditions.

The Analysis of the Permanent Gaseous Residue /

The Analysis of the Permanent Gaseous Residue (see p.22)

The gaseous residue, which was not adsorbed on soda lime or phosphoric oxide, was brought into contact with illuminated titanium dioxide contained in a side tube attached to the reaction vessel. Owing to the high photochemical specificity of the reaction of titanium dioxide with oxygen any pressure decrease observed during the irradiation of a film of this material can be attributed to oxygen.

Experiment II:26

Gauge sensitivity - 0.084 mm./s.d.
Weight of Peroxide - 2.34 mg. (R.E.)
Weight of substrate - 0.1 gm.
Temperature of film - 145°C.

In this experiment the film of titanium dioxide was open to the reaction space throughout the 'run'. The film was protected from condensable vapours by a cotton wool pellet, impregnated with phosphoric oxide, which was placed at the entrance to the side tube. Another side tube, containing about 0.5 gm. phosphoric oxide, was open to the system throughout the reaction.

Referring to Graph II:r, the reaction was allowed to proceed normally until 'A', the pressure being plotted against time. At 'A' the dark cover was removed from around the titanium dioxide tube and the oxide film irradiated with a strong beam from the Osira lamp. The pressure decreased rapidly to 'B', when the cover was replaced. At 'C' the film was re-illuminated and at 'D' the light intensity was slightly increased. The results show that at least 93% of the residual gases were absorbed by the titanium dioxide while the film was being irradiated but not in darkness. The residual gas was therefore oxygen.

In/

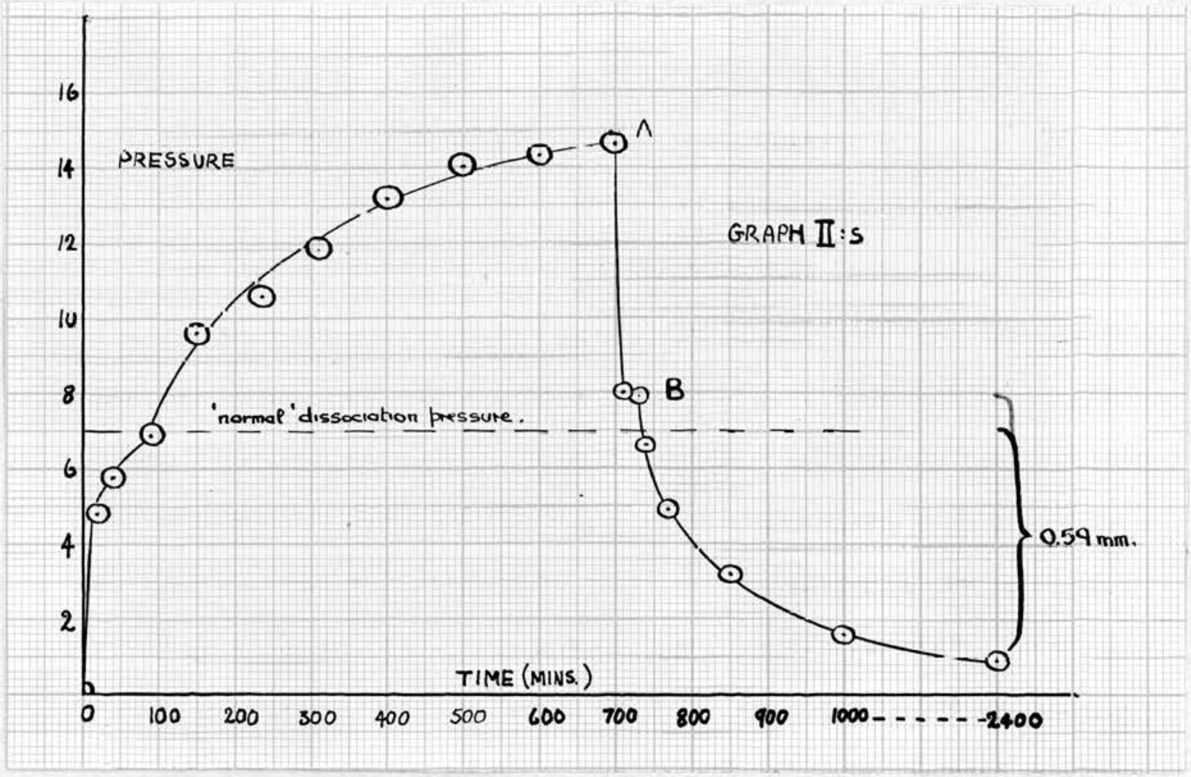
In experiment II:27 the conditions were as above and it can be observed from Graph II:q that during illumination ('A') of the oxide film there occurred a rapid decrease in pressure. For comparison with the above 'runs' the pressure-time curve for experiment II:21 is also drawn on Graph II:r.

The equilibrium pressures in 'runs' :26 and :27 were not in accordance with II:21 which was carried out at the same temperature. Indeed the repeat experiment provided a value for the 'dissociation' pressure at 145°C. which was even lower than the normal value at 130°C. Both of the reactions in question seemed subject to sudden saturation after about 3½ hours of heating. This effect may be connected with the rate of heating the film of peroxide. It is probable that the reaction will cease after the expulsion of all the solvent vapour from the surface. Such a theory would explain why no further decomposition occurs when an equilibrium pressure of gas is pumped off and the film reheated to the same temperature. This point will be enlarged upon during future discussion.

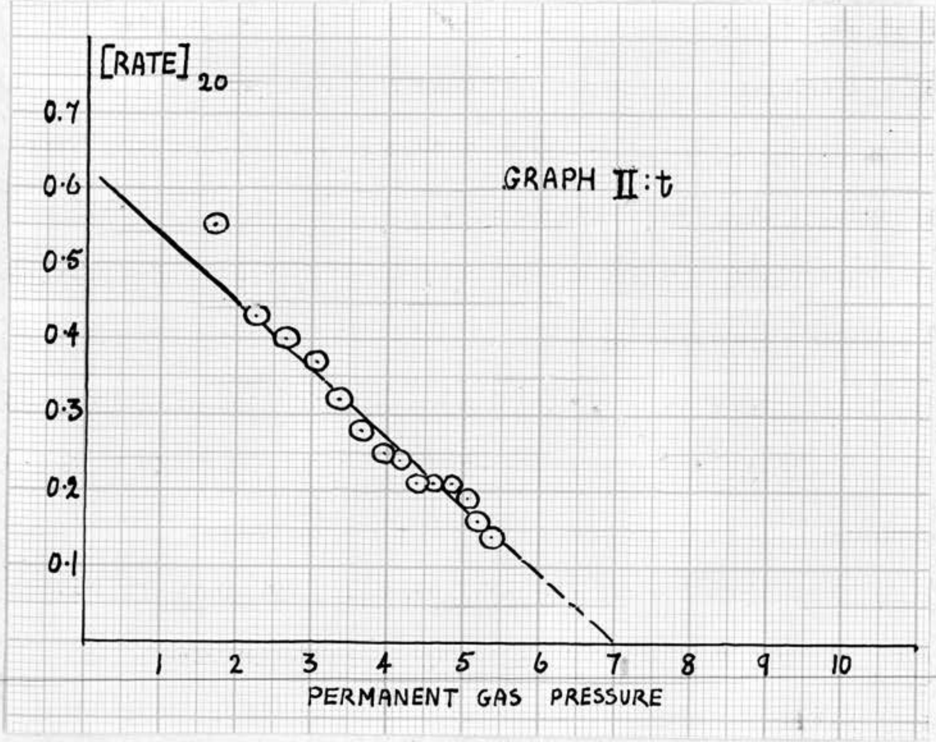
<u>Experiment II:28</u>

The conditions were as above but the ultimate temperature of the decomposition was 129°C. This 'run' proved to be an example of the type during which a much larger gas evolution occurred than expected for this temperature, on the basis of previous results. Such an effect has previously been attributed to inefficient adsorption of the acetone on the phosphoric oxide because of film formation of some other diffusional process. The results are shown, in the form of a pressure-time curve, in Graph II:s.

The /



GRAPH II:s



GRAPH II:t

The titanium dioxide film was contained in a small side tube separated from the reaction vessel by means of a 2mm. vacuum tap. After the system had been evacuated for 15 hours this tap was closed, and the reaction commenced in the presence of phosphoric oxide. At 'A' the tap was opened although the dark cover was not removed from around the titanium dioxide film. Appreciable dark absorption then occurred. When the dark reaction had ceased, the oxide film was illuminated ('B') and a pressure decrease of 0.58 mm. recorded. This agreed well with previous values of the equilibrium pressure at this temperature. The observed dark absorption on the titanium dioxide provided direct evidence in favour of the theory put forward by way of explanation of the anomalous 'dissociation' pressures previously observed.

After the completion of the reaction the film residue was analysed spectrographically for rubrene and the per cent decomposition estimated as 40%. The value obtained by calculation from the total pressure (permanent) increase and the constants of the apparatus was 35.5% (volume of the system 60 mls.) on the assumption of a unit molar ratio.

This discrepancy can probably be accounted for by a very slow evolution of oxygen while the illuminated titanium dioxide film was in the system.

It is now certain that the equilibrium pressures, if they are such, consist of pressures of oxygen in the presence of phosphoric oxide.

Divers Observations in the Decomposition of Rubrene Peroxide /

Divers Observations in the Decomposition of Rubrene Peroxide

In the initial experiments of this section, unimolecular decompositions extrapolable to pressure values corresponding to unit molar evolutions of condensable gas, were obtained in the absence of any adsorbents. The gauge sensitivity in such experiments was 0.16 mm./s.d. and the total extrapolated gas evolutions were of the order of 15 scale divisions for a film consisting of 2.34 mg. (R.E.) of the peroxide at 130°C. More recent data has indicated that a permanent gas is slowly produced, in the presence of phosphoric oxide, until the pressure reaches 0.59 mm. at this temperature. This pressure constitutes about 25% of the total extrapolated evolutions when no adsorbents were in the system. It would therefore appear that the decomposition to rubrene and oxygen had been retarded in some way during these experiments.

In a check experiment 1.35 mg. of the peroxide on 0.1 gm. of glass, was heated at 130°C 'in vacuo' for 350 minutes during which time the acetone vapour pressure was allowed to build up in the vessel. Although the film residue appeared red in parts, spectrographic analysis indicated that less than 1% decomposition to rubrene had occurred. It is probable that the acetone vapour had an adverse effect on the process of 'nucleation'. This process must be overcome before normal dissociation can occur. Visual evidence in favour of this suggestion was gained from an examination of the film residue: the residues were never completely red but consisted of isolated red 'stars' which were probably growth nuclei. After /

After heating in the presence of adsorbents, however, the films were completely red.

Throughout this section every effort has been made to obtain a film which will decompose twice in the same manner - the vapours have often been pumped off and the film reheated. In no case investigated has the pressure produced on reheating even approached the equilibrium (first heating) value.

The initial stages of the decomposition have not been accurately assessed by virtue of the time lag involved in heating the film up to the required temperature. The following experiment was designed to overcome this variable. It was also hoped to remove most of the loosely bound solvent from the surface of the glass before effecting the decomposition in this experiment.

Experimental

Gauge sensitivity - 0.084 mm./s.d.

Weight of peroxide - 4.68 mg.

Weight of substrate - 0.1 gm.

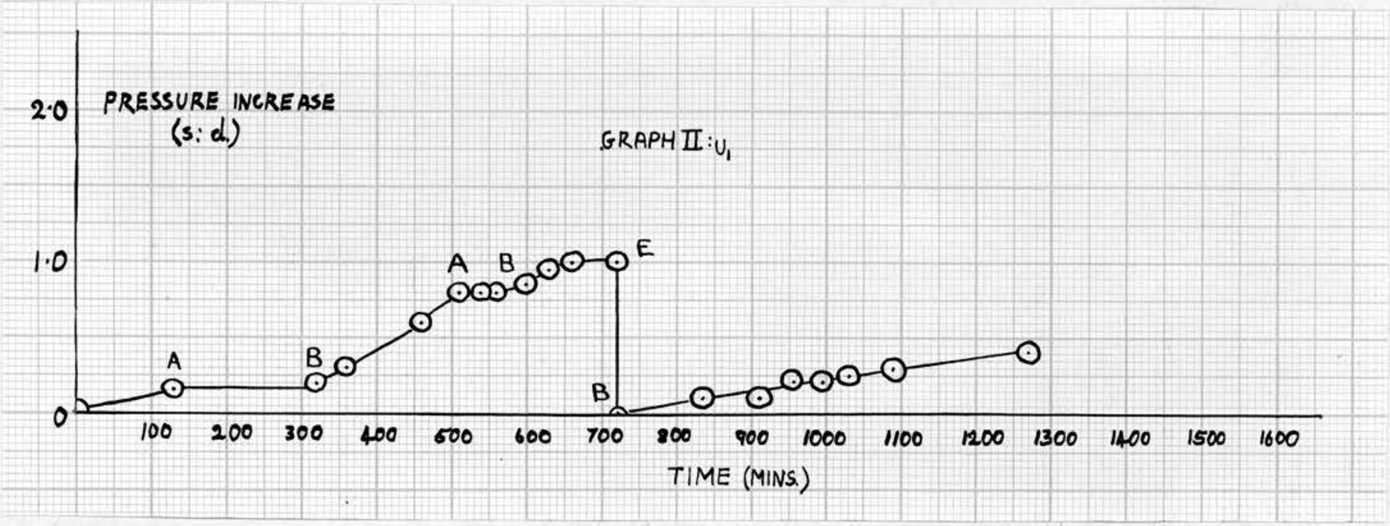
The reaction vessel was fitted with a side arm containing 0.5 gm. of phosphoric oxide. The film was evacuated for 20 hours after which 50 mm. of dry air was introduced into the apparatus while the film temperature was raised to 100°C. After 10 minutes hard evacuation at this temperature the apparatus was filled with 30 mm. of dry air and the film temperature raised to 130°C. When the temperature was steady the system was pumped as rapidly as possible to a pressure of uncondensable gas of 10^{-2} mm. Hg.(McLeod) and the gauge taps closed. The uncertainty time was about 3 minutes. The resulting pressure increases were recorded after known /

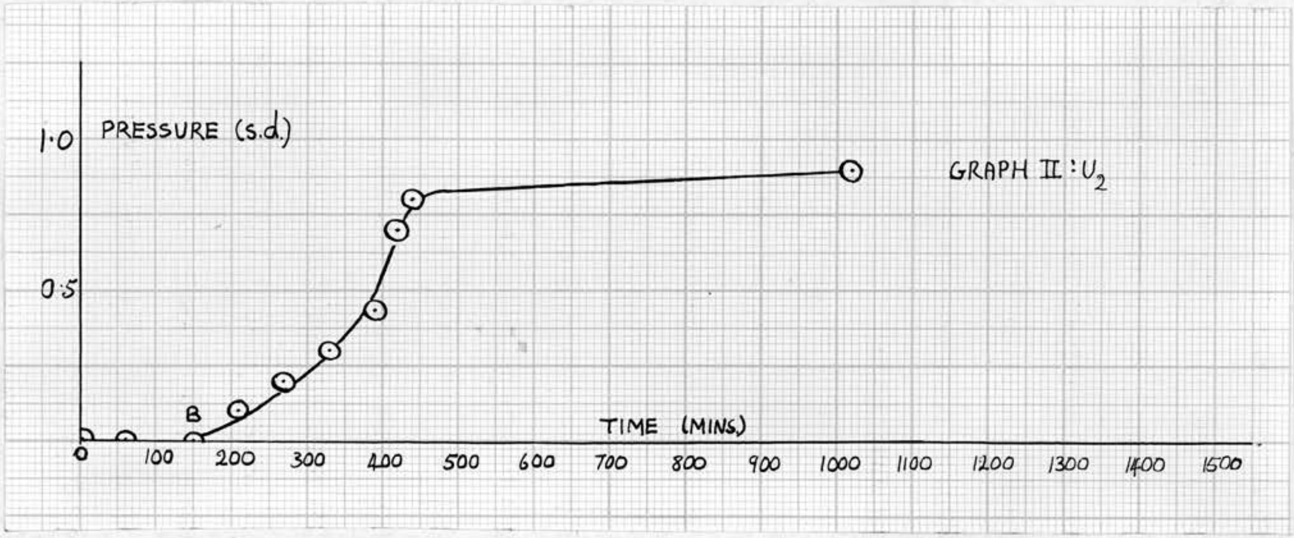
known time intervals while the results for the rate, expressed as scale divisions/20 minutes, at various gas pressures, expressed as scale divisions, are given below.

