

The Kinetics of Gaseous Oxidation Reactions

A Thesis

submitted for the degree

of

Doctor of Philosophy

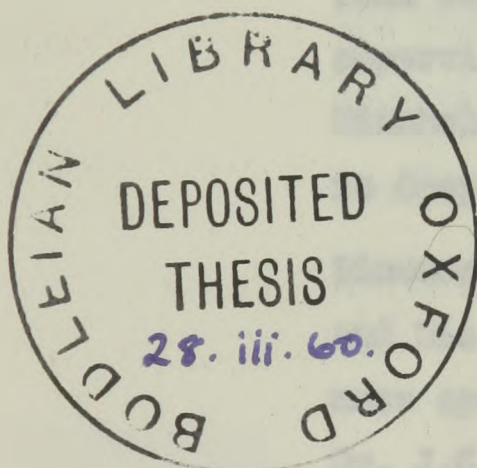
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ABSTRACT

INTRODUCTION

The objective of the work presented in this paper is to study the kinetics of the reaction of hydrogen peroxide with various organic compounds. The reaction of hydrogen peroxide with organic compounds is of great interest because of its importance in many biological and chemical processes. The reaction of hydrogen peroxide with organic compounds is a complex process and the kinetics of this reaction has been studied by many investigators. The present work is a continuation of the work of these investigators and is aimed at determining the rate of reaction of hydrogen peroxide with various organic compounds. The results of this work will be presented in a separate paper.

Experimental Methods and Materials

Many of the experimental observations are based on a study of the reaction of hydrogen peroxide with various organic compounds. The following are considered: the reaction of hydrogen peroxide with organic compounds, the reaction of hydrogen peroxide with organic compounds, and the reaction of hydrogen peroxide with organic compounds.

INTRODUCTION

1) The reaction of hydrogen peroxide with organic compounds is a complex process and the kinetics of this reaction has been studied by many investigators. The present work is a continuation of the work of these investigators and is aimed at determining the rate of reaction of hydrogen peroxide with various organic compounds. The results of this work will be presented in a separate paper.

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Introduction

The objective of the work presented in this thesis has been to obtain data bearing upon the mechanism of gas phase hydrocarbon oxidations. Such reactions have received considerable attention for many years and despite the vast amount of information which has been obtained, there is still disagreement upon some of the quite basic aspects. Before considering these differences and the reasons for them, it will be convenient to review briefly the main features of such oxidations.

Main Features of Hydrocarbon Oxidations

Many of the experimental observations are common to a great variety of normal, substituted and cyclic hydrocarbons. Of these the following are considered most relevant to the present investigation and to the discussion of possible oxidation processes.

i) The oxidation of hydrocarbons in the gas phase may proceed either in an explosive manner or at a measurable rate. The principal conditions determining which type of reaction results are, temperature, nature of the surface of the containing vessel and the concentration of either one or both reactants [1,2].

ii) When a hydrocarbon is oxidised under conditions such that a smooth, non-explosive reaction occurs, a change in pressure can be observed, if the combustion is carried out in a closed system. The pressure/time record usually shows an "induction" period (θ) during which there is little or no pressure rise. At the end of this the rate of pressure change increases to a maximum and then falls off again. This maximum rate of pressure change ($\rho_{\max.}$) has been considered by many workers to be the most significant measure of the rate of reaction [3,4,5]. Some workers however dispute this for reasons which will be considered later [6].

iii) The rate of oxidation ($\rho_{\max.}$) does not always increase smoothly with rising temperature and in the region 500°C to 400°C a maximum and

minimum may often be observed in the relation of rate to temperature [5,4,7]. The two regions on either side of this range of anomalous behaviour are usually designated as "high" and "low" temperature regions, the kinetics of oxidation being held to differ in each case.

iv) At all temperatures, the rate of oxidation increases and the induction period decreases with an increase in the initial pressure of combustible material [4,8]. At "high" temperatures ($>400^{\circ}\text{C}$) the rate is also strongly dependant on oxygen pressure [4], while at "low" temperatures ($<300^{\circ}\text{C}$) the rate can become independant of the concentration of one reactant under certain conditions [8].

v) Both the rate of reaction and the induction period are very sensitive to the state of the reaction vessel surface, and also the surface/volume ratio, the rate being most effected in each case. Seemingly trivial changes in the state of the surface can have large and differing effects, while an increase in the surface to volume ratio usually retards the reaction [4,8,9].

vi) The length of the induction period is usually reduced by any of the following :-

Increase in the pressure of either reactant [8,10]

The addition of small amounts of peroxides [11] and aldehydes [10, 11].

Increase of temperature, except that over a certain range the opposite effect is sometimes found [10,12].

vii) A large number of substances are produced during the oxidation of hydrocarbons. Carbon monoxide, carbon dioxide and water are the principal products and all reach their maximum concentrations at the end of the reaction. Others however, such as peroxides and aldehydes reach a maximum during the period of rapid reaction and do not always appear as end products [8]. These intermediates are most important in the kinetics of the reaction.

viii) At moderate temperatures the combustion of hydrocarbons is often accompanied by "cool flames" through the reaction mixture. These are usually blue in colour, give moderate pressure increases and cause

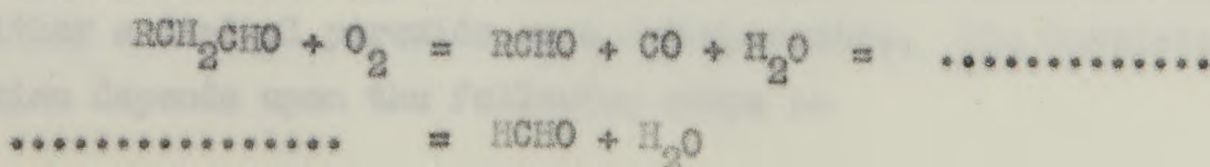
very incomplete combustion, since several such flames can follow each other in succession through the same reaction mixture [15]. The spectra of the cool flames from a number of different organic molecules has been shown to be the same, and identified as that of formaldehyde [14].

ix) In the normal paraffin series the rate of oxidation increases very rapidly with the length of the carbon chain, this increase being out of all proportion to the change in size of the molecule. Branching the chain, however, leads to a marked decrease in the rate of oxidation [15]. This is completely different from what happens in the pyrolysis of hydrocarbons, where increase of chain length or branching has very little effect after butane [16].

x) When a hydrogen atom of a paraffin is substituted by another atom or group, most of the effects listed above are still apparent while the absolute rate is usually changed considerably, especially if it is a hydrogen from a methyl group which has been replaced [5,17,18]. It is also usually found that if a structural factor affects the maximum rate, it will also affect the induction period in a corresponding way.

Theories of Oxidation Reactions

When some of the earlier oxidation theories were proposed, not all the experimental facts listed above were known and several theories were put forward involving somewhat complex rearrangement and substitution reactions. These included, for the low temperature reaction, the hydroxylation theory [19,20] of Bone where the intervention of oxygen atoms was required to degrade the hydrocarbon through alcohols to thermally unstable α diols and glycols. Lewis [21] put forward a primary dehydrogenation theory whereby water was formed from the most active hydrogen in the paraffin, leaving an olefin to be oxidised. Pope, Dykstra and Edgar [22] suggested that the oxidation proceeded through aldehydes which were degraded to lower ones.



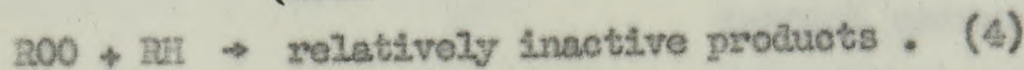
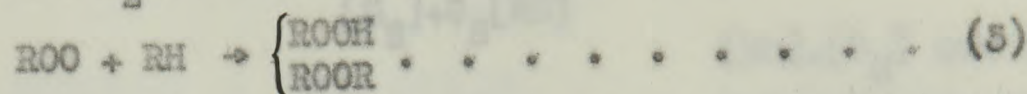
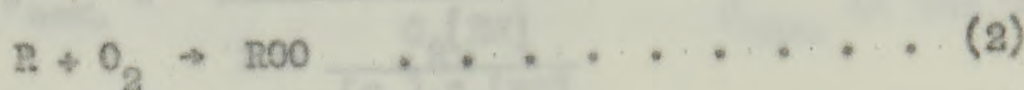
These and other theories have been reviewed by Cullis [23] and Walsh [24], and are all inadmissible on the grounds that they require large scale thermal decomposition or complex molecular reactions. With the accumulation of more data and the formulation of chain reaction schemes, several fairly comprehensive theories were developed. Although it is difficult to produce direct evidence that free radicals take part in oxidation processes, the observed experimental facts are quite consistent with their presence. It is known that chain reactions are very sensitive, to surface conditions, to the presence of catalysts and often show induction periods. All these are markedly present in hydrocarbon oxidations and it is now generally accepted that combustion takes place by a chain process, such as the slow branching mechanism of Semenov [2]. The main points at issue being how the chains are initiated, propagated and ended. According to the concept of degenerate branching the reaction takes place by a straight chain mechanism to produce a comparatively stable intermediate which is occasionally capable of starting fresh reaction chains. If, as is possible, the rate of regeneration of the intermediate is greater than its rate of destruction, then the number of chains will increase and the rate of reaction accelerate. The identity of this intermediate, in both high and low temperature modes of oxidation, has been the subject of considerable discussion and disagreement. Although the initial production of chain carriers could result from pyrolysis of the hydrocarbon, most workers now favour a direct bimolecular reaction of hydrocarbon and oxygen as the most probable method of chain initiation. Either peroxides or aldehydes are considered the most likely intermediates in the low temperature reaction and a few reaction schemes based upon them will now be considered.

1. The Theory of Cullis and Hinshelwood [8]

The key intermediate in the low temperature mode is assumed to be either a dialkyl peroxide or a hydroperoxide. The initiation reaction depends upon the following steps :-



The radicals then react as follows

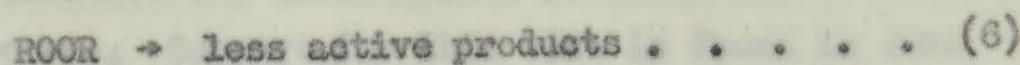


Of the peroxides produced by steps (3) and (4) it is assumed that one will be of predominant importance. This is designated as ROOR, all other reactions being covered by step (4).

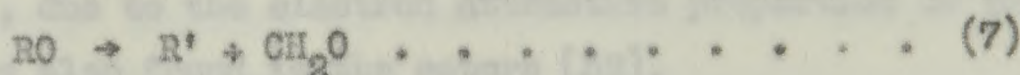
The active peroxide may decompose in two ways,



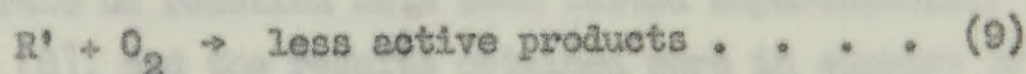
or non-chain degradation



The radical RO is assumed to decompose to give aldehyde and a lower alkyl radical



R' may then react with more RH or with O₂



The whole scheme is simplified by using the experimental fact that the rate decreases very markedly with diminishing number of carbon atoms. Thus it is inferred that step (8) will maintain the rate while the contribution from step (9) can be neglected and it may be treated as a chain breaking reaction. Assuming the reaction to be of a stationary nature ($d[x]/dt$ being equal to zero: $[x]$ being the concentration of the various radical intermediates), Cullis and Hinshelwood obtained the following expression for the maximum rate of reaction :-

$$p_{\max.} = \frac{C_1[RH][O_2]}{1 - \frac{C_2[RH]}{[O_2] + C_3[RH]}}$$

C_1, C_2, C_3 are constants

$p_{\max.}$ is the maximum rate

$[RH], [O_2]$ are the initial pressures of hydrocarbon and oxygen.

The remarkable structural effects with branched chain hydrocarbons are accounted for, in this theory, by the relative stabilities of the labile peroxides, which affect the constants in the denominator of the rate expression and so produce a magnified effect upon the rate. This is believed to occur through the electron repelling powers of the methyl group, which can stabilize the intermediate peroxide and so reduce the chain branching process. Support for this view is found in some substituted hydrocarbons, replacing one hydrogen by chlorine in a methyl group increases the rate of oxidation [50]. It is further demonstrated in the ethers [51], due to the electron attractive properties of the -OR group and it is also found in the esters [52].

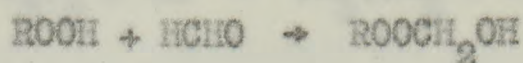
They also deduce that the reciprocal induction period ($1/\theta$) should vary in a linear manner with hydrocarbon or oxygen pressure. Both this and the predicted rate of reaction have been tested experimentally with pentane and hexane [8], and the results obtained were in support of the theory. The point of attack on the hydrocarbon is believed to take place as far from a methyl group as possible.

The substitution of hydroperoxide for dialkyl peroxide does not affect the basic postulates or the mathematical development of the theory.

2. The Theory of Walsh [24,26]

In many ways this theory is similar to that of Cullis and Hinshelwood. Both postulate a peroxide as the intermediate, but there are several differences. In the low temperature region Walsh suggests that decomposition of the peroxide molecule is catalysed by aldehydes, which are known to

condense with hydroperoxides to give hydroxy peroxides:



these are probably less stable than the normal peroxide and would decompose thus

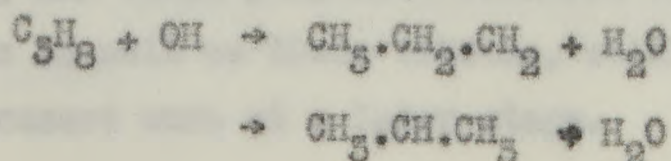


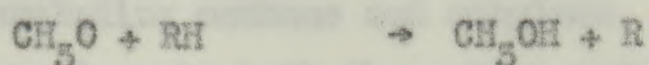
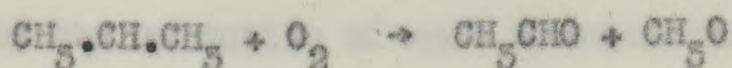
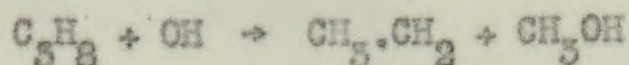
producing the same products as normal peroxide decomposition. It is postulated that the change to high temperature mechanism occurs through increased, non-chain, decomposition of ROO radicals.

The proposed point of attack on the carbon skeleton is at a tertiary carbon atom, in preference to a secondary, and at a secondary in slight preference to a primary. This is based on the work of Rice [28] for the relative probabilities of attack of alkyl radicals on 1°, 2°, and 3° carbon atoms, and is also supported by some recent work by Cullis [29]. It should be borne in mind, however, that the most probable point of attack is not necessarily the one which will give rise to the most rapid chain branching. Although the hydrogen atoms most easily removed from a paraffin are the tertiary ones, it is probable that attack upon the secondary carbon atoms produces branching chains which are of much greater significance in the development of the reaction than those produced from attack on tertiary carbon atoms.

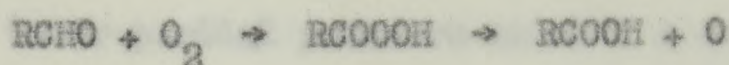
5. The Theory of Norrish

Norrish considers that the agent of degenerate branching is an aldehyde and not a peroxide. Although there is conflicting evidence on whether hydroperoxides are present in oxidation systems [33,34], there is no doubt that higher aldehydes are present and can act as branching intermediates [35,35,36]. A scheme for propane oxidation is as follows [35].





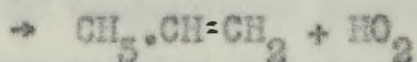
Branching takes place by reaction of the aldehyde with oxygen to give an oxygen atom which initiates two fresh chains.



The transition to high temperature reaction is supposed to occur through an olefine forming reaction tending to replace the production of aldehyde and so bringing about the observed negative temperature coefficient.



is replaced by



thus reducing the chain branching from the oxidation of the aldehyde.

It is difficult to see how this can, in fact, take place since if a reaction, such as the initiating one, can proceed by two routes one having a greater temperature coefficient than the other, then increasing temperature will cause only a relative and not an absolute decrease in the reaction having the lower activation energy. That this will produce a change in slope in the linear Arrhenius plot relating rate to temperature is true but it is difficult to see how it can give the negative temperature dependence observed. To achieve this either the active intermediate or one of its transient precursors must be able to undergo two different types of reaction.

Tipper [37] and Ridge [38] have reviewed various aspects of oxidation kinetics as well as these schemes, which will be discussed in relation to the present work at a later stage.

Cool Flames

A characteristic phenomenon of intermediate temperature oxidation is the appearance of the cool flames mentioned above, they have been noted in the oxidation of most hydrocarbons, including ethane [39] but excluding methane and ethylene. Various theories have been put forward as to both the nature and the periodicity of cool flames. There is considerable support for the view that peroxides play an important part in the mechanism [40,41,42]. They decompose explosively when their partial pressure exceeds a critical limit [41], and it is found that the minimum pressure of peroxides required to induce a cool flame in butane -oxygen mixtures is, in fact, the same as the critical limit for explosion of the peroxides alone [42]. Some workers however consider that it is an aldehyde, not a peroxide, which is built up just before the onset of cool flames [43].

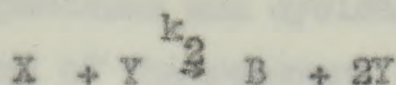
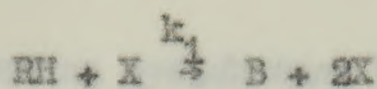
Pease has suggested [44] that the recurrent nature of cool flames is caused by the self-heating accompanying the flame, bringing the reaction mixture into the region of temperature where the rate starts to decrease. The reduced rate then permits the temperature to fall and the whole process to repeat itself again.

Salnikov considers [45] a homogeneous exothermal reaction to be responsible,



where the temperature coefficient of the second step is greater than that of the first. If the second step is highly exothermal and self-heating occurs, the rate may increase until X is depleted. The temperature then drops and X can build up again for a repetition of the process.

Frank-Kamenetski [46] ascribes the repetition to the reaction of one intermediate with another. The following sequence of reactions is supposed to take place.



where RH is a molecule of hydrocarbon, X is an intermediate formed autocatalytically from RH, Y is an intermediate formed autocatalytically from X, and B represents final products.

The rates of increase of the concentrations of X and Y are given by :-

$$d[X]/dt = k_1[RH][X] - k_2[X][Y] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$d[Y]/dt = k_2[X][Y] - k_3[RH][Y] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Consideration of these equations show that the reaction proceeds periodically. If a small amount of X is formed in some way, its concentration will increase in accord with equation (1). If a small amount of Y is also present, it will react with X to produce more Y. The autocatalytic production of Y will eventually lead to a decrease in the concentration of X. When [X] falls below a critical value of $k_3[RH]/k_2$, [Y] will begin to decrease and a repetition of the cycle becomes possible.

Frank-Kamenetski considers that X is a peroxide and Y an aldehyde. This type of system is in accord with the oxidation theory of Walsh [24,26] who identifies Y with formaldehyde.

The Present Work

The systems investigated in this thesis are a series of cycloparaffins and oxygen in a static system, mainly at temperatures below 300°C. Comparisons have been made with the kinetics of similar open chain paraffins and particular reference made to the problems of the rate-structure relationship and the rate. The actual paraffins used for this purpose have been a series from cyclopropane to

Experimental

The investigations to be described were carried out in a similar system but the reactions studied by pressure change and by gas uptake.

Apparatus

The apparatus used in this work was similar in design to those used previously in this laboratory for the oxidation and polymerization of hydrocarbons. The essentials of the system are a reaction vessel heated in a furnace and connected to an overbalancing system, a pressure system for reactants and pure pressure measuring system. A diagram of the apparatus, which was constructed of "Pyrex" glass, is shown in Fig. 1.

The reaction vessels used were cylindrical in shape and connected to the main apparatus by a special capillary tube at one end. Two alloys, packed and unp~~packed~~ EXPERIMENTAL were used, all of which were 1200, long by 600, in diameter, giving a volume of about 200 cc. and a surface/volume ratio of 0.25 cm^{-1} . The alloy vessels were packed with alloy tubes to give surface/volume ratios of 0.2 cm^{-1} and 0.3 cm^{-1} . Two of the glass vessels were coated on the inside with a thin layer of salt, deposited from a strong aqueous solution by heating and drying. The alloy vessels were connected to the main apparatus through an 18° joint and sealed joint sealed with Shimadzu "W" wax; the glass vessels were sealed on. All vessels were cleaned before use, or heating with sodium fluoride oxide and then washed with distilled water.

Capillary tubing of the internal diameter was used in all experiments connected to the reaction vessel and there was care to select at one pressure to eliminate the "dead space". The diameter used was at 20°C assumed to be 0.25 of the volume of the vessel and 0.25 of that of the packed vessel.

The furnace consisted of a vertical alloy tube about 20 cm in diameter lined with nichrome wire and fed with current from a "variac" variable voltage transformer, connected to the mains. The furnace was

Experimental

The investigations to be described were carried out in a static system and the reactions studied by pressure change and by analysis.

Apparatus

The apparatus used in this work was similar in design to those used previously in this laboratory for the oxidation and pyrolysis of hydrocarbons. The essentials of the system are a reaction vessel heated in a furnace and connected to an evacuating system, a storage system for reactants and some pressure measuring device. A diagram of the apparatus, which was constructed of "Pyrex" glass, is shown in Fig.1.

The reaction vessels used were cylindrical in shape and connected to the main apparatus by a co-axial capillary stem at one end. Both silica, packed and unpacked, and pyrex vessels were used, all of which were 10cm. long by 6cm. in diameter, giving a volume of about 280 cc. and a surface/volume ratio of 0.85 cm^{-1} . Two silica vessels were packed with silica tubes to give surface/volume ratios of 5.8 cm^{-1} and 5.2 cm^{-1} . Some of the pyrex vessels were coated on the inside with a thick layer of salt, deposited from a strong aqueous solution by heating and pumping. The silica vessels were connected to the main apparatus through an A7 cone and socket joint sealed with Edwards "W" wax; the pyrex vessels were sealed on. All vessels were cleaned before use, or coating, with boiling fuming nitric acid and then washed with distilled water.

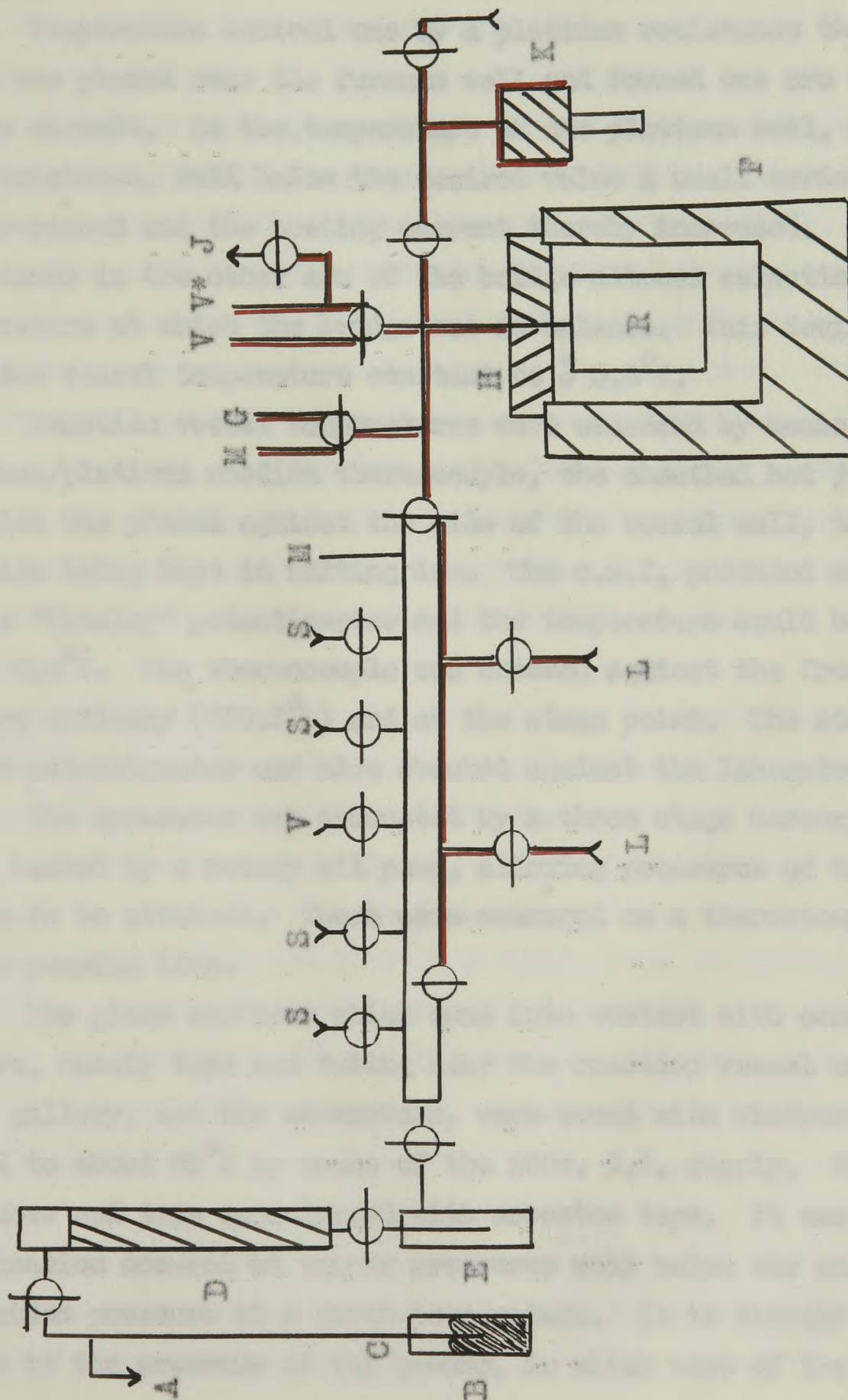
Capillary tubing of 2mm internal diameter was used in all connections contiguous to the reaction vessel and these were made as short as was practicable to minimise the "dead space". The effective dead space at 250°C amounted to 2.3% of the volume of the unpacked and 2.7% of that of the packed vessel.