Total Pressure	Rate s.d./ 20 mins.	Total Pressure	Rate s.d./ 20 mins.
1.73	0.55	4.17	0.24
2.22	0.43	4.39	0.21
2.63	0.40	4.60	0.21
3.02	0.37	4.81	0.21
3.36	0.32	5.01	0.19
3.66	0.28	5.19	0.16
3.92	0.25	5.34	0.14
		5.48	0.14

As can be observed from the rate curve in Graph II:t, the extrapolated pressure increase was about 6.9 scale divisions, i.e., 0.58 mm., which is in excellent agreement with previous values of the equilibrium at this temperature.

At the cessation of the reaction the oxygen pumped off, and the film heated at 130°C. for 56 hours. The resultant pressure increase was only 1.1 divisions.


PRESSURE INCREASE (s: d.)
GRAPH II : U1
2·0
1·0
0
A
B
A
B
E
B
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
TIME (MINS.)


PRESSURE (s.d.)
GRAPH II : U2
1·0
0·5
0
B
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
TIME (MINS.)

The Effect of Light on the Decomposition of Rubrene Peroxide

It was pointed out by C. Dufraisse et al. that rubrene peroxide in benzene solution, when irradiated with light of unspecified energy in the absence of oxygen, shows the fluorescence of rubrene. This would indicate a reversible photochemical reaction involving rubrene, oxygen and rubrene peroxide. The following experiments were carried out in an effort to detect an analagous reaction in the solid state.

Experiment II:28

Gauge sensitivity - 0.050 mm./s.d.
Vessel volume - 60.5 mls.
Temperature - 25°C.
Weight of peroxide - 1.35 mg. (B)

A film was deposited on the plane glass surface of the reaction vessel and evacuated for $2\frac{1}{2}$ hours at 10^{-4} mm. Hg. (McLeod gauge) at room temperature. The gauge taps were closed and the vessel kept in complete darkness for 10 hours at 25°C. during which time no pressure change occurred in the reaction vessel. The film was then illuminated with the beam from the Osira lamp system. The course of the reaction may be followed by inspection of Graph II:u_1 where the symbols A, B and E have the following significance:-

A - Light off
B - Light on
E - Evacuated for 2 hours and left overnight in the dark at 25°C.

When the reaction had ceased the vessel was removed from the apparatus and the film visually examined. Although no red particles /

particles were observed, it was noticed that the film was slightly yellow, particularly under ultra violet light. This may have been the fluorescence emission from the very small amount of rubrene formed.

The results indicate that a definite photochemical reaction has taken place. The pressure increase, however, may have been the result of light activated desorption of solvent vapour; decomposition of the peroxide-solvent complex to produce solvent vapour; or the breakdown of the peroxide to give oxygen and rubrene.

A repeat experiment, using 1.1 mg. of the peroxide deposited in the form of a film on 0.2 gm. Jena glass, provided the results shown on Graph II:u_2. In this case the reaction was allowed to proceed to completion, without interruption, as far as could be estimated by pressure measurement. The total pressure increase in this experiment was only 0.045 mm. (17 hours) while the previous 'run' had yielded a value of about 0.05 mm. after the same time. Although, however, the approach to equilibrium after evacuation was much slower, only 0.025 mm. being evolved in 600 minutes of illumination.

An experiment was carried out in which 2.34 mg. of the peroxide on 0.1 gm. of Jena glass was illuminated while being decomposed at 130°C. in the absence of any adsorbents. The results indicated that a unit molar ratio of acetone was produced from the peroxide-solvent complex; after correcting for the solvent desorbed from the glass. Less than 5% dissociation of oxygen occurred. It can be concluded that light of wavelength longer than 3650 A° had no appreciable /

appreciable effect on the decomposition of rubrene peroxide at 130°C.

This is not surprising in relation to the effect of light at room temperature as the photochemical reaction will have a very small apparent activation energy which may even be negative if the excited state involved is degraded by heat; e.g., the triplet state with a diradical structure.

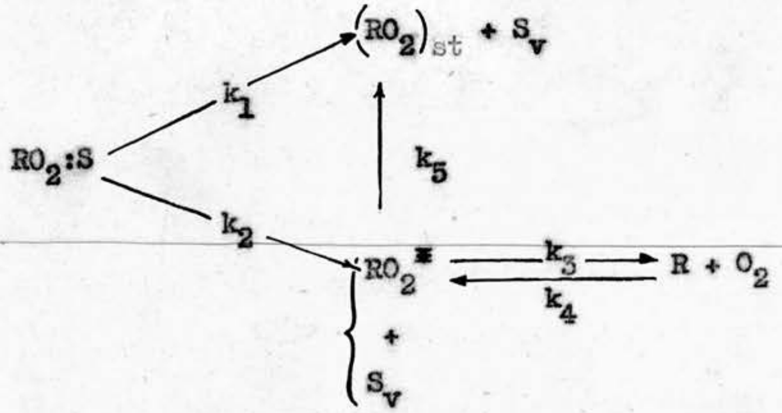
Discussion of the Results from Section II /

Discussion of the Results from Section II

As has been previously described the solutions of rubrene peroxide were prepared by exposing rubrene solutions of known concentration to sunlight until no trace of rubrene could be detected in the absorption spectrum of the product. Absorption spectra and experiments on the photo-oxidation of rubrene films prepared 'in situ' from the peroxide have indicated that such peroxide solutions contained the rubrene equivalent of the original solution.

Rubrene peroxide, associated with a molecule of crystallisation is deposited on a powdered glass surface and the starting material may be written as $RO_2:S$ where R signifies the rubrene, O_2 the associated oxygen and S the solvent of crystallisation. It is postulated that this material may be degraded by heat either into a thermally stable derivative, (RO_2) st., and solvent vapour, S_v, or into the dissociable peroxide RO_2^* and solvent vapour. These processes will occur at the specific rates k_1 and k_2 respectively. The compound RO_2^* may dissociate into oxygen and rubrene or may rearrange to the stable product at a specific rate k_5; this product may or may not be the same as $(RO_2)_{st}$.

The complete reaction scheme is shown below.



In the above scheme $RO_2:S$, RO_2^*, R, and $(RO_2)_{st}$ are solid components while O_2 and S_v are in the gaseous phase.

Rubrene /

Rubrene peroxide as deposited from acetone solution as a thin film on Jena glass produces, when heated, an equi-molar quantity of a vapour. This vapour has been shown to be acetone and it may be concluded that rubrene is associated with one molecule of acetone of crystallisation.

In the presence of phosphoric oxide, which adsorbs acetone, a permanent gas is evolved in amount depending only on the temperature when the other conditions are ideal. This gas has been shown to be oxygen, derived from the rubrene peroxide, and corresponding amounts of rubrene are formed. The pressure values obtained from the extrapolated rate curves indicated an equilibrium system, if only by their reproducibility. Doubling the surface concentration of peroxide did not alter the position of equilibrium, as measured by oxygen pressure increase, although equilibrium was not re-attained at a measurable rate if the pressure was reduced. If, however, the temperature was raised during the reaction the extent of the decomposition was increased.

The fraction of the original peroxide which is transformed into the dissociable form is given by $k_2/k_1 + k_2$. Thus the amount of oxygen formed from the dissociable peroxide, expressed as a fraction of the molar concentration of the original peroxide, will be given by (1)

$$\text{Moles oxygen/Moles } RO_2{:}S = (k_2/k_1 + k_2)(k_3/k_5 + k_3) \text{ ------ } (1)$$

where k_1, k_2 etc., are the specific rates of the noted stages in the reaction.

Formula /

Formula (1) leads in general to the expression:

$$\left(\frac{k_2}{k_1 + k_2}\right)\left(\frac{1}{1 + k_5/k_3}\right)$$

for the fraction of the starting material which will decompose into rubrene and oxygen. The cases then arising are (a) $k_5 \ll k_3$; (b) $k_5 \gg k_3$; and (c) $k_5 \sim k_3$; the latter stipulation constituting a mean value of the extreme conditions. When governed by such limits the above expression will assume the following values:-

(a) $\left(\frac{k_2}{k_1 + k_2}\right)$

(b) Zero

and (c) $\frac{k_2}{2(k_1 + k_2)}$ -------------- (2)

If the mean value (2) is accepted as the best approximation two further cases will result. Case (1): when the fraction of solid RO_2:S which decomposes into rubrene and oxygen is less than that required for a true dissociation pressure to be set up; i.e. when -

$$p_e > \frac{k_2}{2\,(k_1 + k_2)}$$

where p_e is the true dissociation pressure of oxygen expressed as a molar fraction of the amount of RO_2:S. Case (2): when the dissociation pressure expressed as a similar fraction is less than the fraction of RO_2:S which may decompose into rubrene and oxygen; i.e., when -

$$p_e < \frac{k_2}{2\,(k_1 + k_2)}$$

If the temperature, weight of peroxide and the constants of the apparatus satisfy the first case, then the true dissociation pressure may /

may not be measured. Instead an oxygen pressure value equivalent to $\frac{k_2 \times 100}{2\,(k_1 + k_2)}$ % decomposition of RO_2:S will be obtained. When Case (2) arises the produced oxygen pressure will constitute an equilibrium amount as there will always be RO_2 available for dissociation.

When the peroxide complex was decomposed in the absence of any adsorbents either on a plane or on a Jena glass surface, little or no oxygen was formed although equimolar proportions of solvent were evolved. The rate constants for these reactions were all approximately 10×10^{-3} mins.$^{-1}$ and may be identified with k_1. If (k_3) is very much greater than (k_2) then the measured rate of oxygen production will actually be determined by k_2 which is 5.3×10^{-2} mins $^{-1}$ at 130°C. It was observed that the variation of k_1 with temperature was not very great over the examined range.

Thus,

$$k_2/2(k_1 + k_2) \sim \frac{53}{2\,(10 + 53)} = 0.421$$

and the maximum oxygen evolution that may be expected on the basis of this mechanism will therefore be equivalent to a 42.1% decomposition of the peroxide, at 130°C. This value is not extremely temperature sensitive, only rising to 48% at 145°C., however the variation of the specific rate k_5 with temperature is not known.

The decomposition of the peroxide at 145°C. resulted in the production of 0.84 mm. of oxygen from 2.34 mg. of starting material, the pressure-time curve being subject to a sudden saturation effect. The amount of decomposition can be calculated as 41.5% which would suggest that the true equilibrium pressure has not been attained /

attained in this reaction. In other words the reaction is governed by Case (1). The pressure equilibrium set up in 'run' II:13, where a fairly large and more reasonable value of 1.34 mm. was obtained, at 150°C. and from an initial 4.68 mg. of the peroxide, corresponded to a 29% decomposition of the peroxide. It is probable then that this is the true dissociation pressure of oxygen at this temperature; the reaction conforming to Case (2).

The value of 0.59 mm. at 130°C which was obtained independently of the initial peroxide concentration was equivalent to only 29.3% or 14.7% decomposition according to whether the concentration was 2.34 mg. or 4.68 mg./film. Again, on the basis of the proposed mechanism, this was probably the actual dissociation pressure of the reaction.

Such a mechanism as has been postulated would necessitate an induction period due to the building up of the amount of reactive peroxide but if the rate of decomposition of this dissociable peroxide is very large compared to its rate of formation the period of induction becomes infinitely small. This acceleration period is not directly connected with the period of nucleation which may also be a rate determing factor at the commencement of the reaction.

If the solvent pressure was allowed to build up from the commencement of the reaction little or no decomposition of the peroxide to oxygen and rubrene could be detected. Solvent vapour, however, did not inhibit the reaction once the evolution of oxygen had commenced. It would therefore appear that large amounts of solvent vapour, obtained from the glass and the peroxide complex, retarded the initiation step or period of nucleation. That is to say only the stages with rates k_1, k_2 and k_5 took place under these conditions /

conditions; after removal of the solvent vapour towards the end of the reaction, as measured by pressure increase, it is likely that complete conversion to the thermally stable product had been effected and no further pressure increases would be observable in the presence of adsorbents.

It is still possible that the solvent vapour might inhibit the reaction k_2 resulting in all the $RO_2{:}S$ decomposing via reaction k_1 in the absence of adsorbents. Such a mechanism would require that the stage $G{:}RO_2{:}S \xrightarrow{k_2} RO_2^{\ddagger} + S_v$ in the presented scheme be replaced by $G{:}RO_2{:}S \underset{k_6}{\overset{k_2}{\rightleftharpoons}} RO_2^{\ddagger} + S_v$.

According to the empirical results of this section the solvent complex and the peroxide break down independently to produce solvent vapour in the one case and oxygen and rubrene in the other. Evidence is available, however, (see Section III: p. 133) which indicates strongly that these steps occur simultaneously and at the same specific rate, in the ideal case, and are probably associated. This is excellent indication in favour of the theory that the peroxide is in effect stabilised by a surface effect while the solvent remains loosely bound.

The value of 10 Kg.cals./mole for the heat of dissociation obtained from the slope of curve II:m_1 must now, in the light of the present reaction scheme, be modified. The slope of the dotted line on the same graph indicates the true heat of reaction; the point at 145°C. having been discarded for the reasons described above. The new value of 13.5 Kg.cals./mole agrees well with the value obtained from the slope of the line in Graph II:m_2 which was 12.9 Kg.cals./mole.

Enderlin /

Enderlin (62, 63) calculating from the heats of combustion and formation has arrived at a value of $\Delta H = 23.2$ Kg.cals./mole for the formation of rubrene peroxide from rubrene and oxygen. This value is considered to be high for a reversible reaction. The decomposition of diphenylanthracene is also endothermic and the heat of this dissociation has been estimated as +15 Kg.cals./mole. In marked contrast is the dissociation of 1:4-dimethoxy-9:10-diphenylanthracene (64) which is an exothermic reaction, $\Delta H = -15$ Kg.cals./mole, this compound being easily dissociable at room temperature. Audubert and Racz (65) have studied the decomposition of this compound and have shown that the oxygen is molecular when evolved.

It is thus apparent that the results obtained in this work are favourably comparable with the results of other workers on similar compounds.

An apparent activation energy of 40 Kg.cals./mole was measured and attributed (p. 98) to the dissociation of rubrene peroxide into rubrene and oxygen. Further examination of the reaction scheme, however, invalidates this assumption. If the rate determining stage in the decomposition is the formation of the reactive peroxide, which is a basic assumption in the proposed mechanism, then the measured activation energy must apply to this stage. From the present results it may only be said that the peroxide dissociates with an activation energy less than 40 Kg.cals./mole.

The variation of the individual rate constants in the proposed scheme was not accurately assessable but it is likely that stage (5) has a small activation energy. In a normal experiment the film was heated in the presence of phosphoric oxide until the rate curve became /

became extrapolable to the equilibrium pressure. If at this point the film was evacuated rapidly and the system re-isolated without changing the temperature of the film a further small pressure increase would be detected. If on the other hand the temperature was lowered and the film evacuated at room temperature no further pressure was observable on reheating the film over a long period. Thus it is probable that the rate constant k_5 is still appreciable at lower temperatures. By virtue of this stage it is most improbable that any one film, under these conditions, would ever attain equilibrium during a second heating.

No positive conclusion may be reached from the available experimental data regarding the nature of the thermally stable peroxide complex. As similar results were obtained with the film deposited on the plane glass surface of the reaction vessel it is unlikely that the Jena glass substrate played any part in the reaction. On treatment with reducing agents or with dilute acids, rubrene peroxide may rearrange to a variety of stable oxides or hydroxides. It is possible that the experimental conditions were such that would facilitate one of these rearrangements. The reaction (5), which is a solid transformation, may involve a similar chemical stage to the reaction (1). Such rearranged oxides are known to be stable up to their melting points (66).

The scheme, as given, explains the effect of solvent vapour on the decomposition of the peroxide into rubrene and oxygen. The explanation that the vapour effects the nucleation process must, however, include a further stipulation; viz., that the nucleation step in the breakdown of the peroxide to rubrene and oxygen occurs on the surface of the material which is in contract with the vapour phase.

A less probable scheme which would certainly explain the solvent effect is given below.

$$RO_2{:}S_2 \longrightarrow RO_2{:}S + S_v \text{ ------------------------ (a)}$$

$$RO_2{:}S \rightleftharpoons RO_2 + S_v \text{ ------------------------ (b)}$$

$$RO_2 \rightleftharpoons R + O_2 \text{ ------------------------ (c)}$$

In this case it must be assumed that the peroxide molecule is initially associated with two molecules of acetone in the crystalline state. If the adsorptive efficiency of the phosphoric oxide, was not high enough to remove acetone vapour to a residual pressure less than the solvent dissociation pressure of reaction (b) then no decomposition to rubrene and oxygen would occur. Under normal circumstances when the adsorbent is efficient, a dissociation pressure of oxygen would be set up; on the other hand in the absence of any adsorbents, only the stage (a) will take place. There is, however, no evidence which suggests that the peroxide crystallises with two molecules of acetone of crystallisation.

A comparison of the general conclusions from this section with the results of other workers will be presented at the end of Section IV.

Experimental Section III /

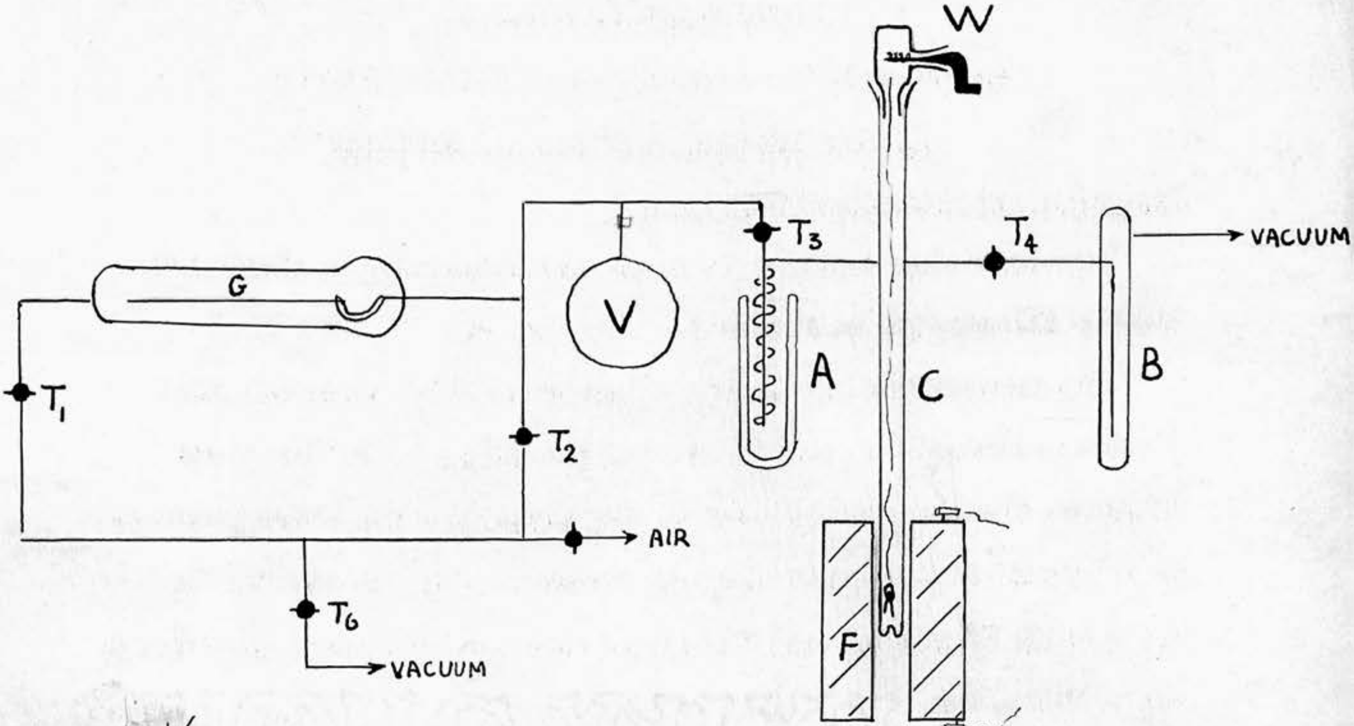
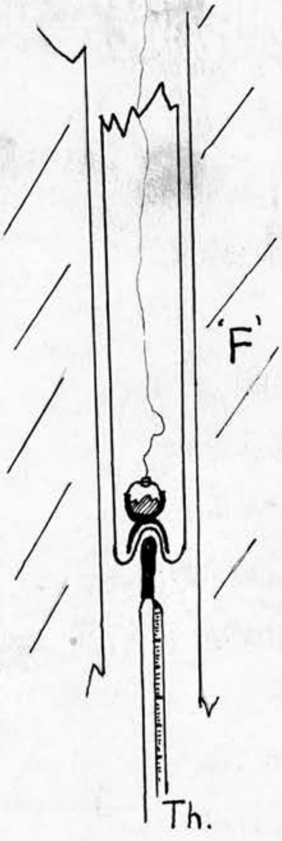
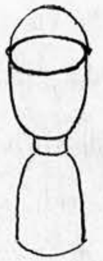


FIGURE 5(a)



5(c)



5(b)

EXPERIMENTAL SECTION III

The 'in vacuo' Decomposition of Rubrene Peroxide as Crystallised from Benzene Solution

Apparatus and Experimental Procedure

The apparatus employed in these investigations is diagrammatically illustrated in Figure 5.

The pressure of gas in the volume V could be measured, from a vacuum standard, on the Bourdon sickle gauge, G, by the usual telescope arrangement focussed on the gauge pointer. The pressure in the gauge could be balanced, if necessary, by introducing dry air through T_1 and T_5 into the gauge jacket. The gauge sensitivity was 0.05 mm./s.d.

The cylindrical furnace, F, was easily fitted coaxially round the tube C. A potential divider arrangement coupled to the 230 volt mains and the furnace allowed the temperature to be controlled to within 1°C. of the required value over a period of a few hours. The temperature was measured with a thermometer.

The peroxide container (see fig. 5b) was fabricated from Pyrex glass and so shaped that it could slip over the small holder at the base of the reaction chamber. Figure 5c shows the vessel in position. In this way it was ensured that the position of the container, relative to the furnace and the thermometer, Th, was reproducible.

The winch, W, enabled the bucket container to be raised and lowered in the reaction chamber on the end of a thin untempered platinum wire. The winch was made from a set of Quickfit joints lubricated with Apiezon 'L' high vacuum grease.

The /

The chamber 'C' and the spiral trap 'A' were so arranged that their combined volumes were small compared with the volume of the cold side of the trap 'A'. This was aided by making the volume 'V' very large (150 mls.).

The bulb 'V' was maintained at 20°C. throughout a reaction. The volume of the space enclosed by the taps T_2 and T_3 was determined in the usual manner. After opening tap T_3 the volume enclosed by T_2 and T_4 was similarly determined. Approximately 5 mls. of the reaction chamber volume was enclosed by the furnace. The results obtained were as follows:-

Volume enclosed by T_2 and T_3 (V_1) - 170 mls.
Volume enclosed by T_2 and T_4 - 206 mls.
Volume enclosed by T_3 and T_4 (by difference) - 36 mls.
Fraction of this volume at furnace temperature (V_3) - 5 mls.
Fraction of T_3T_4 volume at room temperature (V_2) - 31 mls.

At the commencement of an experiment the trap 'A' was surrounded with liquid oxygen. If a reaction occurs in V_3 to produce a condensable vapour and a permanent gas in approximately equimolar proportions the gas pressure in V_2 will equal that in V_1. The gas in V_1, however, will be oxygen (on the assumption that this is the permanent gas) while only half the gas in V_2 will be 'permanent'. If the gas pressure is measured in V_1 and found to be P mm. the total number of moles of oxygen present in the system is then given by:-

$$\frac{P}{760} \cdot \frac{273}{293} \cdot \frac{(V_1 + \frac{1}{2}V_2)}{22.4} = 1.01 \times 10^{-5} . P \text{ moles.}$$

where V_1 and V_2 are expressed in litres.

If /

If the rate of diffusion of vapour to the trap is slow the partial pressure of oxygen in V_2 will decrease as the vapour pressure builds up. The magnitudes of the volumes V_1 and V_2 have been so arranged that the limiting error in this calculation (i.e. when no vapour diffuses to the trap) due to vapour diffusion was less than 8%. It has been assumed in all experiments that the rate of movement of oxygen from V_3 to V_1 was rapid compared to the rate of the decomposition occurring in V_3. The volume V_3 has been excluded from the calculation its effect being considered negligible.

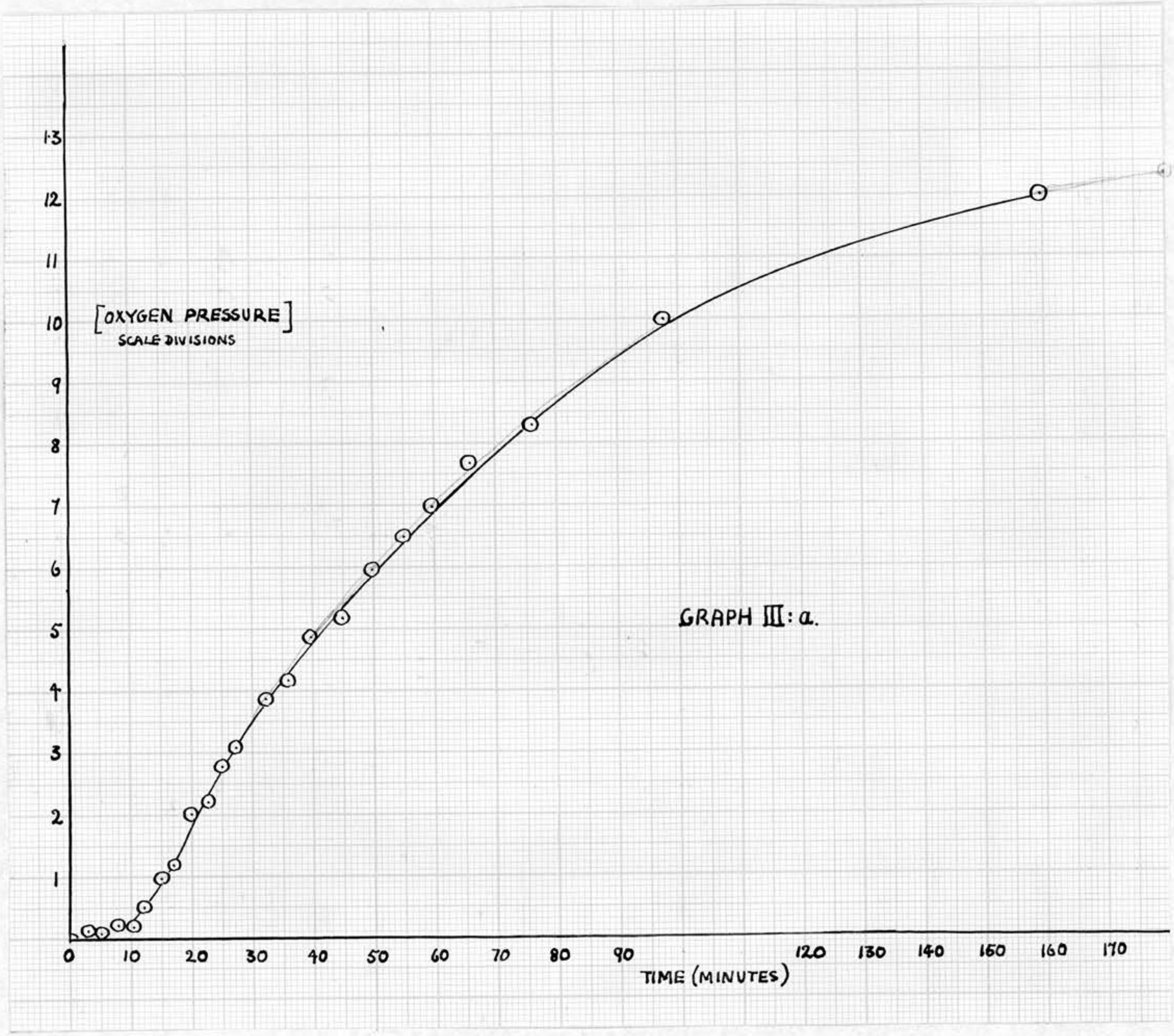
During the experiments the gauge jacket was continually evacuated thus rendering thermostating unnecessary.

A Typical Experiment

7.1 mg. of the rubrene peroxide (for preparation see p. 17) were weighed out in the reaction container and immediately transferred to the winch system. The bucket was suspended about 8 inches above the furnace entrance. The furnace was then switched on and allowed to reach 81°C. The apparatus was evacuated through taps T_2 and T_4, T_3 being open, for 15 hours. The evacuation was effected with the oil and diffusion pumps and the residual pressure, measured by the McLeod gauge, was less than 10^{-4} mm.Hg. During this evacuation the trap 'B' was surrounded with liquid oxygen.

When the evacuation was completed the taps T_2 and T_4 were closed and the trap 'A' surrounded with liquid oxygen. The gauge pointer reading was now noted. The joint comprising the winch axle was slightly warmed, to facilitate turning, and the bucket containing the peroxide quickly lowered into its position as shown on the diagram. The furnace temperature was now noted and found to be 81°C. having remained steady for 15 hours.

Readings /



GRAPH III: a.

[OXYGEN PRESSURE]
SCALE DIVISIONS
1·3
12
11
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
120
130
140
160
160
170
TIME (MINUTES)

Readings of the gauge pointer were recorded at appropriate time intervals until the cessation of the reaction. The actual results obtained are given below while the values are plotted on Graph III:a. 'P' is the recorded pressure in scale divisions at time 't' while P/mg. is the pressure per unit weight of initial rubrene peroxide, obtained by dividing 'P' by 7.1.

t (mins.)	P s.d.	P/mg.	t (mins.)	P s.d.	P/mg.
0	0.0	0.0	36	4.2	0.592
3	0.1	0.014	40	4.9	0.691
5	0.1	0.014	45	5.2	0.733
8	0.2	0.028	50	6.0	0.847
10	0.2	0.028	55	6.5	0.916
12	0.5	0.0704	60	7.0	0.987
15	1.0	0.14	66	7.7	1.08
17	1.2	0.169	76	8.3	1.17
20	2.0	0.282	98	10.0	1.41
22.5	2.2	0.310	160	12.0	1.69
25	2.8	0.436	255	13.0	1.83
27.5	3.1	0.436	180	12.3	1.74
32.5	3.9	0.549	285	13.0	1.83

The bucket was now raised to a cool part of the tube and the system evacuated through the tap T_2 for one hour. After closing this tap the liquid oxygen was removed from around the trap 'A'. When the trap had warmed up sufficiently 12.0 divisions of condensable vapour evaporated into the gauge. The crystalline mass in the bucket was then removed from the apparatus, made up to a known volume in benzene and spectrographically analysed for rubrene.

The /

The rubrene equivalent of the residue was 6.19×10^{-6} moles. The amount decomposed, calculated from the oxygen evolution, was 6.59×10^{-6} moles and from the solvent (benzene) 6.58×10^{-6} moles.

This experiment (III:1) has been described in detail and the results that follow have been obtained from experiments performed in exactly the same manner with the same apparatus. Only the variables of temperature and initial concentration of rubrene peroxide were altered from experiment to experiment.

Experiment III:2

Weight of container peroxide - 1.56310 gm.
Weight of container alone - 1.54424 gm.
Weight of Peroxide -18.86 mg.
Temperature - 91°C.

Time (mins.)	P s.d.	P/mg.	Time (mins.)	P s.d.	P/mg.
0	0	0	18	15.0	0.756
1	0	0	19	16.0	0.849
2	0	0	20	17.0	0.902
3	0.05	0.0027	22	19.0	1.01
4	0.1	0.0054	23	20.0	1.06
5	0.8	0.0043	25	22.1	1.19
6	1.5	0.080	26	22.8	1.21
7	2.2	0.117	27.5	23.1	1.22
8	3.2	0.170	29	24.0	1.27
9	4.2	0.223	30	24.6	1.30
10	5.3	0.281	32	25.6	1.36
11.5	7.1	0.376	33	26.0	1.38
12.5	8.8	0.466	34	26.5	1.40
13	9.0	0.477	35	27.0	1.43
14	10.2	0.541	36	27.5	1.46
15	11.9	0.631	37	28.0	1.48
16	13.0	0.690	40	29.7	1.57
17	14.0	0.744	48	31.1	1.65

Condensable /

Condensable vapours retrieved - 33.1 scale divisions

Rubrene equivalent of the residue - 11.5 mg.

Experiment III:3.

Weight of container Peroxide - 1.56110 gm.

Weight of container alone - 1.54418 gm.

Weight of Peroxide - 16.82 mg.

Temperature - 100°C.

Time (mins.)	P s.d.	P/mg.	Time (mins.)	P s.d.	P/mg.
0	0	0	14	18.9	1.12
1	0	0	15	20.0	1.19
2.5	0	0	17	21.0	1.25
8	8.9	0.53	19	21.9	1.30
9	9.4	0.56	22	22.0	1.30
10	12.0	0.72	25	22.1	1.31
11	14.4	0.85	32	22.1	1.31
12	16.4	0.98	55	22.1	1.31
13	17.9	1.06	60	22.1	1.31

Rubrene equivalent of the residue - 6.7 mg.