The furnace consisted of a vertical silica tube about 11 cm in diameter wound with resistance wire and fed with current from a "Variac" variable voltage transformer, connected to the mains. The furnace was

Key to Fig. 1

- A. Gas inlet
- B. Mercury seal
- C. To atmosphere
- D. Phosphorus pentoxide drying tower
- E. Condensing point
- F. Furnace
- H. Asbestos furnace plug
- J. Sampling point
- K. Storage for liquid hydrocarbons
- L. Storage for liquid additives
- M. Mercury manometers
- S. Gas storage globes
- V. To vacuum line
- V₁ To vacuum line through liquid air trap
-  Taps
-  Cone and socket joints
-  Heated sections

Fig. 1 The Apparatus



well lagged and the top covered by an asbestos wool and board cap. Measurement of the vertical temperature distribution in the furnace, with the reaction vessel in position, showed that the variations over the length of the vessel did not exceed $\pm 1.5^{\circ}\text{C}$ at 515°C .

Temperature control was by a platinum resistance thermometer which was placed near the furnace wall and formed one arm of an A.C. bridge circuit. As the temperature of the platinum coil, and consequently its resistance, fell below the desired value a small series resistance was by-passed and the heating current thereby increased. A variable resistance in the other arm of the bridge allowed selection of the temperature at which the bridge was in balance. This device could keep the vessel temperature constant to $\pm 0.4^{\circ}\text{C}$.

Reaction vessel temperatures were measured by means of a platinum/platinum rhodium thermocouple, the sheathed hot junction of which was placed against the side of the vessel wall, the cold junction being kept in melting ice. The e.m.f. produced was measured with a "Tinsley" potentiometer and the temperature could be read to about 0.2°C . The thermocouple was checked against the freezing point of pure antimony (630.5°C) and at the steam point. The standard cell in the potentiometer was also checked against the laboratory standard.

The apparatus was evacuated by a three stage mercury diffusion pump, backed by a rotary oil pump, allowing pressures of the order of 10^{-5} mm to be attained. These were measured on a thermocouple gauge in the pumping line.

The glass surfaces which came into contact with condensable vapours, namely taps and tubing near the reaction vessel or on the lower gallery, and the manometers, were wound with Nichrome wire and heated to about 60°C by means of the 100v. D.C. supply. Where possible the tubes and taps were lagged with asbestos tape. It was found that condensation occurred at vapour pressures well below the nominal saturation pressure at a given temperature. It is thought that this is due to the presence of tap grease, in which some of the reactants

were soluble, and to the capillary surfaces. A good safety margin was therefore maintained.

Heated taps and joints were lubricated with "Edwards Silicone High Vacuum Grease". For the remainder either "Apiezon L" or "Edwards Soft High Vacuum Grease" was used according to the size of the ground surfaces.

Pressures were measured with a mercury manometer of 2 mm capillary tubing, read to 0.1 mm. Errors introduced into the pressure readings by the heating of the manometer were negligible. An all glass, spoon gauge, manometer was used when working with free halogens, the spoon being surrounded by an outer jacket the pressure in which could be varied and measured on a subsidiary mercury manometer. The gauge was used as a null point instrument by balancing the outer jacket and vessel pressures. Two platinum contacts, one on the spoon and one fixed to the jacket, were used as a switch in an electric circuit to determine the null point at any pressure. The current used was 2 to 5 milliamperes and the gauge was sensitive to a pressure difference of 0.5 mm.

Liquid hydrocarbons were stored in a tube attached to a vapour reservoir, and liquid additives in small bulbs attached to the lower gallery, through cone and socket joints. They were freed of dissolved air by alternate freezing, thawing and pumping. Gaseous hydrocarbons and other gases were stored in five litre globes attached to the upper gallery and were admitted through a drying tube containing phosphorus pentoxide, a mercury blow-off ensuring a positive pressure so as to prevent air leaking in through the cylinder reduction valve. Condensable gases were frozen down and pumped, non-condensable gases passed through a liquid air trap.

Materials

Some of the hydrocarbons used in this investigation were purchased and some were synthesised.

Cyclohexane, cyclopentane, n-pentane, methyl cyclohexane and methyl cyclopentane were supplied by Phillips Petroleum Company and were 99 Mol % minimum. The cyclopentane, with which most of the kinetic work was carried out, contained 1% of 2:2 dimethyl butane as an impurity. This could not be removed by fractionation but tests showed that it did not affect the kinetics of the cyclopentane. 1:1:3 trimethyl cyclopentane was supplied by I.C.I. (Billingham).

Cyclopropane was supplied by the British Oxygen Company (Medical Division). Oxygen, carbon dioxide, nitrogen and neon (spectroscopically pure) were also supplied by B.O.C.. Carbon tetrafluoride was supplied by I.C.I. as "Arcton".

The salts, and other additions used, were obtained from B.D.H. and were, where possible, of AnalaR quality.

1:4 dimethyl cyclohexane was synthesised by the high pressure hydrogenation of p-xylene. This was freed from any o- and m-xylene impurities by freezing. The hydrogenation was carried out at 200°C and 170 atmospheres pressure using a Rayney Nickel catalyst. Two reductions each lasting six hours were required to reduce all the xylene. Mass spectrometric analysis showed only 0.05% of unsaturated material after purification with concentrated sulphuric acid.

1:3:5 trimethyl cyclohexane was prepared, by a method similar to the above, from mesitylene. The product contained 0.05% unchanged mesitylene after purification.

Cycloheptane was prepared from cycloheptanone by reduction, as above, to the alcohol, dehydration to the olefin, by distillation with β -naphthalene sulphonic acid, and finally hydrogenation to the paraffin [54], after purification it contained only 0.05% of unchanged olefin.

Cyclooctane was obtained from Light and Co. and from the hydrogenation of cyclooctatetraene. That supplied by Light contained 15% of benzene and 8% of some unknown substance, as shown by gas chromatography, but was used as such. The hydrogenation was carried out at 150 atmospheres and 100°C for 5 hours. The product was purified

with concentrated sulphuric acid and by freezing and thawing.

Ditertiary butyl peroxide, used as an initiator, was supplied by Laporte Chemicals, and was redistilled when used for rate determinations.

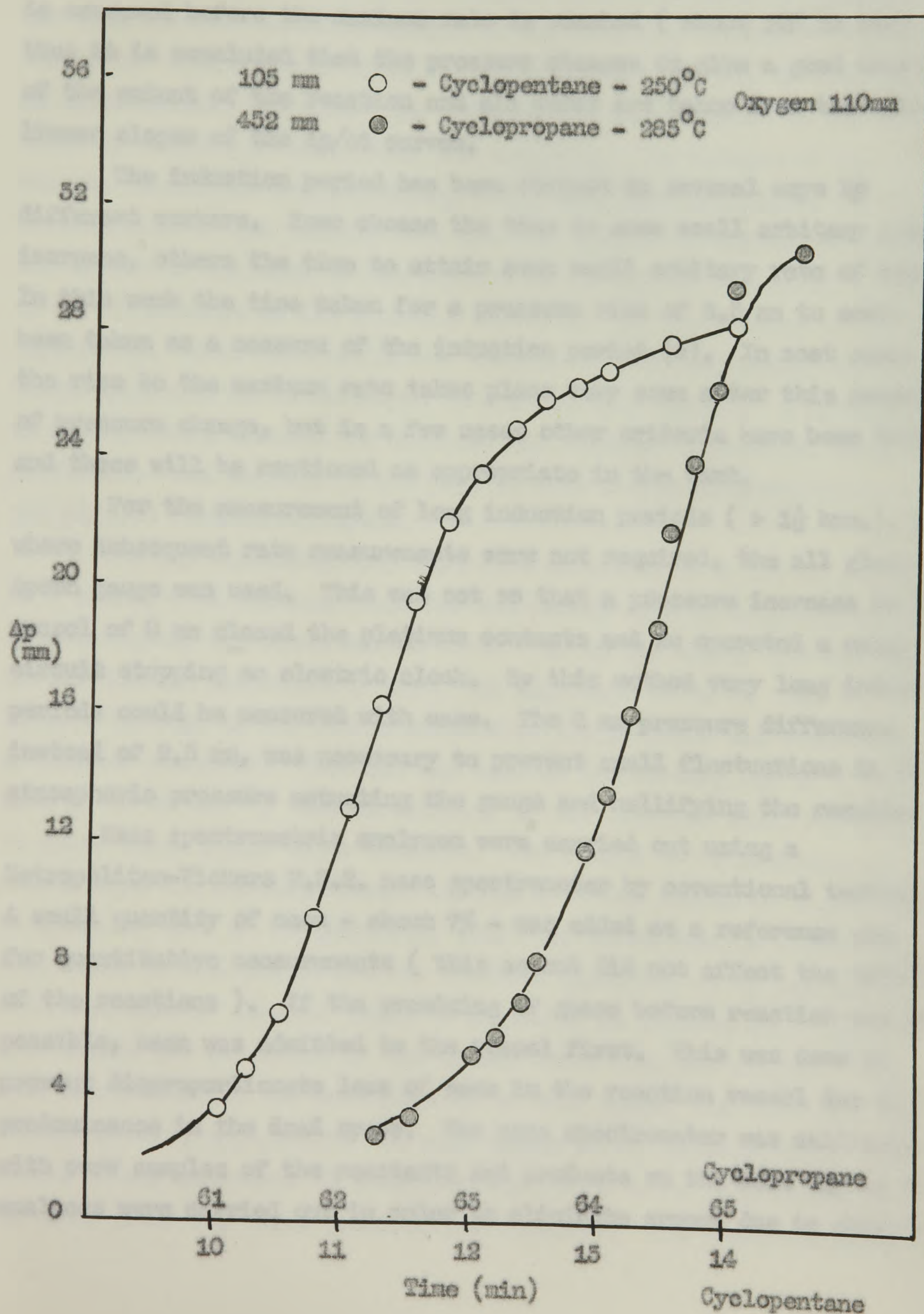
General Experimental Procedure and Validity of Pressure Changes as a Measure of the Absolute Rate

The general procedure in carrying out a "run" was as follows. The reaction vessel having been evacuated, the desired amount of hydrocarbon was admitted from its storage reservoir, heated in hot water if necessary. Oxygen was then added from its storage globe, the pressures measured and a stop watch started. Any small homogeneous additions were added before the hydrocarbon, and inert gases before the oxygen. After the induction period was over, pressure readings were taken at suitable intervals, from one minute to five seconds depending upon the rate of reaction. The manometer was tapped continually to prevent the mercury sticking to the glass. Readings, taken to 0.1 mm, were probably accurate to ± 0.3 mm. A Δp /time curve was constructed and the maximum slope measured, typical curves are drawn in Fig. 2.

It is well known that in oxidation reactions, where after a long induction period, the rate only accelerates slowly to a maximum, there is often a large consumption of reactants before this maximum rate is reached. This raises the question of the validity of pressure measurements as a measure of the absolute rate, which itself can be defined as either the rate of removal of oxygen or of hydrocarbon. The detailed analytical results will be set out in a later section but some of those having a bearing on this problem will be considered now.

The principal products are carbon monoxide, carbon dioxide and water, the pressure rise is due mainly to these and all the other products are found in low concentrations. During the period where the maximum rate prevails the $\Delta p/\Delta t$ curves and the rate of oxygen

Fig. 2 Typical Pressure - Time Curves



disappearance follow each other closely and the rate of hydrocarbon removal follows that of the oxygen. Furthermore very little reactant is consumed before the maximum rate is reached (about 10% in most cases), thus it is concluded that the pressure changes do give a good measure of the extent of the reaction and all rates are taken from the maximum linear slopes of the $\Delta p/\Delta t$ curves.

The induction period has been defined in several ways by different workers. Some choose the time to some small arbitrary pressure increase, others the time to attain some small arbitrary rate of reaction. In this work the time taken for a pressure rise of 2.5 mm to occur has been taken as a measure of the induction period (θ). In most cases the rise to the maximum rate takes place very soon after this amount of pressure change, but in a few cases other criteria have been taken and these will be mentioned as appropriate in the text.

For the measurement of long induction periods ($> 1\frac{1}{2}$ hrs.), and where subsequent rate measurements were not required, the all glass spoon gauge was used. This was set so that a pressure increase in the vessel of 8 mm closed the platinum contacts and so operated a relay circuit stopping an electric clock. By this method very long induction periods could be measured with ease. The 8 mm pressure difference, instead of 2.5 mm, was necessary to prevent small fluctuations in the atmospheric pressure actuating the gauge and nullifying the results.

Mass spectrometric analyses were carried out using a Metropolitan-Vickers M.S.2. mass spectrometer by conventional techniques. A small quantity of neon - about 7% - was added as a reference gas for quantitative measurements (this amount did not affect the kinetics of the reactions). If the premixing of gases before reaction was not possible, neon was admitted to the vessel first. This was done to prevent disproportionate loss of neon in the reaction vessel due to its predominance in the dead space. The mass spectrometer was calibrated with pure samples of the reactants and products on the same day as the analyses were carried out in order to eliminate errors due to changing

sensitivity.

Details of the chemical analyses performed will be given in the next section but some mention of the sampling technique will be made now. Samples were taken from the reaction vessel, by sharing into an approximately one litre gas pipette, the exact volume of which was found by filling it with water and weighing. The volumes of the reaction vessel, dead space and connecting tubes were then calculated by sharing a fixed mass of gas between them and the pipette at different temperatures. The amount of reactant in the pipette could then be expressed in terms of mm Hg pressure in the reaction vessel at the temperature of the experiment. This calibration was checked by chemical estimation of known pressures of formaldehyde in the reaction vessel. A difference of 3% was found between the methods, the chemical estimation being preferred. Gas samples in the pipette were shaken with distilled water and aliquot portions analysed.

The gas chromatography apparatus consisted of a 150 cm column of U shape, 8 mm internal diameter and packed with di-nonyl-phthalate on keisulguhr, the whole heated to 60°C by an air bath. The detector, of the thermal conductivity type, was also kept at 60°C. The out of balance voltage in the bridge circuit of the detector was measured on a "Sunvic" recorder. Nitrogen was used as the eluting gas at a flow rate of 20 ml min⁻¹. The sensitivity of the recorder could be changed to allow large peaks to be measured. The sample to be analysed was pumped from the reaction vessel through a U-trap cooled in liquid air to condense most of the products, this trap could then be fitted to the inlet side of the column and its contents distilled on by heating it with warm water. Samples could be collected as desired in a trap cooled with liquid air at either of two outlet tubes from the column. Much peak identification was accomplished by this means, the individual peak effluents being analysed on the mass spectrometer qualitatively. The amount of any substance in a mixture was found to be proportional to the area under the curve drawn by the recorder. The proportionality

Table 1

Gas Chromatography Calibration Data

Column is packed with di-nonyl- phthalate on kalsulghur, 150 cm long.
Column and detector temperature 60°C. Nitrogen flow rate 20 ml min⁻¹.
The sensitivity refers to pressure in the reaction vessel at 250°C.

<u>Compound</u>	<u>Peak Time</u> (min)	<u>Peak Direction</u>	<u>Sensitivity</u>	
			<u>mm cm⁻²</u>	<u>10⁻⁶ mol cm⁻²</u>
Carbon dioxide *	3-5	+ve	0.04	0.35 *
Cyclopropane	3-5	+ve	?	?
Propane	3-5	+ve	0.13	1.4
Propylene	3-5	+ve	0.13	1.4
Butene	6-7	+ve	0.10	0.8
Acetaldehyde	9-10	+ve	0.13	1.0
Water	12-	-ve	?	?
2:2 dimethyl butane	15-17	+ve	?	?
Cyclopentane	18-24	+ve	0.10	0.8
n-butyric aldehyde	41-45	+ve	0.13	1.0
Benzene	65-72	+ve	?	?
Cyclooctatetraene	90-100	+ve	?	?

* Peak height only, and not peak area is referred to with carbon dioxide*

Reaction of peroxide with hydrocarbon in the presence of cobalt
 catalyst

Reaction of peroxide and cobaltous chloride in benzene

It was first ascertained that some experiments should be made before beginning the investigation. They are both typical members of their hydrocarbon series and both have already been investigated [2, 10], although under conditions different from those used here. A comparison could show not only how far results could be compared as general, but also whether the apparatus and technique used gave results comparable with those of other workers. It is unfortunate that in oxidation reactions results may vary from apparatus to apparatus and from worker to worker, even though the same systems are being investigated. The reaction parameters are

RESULTS

The reaction parameters are k_p and $t_{1/2}$. A comparison is made of the two peroxide systems found to be 20°C (the effect of temperature as a variable will be considered later) and both systems and oxygen pressure were varied slightly. The effect of rate of addition and induction period is shown in Figs. 1, 2, 3, and 4. In Fig. 1 the induction period ($t_{1/2}$) is plotted against the rate of addition of peroxide to hydrocarbon. For the rate of addition and all the experimental points have been plotted on the graph but all the results are given in the tables in Appendix A.

In some cases, where the induction periods were very long, a few millimoles of di-tert-butyl peroxide were added as an initiator. Since at the temperature of the experiment the peroxide decomposes very rapidly (half life is 0.5 sec at 20°C) it was necessary to add it with the oxygen to the reaction vessel. The lower gallery was used for this purpose as a gas syringe, being filled with peroxide vapor at room temperature. The oxygen was then admitted through the lower gallery carrying the peroxide into the reaction vessel. In this way 2 cc of peroxide could be added, which was sufficient to remove the

Results

Comparison of n-Pentane and Cyclopentane Oxidation Kinetics

It was first considered desirable that some comparison should be made between n-pentane and cyclopentane. They are both typical members of their homologous series and both have already been investigated [8,55], although under conditions different from those used here. A comparison would show not only how far results could be regarded as general, but also whether the apparatus and technique used gave results comparable with those of other workers. It is unfortunate that in oxidation reactions results may vary from apparatus to apparatus and from worker to worker, even though the same systems are being investigated. Two reaction parameters were measured throughout this work, the induction period (θ) and the maximum rate ($\rho_{\max}$). A convenient temperature to compare the two paraffins was found to be 250°C (the effect of temperature as a variable will be considered later) and both hydrocarbon and oxygen pressures were varied widely. The effect of this upon maximum rate and induction period is shown in Figs. 3,4,5, and 6. In fact reciprocal induction period ($1/\theta$) is plotted since this seems to bear a linear relationship to reactant pressure. For the sake of clarity not all the experimental points have been plotted on the graphs but all the results are given in the tables in Appendix A.

In some cases, where the induction periods were very long, a few millimetres of ditertiary butylperoxide were added as an initiator. Since at the temperature of the experiment the peroxide decomposes very rapidly (half life is 0.8 sec at 250°C) it was necessary to add it with the oxygen to the reaction vessel. The lower gallery was used for this purpose as a gas pipette, being filled with peroxide vapour at room temperature. The oxygen was then admitted through the lower gallery sweeping the peroxide into the reaction vessel. In this way 2 mm of peroxide could be added, which was sufficient to remove the

Fig. 5 Variation of Maximum Rate with pressure of n-pentane and cyclopentane at different oxygen pressures

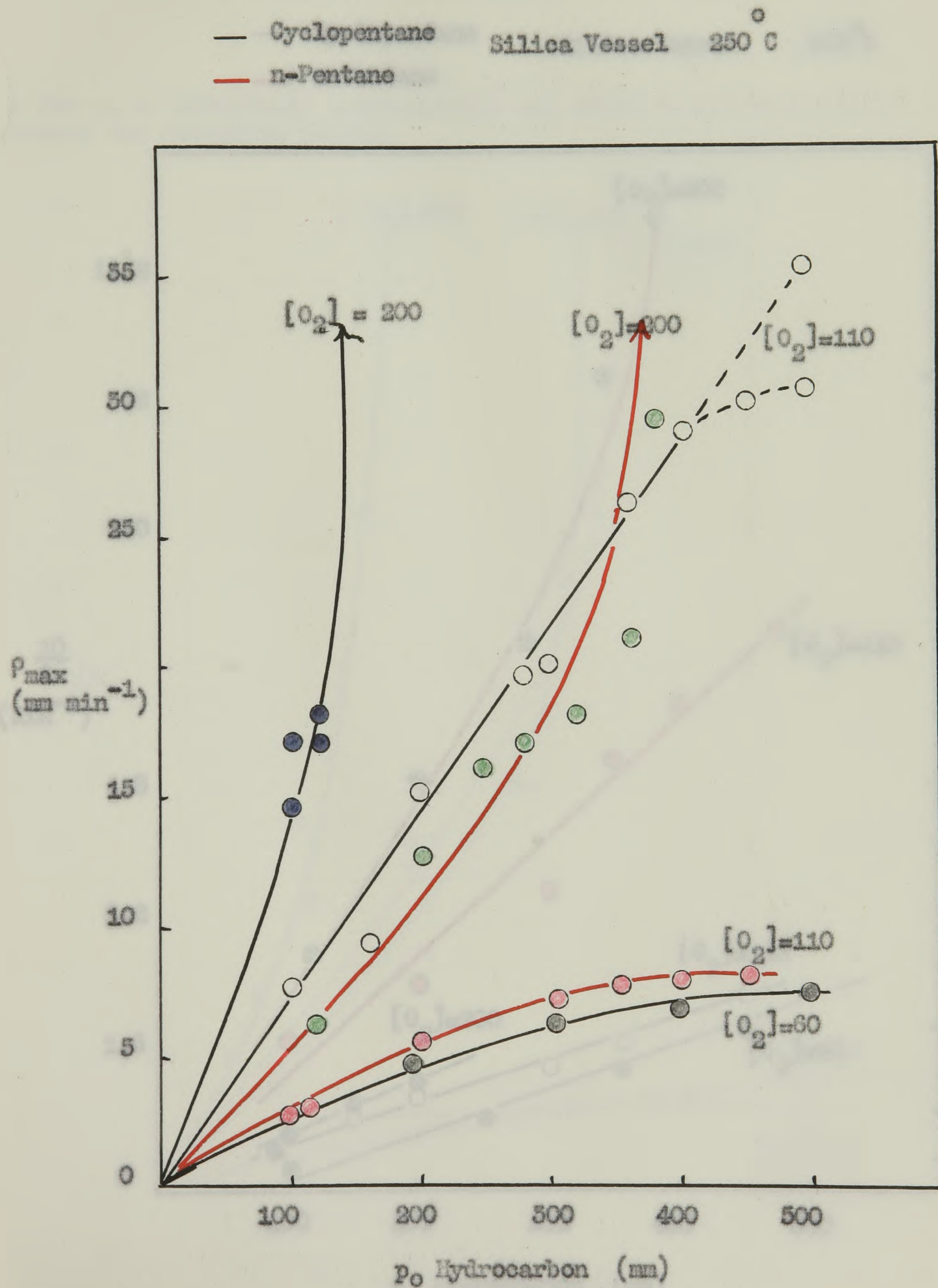


Fig. 4

Variation of Reciprocal Induction Period with pressure of n-Pentane and Cyclopentane at different Oxygen pressures