Experiment III:4

Weight of container peroxide - 1.55103 gm.

Weight of container alone - 1.54417 gm.

Weight of Peroxide - 6.86 mg.

Temperature - 100°C.

Time (mins.)	P s.d.	P/mg.	Time (mins.)	P s.d.	P/mg.
0	0	0	10	7.7	1.12
1	0	0	10.5	8.0	1.17
2	0	0	11	8.8	1.27
3	0	0	12	9.5	1.38
4	0.1	0.018	13	10.0	1.46
5	1.1	0.161	14.5	10.9	1.59
6	2.2	0.324	16	11.1	1.62
6.5	3.0	0.439	17.5	11.5	1.68
7	3.8	0.555	19	11.9	1.74

7.5 /

Time (mins.)	P s.d.	P/mg.	Time (mins.)	P s.d.	P/mg.
7.5	4.5	0.659	21.5	12.0	1.75
8	5.1	0.743	24	12.0	1.75
8.5	5.7	0.835	32	12.1	1.76
9	6.5	0.949	38	12.1	1.76

Rubrene equivalent of the residue - 3.3 mg.

Experiment III:5.

Weight of container Peroxide - 1.53040 gm.
Weight of container alone - 1.49800 gm.

Weight of peroxide - 32.4 mg.
Temperature - 104°C.

Time (mins.)	P s.d.	P/mg.	Time (mins.)	P s.d.	P/mg.
0	0	0	13	56.8	1.75
1	0	0	14	58.0	1.79
2	0.1	0.0031	15	59.7	1.84
3	2.5	0.077	16	60.7	1.87
4	7.2	0.223	17	61.4	1.89
5	14.0	0.434	18.5	62.2	1.92
6	23.0	0.710	20	63.0	1.94
7	30.8	0.955	22	63.8	1.97
8	38.5	1.19	24	64.0	1.98
9	44.0	1.39	26	64.2	1.98
10	48.2	1.49	28	64.7	2.00
11	52.0	1.61	30	64.8	2.00
12	54.4	1.71	35	65.0	2.02
			60	65.0	2.02

Condensable vapour retrieved - 61.5 divisions.

Rubrene equivalent of residue - 20.4 mg.

Experiment III:6

Weight of container Peroxide - 1.55664 gm.
Weight of container alone - 1.54417 gm.

Weight of peroxide - 12.47 mg.
Temperature - 107°C.

Time /

Time (mins.)	P s.d.	P/mg.	Time (mins.)	P s.d.	P/mg.
0	0	0	5.5	19.7	1.56
1	0	0	6.5	21.9	1.75
2	0	0	7.0	22.2	1.78
3	3.1	0.25	8	22.8	1.82
3.5	6.7	0.54	9.5	23.0	1.84
4	9.9	0.79	11	23.0	1.84
4.5	13.9	1.11	13	23.0	1.84
5	16.9	1.35	15	23.0	1.84

Condensable vapour retrieved - 24.0 divisions.

Rubrene equivalent of the residue - 6.6 mg.

Experiment III:7

Weight of the container Peroxide - 1.55360 gm.
Weight of the container alone - 1.54420 gm.

Weight of Peroxide - 9.40 mg.
Temperature - 111°C.

Time (mins.)	P s.d.	P/mg.	Time (mins.)	P s.d.	P/mg.
0	0	0	6.5	15.2	1.60
0	0	0	7.0	16.2	1.73
3	0	0	7.5	16.7	1.79
4	1.2	0.13	8.5	17.0	1.81
4.5	4.1	0.445	10	17.1	1.84
5.0	7.7	0.84	13	17.1	1.84
5.5	11.1	1.18	16	16.9	1.80
6.0	13.9	1.49	23	16.5	1.76

Condensable vapours retrieved - 21.8 divisions

Rubrene equivalent of the residue - 6.0 mg.

Experiment III:8

Weight of the container Peroxide - 1.56329 gm.
Weight of the container alone - 1.54417 gm.

Weight of Peroxide - 19.12 mg.
Temperature - 118°C.

Time /

Time (mins.)	P s.d.	P/mg.	Time (mins.)	P s.d.	P/mg.
0	0	0	6.5	33.0	1.72
1	0	0	7.0	33.2	1.73
3	1.0	0.052	8.0	33.5	1.75
3.5	12.0	0.63	9	33.8	1.77
4.0	18.0	0.94	10	33.9	1.77
4.5	27.0	1.41	11	33.9	1.77
5.0	30.5	1.60	12	33.9	1.77
5.5	32.0	1.675	18	33.4	1.75
6.0	32.8	1.71	25	33.1	1.72

Rubrene equivalent of the residue - 9.8 mg.

The Stoichiometry of the Decomposition /

The Stoichiometry of the Decomposition

Rubrene peroxide crystallises with solvent of crystallisation in amount depending on the solvent. In this case benzene was the solvent and on the assumption that the one mole of benzene is combined with one mole of peroxide the molecular weight of the complex is 642 gm. The numbers of moles of oxygen, benzene and rubrene that were recovered from one mole of peroxide complex in a series of reactions are shown in the table below. The yields are expressed as percentages of the initial molar concentration of peroxide, assuming its molecular weight to be 642. Included in this table are the results of Experiments III:9 - 13 in which it was not possible to estimate the form of the pressure-time curve although the routine analyses were carried out.

Number	Oxygen %	Benzene %	Rubrene %
III: 1	60	60	57
2	73	64	73
3	48	-	48
4	64	-	58
5	70	69	70
6	67	69	64
7	69	84	77
8	65	-	62
9	72	70	78
10	77	-	80
11	69	65	73
12	70	63	73
13	64	74	69

The /

The constancy of these figures indicates that the peroxide complex normally decomposes to about 70% thus producing equimolar proportions of oxygen, benzene and rubrene. The reaction may then be represented by the stoichiometric relationship:-

Rubrene peroxide:benzene → Rubrene + Oxygen + Benzene

or $C_{42}H_{28}O_2 : C_6H_6 \longrightarrow C_{42}H_{28} + O_2 + C_6H_6$

The analysis results suggest that the splitting off of solvent and the evolution of oxygen have occurred at the same specific rate and are thus probably concerned with the same chemical stage of the reaction.

The Dependence of Maximum Rate on Peroxide Concentration /

The Dependence of Maximum Rate on Peroxide Concentration

The maximum rates of oxygen evolution in 'runs' :3 and :4 were computed to be 29.1 and 13.6 scale divisions per minute respectively while the initial peroxide concentrations were 16.83 and 6.86 mg. It can be seen that the ratio of rate to weight of peroxide is constant within the limits of experimental error. This maximum rate of production of oxygen occurred and was measured along the same P/mg. abscissa.

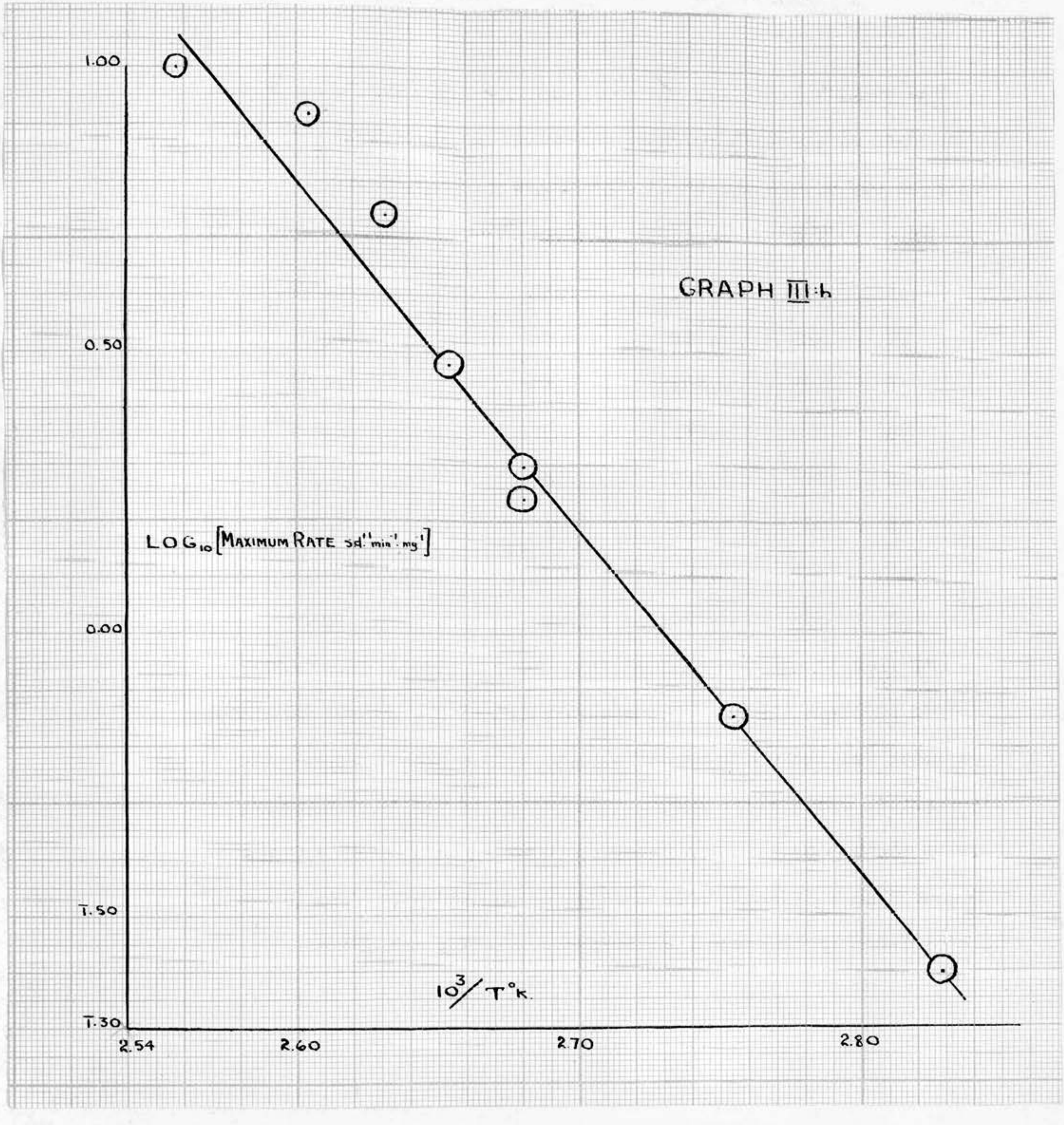
Thus:

$$\text{Maximum Rate} = \text{constant.} \left[\text{peroxide}\right]$$

$$\frac{d\left[O_2\right]}{dt} = k. \left[RO_2\text{:Benzene}\right]_{\text{initial}}$$

An examination of the typical curve drawn on Graph III:a manifests the existence of three distinct stages in the reaction; viz., the 'induction' or acceleration period, the inflective portion involving the maximum rate and finally the decay process. In order to aid the process of derivation the maximum rate portion will be the first to be discussed.

The Energetics of the Maximum Rate Process /


GRAPH III·h
1.00
0.50
0.00
1̄.50
1̄.30
LOG₁₀ [MAXIMUM RATE sd⁻¹ min⁻¹ mg⁻¹]
10³/T°K.
2.54
2.60
2.70
2.80

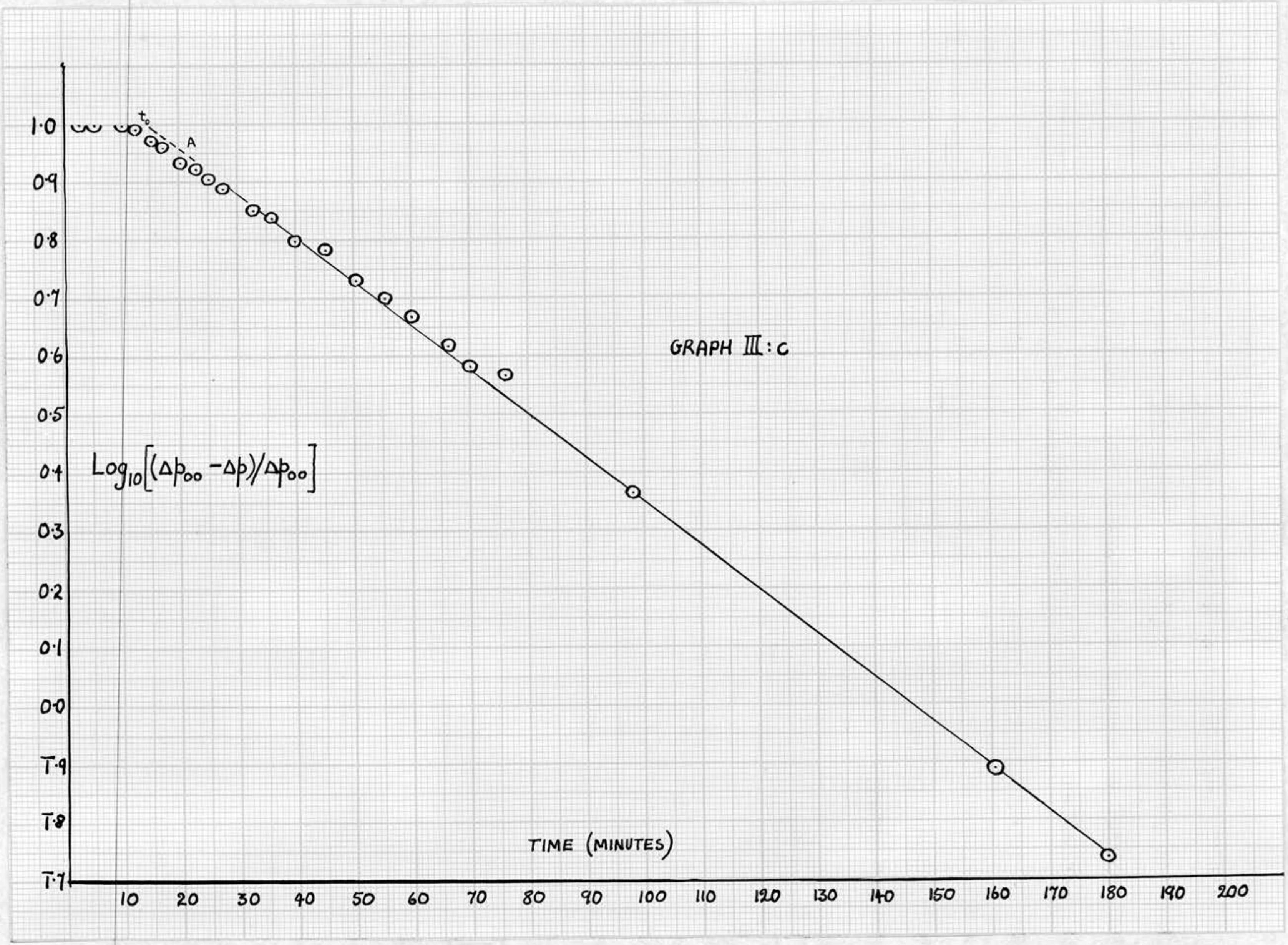
The Energetics of the Maximum Rate Process.

The table below lists the computations from 'runs' III: 1 - 8 in the form of the maximum rates expressed as scale divisions per milligram per minute and their dependence on temperature.

No.	$T^{o}K$	$10^3/T$	Maximum Rate	$\log_{10}$ Maximum Rate
III:1	354	2.828	0.25	$\bar{1}.398$
:2	363	2.754	0.71	$\bar{1}.851$
:3	373	2.681	1.73	0.238
:4	373	2.681	1.98	0.297
:5	377	2.653	2.80	0.477
:6	380	2.631	5.5	0.740
:7	384	2.604	8.2	0.914
:8	391	2.557	10.0	1.00

The plot of maximum rate against the reciprocal temperature is shown in Graph III:b. The distribution of the points indicates that these functions are connected by a linear relationship over the examined temperature range. The slope of the best straight line is -6.41×10^3. This corresponds to an activation energy, ΔE_r, of 29.3 - Kg.cals./mole for the decomposition. The accuracy of this determination was approximately ±1.5Kg. cals./mole.