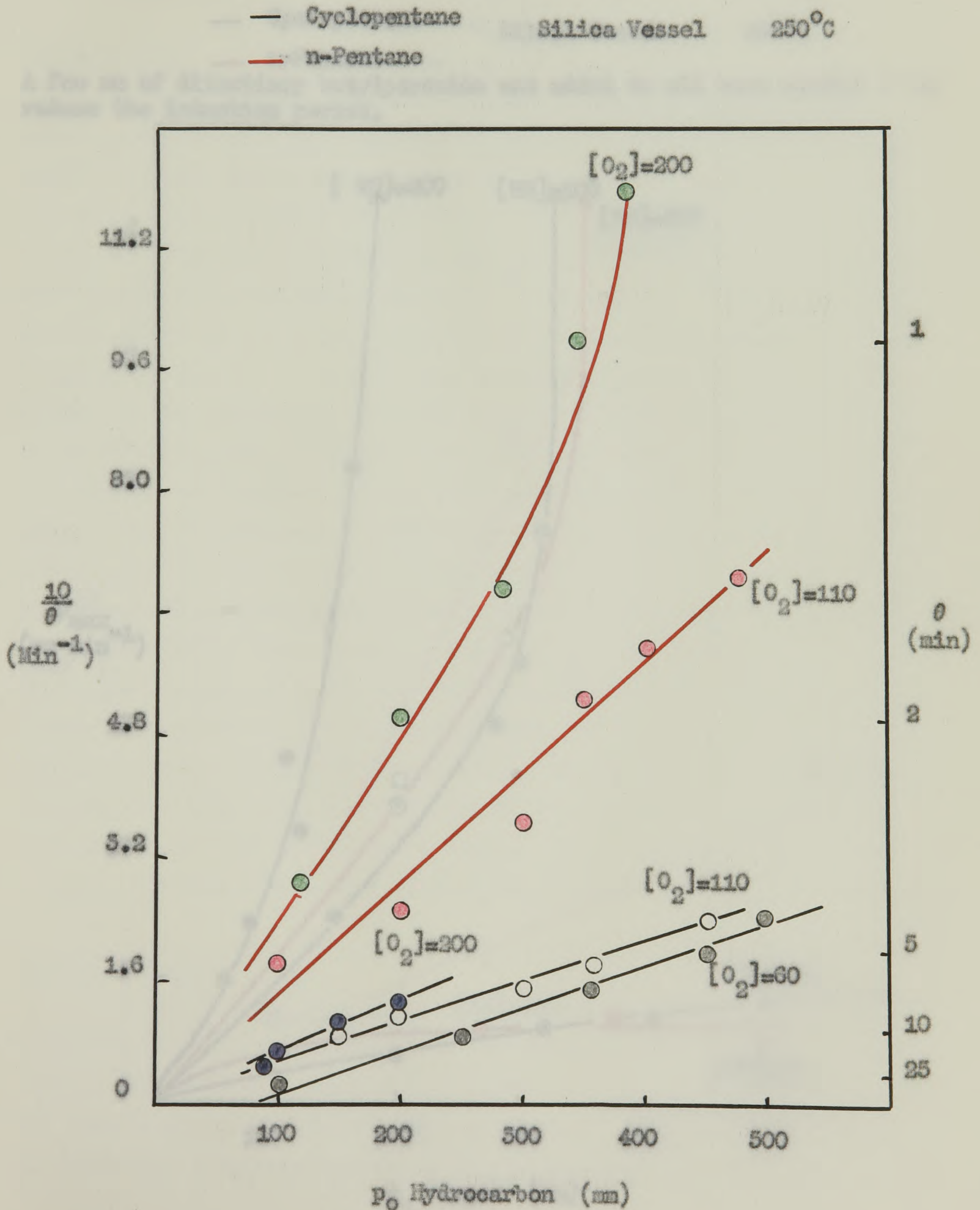


Fig. 5 Variation of Maximum Rate with pressure of oxygen at different
n-pentane and cyclopentane pressures

— Cyclopentane Silica Vessel 250°C
— n-Pentane

A few mm of ditertiary butylperoxide was added to all runs marked ⊙ to reduce the induction period.

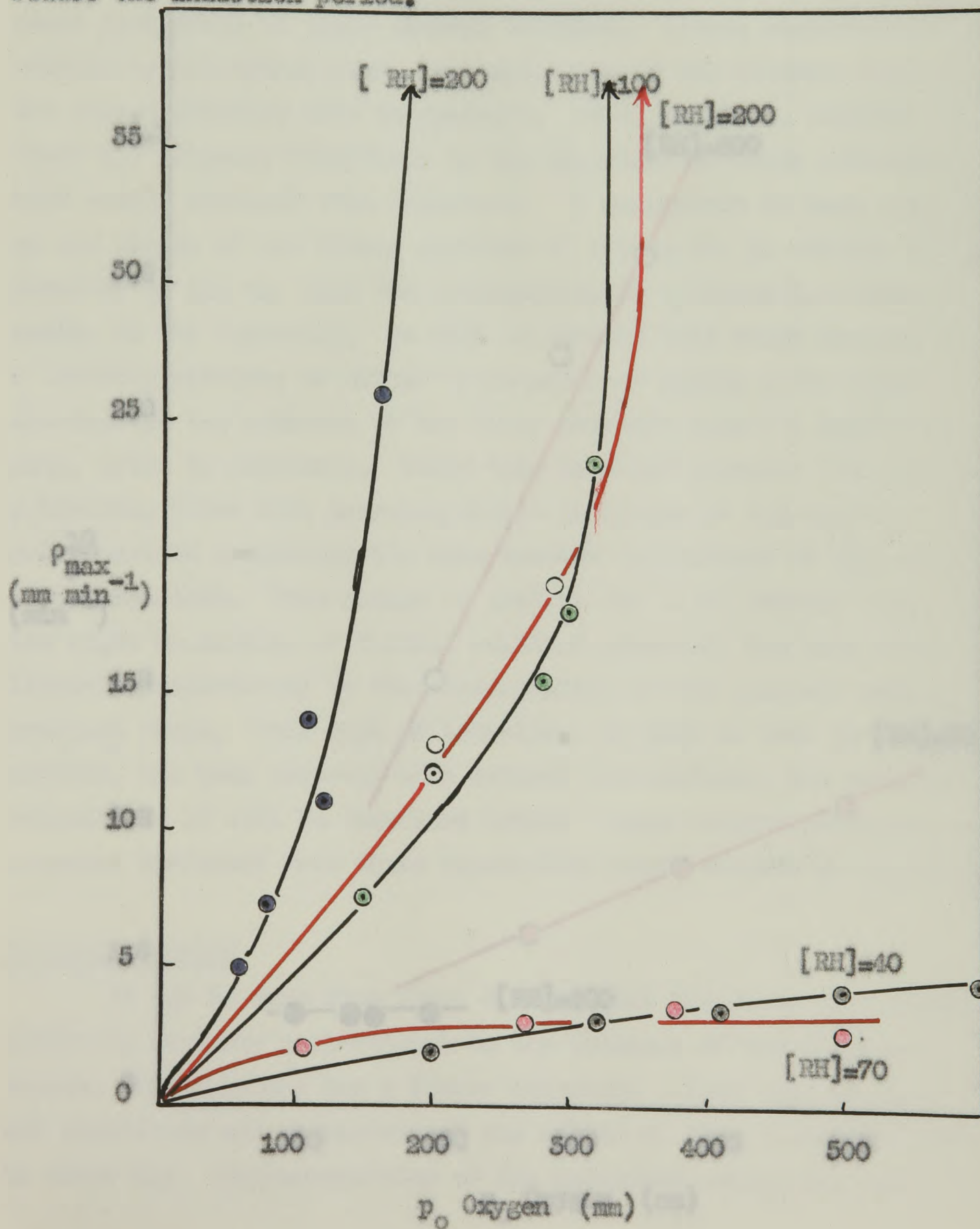
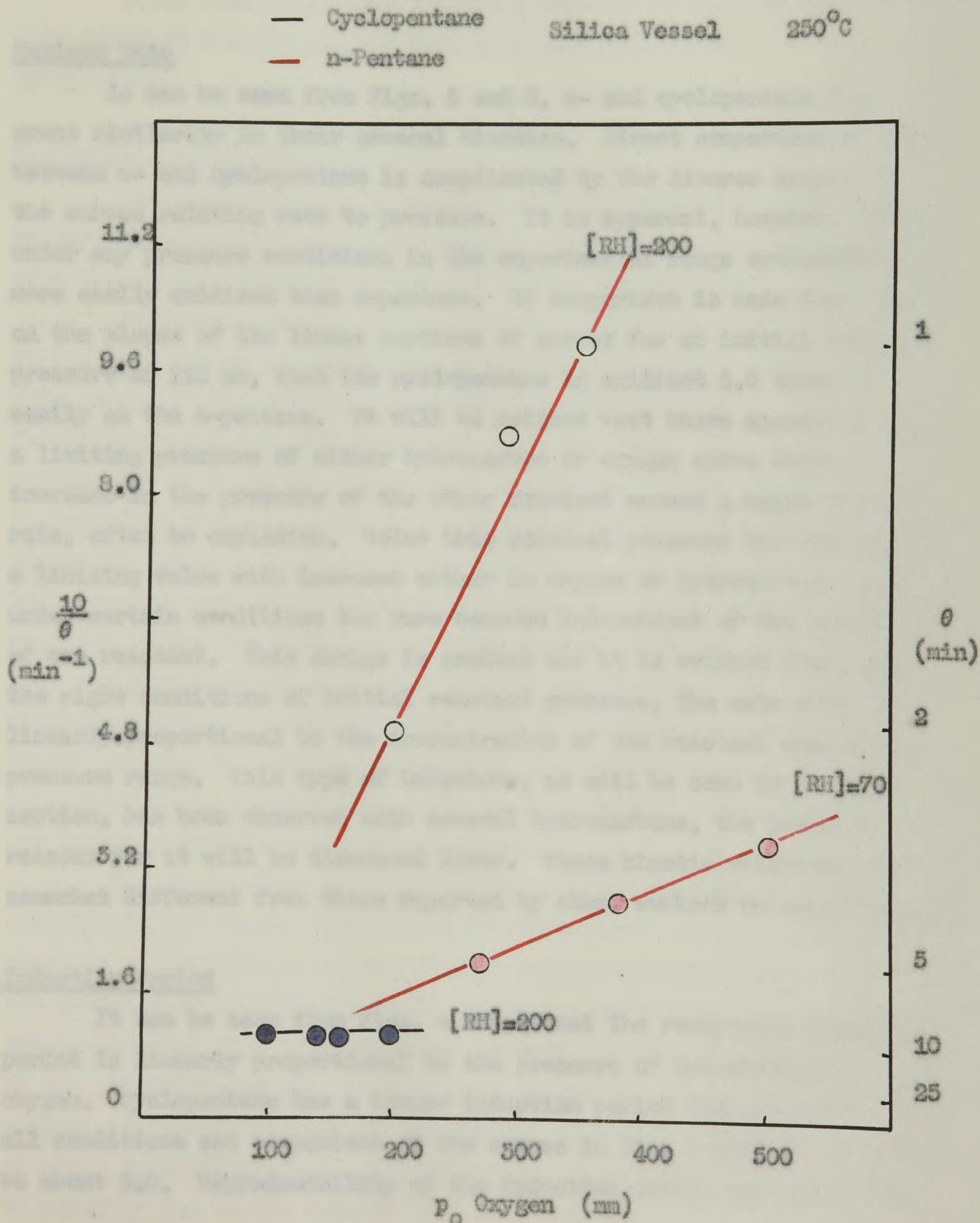


Fig. 6 Variation of Reciprocal Induction Period with pressure of oxygen at different n-pentane and cyclopentane pressures



induction period but left the rate unaffected. The probable reasons for the action of peroxide as an initiator will be discussed later.

Maximum Rate

As can be seen from Figs. 3 and 5, n- and cyclopentane show great similarity in their general kinetics. Direct comparison of rates between n- and cyclopentane is complicated by the diverse shapes of the curves relating rate to pressure. It is apparent, however, that under any pressure conditions in the experimental range cyclopentane is more easily oxidised than n-pentane. If comparison is made from Fig. 5 on the slopes of the linear portions of curves for an initial oxygen pressure of 110 mm, then the cyclopentane is oxidised 2.5 times as easily as the n-pentane. It will be noticed that there appears to be a limiting pressure of either hydrocarbon or oxygen above which increase in the pressure of the other reactant causes a rapid rise in rate, often to explosion. Below this critical pressure the rate attains a limiting value with increase either in oxygen or hydrocarbon. Thus under certain conditions the rate becomes independent of the concentration of one reactant. This change is gradual and it is evident that, under the right conditions of initial reactant pressure, the rate would be linearly proportional to the concentration of one reactant over a wide pressure range. This type of behaviour, as will be seen in the next section, has been observed with several hydrocarbons, the possible reasons for it will be discussed later. These kinetic relations are somewhat different from those reported by other workers on n-pentane [8].

Induction Period

It can be seen from Figs. 4 and 6 that the reciprocal induction period is linearly proportional to the pressure of hydrocarbon or oxygen. Cyclopentane has a longer induction period than n-pentane under all conditions and comparison of the curves in Fig. 4 show the ratio to be about 2.6. Reproducibility of the induction period was not as good

as that of the maximum rate probably on account of incidental variations in the surface of the reaction vessel.

A few remarks on this variation seem to be in place and though they apply to all the present work they will not be repeated for every hydrocarbon.

Incidental Surface Effects

Systematic changes in surface will be considered later but day to day variations and seemingly trivial incidents have a profound effect upon the induction period and often upon the rate.

Prolonged pumping between runs (> 1 hour) was usually followed in the next run by an abnormally long induction period, although the rate showed little change. Conversely, inadequate pumping reduced the induction period and also tended to raise the rate. It was found that pumping for 15 to 20 min was usually required to obtain fairly reproducible results. Leaving the vessel overnight had little effect either on the rate or on the induction period, but after the vessel was left standing for longer periods (48 hours or longer) several runs were required before the rate and induction period attained constant values. This was also true for a freshly cleaned vessel where explosions usually resulted under the same conditions that gave a smooth reaction in an "aged" vessel. A number of explosions were usually carried out intentionally in a new vessel so as to age it, this effect and treatment are commonly found in work on oxidations.

The explanation of these rather peculiar variations of surface activity is not at all obvious but it may be that under normal conditions there is a thin film of carbon or some other non-volatile material on the vessel surface which tends to adsorb intermediates or products. It would seem that this adsorbed layer governs, to some extent, the length of the induction period, since removal by pumping lengthens the induction period, presumably because of the removal of some necessary intermediate or chain initiating agent. The explosion effect with a clean surface is possibly due to the removal of a chain breaking action of the postulated non-volatile film.

The Kinetics of the Oxidation of a Series of Cycloparaffins in
Relation to Structure

There is some previous work [8] on the comparison of a series of n-paraffins and the remarkable effect of chain length and structure upon the rate. It was found that increasing the length of the carbon chain greatly increased the rate and that branching the chain had the opposite effect. Experiments were carried out to determine whether or not the same phenomena occurred in the cycloparaffins on increasing ring size and on methyl substitution. The paraffins investigated were cyclopropane, cyclopentane, methyl cyclopentane, 1:1:5 trimethyl cyclopentane, cyclohexane, methyl cyclohexane, 1:4 dimethyl cyclohexane, 1:3:5 trimethyl cyclohexane, cycloheptane and cyclooctane.

With the exception of cyclopropane, all the paraffins listed above were examined at 250°C and comparison made at one fixed oxygen pressure. Cyclopropane was examined at 285°C and the rate extrapolated on an Arrhenius plot down to 250°C. This gives an activation energy of 55.6 Kcals/mole. The kinetics of cyclopentane have already been mentioned: two other paraffins were examined in a similar manner, 1:1:5 trimethyl cyclopentane and cycloheptane (the latter at two temperatures, 250°C for comparison with the other paraffins and 245°C for more detailed kinetics). The remaining hydrocarbons were examined more briefly by measuring the rates and induction periods at one temperature and varying the hydrocarbon pressure while keeping the oxygen constant at 110 mm. Fig. 7 shows the maximum rates of oxidation as a function of hydrocarbon pressure for a series of paraffins. In the course of the investigations two sets of data were obtained for cyclopentane and methyl cyclohexane which differed slightly as a result of some surface effect of the vessel. The most recent data for methyl cyclohexane have been used throughout this thesis and the cyclopentane results kept separate. One set is consistent with and was obtained at the same time as the data on Figs. 3,4,5 and 6, the other for Figs. 7 and 8. No

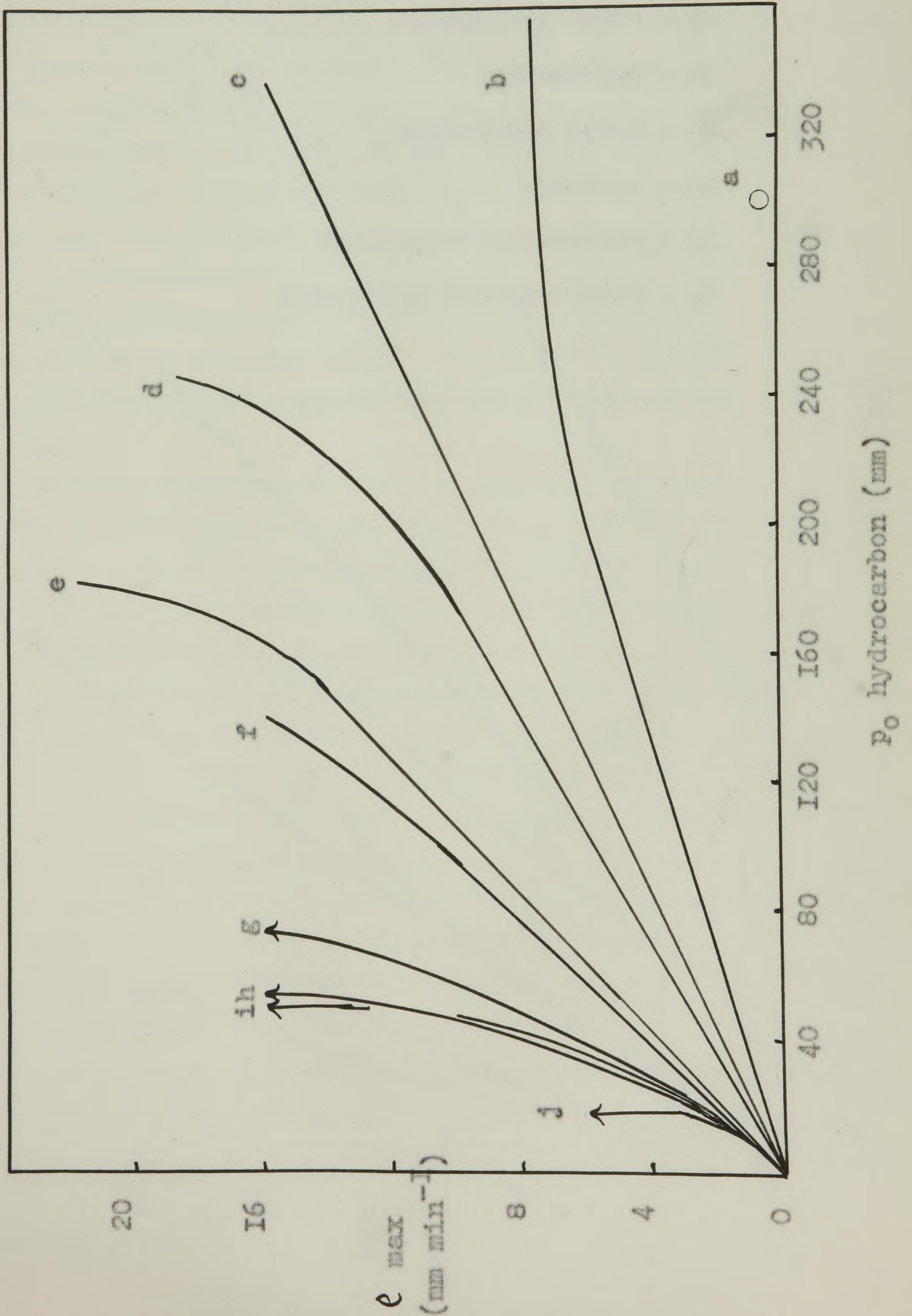
Key to Fig. 7

- a. - cyclopropane
- b. - n-pentane
- c. - cyclopentane
- d. - methyl cyclopentane
- e. - 1:1:5 trimethyl cyclopentane
- f. - cyclohexane
- g. - methyl cyclohexane
- h. - 1:4 dimethyl cyclohexane
- i. - 1:3:5 trimethyl cyclohexane
- j. - cycloheptane

Fig. 7

Maximum Rate of various hydrocarbons as a function of hydrocarbon
pressure

Oxygen = 110 mm Silica Vessel 250°C

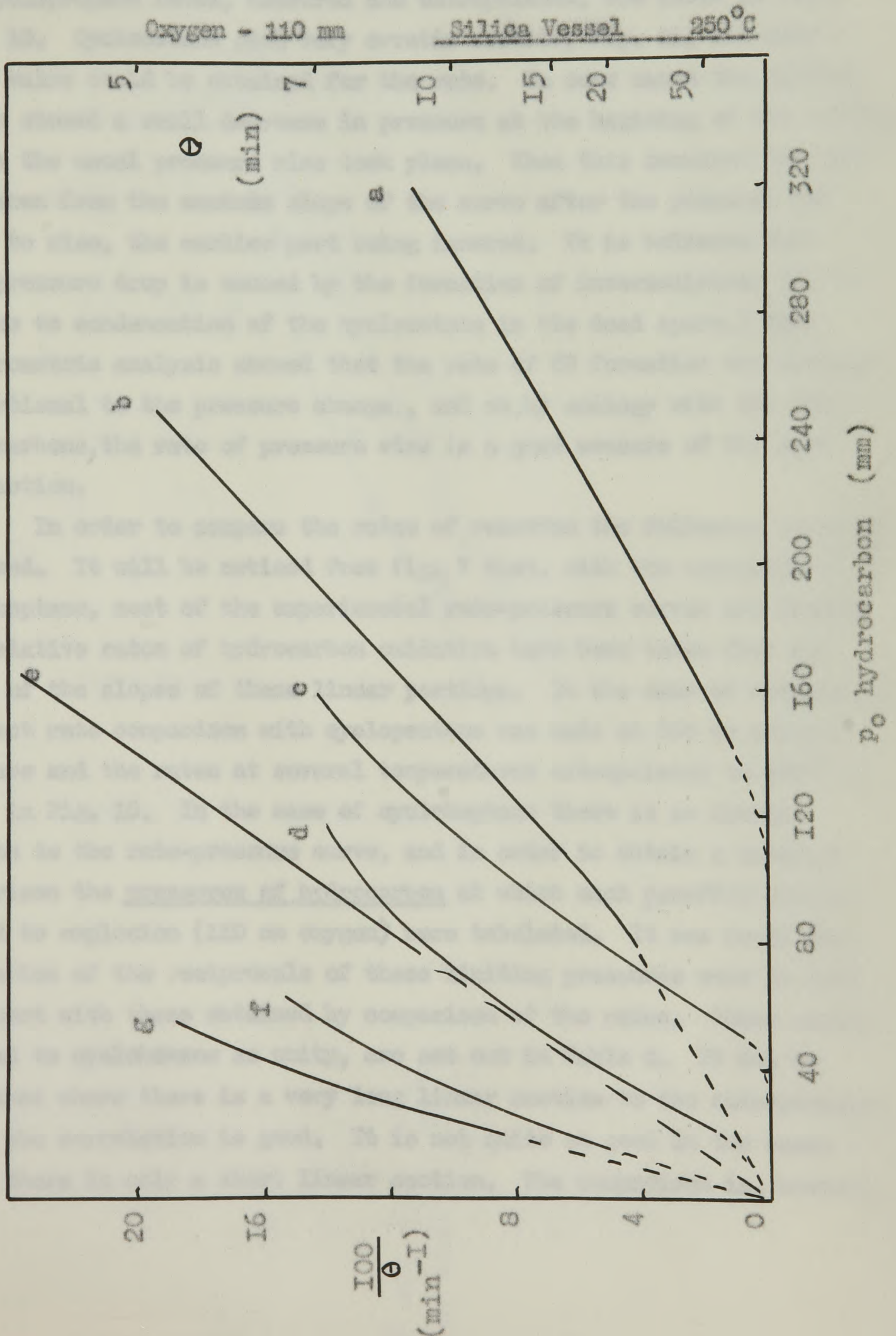


Key to Fig. 8

- a. - cyclopentane
- b. - methyl cyclopentane
- c. - cyclohexane
- d. - methyl cyclohexane
- e. - n-pentane
- f. - 1:4 dimethyl cyclohexane
- g. - 1:3:5 trimethyl cyclohexane

Fig. 8

Reciprocal Induction Periods of various hydrocarbons as a function of hydrocarbon pressure



significance has been attached to these differences. The induction periods corresponding to the rates in Fig. 7 are plotted in Fig. 8. The cyclopropane rates, measured and extrapolated, are given in Figs. 9 and 10. Cyclooctane gave very erratic results, Fig. 11, and only a rough value could be obtained for the rate. In some cases the $\Delta p/\text{time}$ curves showed a small decrease in pressure at the beginning of the reaction before the usual pressure rise took place. When this occurred the rate was taken from the maximum slope of the curve after the pressure had begun to rise, the earlier part being ignored. It is believed that this pressure drop is caused by the formation of intermediates. (It is not due to condensation of the cyclooctane in the dead space.) Mass spectrometric analysis showed that the rate of CO formation was linearly proportional to the pressure change, and so, by analogy with the other hydrocarbons, the rate of pressure rise is a good measure of the rate of reaction.