The Decay Process



GRAPH III : C

Log$_{10}$[(Δp_{00} − Δp)/Δp_{00}]
TIME (MINUTES)
t_0
A
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
$\bar{1}$·9
$\bar{1}$·8
$\bar{1}$·7
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

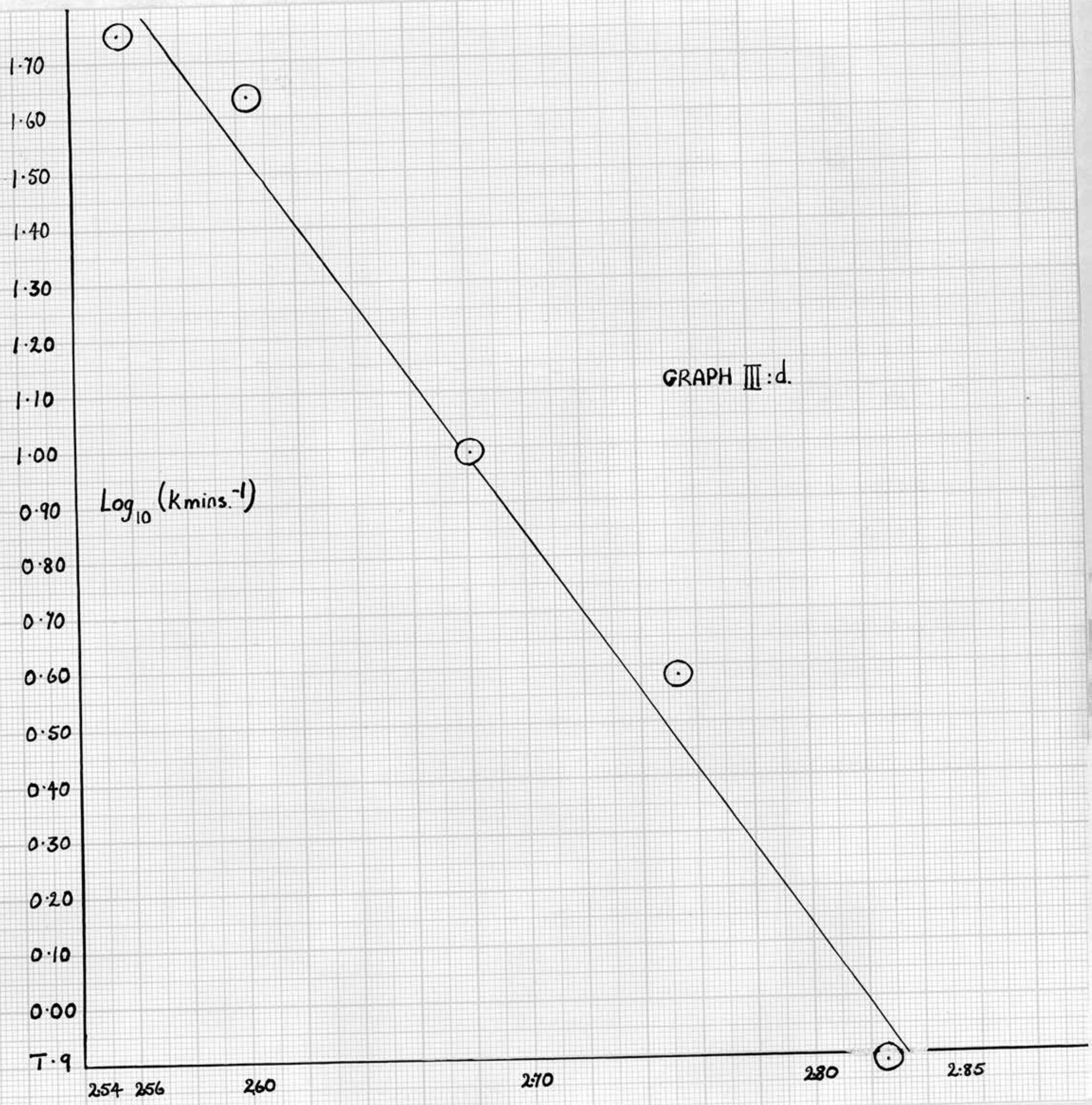
The Decay Process

It was possible to estimate, in most experiments, the final amount of peroxide that would have decomposed had the reaction been allowed to proceed to completion: this value was termed ΔP_{oo} scale divisions. A typical plot of $\log_{10}(\Delta P_{oo} - \Delta P/\Delta P_{oo})$ against time is shown in Graph III:c while the actual results, calculated on the basis of a value of 13.0 scale divisions for ΔP_{oo}, are given in the table below. These figures were computed from the results of 'run' III:1.

Time (mins.)	$\text{Log}_{10}(\Delta P_{oo} - \Delta P/\Delta P_{oo}).10$	Time (mins.)	$\text{Log}_{10}(\Delta P_{oo} - \Delta P/\Delta P_{oo})$
0	0	36	0.833
3	0.996	40	0.792
5	0.996	45	0.778
10	0.991	50	0.724
12	0.982	55	0.699
15	0.966	60	0.663
17	0.959	66	0.613
20	0.929	70	0.580
22.5	0.919	76	0.556
25	0.898	98	0.362
27.5	0.881	160	$\bar{1}.887$
32.5	0.845	180	$\bar{1}.732$

When the acceleration ceases to be rate determining: i.e., at 'A' on Graph III:c, the curve becomes linear. The 'first order' rate constant in this case was 7.75×10^{-3} mins.$^{-1}$. A series of plots of this type illustrated further that the decay process was unimolecular. The following table has been drawn up relating the various unimolecular rate constants (k) to the absolute temperature.

No. /

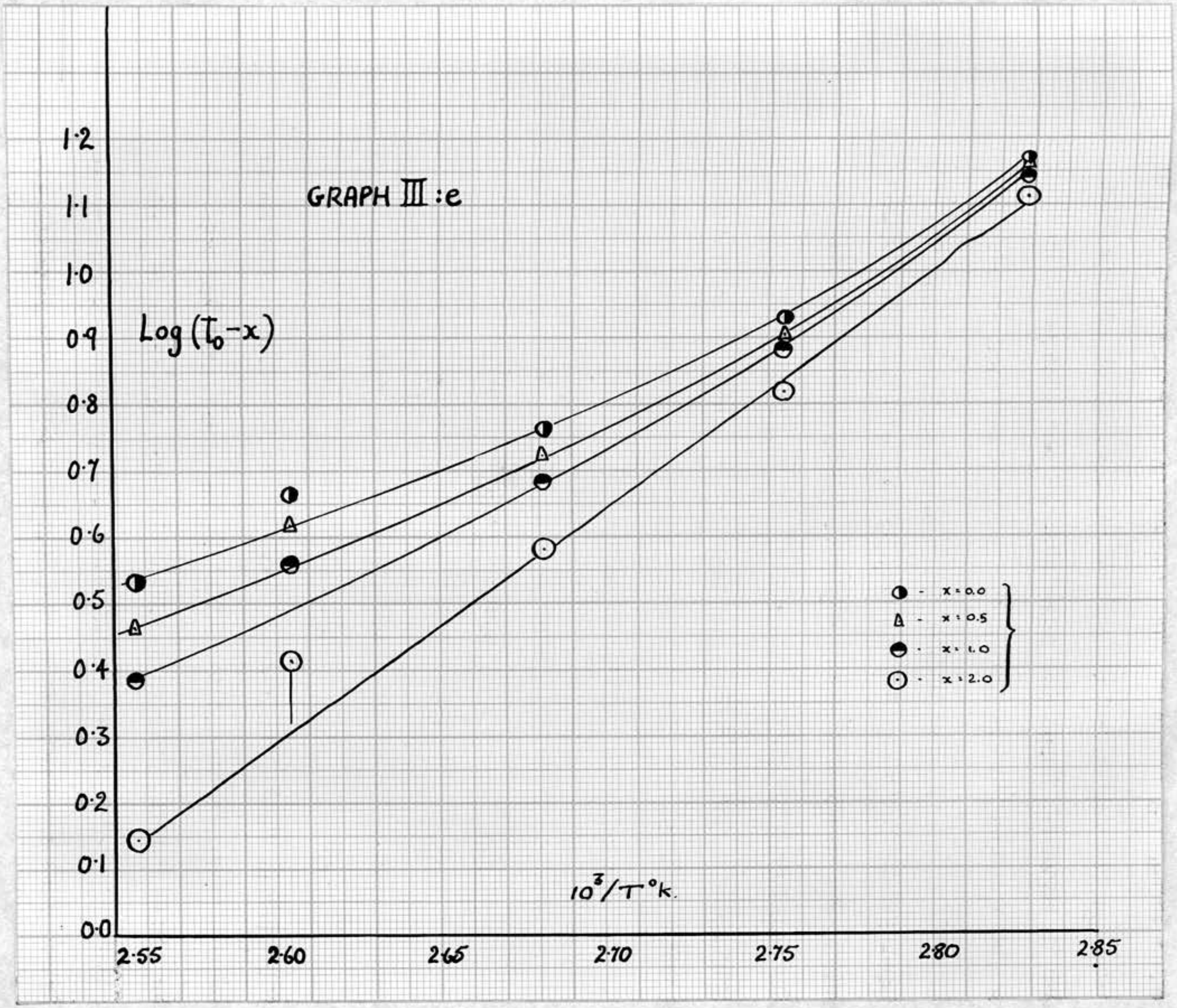

GRAPH III : d.
1·70
1·60
1·50
1·40
1·30
1·20
1·10
1·00
0·90
0·80
0·70
0·60
0·50
0·40
0·30
0·20
0·10
0·00
T·9
Log$_{10}$ (k mins.$^{-1}$)
254
256
260
270
280
2·85

No.	$10^3/T^{o}k$	k x 10^2min.$^{-1}$	Log (k x 10^2min.$^{-1}$)
III:1	2.828	0.775	$\bar{1}$.889
:2	2.754	3.85	0.586
:4	2.681	9.8	0.991
:7	2.604	43.5	1.639
:8	2.557	56.0	1.748

The slope of the best straight line in the Graph III:d, where $\log_{10}(k.10^2 \text{mins.}^{-1})$ is plotted against reciprocal temperature, was -7.25×10^3 which corresponds to an activation energy (ΔE_u) of 33.2 Kg.cals./mole for the unimolecular decay process. All the 'runs' were not included in this table because it was often impossible to estimate the true amount of oxygen evolved at the completion of the reaction.

The two methods of determining the activation energy for the decomposition have produced approximately the same result within the limits of experimental error. This result lends support for the contention that the maximum rate and the decay process actually depict chemically identical stages in the reaction.

The 'Induction' Period /



GRAPH III:e

Log (T0-x)
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
2·55
2·60
2·65
2·70
2·75
2·80
2·85
10³/T °k
◐ - x = 0.0
Δ - x = 0.5
◒ - x = 1.0
⊙ - x = 2.0

The 'Induction' Period

Such an acceleratory process may be due to two factors: viz. the finite time, t_{ϕ}, taken to heat the furnace temperature and/or the time, t_n, corresponding to a chemical process of nucleation. In order to separate these two processes it was necessary to obtain a value for t_{ϕ}, this being effected in the manner now described.

An examination of the curves of $\log_{10}(\Delta P_{oo} - \Delta P/\Delta P_{oo})$ against time, exemplified by Graph III:c, suggested that the interpolated time value, t_o, would provide a figure for the sum of the two possible acceleration stages (t_{ϕ} and t_n respectively) in a particular experiment. The values t_o at various temperatures are shown in the table below.

No.	t_o mins.	T°K
III:1	15.0	354
:2	8.6	363
:4	5.8	373
:7	4.6	383
:8	3.4	391

Graph III:d shows the plot of $\log_{10}(t_o - x)$ against reciprocal temperature, where 'x' has the values 0, 0.5, 1.0, and 2.0 minutes. That the curve tended towards a straight line, including all the points within the limits of experimental error, at $x = 2$ was taken as evidence that the value of t_{ϕ} was approximately two minutes and that the nucleation period, t_n, was $(t_o - 2)$. The slope of this line is $+4.1 \times 10^3$ this being equivalent to an energy value of +18.8 Kg.cals./mole. It is realised that this two minute time value will depend on the temperature, however, it is thought unlikely that this effect will be appreciable over the present temperature /

temperature range and under the given experimental conditions.

The energy values that have been calculated in this section will be interlinked in the discussion that follows Section IV in an effort to aid the effective elucidation of the scheme of the reversible photo-oxidation of rubrene.

EXPERIMENTAL SECTION IV /

EXPERIMENTAL SECTION IV

An Investigation of the Properties of Solutions of Rubrene and Rubrene Peroxide

The Photo-oxidation of Rubrene in Solution

It was hoped in this section to obtain verification of the unit molar combinations of oxygen and rubrene in solution. Previous experiments involving solutions of the peroxide, prepared in the standard manner, have not resulted, as a rule, in a 100% evolution of oxygen on decomposition; indeed the values have been as low as 12%. By employing the usual constant volume system and accurate pressure gauge it was hoped to be able to measure unambiguously the previously reported (43) dissociation pressure of oxygen below which no oxidation will occur.

The initial experiments consisted of an attempt to measure the amount of oxygen taken up by a benzene solution of rubrene under irradiation. These, however, proved unsuccessful in every way owing to the difficulty of thermostating the liquid in the reaction vessel. Even when a compensating vessel, containing pure benzene open to the gauge jacket, was placed along-side the reaction vessel in the thermostat bath it was found that the vapour pressure of benzene changed too rapidly with temperature to enable significance to be attached to pressure measure measurements on the system.

Cymene (p-isopropylbenzene) was tried as a solvent because of its very low and slow changing vapour pressure. It was found that the gauge pointer remained steady on the scale while a gas free solution of cymene was maintained at 25°C. On the introduction of pure oxygen (measured value, 30 scale divisions) no pressure decrease was observed in the dark but on illuminating the liquid, oxygen /

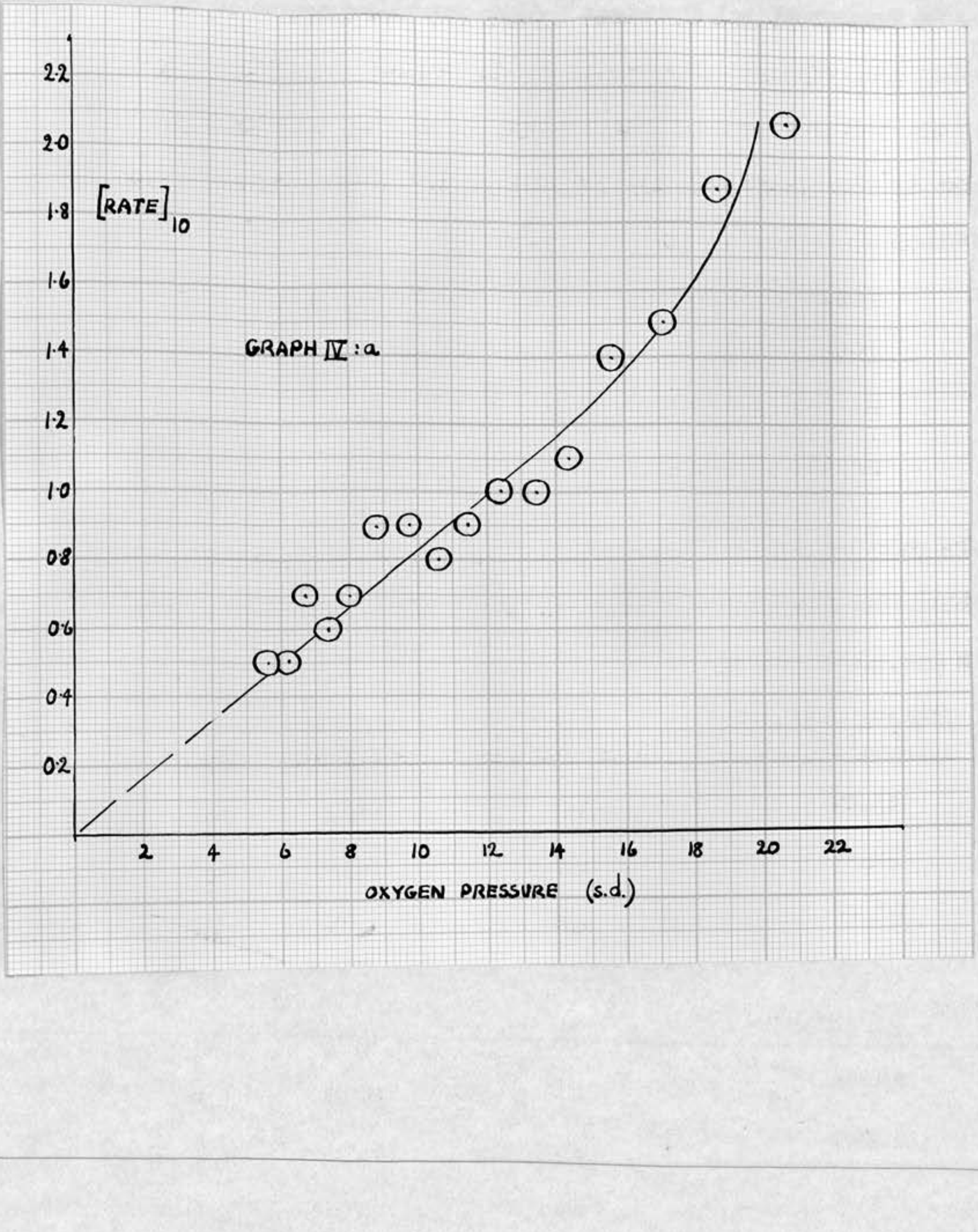
oxygen was absorbed at an appreciable rate.