In order to compare the rates of reaction the following procedure was used. It will be noticed from Fig. 7 that, with the exception of cycloheptane, most of the experimental rate-pressure curves are linear. The relative rates of hydrocarbon oxidation have been taken from the ratio of the slopes of these linear portions. In the case of cyclopropane a direct rate comparison with cyclopentane was made at 500 mm initial pressure and the rates at several temperatures extrapolated to 250°C as shown in Fig. 10. In the case of cycloheptane there is no linear portion to the rate-pressure curve, and in order to obtain a numerical comparison the pressures of hydrocarbon at which each paraffin studied tended to explosion (110 mm oxygen) were tabulated. It was found that the ratios of the reciprocals of these limiting pressures were in good agreement with those obtained by comparison of the rates. These ratios, related to cyclohexane as unity, are set out in Table 2. It can be seen that where there is a very long linear section to the rate-pressure curve the correlation is good. It is not quite so good in the cases where there is only a short linear section. The comparison is, however,

Fig. 9

-57-

Variation of Maximum Rate and Reciprocal Induction Period of
Cyclopropane. Oxygen - 110 mm Silica Vessel 285°C

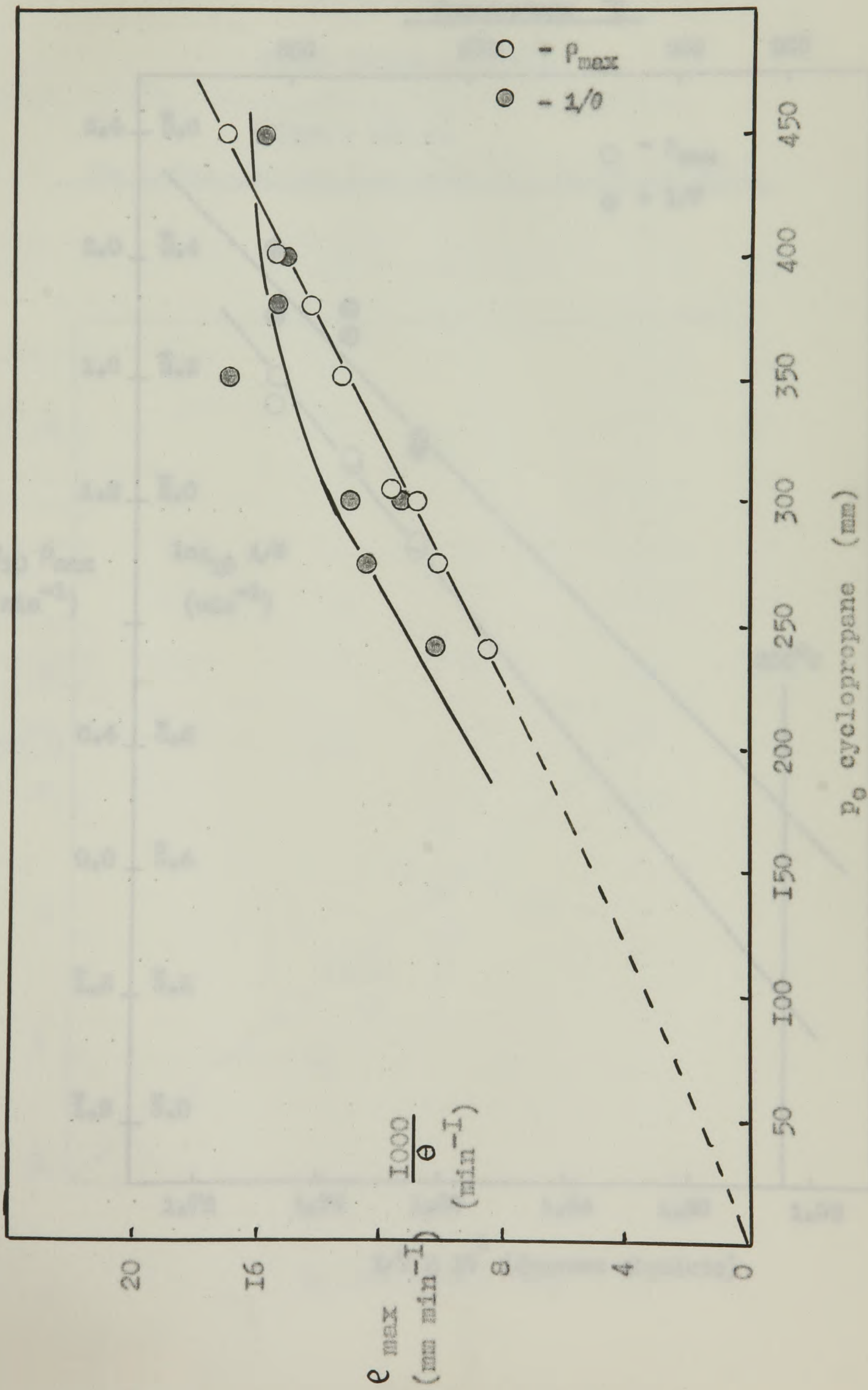


Fig. 10

-38-

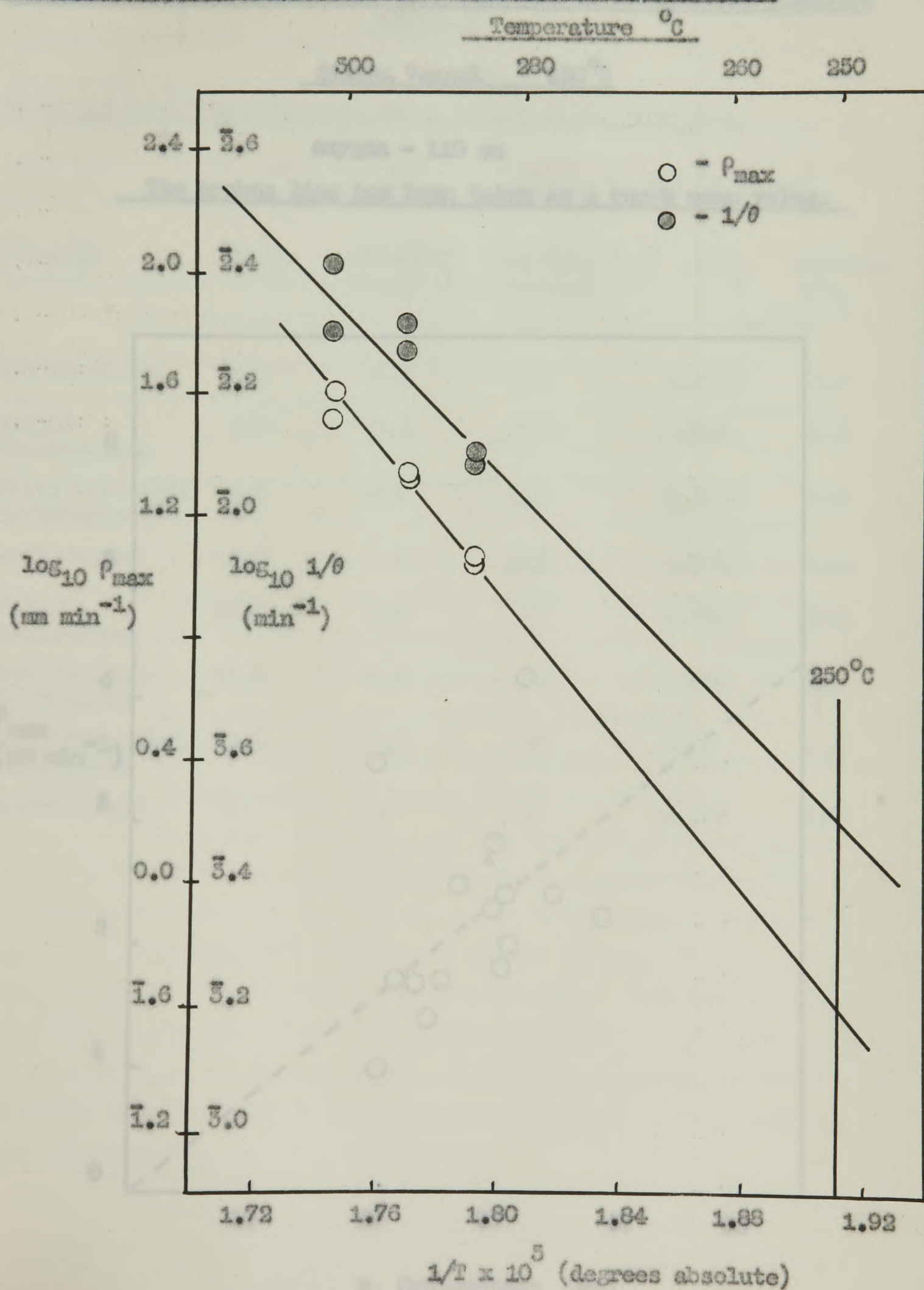
Maximum Rate and Reciprocal Induction Period of Cyclopropane

Fig. 11 Rate of Cyclooctane as a function of cyclooctane pressure

Silica Vessel 250°C

oxygen - 110 mm

The broken line has been taken as a rough mean value.

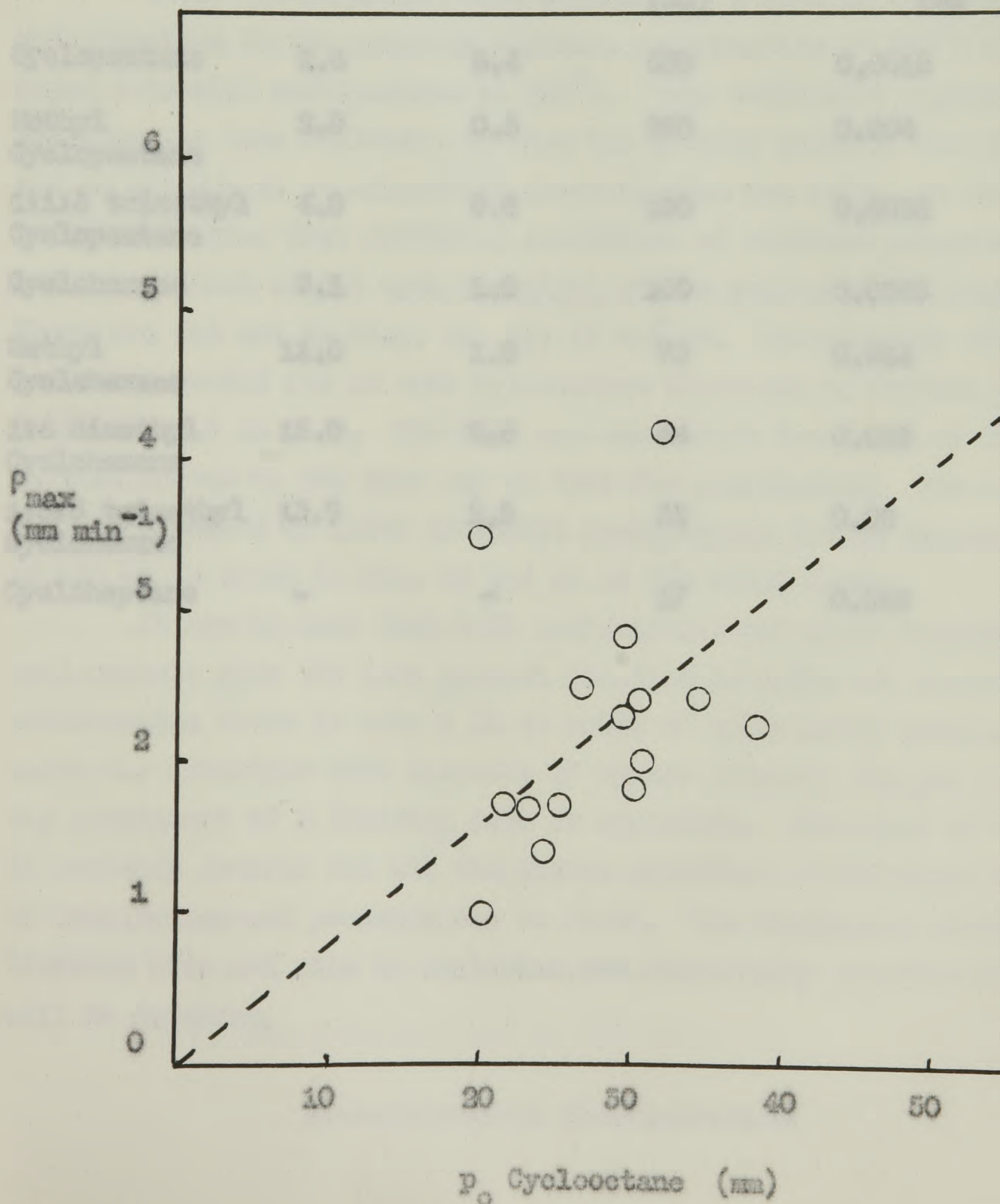


Table 2

Rates and Limiting Pressures for a series of Hydrocarbons

250°C : Silica Vessel

Compound	Slope	Adjusted Slope	Limiting Pressure (mm)	$1/L_p$ (mm ⁻¹)	Adjusted $1/L_p$
Cyclopentane	2.4	0.4	550	0.0018	0.5
Methyl Cyclopentane	2.9	0.5	250	0.004	0.6
1:1:3 trimethyl Cyclopentane	4.8	0.8	190	0.0053	0.8
Cyclohexane	6.1	1.0	160	0.0063	1.0
Methyl Cyclohexane	11.0	1.8	75	0.014	2.2
1:4 dimethyl Cyclohexane	15.0	2.5	54	0.019	3.0
1:3:5 trimethyl Cyclohexane	15.0	2.5	50	0.02	3.2
Cycloheptane	-	-	17	0.059	9.4

Table 5Relationship between Rate and Structure for a series of CycloparaffinsAdjusted to 250°C where necessary

<u>Unsubstituted</u>	<u>All rates related to cyclohexane as unity</u>
cyclopropane	0.016*
cyclopentane	0.4
cyclohexane	1.00
cycloheptane	9.4
cyclooctane	no accurate value but between 0.5 and 0.8
n-pentane	0.16
<u>Substituted</u>	
methyl cyclopentane	0.5
1:1:3 trimethyl cyclopentane	0.8
methyl cyclohexane	1.8
1:4 dimethyl cyclohexane	2.5
1:3:5 trimethyl cyclohexane	2.5

* Value extrapolated from higher temperatures.

Fig. 12 Variation of maximum rate of cycloheptane with oxygen pressure at different hydrocarbon pressures.

245°C : Silica Vessel

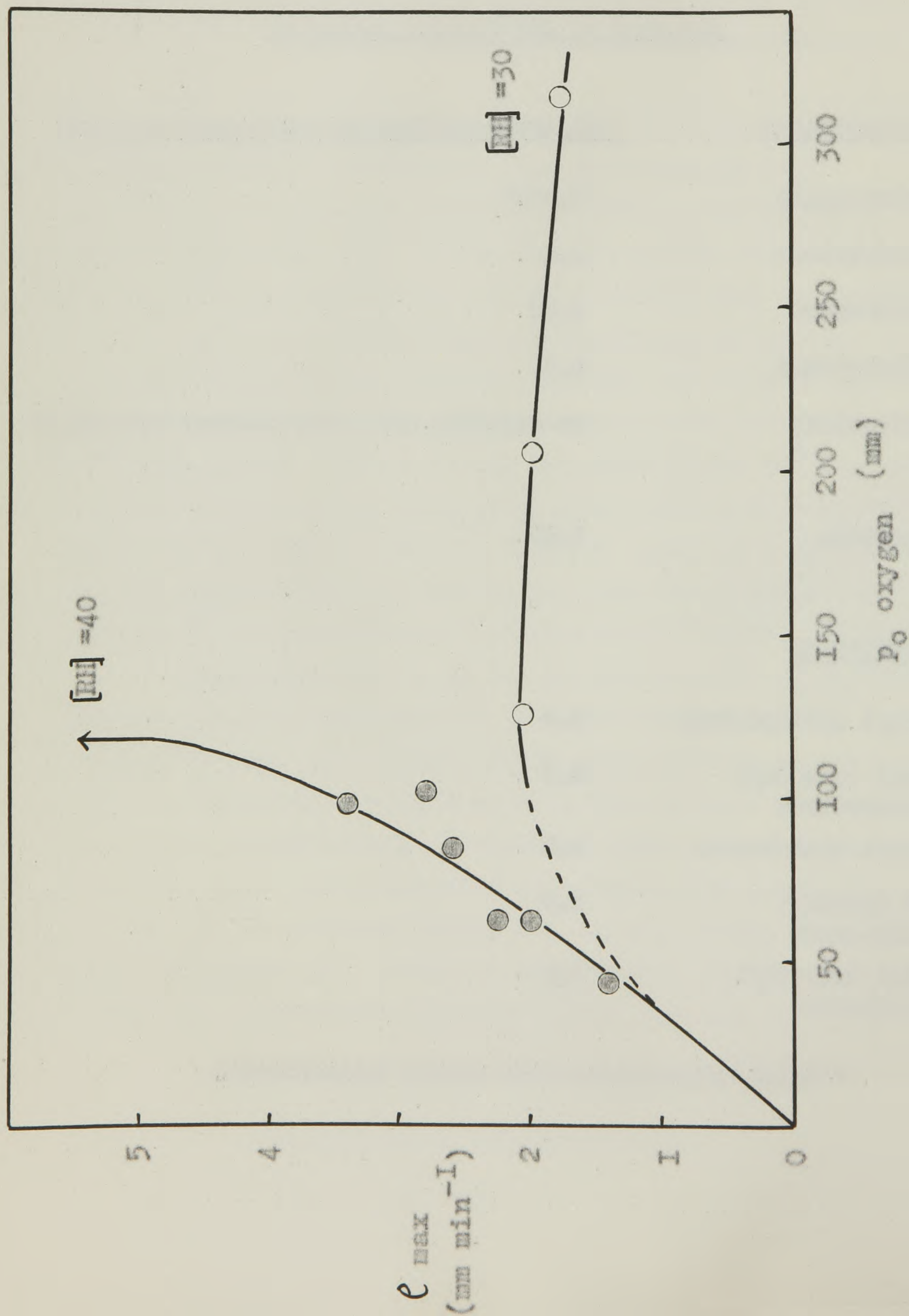


Fig. 13 Variation of maximum rate of cycloheptane with hydrocarbon pressure at different oxygen pressures

245°C : Silica Vessel

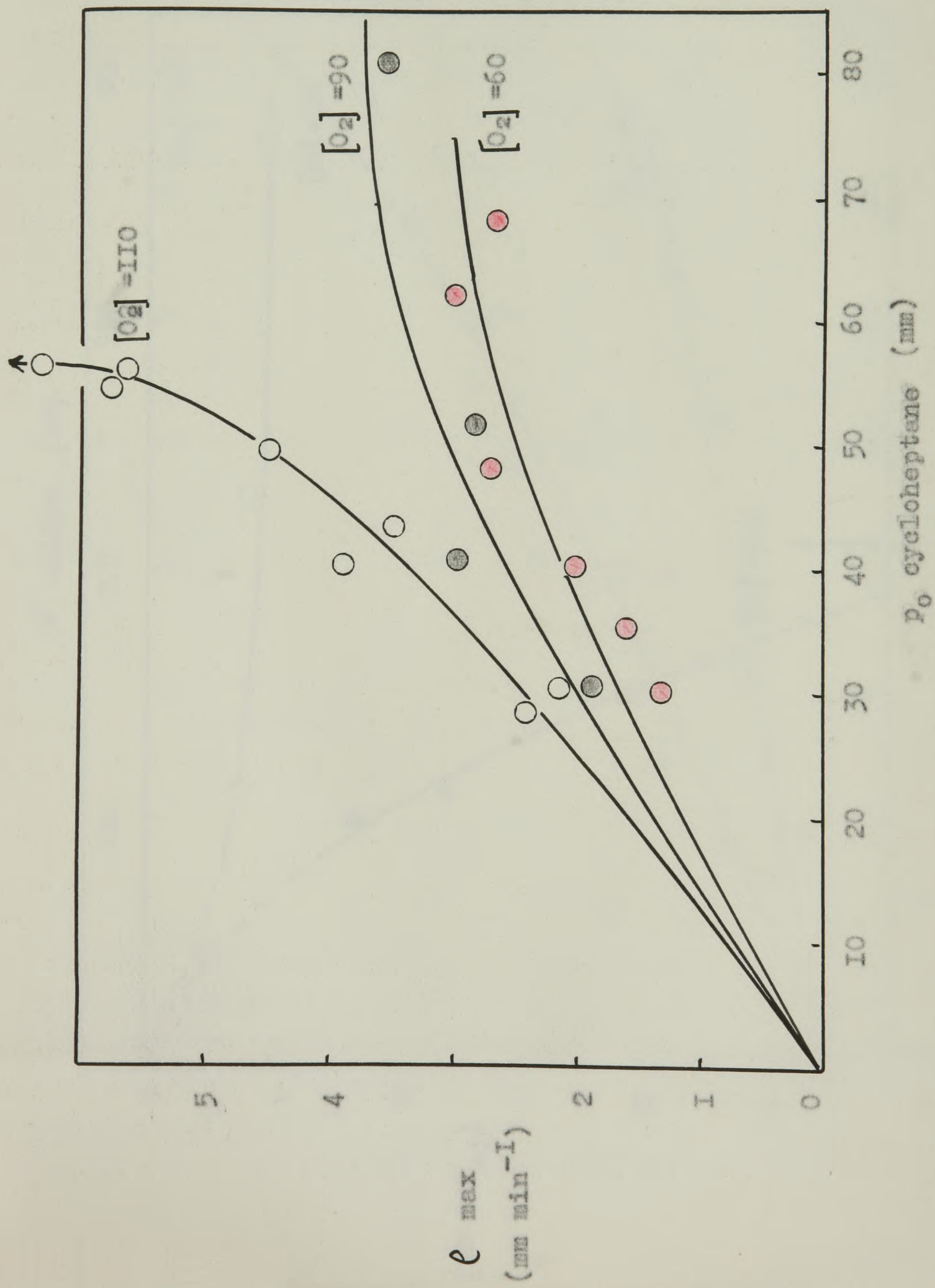


Fig. 14 Variation of maximum rate of 1:1:3 trimethyl cyclopentane with oxygen pressure at different hydrocarbon pressures

250°C : Silica Vessel

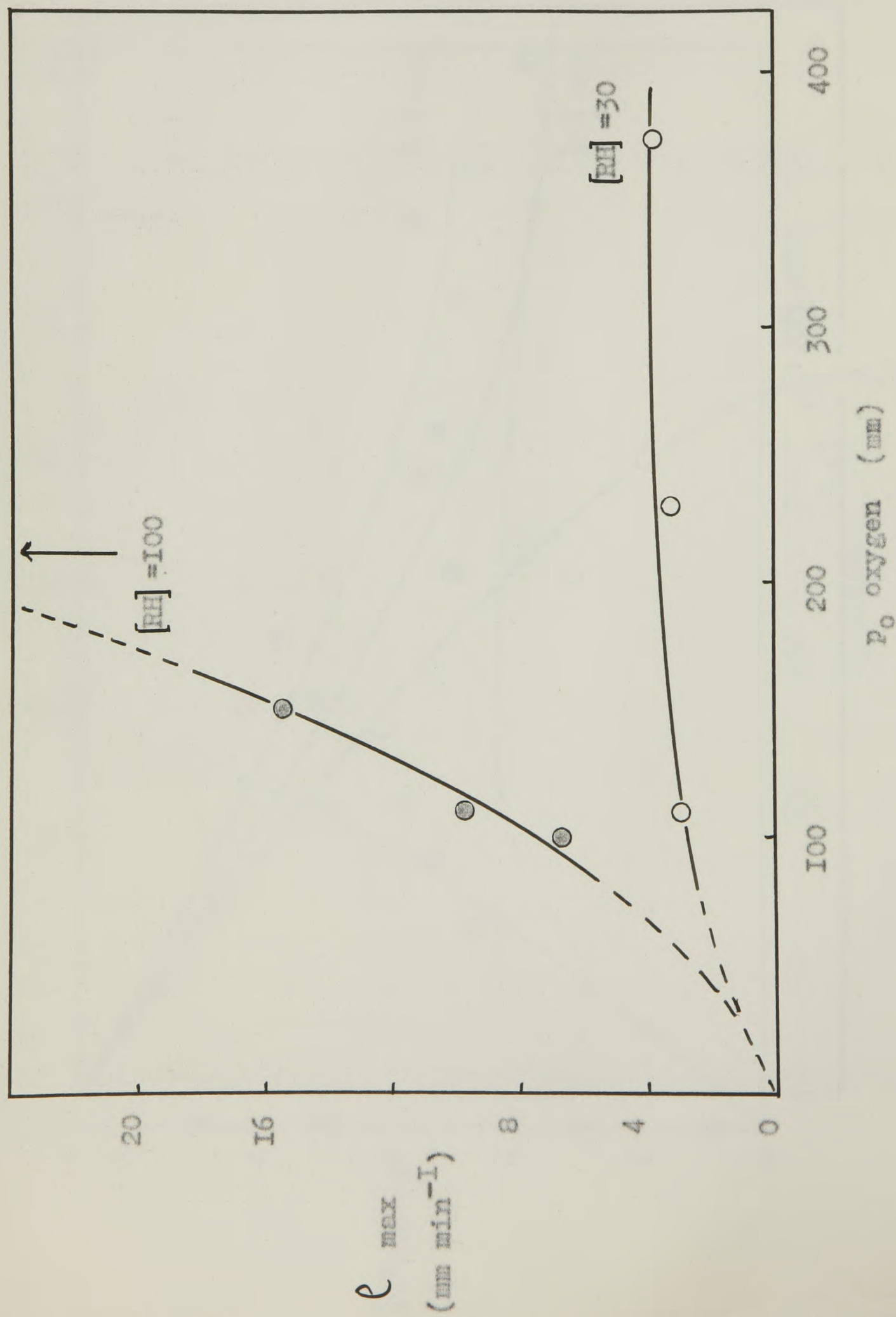


Fig. 15 Variation of maximum rate of 1:1:5 trimethyl cyclopentane
with hydrocarbon pressure at different oxygen pressures

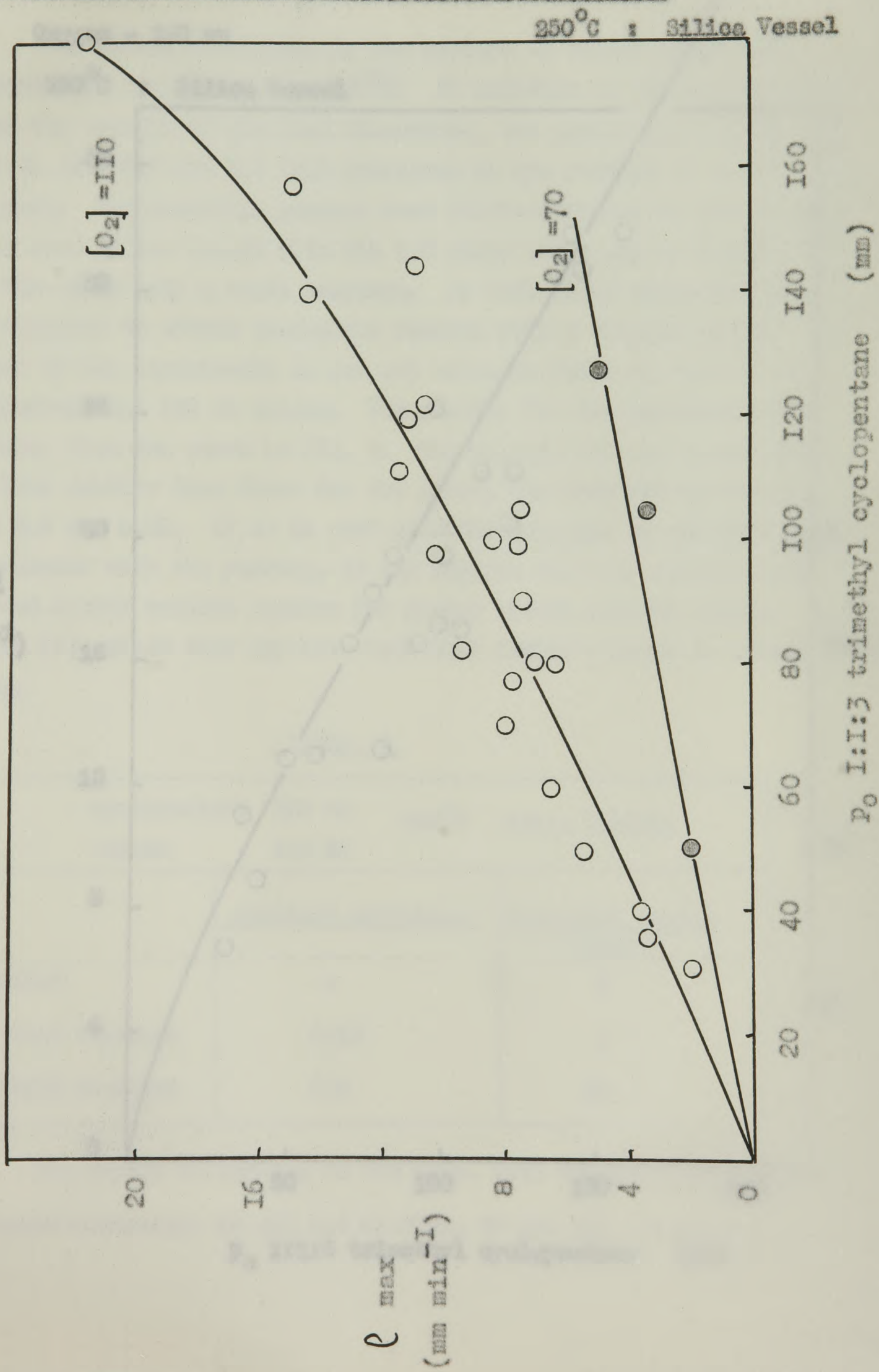
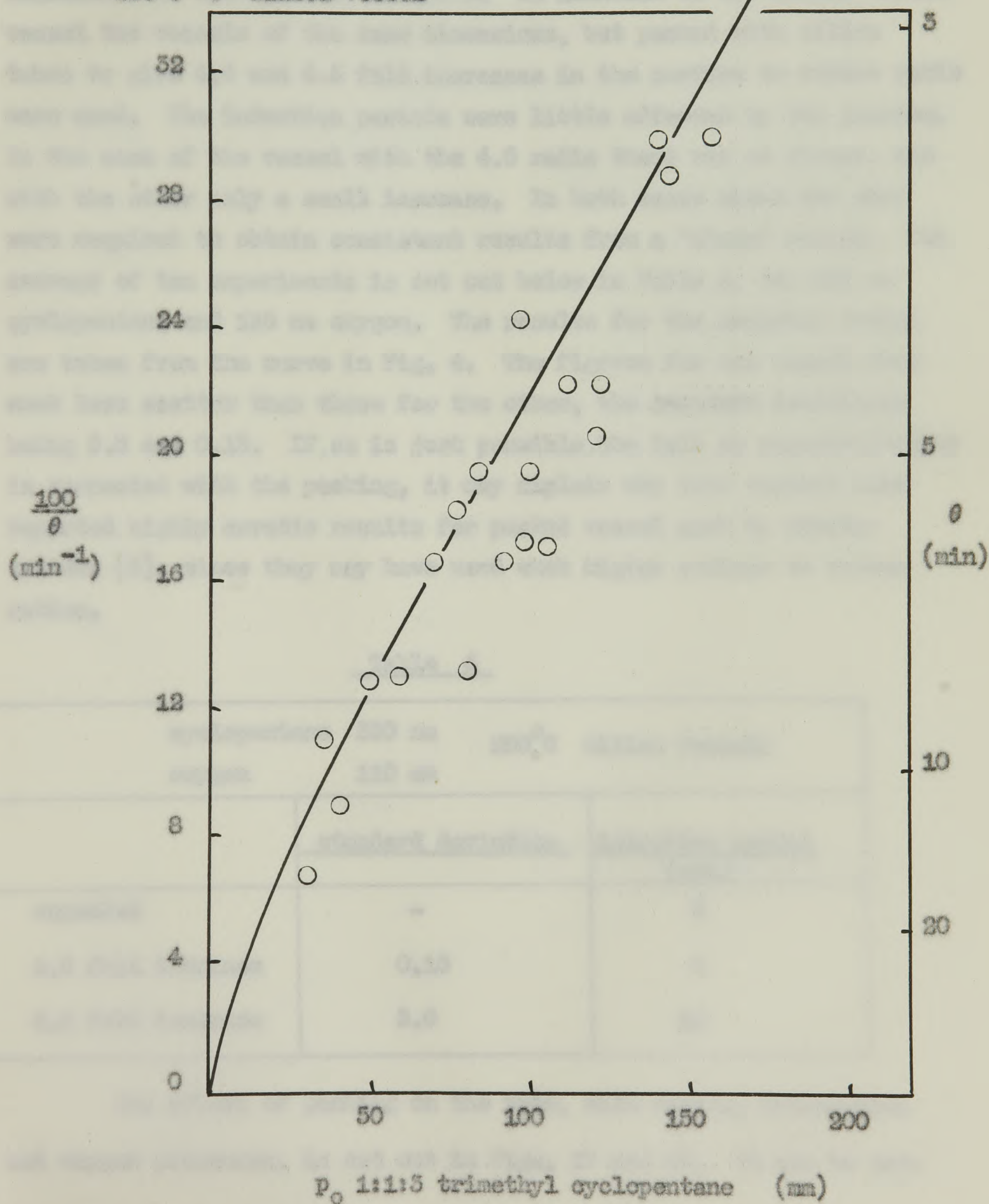


Fig. 16 Variation of reciprocal induction period of 1:1:5 trimethyl cyclopentane with hydrocarbon pressure

Oxygen - 110 mm

250°C : Silica Vessel



Effect of Changes in the Surface to Volume Ratio

The effect of changes in the surface to volume ratio were examined with cyclopentane at 250°C. In addition to the normal silica vessel two vessels of the same dimensions, but packed with silica tubes to give 4.6 and 6.3 fold increases in the surface to volume ratio were used. The induction periods were little affected by the packing. In the case of the vessel with the 4.6 ratio there was no change, and with the other only a small increase. In both cases about ten runs were required to obtain consistent results from a "clean" vessel. The average of ten experiments is set out below in Table 4, for 550 mm cyclopentane and 110 mm oxygen. The results for the unpacked vessel are taken from the curve in Fig. 4. The figures for one vessel show much less scatter than those for the other, the standard deviations being 5.8 and 0.15. If, as is just possible, the fall in reproducibility is connected with the packing, it may explain why some workers have reported highly erratic results for packed vessel work in similar systems [8], since they may have used much higher surface to volume ratios.

Table 4

cyclopentane 550 mm oxygen 110 mm 250°C Silica Vessels		
	<u>standard deviation</u>	<u>induction period</u> (min)
unpacked	-	6
4.6 fold increase	0.15	6
6.3 fold increase	5.8	12

The effect of packing on the rate, with varying hydrocarbon and oxygen pressures, is set out in Figs. 17 and 18. It can be seen

Key to Fig. 17

Red lines - unpacked vessel

○ - 4.6 fold increase

● - 6.5 fold increase

a - $[O_2] = 110$ mm

b - $[O_2] = 110$ mm

c - $[O_2] = 200$ mm

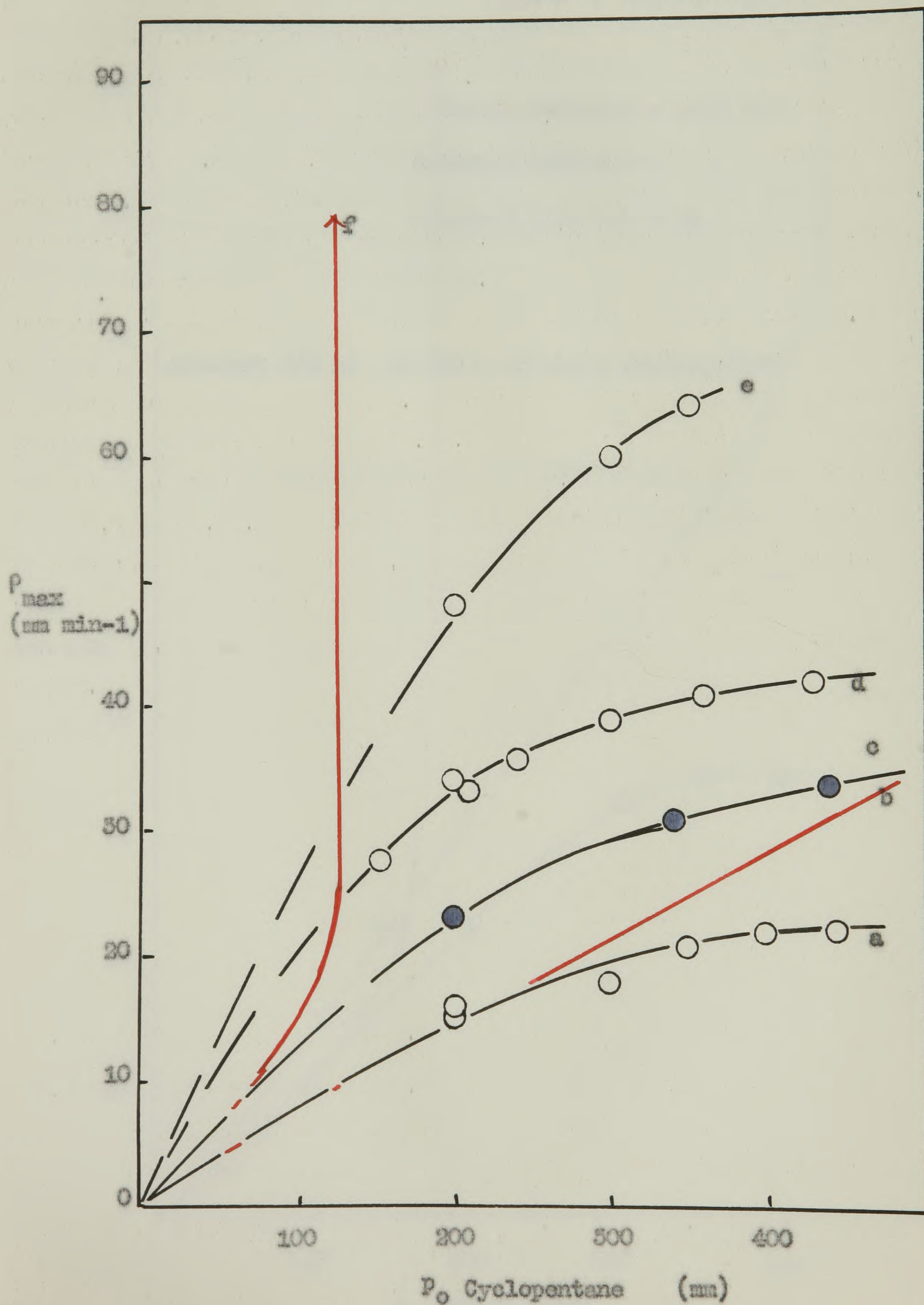
d - $[O_2] = 200$ mm

e - $[O_2] = 500$ mm

f - $[O_2] = 200$ mm

Fig. 17 Variation of maximum rate of cyclopentane with different oxygen pressures in packed vessels

250°C : Silica Vessels



Key to Fig. 18

Red line - unpacked vessel

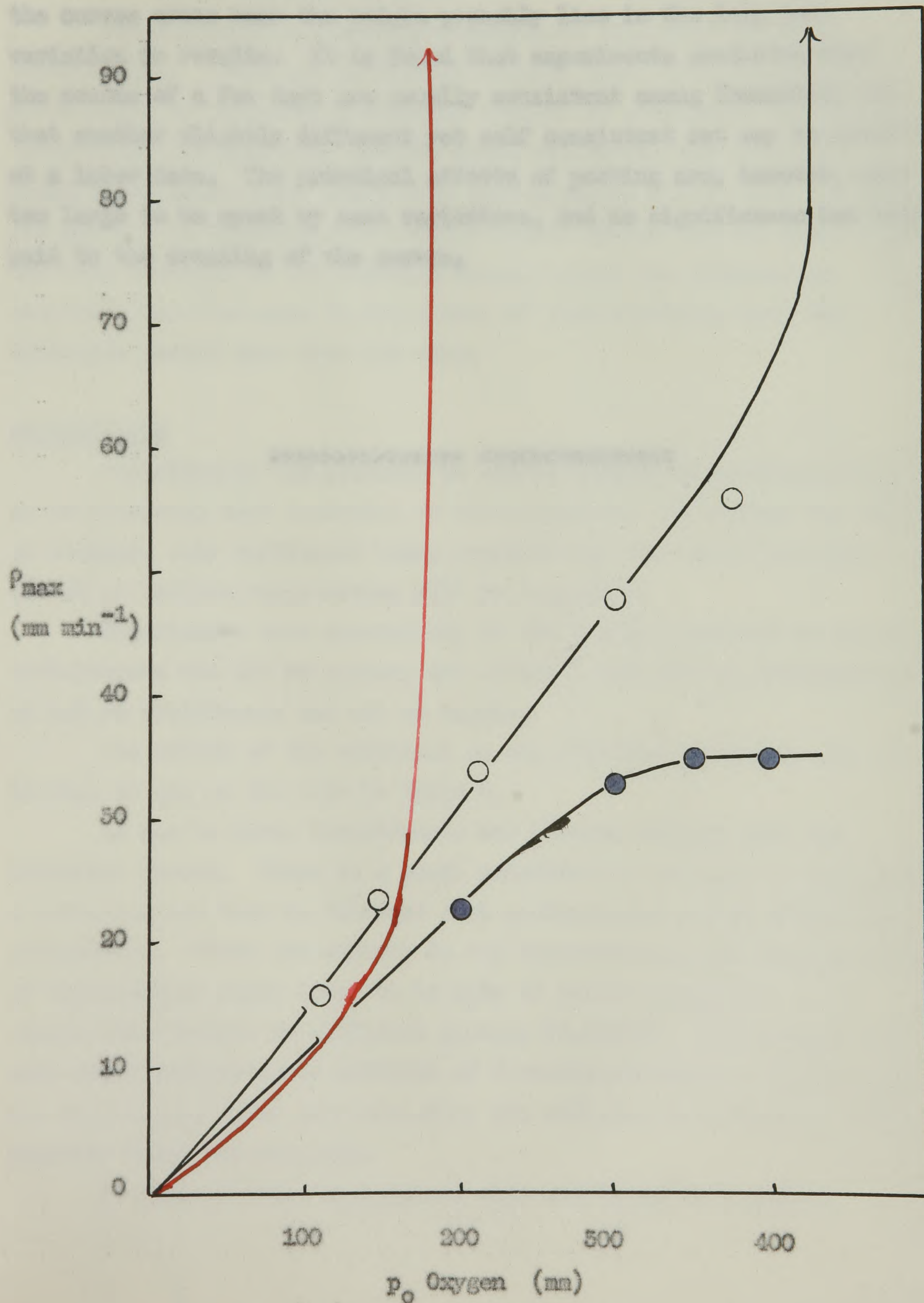
○ - 4.6 fold increase

● - 6.5 fold increase

Cyclopentane pressure - 200 mm in all vessels.

Fig. 18 Variations of maximum rate of cyclopentane with oxygen pressure at different vessel packings.

250°C : Silica Vessels



The Effect of Various Homogeneous Additions

The effect of a number of homogeneous additions has been investigated. These may be divided roughly into three groups, those which might be expected on chemical grounds to accelerate the reaction, those which for analogous reasons might retard it, and chemically indifferent gases which might have some physical effect upon the kinetics. The amounts of additive were usually small, except for the inert gases, and were admitted to the reaction vessel before the hydrocarbon. More attention has been paid to the effect of such additions upon the induction period than upon the rate.

Formaldehyde

Formaldehyde was produced by gentle warming of paraformaldehyde in an evacuated tube connected to the apparatus. No attempt was made at storage, only sufficient being prepared for the run in progress. Its effect on various hydrocarbons will be described.

Experiments were carried out at 235°C with a mixture of 500 mm cyclopropane and 110 mm oxygen, and at 250°C with 250 mm cyclopentane or 110 mm cyclohexane and 110 mm oxygen.

The effect of the additions on the induction period is set out in Fig. 19 and on the rate in Table 5.

As can be seen, formaldehyde has diverse effects upon the induction period. There is a small reduction in the case of cyclopentane, a reduction and then an increase with cyclopropane and no effect with cyclohexane. There are reports in the literature on the varying effects of formaldehyde which seems to be able to either accelerate or to retard the reaction in different systems [8,55,56]. The cyclopentane rate seems unaffected by addition of formaldehyde but the cyclopropane and cyclohexane rates are reduced by the addition to a constant value slightly below the original.