Although this blank experiment showed that the apparatus was adaptable to solution work it was apparent that p-cymene was useless as a solvent in which to study photo-oxidations as it was itself photo-oxidisable, even at low oxygen pressures.

The next solvent employed was m-xylene with which no 'blank' oxygen uptake was observed over a period of a few hours.

The liquid was thermostated by immersing the reaction vessel in a water bath maintained at $24^{\circ}C \pm 0.05^{\circ}$ by means of a 15 Watt heater and a mercury toluene regulator in conjunction with a Sunvic relay, and an efficient stirrer. Attached to the stirrer was a small horseshoe magnet, the top of which lay about 2mm. below the base of the reaction vessel. A nail in a glass envelope was placed in the reaction vessel thus enabling the liquid to be stirred while under examination. The remainder of the apparatus employed was as previously described although a special type of vessel, small and with a flat bottom, was used. The thermostat tank was fitted with glass windows through which a beam from the Osira lamp system could pass during period of illumination.

The solvent was purified by distillation (sample Hopkins and Williams) over calcium chloride the distillate being kept as free from air as possible. A solution containing 1.966×10^{-3} moles of rubrene per litre of m-xylene was prepared and stored in the dark. 3 mls. of this solution were measured into the reaction vessel and after the addition of the magnetic stirring element the vessel was transferred to the apparatus and cooled in liquid oxygen. The reaction space was then evacuated, the gauge taps closed and the vessel allowed to warm up. At equilibrium the vessel was again /


[RATE]$_{10}$
GRAPH IV : a
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
2
4
6
8
10
12
14
16
18
20
22
OXYGEN PRESSURE (s.d.)

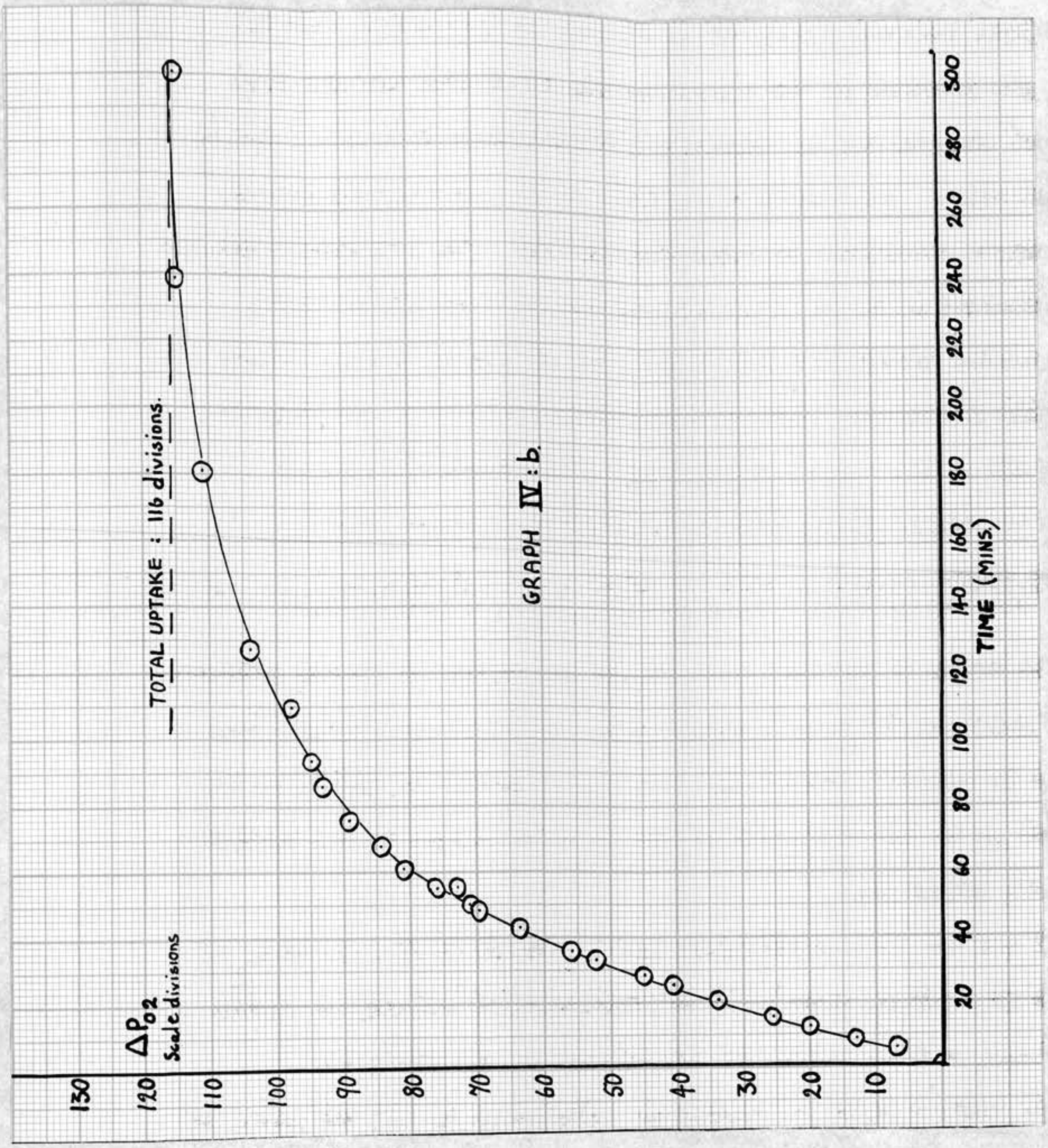
again cooled in liquid oxygen and the apparatus evacuated. This process was repeated until the vapour pressure-temperature curve for the solution was virtually identical with curve drawn from the values in International Critical Tables for m-xylene. This degassing process was carried out in the dark. At this stage oxygen was allowed to enter the vessel to a known pressure as measured by the gauge pointer deflection and after thermal stability was reached the solution was illuminated.

Gauge sensitivity - 0.038 mm./s.d.
Temperature - 24°C.
Gas volume of the vessel - 23.4 mls.
Oxygen pressure - 21.9 s.d. after dark equilibrium.

The rate of oxygen absorption at various oxygen pressures throughout the reaction are shown in Graph IV:a while the actual results are given below.

Oxygen Pressure (s.d.)	Rate (s.d./10mins.)	Oxygen Pressure	Rate
20.95	2.1	10.70	0.8
18.90	1.9	9.85	0.9
17.25	1.5	8.95	0.9
15.80	1.4	8.15	0.7
14.55	1.1	7.50	0.6
13.50	1.0	6.85	0.7
12.50	1.0	6.25	0.5
11.55	0.9	5.75	0.5

Extrapolation of the curve in Graph IV:a indicates the rate only becomes zero when the oxygen pressure is zero, within the limits of experimental error. This would suggest that the equilibrium pressure of oxygen, if such exists, is immeasurably small, i.e.



GRAPH IV : b

TOTAL UPTAKE : 116 divisions.
ΔP_{O_2}
Scale divisions
130
120
110
100
90
80
70
60
50
40
30
20
10
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
TIME (MINS.)

less than 0.038 mm.

At this stage in the reaction the light was extinguished and the oxygen pressure increased to 30 mm. This implied that the total gas pressure in the apparatus was about 38.5 mm. and that pressure changes due to temperature fluctuations were still easily controllable. The solution was left in the dark and in contact with oxygen overnight and then illuminated. The pressure decreases were recorded at known times and plotted on Graph IV:b. This curve tended towards a saturation value at a total oxygen uptake of 116 scale divisions. The overall oxygen absorption was therefore 15.7 + 116 = 131.7 scale divisions. The molecular ratio of oxygen to rubrene could then be calculated as shown below.

$$\frac{\text{Moles oxygen uptake}}{\text{Moles rubrene present}} = \frac{131.7 \times 0.038 \times 273 \times 23.4 \times 10^{-3}}{760 \times 297 \times 22.4 \times 3 \times 1.966 \times 10^{-6}} = 1.07$$

The extra 7% may have been due to the change in vapour pressure of the solution which will result when the solute is changed from rubrene to rubrene peroxide <u>or</u> to a slight uptake of oxygen by the m-xylene <u>or</u> to the different solubilities of oxygen in the initial and final solutions.

It has now been established that irradiation of a solution of rubrene in m-xylene results in an absorption of oxygen, in amount equivalent, mole for mole, to the rubrene in the solution.

The initial rates of oxidation, s.d./min., in the two parts of this experiment were 0.382 and 1.78 respectively at 0.8 mm. and 30 mm. initial oxygen pressure. The ratio was thus 4.66:1 which when multiplied by the ratio of the respective rubrene concentrations (in terms of availability); i.e., $\frac{116}{20}$, the result is a rate ratio of 37.3:1. The pressures were in the ratio of 37.6:1 indicating that the rate of pressure decrease is proportional to the oxygen pressure over this range.

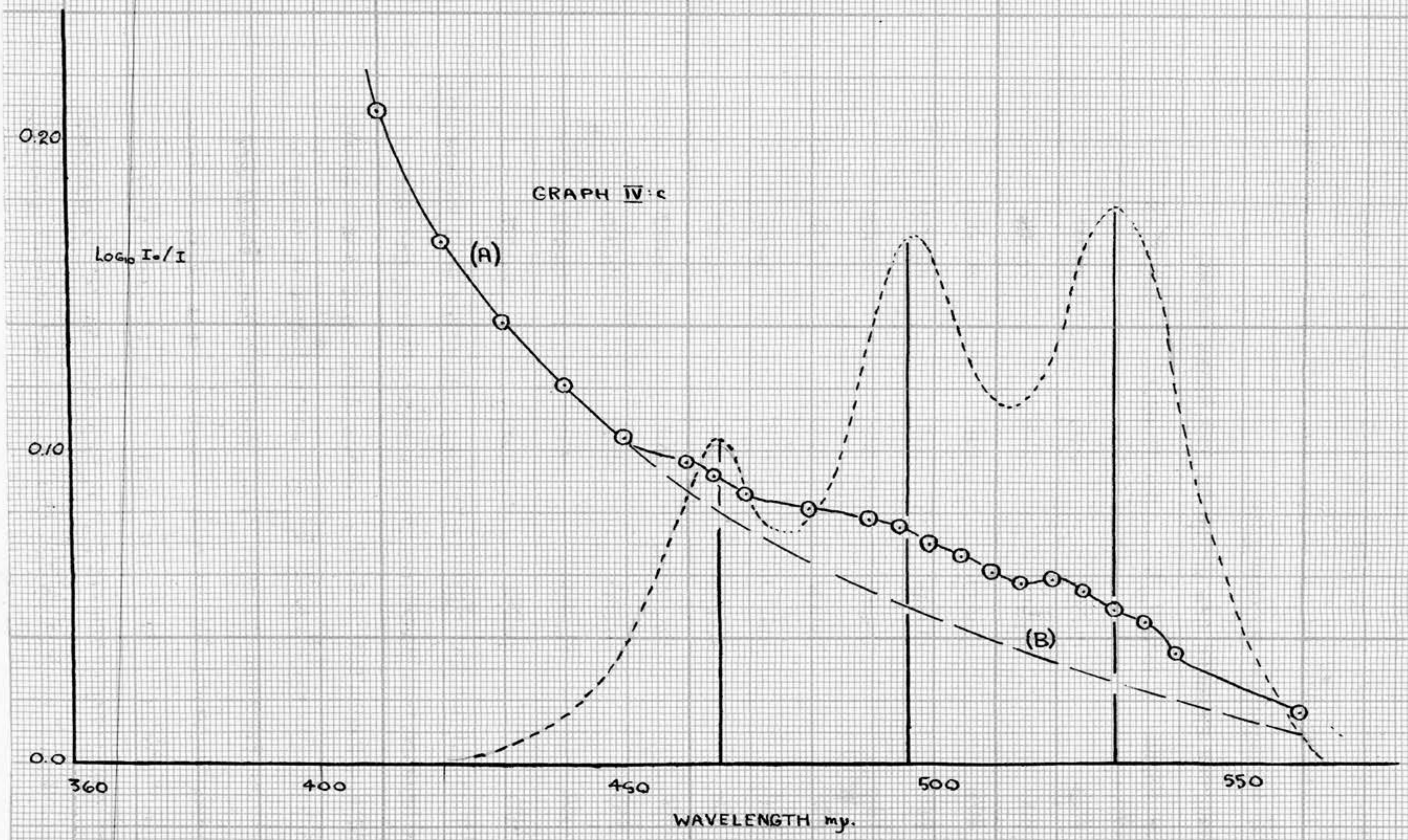
The results have indicated that there is no measurable pressure equilibrium set up when the rubrene is oxidised in m-xylene. It was not possible to check this with benzene as solvent as has been previously mentioned but a series of experiments were arranged in an attempt to measure the extent of the reverse reaction; i.e., the decomposition of the peroxide in light.

Five mls. of a standard solution of rubrene peroxide in benzene contained in a small soft-glass tube, was connected to the high vacuum system. After freezing the solution with liquid oxygen the tube was evacuated. The peroxide solution at this stage in the experiment did absorb visible light, as detected by the Unicam SP600 spectrophotometer. The solution was then allowed to warm up to 15°C. and isothermally degassed for 10 minutes over a liquid oxygen trap. This process was repeated several times to remove, as far as possible, all oxygen from the solution. At this stage the tube was sealed off and the liquid illuminated with a powerful ultra-violet lamp. This illumination was continued for 48 hours after which the tube was left in daylight for 4 weeks. Again the solution was irradiated with the ultra-violet lamp for 48 hours.

By this time the liquid had changed from being completely colourless to a very pale yellow. This yellow colour appeared to be a fluorescence as it was more easily observed at right angles to an incident light beam.

Once the existence of the yellow colour had been confirmed, the seal on the tube was broken while the liquid was obscured from light. The solution was then transferred to a lcm. glass absorption cell and the absorption spectrum examined over the range 350 - 600 mu on the Unicam SP600 instrument.

The /


GRAPH IV:c
LOG10 I0/I
0.20
0.10
0.0
(A)
(B)
360
400
450
500
550
WAVELENGTH mμ.

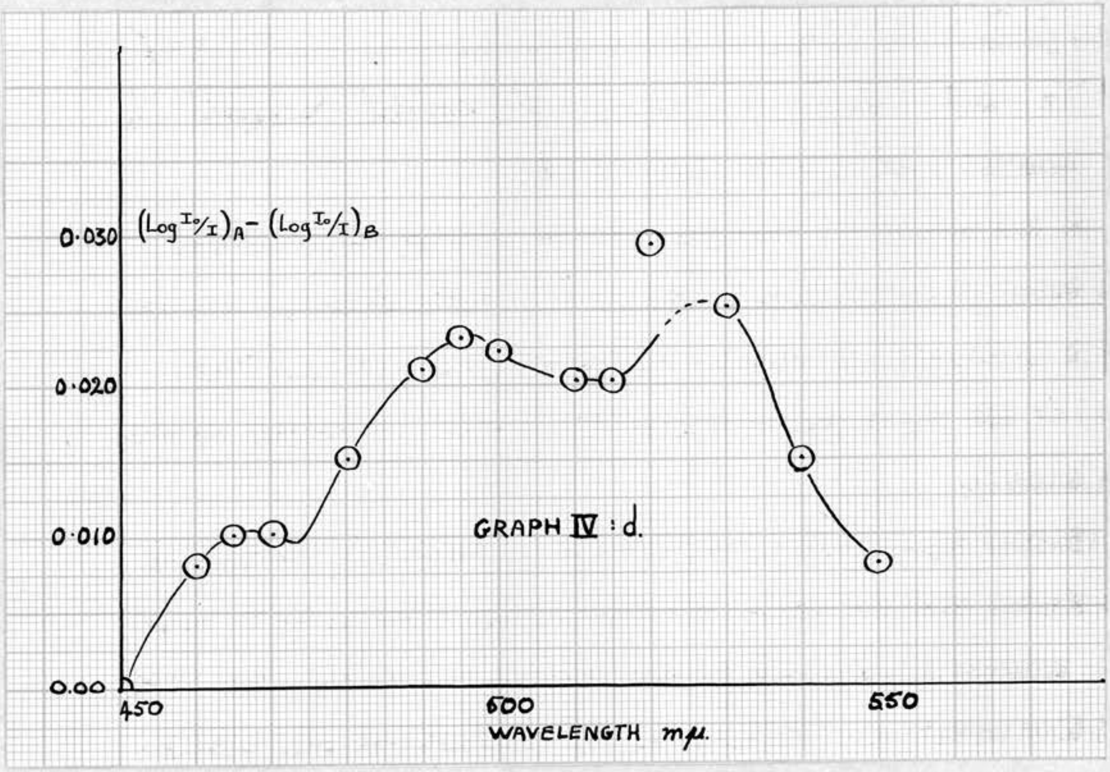
The results are shown on Graph IV:c(A) while the main absorption bands of rubrene are drawn, for reference, as vertical lines at the appropriate wavelengths.