In most of these experiments with additions, the initial

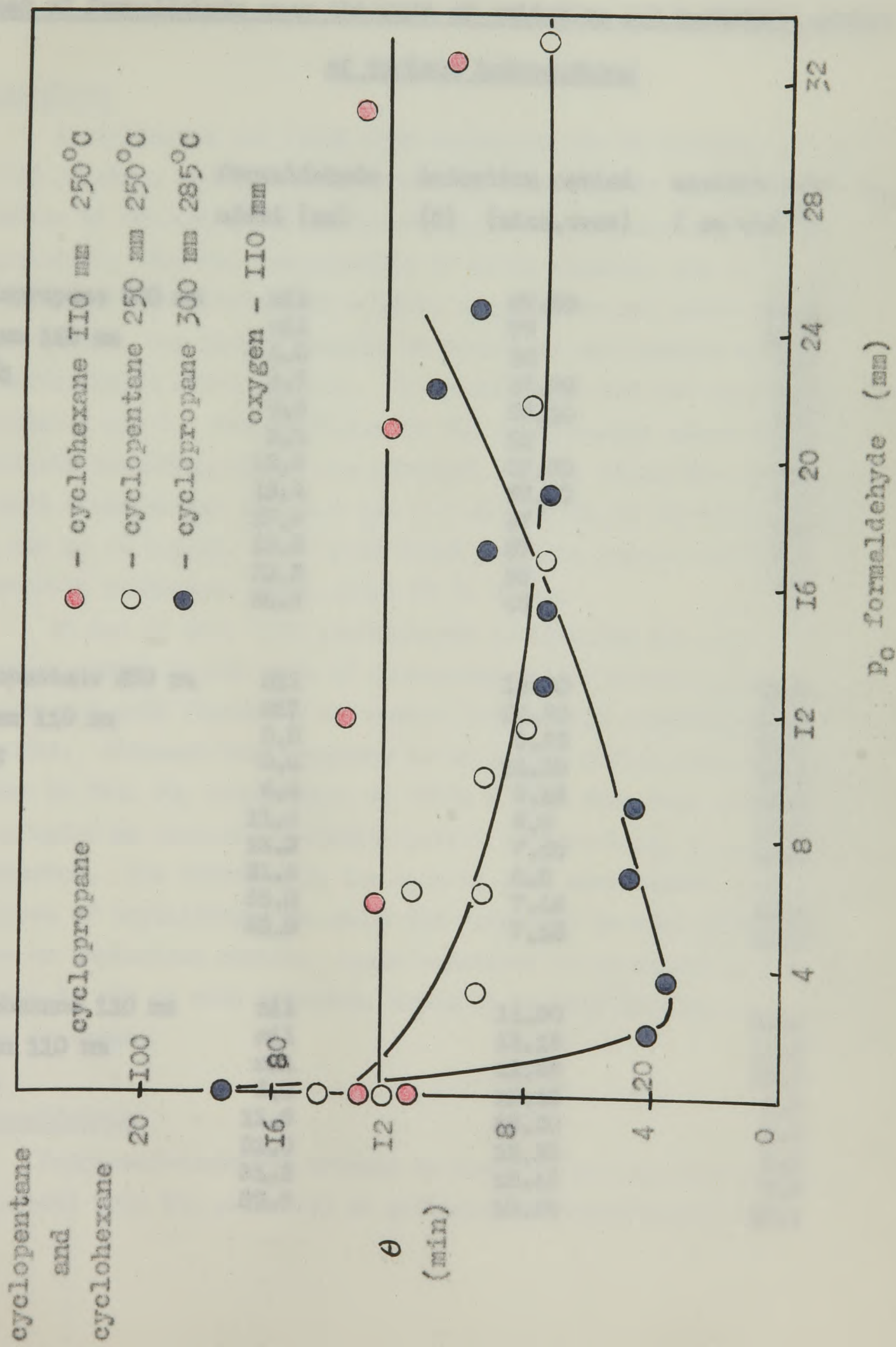
Effect of formaldehyde upon the induction period of cyclonpropanecyclopentane and cyclohexaneSilica Vessel

Table 5

Effect of formaldehyde upon the rate of oxidation and induction period
of various hydrocarbons

	formaldehyde added (mm)	induction period (θ) (mins.secs)	maximum rate (mm min ⁻¹)	p _{max}
cyclopropane 300 mm	nil	87.50	11.0	
oxygen 110 mm	nil	77	11.8	
285°C	2.0	20	6.3	
	3.7	17.50	6.4	
	6.9	25.50	6.0	
	9.1	25	7.4	
	12.9	57.50	6.5	
	15.4	57.50	6.5	
	17.5	47	6.0	
	19.0	57	7.5	
	22.5	55	6.0	
	24.9	48	-	
cyclopentane 250 mm	nil	12.50	15.8	
oxygen 110 mm	nil	14.50	12.3	
250°C	3.2	9.50	16.4	
	6.4	11.50	15.1	
	6.4	9.15	15.0	
	11.6	8.0	15.0	
	16.9	7.50	13.8	
	21.8	8.0	-	
	35.2	7.45	12.4	
	42.0	7.15	13.0	
cyclohexane 110 mm	nil	11.50	11.8	
oxygen 110 mm	nil	13.15	11.9	
250°C	nil	11.40	12.0	
	6.0	12.45	9.9	
	11.9	13.50	9.9	
	21.0	12.30	9.9	
	31.2	13.15	9.8	
	32.5	10.30	10.1	

hydrocarbon and oxygen pressures have, when possible, been so chosen that the induction periods have been long. In this way small changes are more easily seen than when the induction periods are short.

Acetaldehyde

Acetaldehyde was freed from dissolved air by freezing in solid CO_2 and pumping, refreezing and pumping. Its effects upon the oxidation of cyclopropane, cyclopentane, n-pentane and cyclohexane were studied. For the introduction of small amounts, the acetaldehyde was premixed with nitrogen to a known composition and admitted to the vessel first. For larger amounts no premixing was carried out and the acetaldehyde added as such. The results are set out in Fig. 20 and in Tables 6 and 7. The oxidation of the acetaldehyde alone did not contribute significantly to the pressure change, since the maximum rise and fall observed was only + 2 and - 3 mm with 11 mm of acetaldehyde and 110 mm of oxygen. The usual total pressure change for the hydrocarbon oxidations being about 25 to 40 mm.

It can be seen that acetaldehyde accelerates the rate very markedly, except in the case of cyclopropane, where small amounts lower the rate and cool flames do not appear until large quantities of aldehyde are added. Although there appears to be little effect with n-pentane, as seen in Fig. 20, examination of Table 7 will show that when conditions are adjusted so that the induction period becomes long, a marked effect is observed. The effect upon the rate is even more marked and moderate pressures of acetaldehyde so raise the rate that in some cases cool flames or explosions result. Again n-pentane is an exception in that the rate is not so much affected, although it does increase by a factor of two or three.

Propionaldehyde

Propionaldehyde was treated in the same way as acetaldehyde. Its effects upon the oxidation of cyclopropane, cyclopentane and

Effect of acetaldehyde upon the induction period of various hydrocarbons

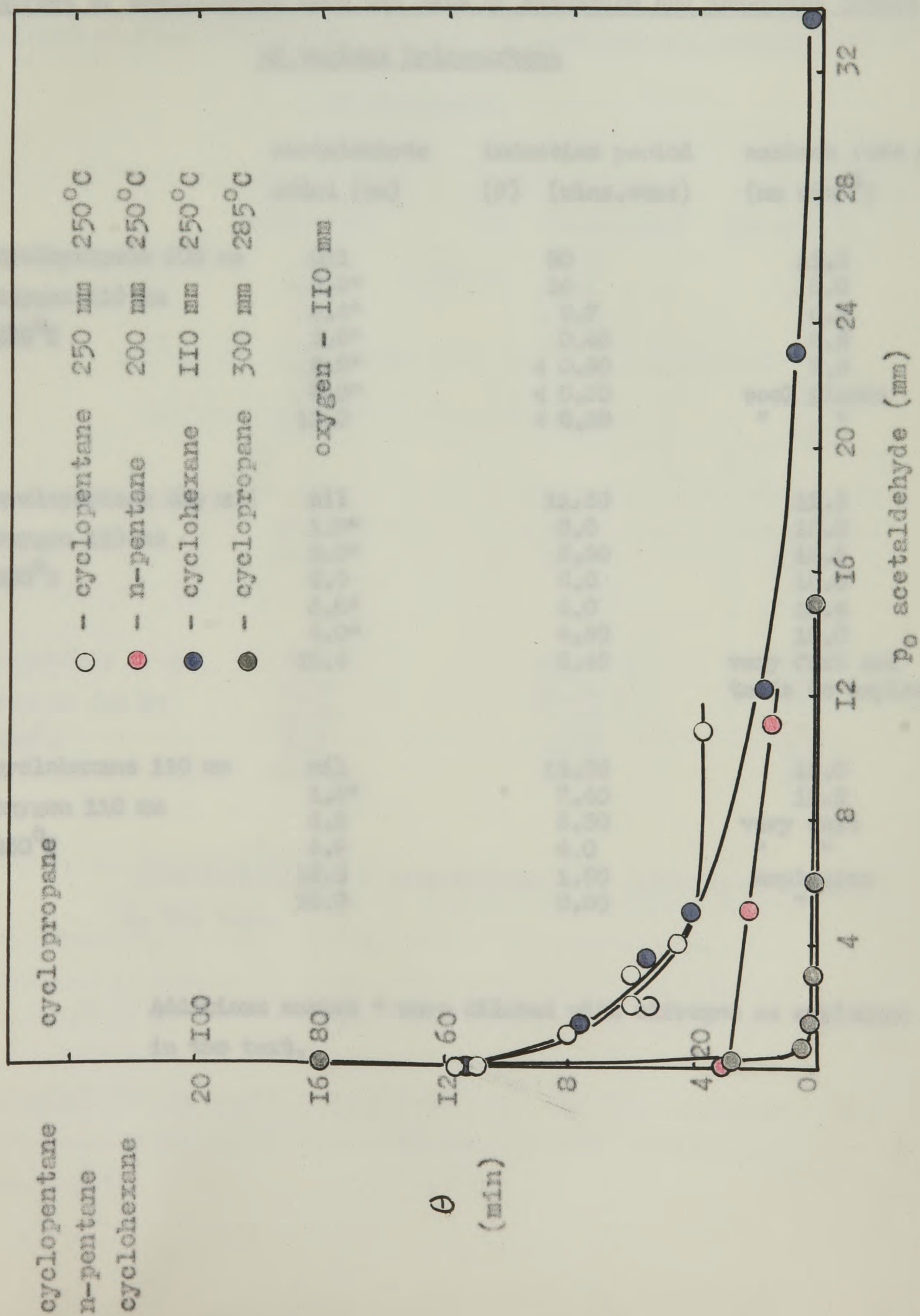


Table 6

Effect of acetaldehyde upon the rate of oxidation and induction period
of various hydrocarbons

	acetaldehyde added (mm)	induction period (θ) (mins.secs)	maximum rate $\rho_{\max}$ (mm min ⁻¹)
cyclopropane 500 mm	nil	80	11.5
oxygen 110 mm	0.3*	14	6.9
285°C	0.6*	2.7	6.2
	1.5*	0.45	6.2
	5.0*	< 0.30	7.0
	6.0*	< 0.30	cool flames
	15.0	< 0.30	" "
cyclopentane 250 mm	nil	11.50	12.5
oxygen 110 mm	1.0*	8.0	15.8
250°C	2.0*	5.50	16.5
	2.0	6.0	16.0
	3.0*	6.0	18.4
	4.0*	4.50	18.0
	10.4	3.45	very fast and tends to explosion
cyclohexane 110 mm	nil	11.50	15.0
oxygen 110 mm	1.3*	7.40	16.2
250°C	5.5	5.50	very fast
	4.9	4.0	" "
	12.2	1.50	explosion
	22.9	0.50	"

Additions marked * were diluted with nitrogen as explained in the text.

Table 7

Effect of acetaldehyde upon the rate of oxidation and induction period

of n-pentane

	acetaldehyde added (mm)	induction period (θ) (mins.secs)	maximum rate $\rho_{\max}$ (mm min ⁻¹)
n-pentane 200 mm	nil	25.50	1.6
oxygen 110 mm	nil	22.0	1.9
255°C	0.5*	16.50	-
	1.0*	16.10	-
	2.0*	14.50	-
	5.5	12.0	-
	11.0	7.45	4.1
n-pentane 200 mm	nil	5.0	6.5
oxygen 110 mm	5.2	2.10	8.1
250°C	10.4	1.50	11.5
n-pentane 50 mm	nil	19.0	0.9
oxygen 110 mm	1.4*	14.15	-
250°C	2.8*	7.15	-
	5.5	4.50	1.6
	11.0	2.45	2.9

Additions marked * were diluted with nitrogen as explained in the text.

cyclohexane were studied and are set out in Fig. 21 and in Table 8. The results follow those of added acetaldehyde very closely.

Benzaldehyde

The effect of benzaldehyde upon the oxidation of cyclopropane was studied. The results run parallel to those of acetaldehyde and propionaldehyde as can be seen from Table 9 below.

Table 9

Effect of benzaldehyde upon the rate of oxidation
and induction period of cyclopropane

	benzaldehyde added (mm)	induction period (θ) (mins.secs)	maximum rate $\rho_{\max}$ (mm min ⁻¹)
cyclopropane 500 mm	nil	75	11.1
oxygen 110 mm	2.9	26	8.6
285°C	6.6	< 0.50	6.3
	8.0	1.0	6.8
	8.5	1.50	6.0

Ditertiary Butylperoxide

Unlike any of the other homogeneous additions, ditertiary butylperoxide is very unstable at the temperatures used for hydrocarbon oxidation. Birss [57] gives a value for the rate constant of $k = 10^{15.95} e^{-38,000/RT}$ whence the half lives at 285°C and 250°C may be calculated as 0.07 sec and 0.8 sec respectively. Thus if the peroxide is added to the vessel first, by the time the hydrocarbon and oxygen have been added (about thirty seconds) all the peroxide will have decomposed.

Effect of propionaldehyde upon the induction period of various hydrocarbons

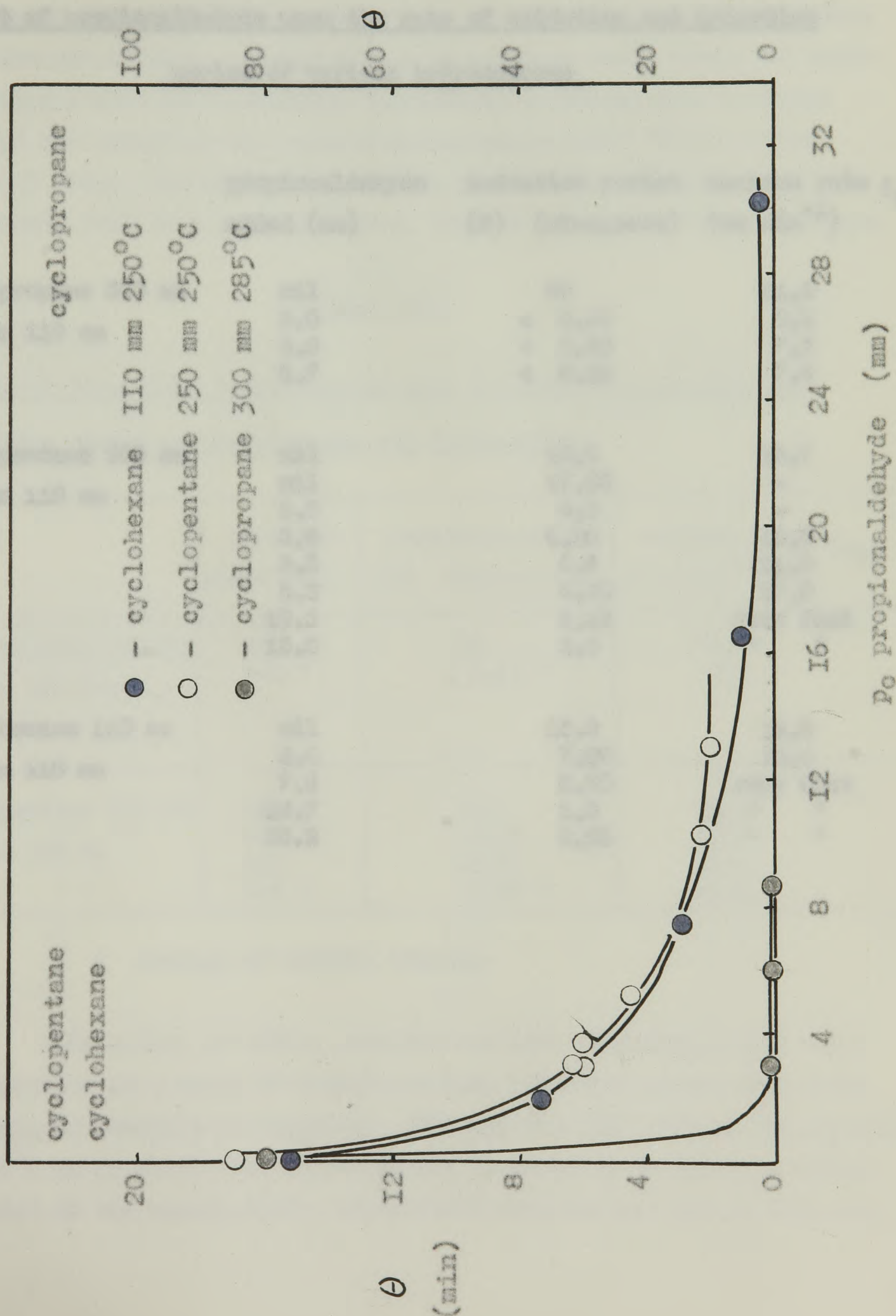


Table 8

Effect of propionaldehyde upon the rate of oxidation and induction
period of various hydrocarbons

	propionaldehyde added (mm)	induction period (θ) (mins.secs)	maximum rate $\rho_{\max}$ (mm min ⁻¹)
cyclopropane 500 mm	nil	80	11.5
oxygen 110 mm	3.0	< 0.50	6.4
285°C	6.0	< 0.50	7.5
	8.7	< 0.50	7.6
cyclopentane 250 mm	nil	16.0	15.7
oxygen 110 mm	nil	17.50	-
250°C	3.0	6.0	-
	3.0	6.20	18.0
	5.8	6.5	21.0
	5.2	4.30	27.0
	10.3	2.15	very fast
	15.0	2.0	" "
cyclohexane 110 mm	nil	15.0	12.0
oxygen 110 mm	2.0	7.20	15.4
250°C	7.6	2.50	very fast
	16.7	1.0	" "
	50.2	0.25	" "

* Average of several values.

This method of adding peroxide has been used extensively with cyclohexane as a means of reducing a long induction period when only the path of reaction is required. Although the half life of the peroxide at 25°C is so short that it can hardly be expected to have any effect if added at the usual time, experiments were carried out in this way.

Experiments were carried out with cyclopropane at 285°C and cyclopentane at 250°C. In the first instance peroxide was added with the oxygen using the lower gallery as a pipette (v.s.) or by premixing peroxide and oxygen. Between 2 to 4 mm could be added using the lower gallery and with both paraffins the induction periods were markedly reduced and except in the case of cyclopropane there was no effect upon the rate. The cyclopropane rate, as with the additions of aldehydes, fell to a constant value, this is set out in Table 10 below.

Table 10

Effect of ditertiary butylperoxide upon the rate of oxidation and induction period of cyclopropane and cyclopentane

	peroxide added (mm)	induction period (θ) (mins.secs)	maximum rate $\rho_{\max}$ (mm min ⁻¹)
cyclopropane 300 mm oxygen 110 mm 285°C	nil 2-4 *	80 < 0.50 *	11.5 6.1 *
cyclopentane 250 mm oxygen 110 mm 250°C	nil nil nil 2-4 *	11.0 10.45 11.45 1.10 *	15.2 15.9 14.1 14.0 *

* Average of several values.

This method of adding peroxide has been used extensively with cyclopentane as a means of reducing a long induction period when only the rate of reaction is required. Although the half life of the peroxide at 250°C is so short that it can hardly be expected to have any effect if added to the vessel first, experiments were carried out in this way.

In order to be sure that there was in the dead space no peroxide which could be pushed into the vessel by the hydrocarbon and oxygen, the following procedure was used. 10 mm of peroxide were admitted to the vessel followed by 40 mm of nitrogen to sweep the peroxide out of the dead space. The peroxide was left in the vessel for varying times before the admission of paraffin and oxygen. The results of experiments based on this procedure with cyclopentane are set out below in Table 11.

Table 11

Effect of ditertiary butylperoxide upon the rate of oxidation and induction period of cyclopentane after varying periods of time

cyclopentane - 250 mm

oxygen 110 mm

250°C

10 mm peroxide followed by 40 mm nitrogen and left in the vessel for the following number of minutes.	induction period (θ) (mins.secs)	maximum rate $\rho_{\max}$ (mm min ⁻¹)
no additions	11.0	13.2
" "	10.45	13.9
" "	11.45	14.1
3	7.30	13.4
5	6.30	16.0
5.50	8.0	14.8
11	8.15	15.4
20	7.30	15.8
32	7.45	14.8
560	11.0	13.4

It can be seen that though the induction period is not reduced to the same extent as when peroxide is added with the oxygen, there is a small reduction and it would seem that the vessel has been "activated" in some way. It seems unlikely that the products from the decomposition

Table 12

Effect of isopropyl halides upon the rate of oxidation and induction
period of cyclopentane

cyclopentane - 550 mm		
oxygen - 110 mm		
250°C		
isopropyl chloride added (mm)	induction period (θ) (mins.secs)	maximum rate $\rho_{\max}$ (mm min ⁻¹)
nil	6.50	25.5
nil	8.0	21.2
nil	7.10	19.5
nil	7.20	21.2
6.2	7.15	18.4
22.5	7.50	19.2
55.5	6.45	20.0

isopropyl bromide

5.0	8.0	20.5
17.5	8.0	20.0
51.0	7.0	25.4

isopropyl iodide

nil	7.50	20.0
5.0	5.30	18.6
10.0	5.50	12.6
15.5	6.10	15.0
19.8	5.50	14.8
25.5	4.50	11.5
51.5	4.50	9.4
58.9	5.25	6.1
45.6	5.15	8.2
61.5	4.50	5.6

Table 15

Effect of aniline upon the rate of oxidation and induction period of
cyclopentane

	aniline added (mm)	induction period (θ) (mins.secs)	maximum rate $\rho_{\max}$ (mm min ⁻¹)
cyclopentane 550 mm oxygen 110 mm 250°C	nil	7.0	No exact rate measurements were made but general observatio- ns showed that there was very little change in the maximum rate from its normal value of about 22 mm min ⁻¹ .
	nil	6.0	
	2.0	6.0	
	2.5	10.0	
	3.2	7.50	
	3.5	9.15	
	3.7	8.15	
	5.0	4.50	
	5.5	5.0	
	7.0	7.50	
	7.4	4.0	
	8.5	6.0	
	9.4	5.50	
	20.0	4.0	

Carbon tetrachloride and Carbon tetrafluoride

These two compounds admitted in moderate amounts in the same way as the others, had no effect upon either the induction period or rate. This can be seen in Table 14 below.

Table 14

Effect of carbon tetrachloride and carbon tetrafluoride upon the rate of oxidation and induction period of cyclopentane.

	CCl ₄ added (mm)	induction period (θ) (mins.secs)	maximum rate $\rho_{\max}$ (mm min ⁻¹)
cyclopentane 350 mm oxygen 110 mm 250°C	nil	4.0	22.0
	5.4	4.5	21.2
	12.1	4.10	19.5
	17.3	4.5	23.4
	24.6	5.0	20.1
	CF ₄ added (mm)		
	9.2	4.50	21.7
	21.8	4.0	22.4
	29.5	5.0	19.9

Mono-, di- and triethylamine and ammonia

It is known that these amines will inhibit the oxidation of acetaldehyde [58] and they were added to a cyclopentane-oxygen system to see if they would retard the reaction. The results of this are shown in Fig. 22

Only triethylamine showed any marked reaction with oxygen at the temperature of the experiment, but the rate of pressure rise due to this was not sufficient to invalidate the measurements of induction period. The maximum rate was markedly increased, often to explosion, by di- and triethylamine. Ethylamine and ammonia had little or no effect. These results, as will be seen later, can be explained by the production of

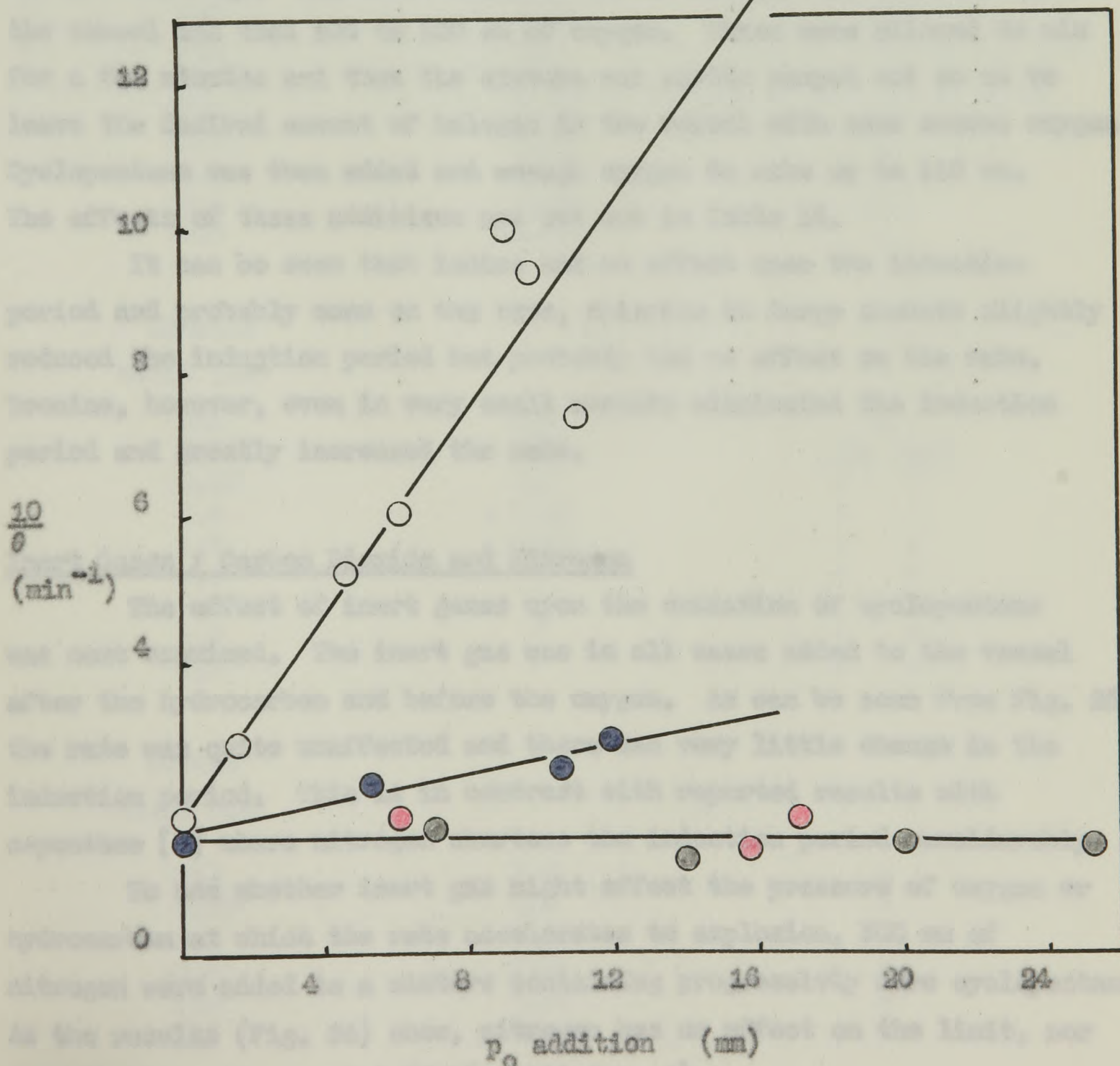
Fig. 22 Effect of various amines and ammonia upon the induction
period of cyclopentane

cyclopentane - 350 mm

oxygen - 110 mm

250°C

- - triethylamine
- - diethylamine
- - ethylamine
- - ammonia



acetaldehyde from the higher amines under the conditions of the experiment.

Chlorine, Bromine and Iodine

In view of the previous results with isopropyl iodide and the known inhibiting action of iodine upon the hydrogen-oxygen reaction [59], the effect of free halogens upon the oxidation of cyclopentane was examined. It was not possible, in an apparatus with mercury manometers, to premix nitrogen and halogen so that very small amounts could be added in the usual way. Instead a small amount of halogen was admitted to the vessel and then 100 to 200 mm of oxygen. These were allowed to mix for a few minutes and then the mixture was partly pumped out so as to leave the desired amount of halogen in the vessel with some excess oxygen. Cyclopentane was then added and enough oxygen to make up to 110 mm. The effects of these additions are set out in Table 15.

It can be seen that iodine had no effect upon the induction period and probably none on the rate, chlorine in large amounts slightly reduced the induction period but probably had no effect on the rate. Bromine, however, even in very small amounts eliminated the induction period and greatly increased the rate.

Inert Gases : Carbon Dioxide and Nitrogen

The effect of inert gases upon the oxidation of cyclopentane was next examined. The inert gas was in all cases added to the vessel after the hydrocarbon and before the oxygen. As can be seen from Fig. 25 the rate was quite unaffected and there was very little change in the induction period. This is in contrast with reported results with n-pentane [8] where nitrogen shortens the induction period considerably.

To see whether inert gas might affect the pressure of oxygen or hydrocarbon at which the rate accelerates to explosion, 500 mm of nitrogen were added to a mixture containing progressively more cyclopentane. As the results (Fig. 24) show, nitrogen has no effect on the limit, nor upon the induction period (Table xiii App. A).

Table 15Effect of halogens upon the rate of oxidation and induction period ofcyclopentane

cyclopentane - 350 mm

oxygen - 110 mm

250°C

chlorine added (mm)	induction period (θ) (mins.secs)	maximum rate $p_{\max}$ * (mm min ⁻¹)
nil	6.0	-
nil	6.50	25
0.1	6.0	-
5.2	5.30	-
13.0	4.30	-
20.0	5.30	-
50.5	4.30	-
42.0	5.30	30
70.0	2.50	-

bromine added (mm)		
nil	8.0	-
0.006	3.0	very fast
0.05	2.0	" "
0.4	< 0.20	" "
1.0	< 0.10	" "
2.0	"	" "
2.5	"	" "
5.0	"	" "
9.0	"	" "

iodine
added (mm)

nil	7.0	-
0.05	5.0	-
0.1	4.45	-
0.3	6.0	-
1.4	5.30	-
1.5	5.30	-

Table 15 cont.

iodine added (mm)	induction period (θ) (mins.secs)	maximum rate $\rho_{\max}$ * (mm min ⁻¹)
2.0	7.15	-
nil	6.50	-

* The rates are very difficult to measure with the type of gauge used. The two actual figures given are approximate. Where no figure is given the rates were approximately normal. Very fast means that the reaction was completed in less than ten seconds, after the end of the induction period.

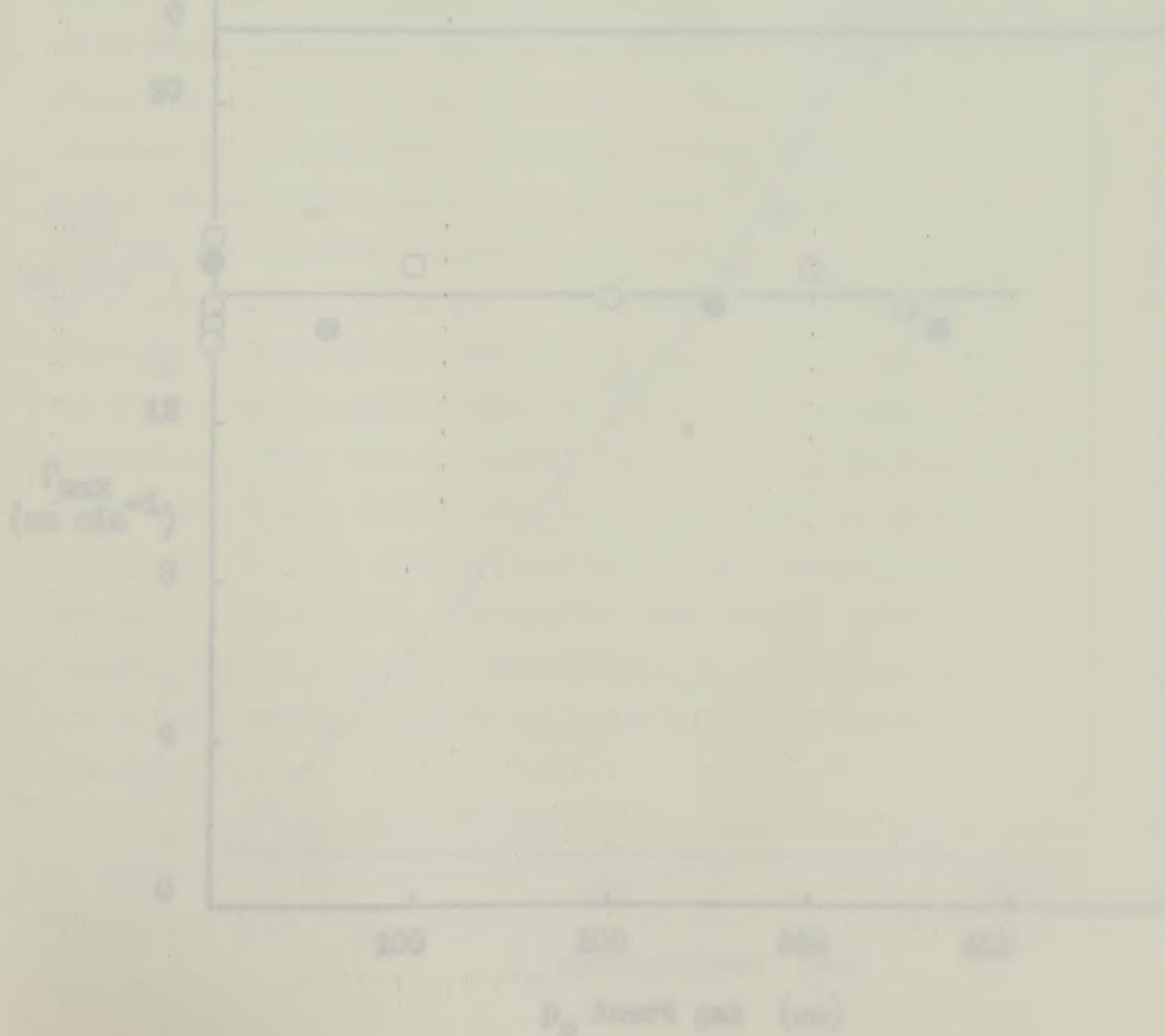


Fig. 25 Effect of nitrogen and carbon dioxide upon the rate of oxidation and induction period of cyclopentane

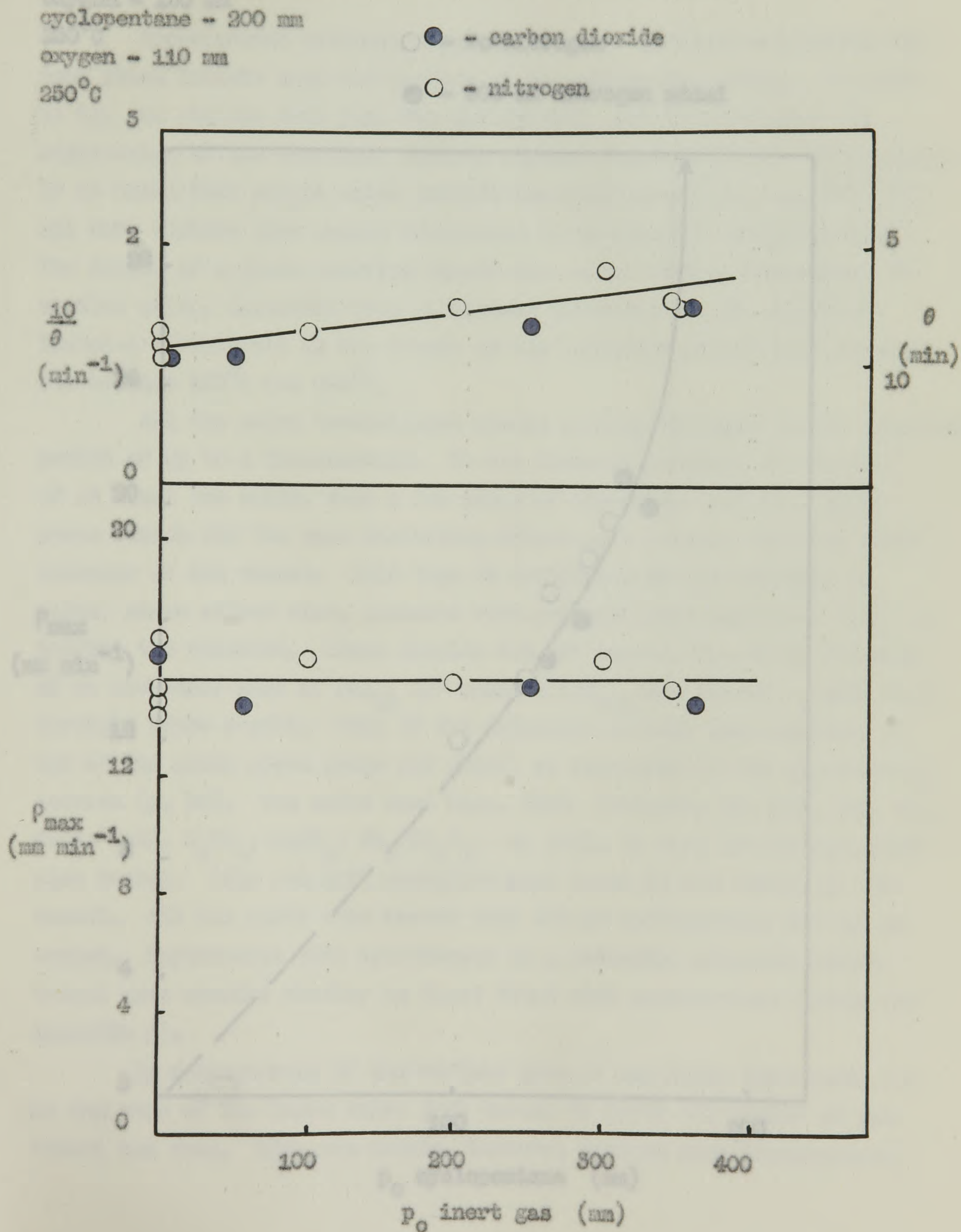


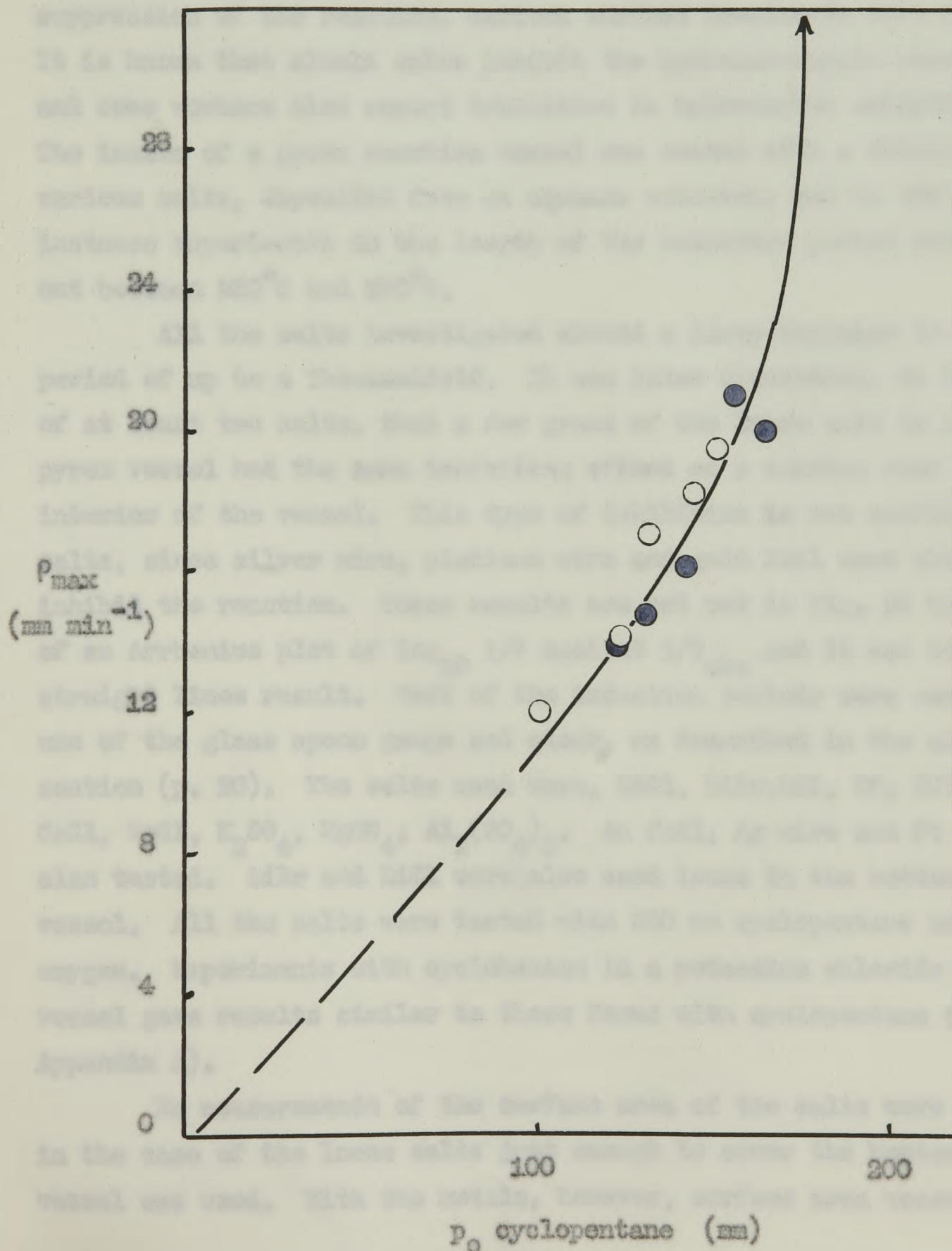
Fig. 24 Effect of nitrogen upon the explosion limit of cyclopentane

oxygen - 150 mm

250°C

○ - No nitrogen

● - 500 mm nitrogen added



The Effect of Various Surface Treatments

Experimental evidence suggests that the initiation reaction may take place largely upon the surface of the containing vessel. In order to try and utilize this fact for the control, and in particular for suppression of the reaction, various surface treatments were investigated. It is known that alkali salts inhibit the hydrogen-oxygen reaction [60] and some workers also report inhibition in hydrocarbon oxidation [61]. The inside of a pyrex reaction vessel was coated with a thick layer of various salts, deposited from an aqueous solution, and in the first instance experiments on the length of the induction period were carried out between 250°C and 290°C.

All the salts investigated showed a large increase in the induction period of up to a thousandfold. It was later discovered, in the case of at least two salts, that a few grams of the loose salt in a clean pyrex vessel had the same inhibiting effect as a coating over the whole interior of the vessel. This type of inhibition is not confined to salts, since silver wire, platinum wire and gold foil were also found to inhibit the reaction. These results are set out in Fig. 25 in the form of an Arrhenius plot of $\log_{10} 1/\theta$ against $1/T_{\text{abs}}$ and it can be seen that straight lines result. Most of the induction periods were measured by use of the glass spoon gauge and clock, as described in the experimental section (p. 20). The salts used were, LiCl, LiBr, LiI, KF, KCl, KBr, KI, CsCl, MgCl, K_2SO_4 , $MgSO_4$, $Al_2(SO_4)_3$. Au foil, Ag wire and Pt wire were also tested. LiBr and LiCl were also used loose in the bottom of the vessel. All the salts were tested with 350 mm cyclopentane and 110 mm oxygen. Experiments with cyclohexane in a potassium chloride coated vessel gave results similar to those found with cyclopentane (Table xiv Appendix A).

No measurements of the surface area of the salts were made, and in the case of the loose salts just enough to cover the bottom of the vessel was used. With the metals, however, surface area measurements

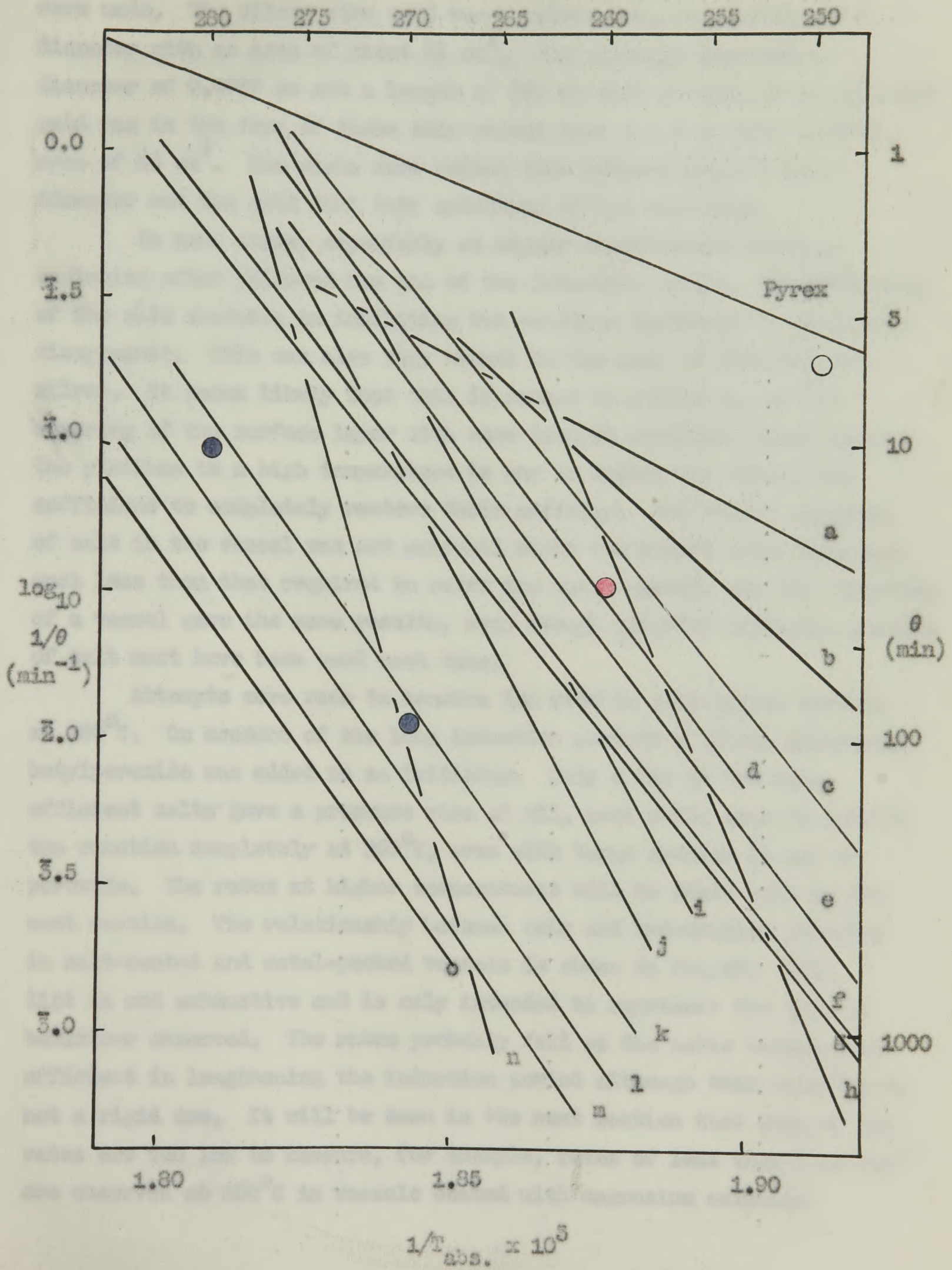
Key to Fig. 25

Effect of various salts upon the induction period of
cyclopentane

a - KF	Cyclopentane - 550 mm
b - Au foil	Oxygen - 110 mm
c - KI	
d - MgSO_4	
e - LiCl	● - LiBr loose
f - KBr	● - LiCl loose
g - KCl	○ - Silica vessel
h - K_2SO_4	
i - Ag wire	
j - $\text{Al}_2(\text{SO}_4)_3$	
k - LiBr	
l - LiI	
m - MgCl_2	
n - CsCl	
o - Pt wire	

Fig. 25

Temperature °C



were made. The silver wire used was 4 metres long and 0.0711 cm in diameter with an area of about 89 cm^2 . The platinum wire had a diameter of 0.0587 cm and a length of 550 cm with an area of 65 cm^2 . The gold was in the form of three thin sheets each $3 \times 5 \text{ cm}$ with a total area of 90 cm^2 . The wires were coiled into helices about 8 mm in diameter and the gold foil into cylinders of the same size.