The analysis results are given in the table below.

Wavelength mu	Log I_o/I	Wavelength mu	Log I_o/I
560	0.016	480	0.081
540	0.035	470	0.086
535	0.045	465	0.091
530	0.049	460	0.096
525	0.055	450	0.104
520	0.059	440	0.121
515	0.057	430	0.141
510	0.061	420	0.167
505	0.066	410	0.209
500	0.070	400	0.275
495	0.075	380	0.406
490	0.078	365	0.592

An examination of the absorption curve on Graph IV:c indicated that the absorption was practically continuous throughout the visible range. There was however, evidence of small peaks in the neighbourhood of the wavelengths of the visible absorption bands of rubrene. As rubrene, in such small concentration, would not absorb appreciably above 560 mu or below 430mu (see curve 2) it was considered reasonable to assume that the other material in the solution was absorbing continuously between 560 and 430 mu, according to the dotted line B in Graph IV:c. The absorption spectrum of the unirradiated solution of rubrene peroxide in benzene (see curve 4) showed little absorption above 400 mu although increasing

to /


GRAPH IV : d.
0·030
0·020
0·010
0.00
$(\mathrm{Log}\, I_0/I)_A - (\mathrm{Log}\, I_0/I)_B$
450
500
550
WAVELENGTH mμ.

to a maximum between 400 mu and 300 mu.

The difference between (A) and (B) is plotted against the wavelength of absorption in Graph IV:d. As can be observed the result is a fair duplication of the absorption spectrum of rubrene. The concentration of the original solution was 1.028 gm./litre of the peroxide in rubrene equivalents. The concentration of rubrene in the product was estimated as 1 mg./litre., i.e., 5.10^{-3}mg./5mls., from the standard calibration curve. The per cent decomposition that occurred was therefore about 0.0004%.

On the assumption that the above percentage decomposition represented an equilibrium condition then the equilibrium pressure for the decomposition would be approximately $3.5.10^{-4}$mm. (the volume of the vessel was approximately 50 mls.) of oxygen, at room temperature.

Similar experiments were performed in which the irradiation was effected with the Osira lamp for varying times up to 72 hours but no rubrene was detected in the resulting solution. The broad absorption across the visible range of the spectrum was, however, present in all cases.

In an attempt to photo-oxidise solutions of rubrene in benzene sealed into tubes under varying oxygen pressures, Dufraisse found that no oxidation would occur below a certain oxygen pressure. The pressure was determined and found to lie between 2 and 8 mm. Hg. of oxygen at 16°C. The experiments on the photo-oxidation of rubrene in m-xylene have not indicated any such limitation. Dufraisse also observed the yellow colouration during the vacuum illumination and although this was attributed to the fluorescence of rubrene no analyses were carried out.

The /

The results for the decomposition and oxidation experiments in this section are in accord in as much as the apparent dissociation pressure estimated in the former would not be detectable in the latter. In general, therefore, the results of this section do not indicate that a dissociation pressure of the magnitude suggested by previous workers governs the reaction equilibrium.

The Effect of Light on Rubrene Peroxide crystals 'in vacuo'. /

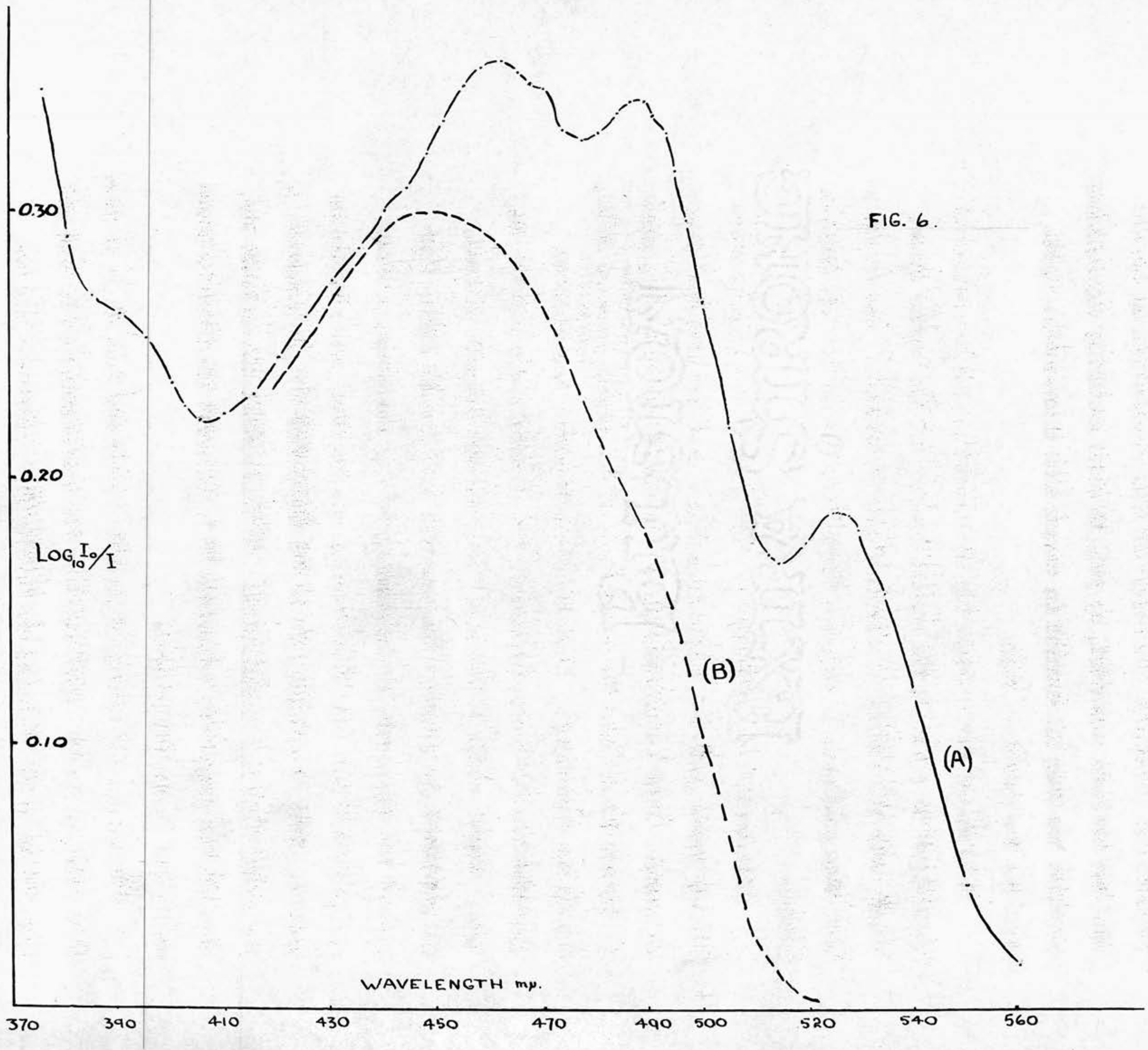

0.30
0.20
0.10
LOG₁₀ I₀/I
(A)
(B)
WAVELENGTH mμ.
370
390
410
430
450
470
490
500
520
540
560

FIG. 6.

The Effect of Light on Rubrene Peroxide crystals 'in vacuo'.

Although little effect was observed when a thin film of the peroxide was irradiated 'in vacuo' at room temperature, an experiment has not been conducted, as yet, in which carefully crystallised peroxide has been illuminated in vacuum with ultra-violet light. Such was the intention here.

8.25 mg. of the crystals (crystallised from benzene solution) were placed in a thin Pyrex reaction vessel and the powder spread evenly over the surface by adding a drop of benzene. The crystals were then evacuated in darkness for 15 hours at 10^{-4} mm. Hg. (McLeod gauge).

Illumination was commenced at this stage with a high pressure mercury vapour lamp and silica focussing device and continued for 48 hours. From a consideration of the dimensions of the apparatus it was not likely that the temperature of the vessel exceeded 30°C., during the experiment. Over the first 24 hours, illumination approximately 0.7 scale divisions - (Gauge sensitivity - 0.004 mm./s.d.; vessel volume = 55.0 mls.) of permanent gas were evolved. The permanent gas pressure was measured continuously during this part of the experiment by surrounding part of the reaction vessel system with liquid air, thus freezing out 'in situ' any condensable vapour. Over the second part of the experiment the gas pressure in the gauge could not be estimated. After 24 hours the crystals had changed from completely colourless to a red-brown and after 48 hours no further change was evident.

The residue was dissolved in A.R. benzene and made up to 10 mls. in a standard flask. This solution was spectrographically analysed from 360 mu to 560 mu using the Unicam SP600 instrument and the resulting absorption spectrum is indicated in Fig.6(A).

It /

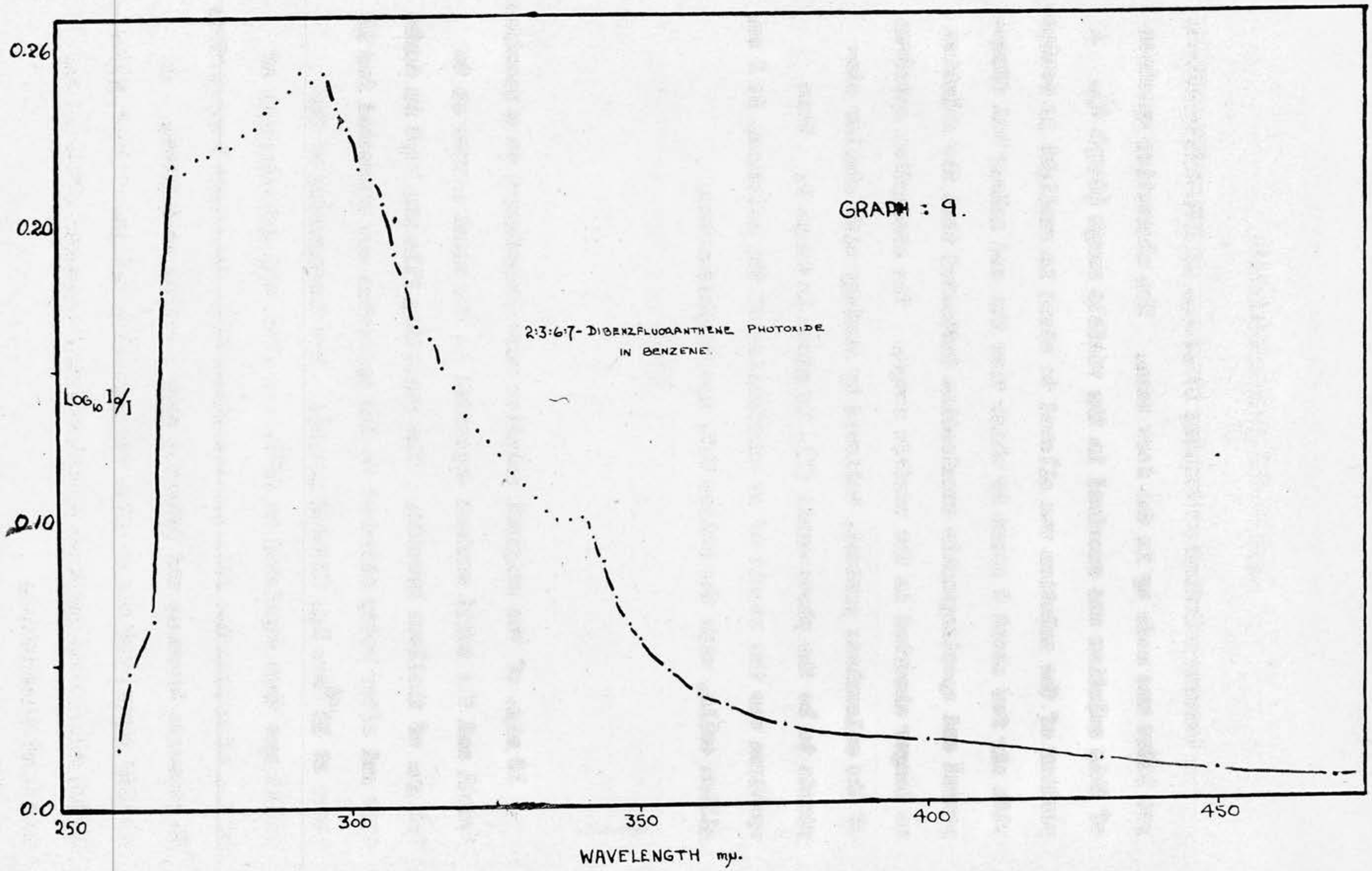
It was apparent from this spectrum and from the colour of the solution that the main absorbing material present was not rubrene. The fact that the curve does exhibit maxima in the region of the three rubrene maxima at 465, 495 and 530 mu., however, strongly indicated that the resultant curve was due to rubrene and another material which absorbs strongly around 460 - 470 mu. and weakly above 560 mu.

The 0.6 divisions of gas evolved, assumed to be oxygen, would correspond to 3×10^{-2} mg. of rubrene in this system. Reading from the calibration curve (see p. 20) this amount in 10 mls. benzene would result in a log I_o/I value of 0.068 at 530 mu. and 0.034 at 465 mu.

A complete absorption spectrum of rubrene was calculated from about double these Log I_o/I values and substracted from the original curve (A) resulting in the dotted curve (B). The doubled values were employed as it was at this limit that all traces of rubrene (detected by 'bumps' in the absorption curve at the wavelengths of the rubrene maxima) disappeared from the curve (B).

The absorption curve (B) is probably a good approximation to the spectrum of the main product of the light activated decomposition of rubrene peroxide in the crystalline state. This unknown compound exhibits a maximum at 450 mu. It must be pointed out that rubrene peroxide which is in very high concentration in this solution does not absorb light of wavelength higher than 400 mu.

Unfortunately it was not possible to identify or examine further this second product, but this experiment has provided evidence which indicates that there are probably two distinct modes of decomposition of the peroxide. As far as could be ascertained, the unverified stage did not involve the production of an uncondensable gas.

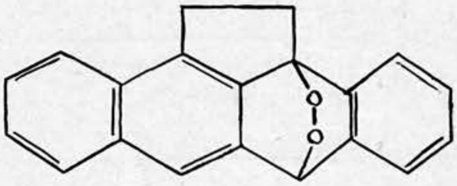

GRAPH : 9.

2:3:6:7-DIBENZFLUORANTHENE PHOTOXIDE
IN BENZENE.
LOG10 I0/I
0.26
0.20
0.10
0.0
250
300
350
400
450
WAVELENGTH mμ.

Note on the Attempted Photo-oxidation of

2:3:6:7 - Dibenzfluoranthene

A benzene solution containing 234.0 mg. of dibenzfluoranthene per litre was made up in the dark room. The absorption spectrum of this solution was examined in the visible range (Graph 8). A portion of the solution was allowed to stand in sunlight in contact with air for about 8 hours by which time the red colour had disappeared and spectrographic examination indicated that the solution no longer absorbed in the visible range. The absorption spectrum of the colourless product, believed by analogy with similar compounds to be the photo-oxide (I), is given in Graph 9. This spectrum was the result of an examination of the solution, in 2 mm. silica cells, with the Unicam U.V. spectrophotometer.



(1)

10 mls. of the original solution were transferred to a reaction vessel and the solid content deposited in the usual manner on to 0.3 gm. of thallous bromide. The resulting film was kept in darkness and after being attached to the apparatus was evacuated for 15 hours at 10^{-4} mm. Hg. (McLeod gauge). The temperature of the vessel was then regulated to 25°C. and after the introduction of 50 mm. of oxygen the film was irradiated with the Csira lamp system. No pressure decrease was detected over a period of 8 hours. A similar experiment was carried out employing 0.2 gm. of Jena glass as the substrate, again no pressure change occurred after a long period of irradiation.

Thus although 2:3:6:7 - dibenzfluoranthene was readily photo-oxidised in solution there appears to be no evidence of such an oxidation occurring in the solid state under such experimental conditions. In this respect dibenzfluoranthene differs from rubrene.

A General Discussion of the Results.

Although the main features of this work indicate that the reaction between rubrene and oxygen is reversible, no evidence of a dissociation pressure of oxygen of the order of 5 mm., at room temperature, as indicated by previous work done on solutions (43) has been apparent. A similar oxygen pressure limit below which the dissociation of peroxide may occur but above which the evolution of oxygen ceases, was detected during a study of the oxidation of dibeterocoerdianthone in pyridine (68). No previous workers have attempted to measure the equilibrium conditions of the photo-oxidation of photodissociation of such polyacenes in the crystalline state. As the solvent plays an important role in solution reactions it is probable that solvent molecules are fundamental in determining the oxygen pressure limit. It is interesting to point out that in pyridine such a pressure limit is often observed although in other solvents this is not the case (17).

The analogy between the addition of oxygen to polycyclic hydrocarbons containing the anthracene nucleus and the corresponding addition of dienophilic reagents such as maleic anhydride is very close although several important differences have been observed. The presence of meso-phenyl group, for example, retards the addition of moleic anhydride yet promotes the addition of oxygen (69). The most marked difference, however, lies in the fact that although the activation energy for the dienophilic addition may be supplied by heat the addition of oxygen requires light. Ample evidence is available which shows that rubrene does not react with oxygen in the dark, even over a period of 7 years (70). No catalyst has been found which will promote the dark oxidation of rubrene, anthracene or meso-diphenylanthracene (71). The decomposition /

decomposition of the peroxide on the other hand may be effected either thermally or photochemically.

Linear polynuclear hydrocarbons in general exhibit similar absorption spectra. As the number of benzene rings increases the molecules absorb light of decreasing energy; i.e. the spectra are shifted towards the red end of the spectrum. Examination of the spectra of such materials indicates that there are two main regions of absorption (72). The first (A) type absorption is detected in the ultra violet region, reaching a maximum at about 265 mu., in the case of naphthacene and 290 mu., in the case of rubrene. The second (B) type absorption is in the near ultra violet tending towards the visible as the series approaches naphthacene and higher homologues. It has been the case with all polyacenes so far studied, that sunlight has been an efficient source of illumination to bring about the photo-oxidation. In the case of rubrene monochromatic light of wavelength around 500 mu., proved an efficient illumination source (12). As such light contains no wavelength of energy high enough to excite the molecule through the A-type band system it follows that photochemical reactions of this type must involve B-type absorption. This process is visualised as constituting the passage of molecules from the ground to the lowest singlet excited state.

In the case of rubrene the most probable B-type absorption occurs at 465 mu., 495 mu., and 530 mu., the absorption falling to about zero around 560 mu. The excitation energy involved in such processes will be approximately 62.5, 57.0 and 53.4 Kg. Cals./mole respectively for the most probable transitions and 50.5 Kg.cals./ mole for the minimum amount of energy that will bring about this transition /

transition. This latter value may be identified with the light activation energy (E_1) of the first stage in the photo-oxidation.

Once in the excited state the molecule may revert to the ground state although not necessarily to the same vibrational level. In the case of rubrene the fluorescence emission has an approximate light energy of 40 Kg.cals./mole, the molecule in the ground state after fluorescence thus having less than 10 Kg.cals./mole vibrational energy in excess of the ground state energy. Bowen (15) believes that molecules in this state may now combine with oxygen.

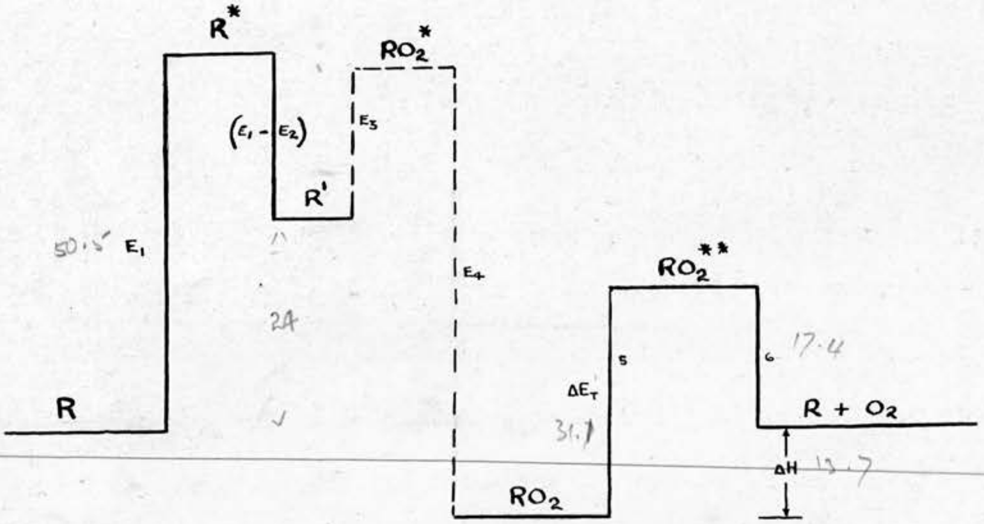
Recent studies (73, 74) of the electronic levels of polyacene hydrocarbons have indicated that assignments of transitions in this series agree with the theoretical assignments for the singlet states. For the triplet states, however, the same agreement has not been apparent (75). The value of 10.250 cm^{-1} for the lowest singlet triplet absorption in naphthacene has been determined (76) and this value agrees with theory. The energy of such a singlet triplet transition is about 29 Kg.cals./mole.

Jones (77) has carried out calculations involving the angles made by phenyl substituent planes to anthracene nuclei. The results indicate that the two ring systems cannot be planar. This implies that very many meso-substituted anthracenes and other substituted polycyclics cannot show the degree of conjugation between the substituent and the ring system which might be expected from a consideration of the source substituents in benzene or in other molecules where such steric inhibition of resonance does not occur. That the above theory is applicable to rubrene is indicated by the similarity of the absorption spectra of rubrene and naphthacene.

Thus /

Thus it is possible to predict a probable value for the energy of the singlet-triplet transition in rubrene by analogy with the value for naphthacene and a comparison of the absorption spectra of rubrene and naphthacene. Such an approximation is made with the knowledge that the lower triplet excitation energy decreases as the polyacene series increases and eventually this triplet level approaches the ground (singlet) state (<u>76</u>). If the spectral positions of the singlet-singlet absorption bands in rubrene and naphthacene, relative to the weaker singlet-triplet absorption remain similar then the lowest triplet level of rubrene will involve an excitation energy of about 24 Kg.cals./mole (E_2).

A combination of the computed values of E_1 and E_2 with the mean measured thermal activation energy for the decomposition of rubrene peroxide (ΔE_t) and the estimated heat of the reaction (ΔH) results in the following energy diagram for the reversible combination of rubrene and oxygen.



The fact that two molecules of rubrene must collide before optimum activation and hence photo-oxidation will occur will not interfere with this energy cycle. In this scheme R indicates rubrene in the ground state, R^* indicates rubrene in the singlet excited /

excited state, R^1 the triplet state, RO_2^{*} an unstable intermediate which may stabilise to the peroxide RO_2 and RO_2^{**} an unstable intermediate reached by thermal activation of the rubrene peroxide.

As the diradical, R^1, is relatively stable, having an apparent lifetime of 2 seconds in benzene solution (14), it has been considered as occupying a position of minimum potential energy. The energy values E_3 and E_4 are not accurately assessable although inspection of the diagram indicates that limits for these values may be computed. E_3, for example, must be less than $(E_1 - E_2)$; i.e., less than 26.5 Kg.cals./mole, while E_4 must be less than $(E_1 + \Delta H)$ which is 63.7 Kg.cals./mole.

50.5 - 24

The first deduction which may be made from this energy scheme involves the reaction,

$$RO_2^{**} \longrightarrow R + O_2 + E_6$$

31.1 - 13.7

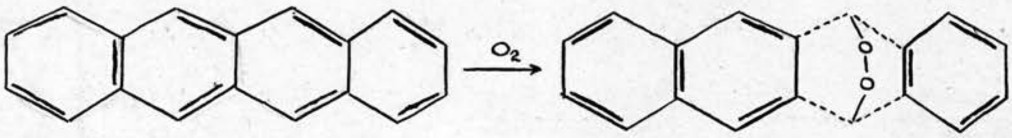
13.7

The value of E_6 is given by $(\Delta E_t - \Delta H)$ which is 17.4 Kg.cals./mole. As the heat of dissociation of an oxygen molecule into two oxygen atoms is about 120 Kg.cals./mole it is evident that in this case the oxygen must have been molecular when evolved. A similar calculation has been made (66) in the decomposition of 1:4 - dimethoxy-9:10-diphenylanthracene. The value for E_t in this case was computed from the reaction rate at only two temperatures (78) and found to be 24 Kg. cals./mole. It is interesting to note, at this stage, that this activation energy is very close to the value determined in this work.

The photo-oxidation of anthracene and naphthacene proceeds smoothly in carbon disulphide, although the photo-oxides do not regenerate oxygen on heating (79, 56). Indeed the decomposition of these oxides occurs explosively at about 120°C. An approximate value /

value of the heat of such a decomposition may be estimated from a knowledge of the resonance energies involved. In polyacenes the π-electrons associated with each double bond may be visualised as moving freely throughout the whole molecule. Such saturation, as is involved in the formation of a photo-oxide, must thus result in the localisation of two π-electrons and a corresponding alteration in the resonance energy of the molecule as a whole.

The photo-oxidation of naphthacene may be written as follows:



Contributing to the nett energy change will be on the one hand a loss of the resonance energy of naphthacene (R_{nc}) and of the energy involved in the transformation $O=O \rightarrow -O-O-$(E_{o-o}); on the other hand the resonance energies of naphthalene (R_n) and benzene (R_b) combined with the energy of two carbon-oxygen (D_{c-o}) bonds will be gained. The nett energy gain will thus be given by -

$$R_n + R_b + 2D_{c-o} - E_{o-o} - R_{nc}$$

If the values of these factors are taken as R_n, 75 Kg.cals./mole; R_b, 39 Kg.cals./mole; D_{c-o}, 70 Kg.cals./mole; E_{o-o}, 61 Kg.cals./mole (80) and R_{nc}, 136.2 Kg.cals./mole (81) then the total energy gain will be 56.8 Kg.cals./mole. The dissociation of such photo-oxides would thus be exothermic to the extent of 56.8 Kg.cals./mole which is very high and would account for the explosive violence of the decomposition.

When substituted in the meso-position, naphthacenic photo-oxides dissociate readily into the parent hydrocarbon and oxygen. This may be explained by the function of the phenyl substituents, in /

in the case of rubrene, in contributing to the resonance energy of the molecule.

Little doubt remains as to the structure of this type of photo-oxide. Their absorption spectra are entirely different from those of the parent hydrocarbons and in the case of rubrene photo-oxide the spectrum resembles closely that of diphenylnaphthalene (82). Calculations have also indicated (83) that the substituted phenyl groups become planar with the basic nucleus after oxidation.

With reference to the energy diagram above and in particular to the stage E_2 involving the production of the triplet state molecule from the light saturated material, in the formation of the rubrene diradical a net energy absorption of $(E_1 - E_2)$; i.e. 26.5 Kg.cals./mole must occur. In the case of naphthacene this value will not be markedly different and the energy involved in the localisation of the two π-electrons will be given approximately by the value of $R_{nc} - (R_b + R_n)$ which is 22.2 Kg.cals./mole.

Such a calculation is very approximate but is in agreement with present ideas on the structure of the diradical.

One aspect of the photo-oxidation which has not been treated specifically in this work is the emission of light during the decomposition of the peroxide. Moureau, Dufraisse and Butler (84) observed this effect with rubrene peroxide and a similar light emission was observed during the decomposition of 1:4-dimethoxy-9:10-diphenylanthracene by Dufraisse and Velluz (85). The observed light energy was estimated as about 40 Kg.cals./mole.

There is no process apparent in the energy diagram which could account for such an emission of light although it is possible that absorbed thermal energy may be recovered as light energy from either of /

of the proposed unstable peroxide intermediates.

On the other hand the reverse photo-oxidation, which was effected by irradiating rubrene peroxide both in the liquid and crystalline states may be visualised as having a light activation energy E_4. According to the limits on E_4 the maximum wavelength of light which will bring about this dissociation, in vacuum, should lie between 750 mu and 440 mu. An examination of the absorption spectrum of rubrene photo-oxide indicates that light absorption becomes appreciable at about 400 mu. This is in reasonable agreement with the maximum light activation energy as predicted by the theory. Such an explanation, however, assumes that the reverse photochemical reaction proceeds according to the same mechanism as the photo-oxidation.

Rubrene in a solid state has been photo-oxidised but 2:3:6:7 - dibenzfluoranthene, which was just as readily photo-oxidised in solution, could not be oxidised either on thallous bromide or Jena glass.

Ease of photo-oxidation of crystals of such hydrocarbons may be related to the shape of the molecule. It has been suggested that the oxygen uptakes observed in this work were due to the oxidation of surface layers in the neighbourhood of crystal irregularities. It is likely that a looser packing than is found in the bulk of the crystal is necessary before the configurational changes accompanying oxidation may occur. In the case of rubrene this change may be able to take place by virtue of the phenyl groups being out of the plane of the naphthacene nucleus before oxidation thus permitting the molecule to change its configuration relatively easily after the absorption of the energy of an 'exciton'. Similar arguments /

arguments in the case of dibenzfluoranthene would suggest that it would be much more difficult to bring about the change in this case because of the close packing of molecules; there being a higher energy barrier to overcome in order to alter the crystal structure of the hydrocarbon.

An important extension of this theory has recently come to light following the synthesis of tetra-p-tolylnaphthacene (tetramethyl rubrene) (86). This molecule will occupy an even greater volume than rubrene and according to this theory should be readily photo-oxidisable in the solid state. It was observed (86) that tetramethyl rubrene crystals were decolourised in sunlight and the product was found to be the photo-oxide. This report (86) constitutes the first example of the direct photo-oxidation of a naphthacenic hydrocarbon in the crystalline state, and a manometric study of films of terametheyl rubrene in an apparatus of the type used in the present work might prove of great value.

This work cannot claim to have elucidated complete mechanisms for the photo-oxidation although studies on the decomposition of thin films and crystals have provided useful energy values which enabled a possible complete energy scheme for the reversible combination of rubrene and oxygen to be proposed. The conclusions have, however, opened up possible lines of approach to the general problem of the photo-oxidation of solid hydrocarbons.

SUMMARY

The effects of light on materials exposed to oxygen are varied and the mechanisms of the ensuing reactions are obscure. The object of this work was to contribute to the elucidation of the mechanism of photobleaching in the solid state by utilising the reversible photo-oxidative properties of 5:6:11:12-tetraphenylnaphthacene (rubrene).

Examination has been made of the photo-oxidation in visible light of thin films of rubrene on thallous bromide and on Jena glass by means of the direct measurement of oxygen pressure decrease. The oxygen uptakes were irreproducible, varying from 0 - 60% of the available material on the assumption that a unit molar combination of rubrene and oxygen had occurred. No pressure below which oxidation would not occur was detected and experiments on the photo-oxidation of rubrene in m-xylene extended this conclusion beyond the solid state. The rate of oxidation on glass was proportional to the surface concentration of oxygen, although the variation of the rate with solid phase concentration was complex.

A study was made of the decomposition of thin films of rubrene peroxide on glass, at various temperatures and the results indicated that the oxygen pressure developed in the presence of solvent vapour adsorbents was solely determined by the temperature of the film. A mechanism was proposed which explained the main features of the decomposition and a mean value of $\Delta H = 13.2$ Kg.cals./mole estimated for the heat of the dissociation.

The energy of activation of the decomposition of the peroxide was calculated from the results of a series of experiments on the decomposition of ground crystals at various temperatures. The mean energy value was $\Delta E = 31.5$ Kg.cals./mole.

An /

An examination was made of the light activated decomposition of the peroxide 'in vacuo', both in solution and in the solid state. In each case the results indicated that rubrene was regenerated along with an unidentified material.

A possible mechanism of the photo-oxidation and an energy scheme linking the photo- and thermal processes has been discussed in relation to the general nature of the preparations.

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