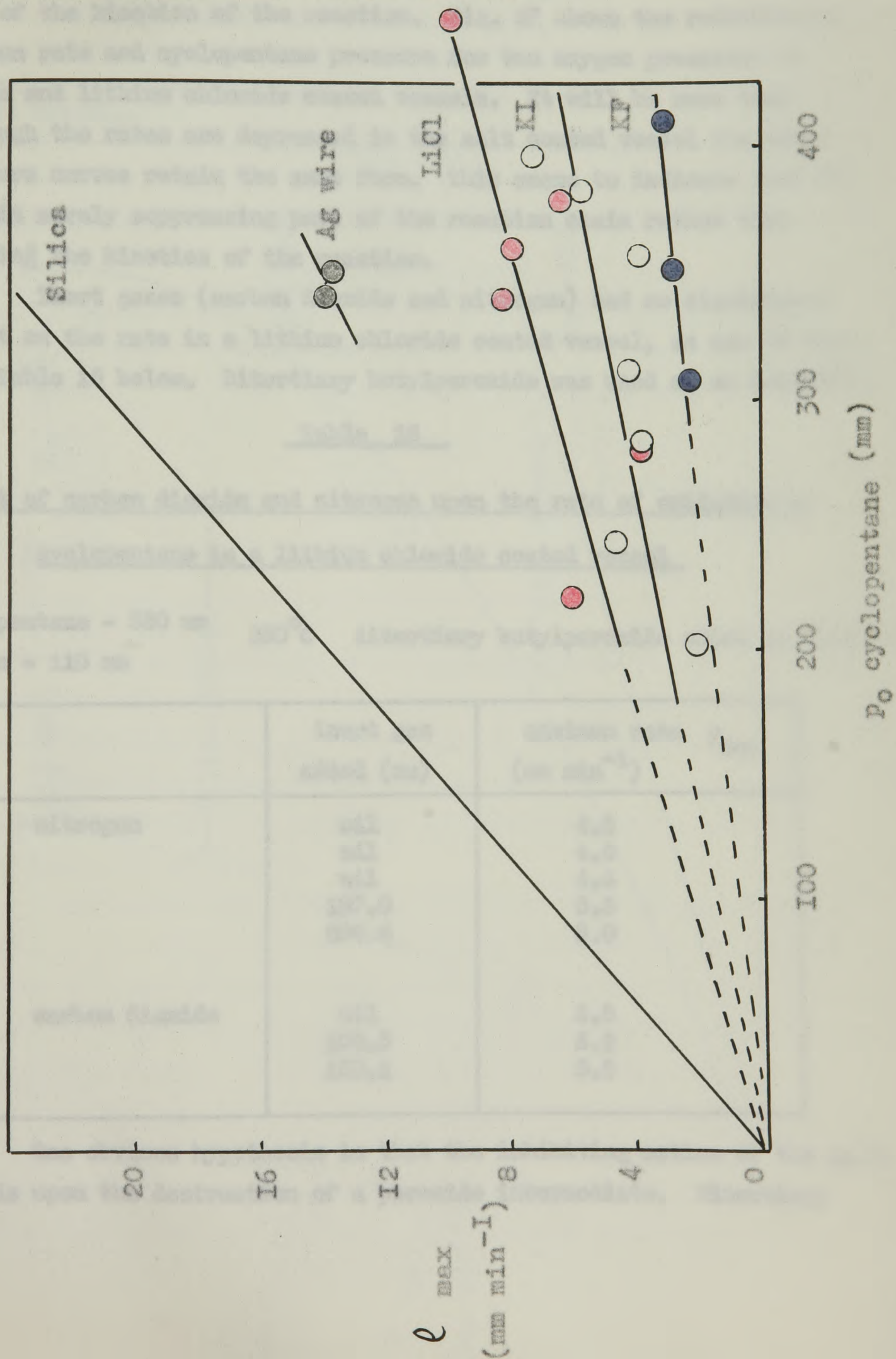
In some cases, especially at higher temperatures where an explosion often followed the end of the induction period, the efficiency of the salt surfaces in inhibiting the reaction decreased or completely disappeared. This was also very marked in the case of platinum and silver. It seems likely that this is caused by poisoning, or the covering of the surface layer with some product material, since heating the platinum to a high temperature in air or wiping the silver was sufficient to completely restore their activity. The actual quantity of salt in the vessel was not critical since the amount used loose was much less than that required to cover the whole vessel, and the recoating of a vessel gave the same results, even though slightly differing amounts of salt must have been used each time.

Attempts were made to measure the rate in salt-coated vessels at 250°C . On account of the long induction periods a little ditertiary butylperoxide was added as an initiator. Only a few of the less efficient salts gave a pressure rise at all, most salts seem to inhibit the reaction completely at 250°C , even with large amounts (5 mm) of peroxide. The rates at higher temperatures will be dealt with in the next section. The relationship between rate and hydrocarbon pressure in salt-coated and metal-packed vessels is shown in Fig. 26. This list is not exhaustive and is only intended to represent the type of behaviour observed. The rates probably fall as the salts become more efficient in lengthening the induction period although this relation is not a rigid one. It will be seen in the next section that some of the rates are too low to measure, for example, rates of less than 1 mm min^{-1} are observed at 350°C in vessels coated with magnesium sulphate.

Fig. 23 Effect of salt coating upon the rate of oxidation of

cyclopentane 250°C

All runs have ditertiary butylperoxide added



Although the salts and metals have such large effects upon the rate and induction periods, they do not seem to affect the general form of the kinetics of the reaction. Fig. 27 shows the relationship between rate and cyclopentane pressure for two oxygen pressures in silica and lithium chloride coated vessels. It will be seen that although the rates are depressed in the salt coated vessel the rate/pressure curves retain the same form. This seems to indicate that the salt is merely suppressing part of the reaction chain rather than changing the kinetics of the reaction.

Inert gases (carbon dioxide and nitrogen) had no significant effect on the rate in a lithium chloride coated vessel, as can be seen from Table 16 below. Ditertiary butylperoxide was used as an initiator.

Table 16

Effect of carbon dioxide and nitrogen upon the rate of oxidation of cyclopentane in a lithium chloride coated vessel

cyclopentane - 550 mm 250°C ditertiary butylperoxide added as initiator
oxygen - 110 mm

	inert gas added (mm)	maximum rate $\rho_{\max}$ (mm min ⁻¹)
nitrogen	nil	4.5
	nil	4.6
	nil	4.4
	187.0	5.5
	204.4	5.0
carbon dioxide	nil	5.8
	102.5	5.2
	180.1	5.5

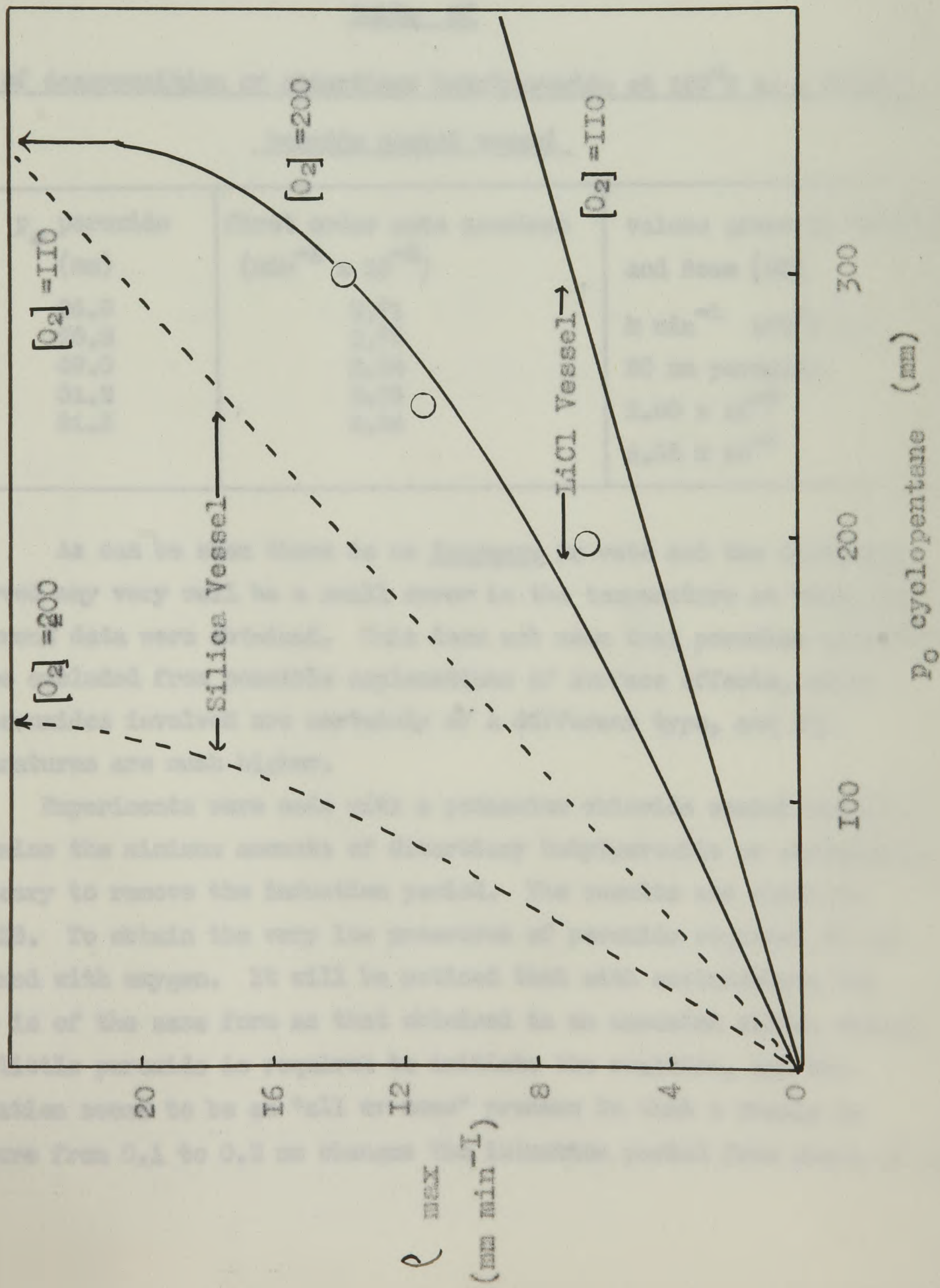
One obvious hypothesis is that the inhibiting action of the salts depends upon the destruction of a peroxide intermediate. Ditertiary

Fig. 27 Effect of a lithium chloride coating on cyclopentane

oxidation at different oxygen pressures 250°C

(three curves are taken from Figs. 3 and 26)

ditertiary butylperoxide added as initiator to runs in lithium chloride coated vessels.



butylperoxide being available its rate of decomposition was measured in a lithium bromide coated vessel at 160°C for comparison with the known rates measured in the absence of salts. The results are shown in Table 17, the first order rate constants being calculated from the initial slopes of the Δp /time curves.

Table 17

Rate of decomposition of ditertiary butylperoxide at 160°C in a lithium bromide coated vessel

P_o peroxide (mm)	first order rate constant ($\text{min}^{-1} \times 10^{-2}$)	values given by Birss [57] and Bose [62]
24.9	2.71	$k \text{ min}^{-1} \text{ } 160^\circ\text{C for}$ 50 mm peroxide. 2.90×10^{-2} 2.85×10^{-2}
25.2	2.78	
49.0	2.64	
51.2	2.65	
51.5	2.64	

As can be seen there is no increase in rate and the difference observed may very well be a small error in the temperature at which the different data were obtained. This does not mean that peroxide destruction can be excluded from possible explanations of surface effects, since the peroxides involved are certainly of a different type, and the temperatures are much higher.

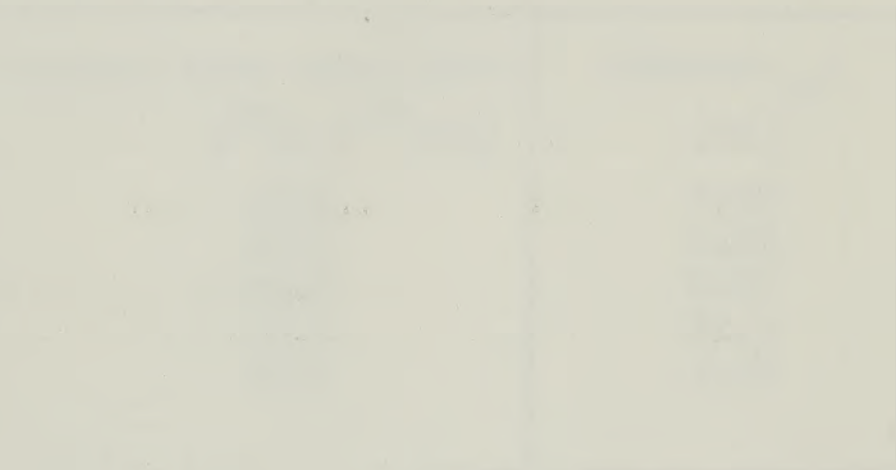
Experiments were made with a potassium chloride coated vessel to determine the minimum amounts of ditertiary butylperoxide or acetaldehyde necessary to remove the induction period. The results are shown in Fig. 28. To obtain the very low pressures of peroxide required it was premixed with oxygen. It will be noticed that with acetaldehyde the curve is of the same form as that obtained in an uncoated silica vessel. Very little peroxide is required to initiate the reaction, and the initiation seems to be an "all or none" process in that a change in pressure from 0.1 to 0.2 mm changes the induction period from about 12 hrs

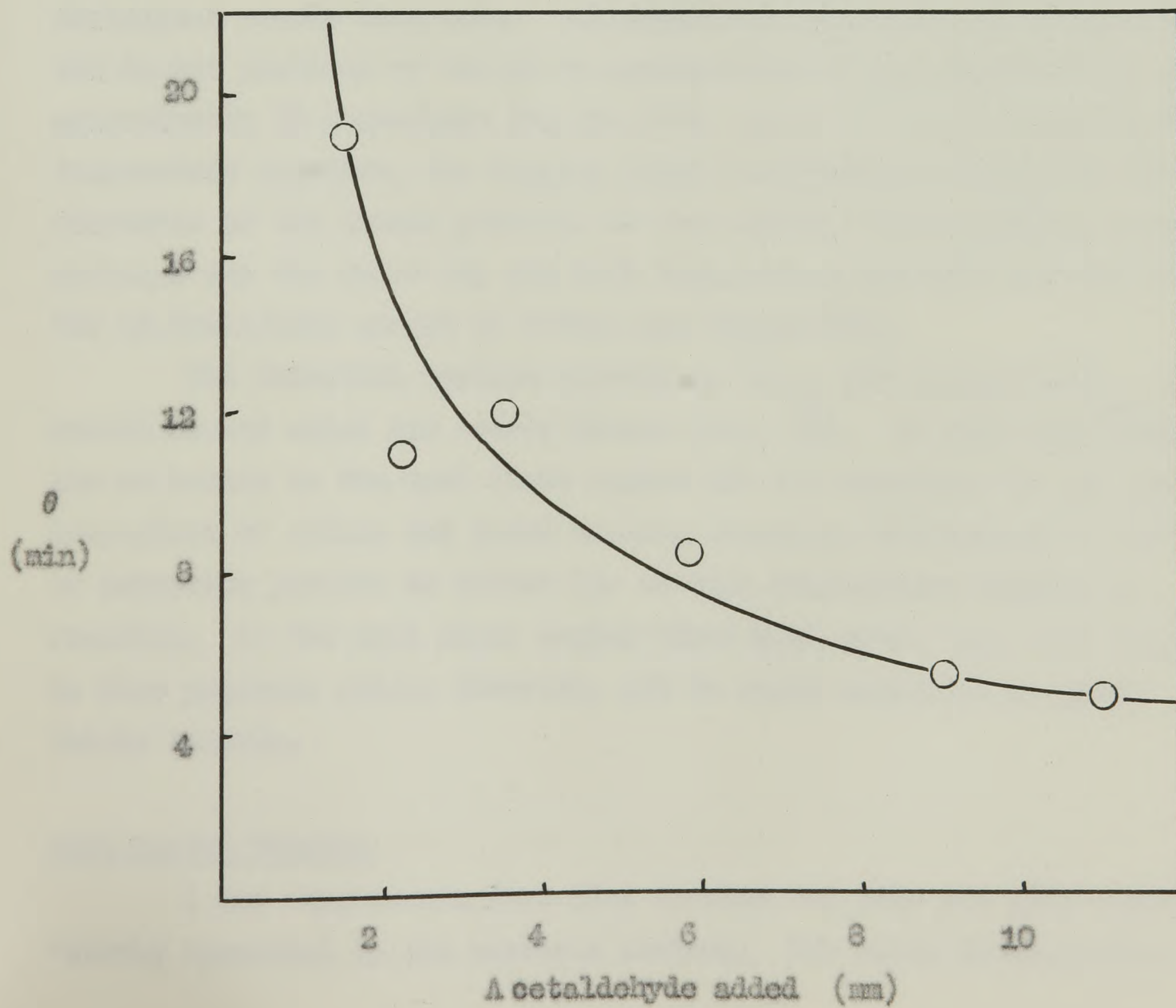
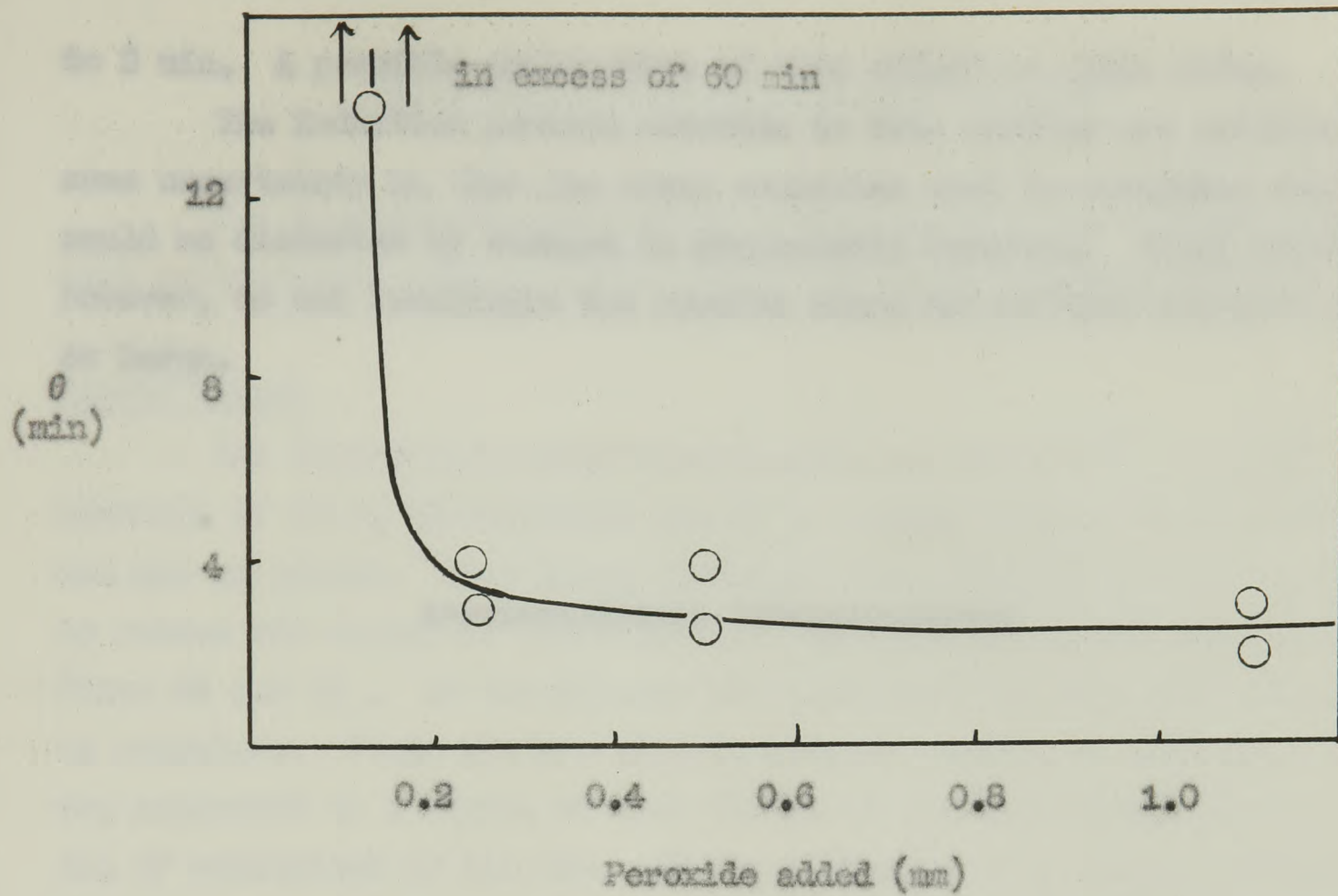
Fig. 28 Effect of ditertiary butylperoxide and acetaldehyde
on the induction period of cyclopentane in a vessel coated
with potassium chloride

Cyclopentane - 500 mm

250°C

Oxygen - 110 mm





to 2 min. A possible explanation of this effect is given later.

The induction periods recorded in this section are subject to some uncertainty in that the clock mechanism used in measuring them could be disturbed by changes in atmospheric pressure. These errors, however, do not invalidate the results since the effects observed are so large.

Allicin Vessels

The temperature range investigated was from 200°C to 400°C with mixtures of 40 cc cyclopentane and 60 cc oxygen, and of 50 cc cyclopentane and 50 cc oxygen. In a large number of runs possible had to be added to reduce the length of the induction period. The results are shown in Figs. 29 and 30. As can be seen the dependence of rate upon temperature is anomalous. There are two clearly defined regions of reaction, which are separated by a region of cool flame at the high temperature end and of explosion at the low. If the temperature is raised sufficiently explosions result once more. The activation energies, as measured from the linear portions of the 40 cc cyclopentane 60 cc oxygen curve, are approximately 30 Kcal/mole for the "low" and 2 Kcal/mole for the "high" temperature reaction, the figures being somewhat in excess of the shortness of the linear portions of the curve, which probably also explains why the value for the high temperature reaction differs from the 12 Kcal/mole quoted by Cohen and Vayer [35].

The induction periods plotted as $\log_{10} 1/t$ against $1/T_{\text{ind}}$ show smooth curves which are nearly linear (Fig. 30). In this case there are no breaks in the cool flame region and the behavior is not anomalous. Comparison of allicin and pyrex vessels showed no difference in the values of induction periods in either low or high temperature regions of reaction. In the cool flame region there were never less than three to five pressure pulses observed, all in rapid succession in about thirty seconds.

Salt Coated Vessels

A few experiments were also carried out with the salt coated vessels described in the previous section. The salts investigated were

Temperature Coefficient of the Reaction

The temperature coefficient of the reaction was investigated with cyclopentane both in plain silica and in salt coated vessels.

Silica Vessel

The temperature range investigated was from 250°C to 450°C with mixtures of 40 mm cyclopentane and 80 mm oxygen, and of 50 mm cyclopentane and 110 mm oxygen. In a large number of runs peroxide had to be added to reduce the length of the induction period. The results are shown in Figs. 29 and 50. As can be seen the dependence of rate upon temperature is anomalous. There are two clearly defined regions of reaction, which are separated by a region of cool flames at the high temperature end and of explosions at the low. If the temperature is raised sufficiently explosions result once more. The activation energies, as measured from the linear portions of the 40 mm cyclopentane 80 mm oxygen curve, are approximately 60 Kcals/mole for the "low" and 9 Kcals/mole for the "high" temperature reaction, the figures being uncertain on account of the shortness of the linear portions of the curves, which probably also explains why the value for the high temperature reaction differs from the 12 Kcals/mole quoted by McEwan and Tipper [53].

The induction periods plotted as $\log_{10} 1/\theta$ against $1/T_{\text{abs}}$ give smooth curves which are nearly linear (Fig. 50). In this case there are no breaks in the cool flame region and the behaviour is not anomalous. Comparison of silica and pyrex vessels showed no difference in the rates or induction periods in either low or high temperature regions of reaction. In the cool flame region there were never less than three to five pressure pulses observed, all in rapid succession in about thirty seconds.

Salt Coated Vessels

A few experiments were also carried out with the salt coated vessels described in the previous section. The salts investigated were

Key to Fig. 29

Effect of temperature upon the maximum rate of

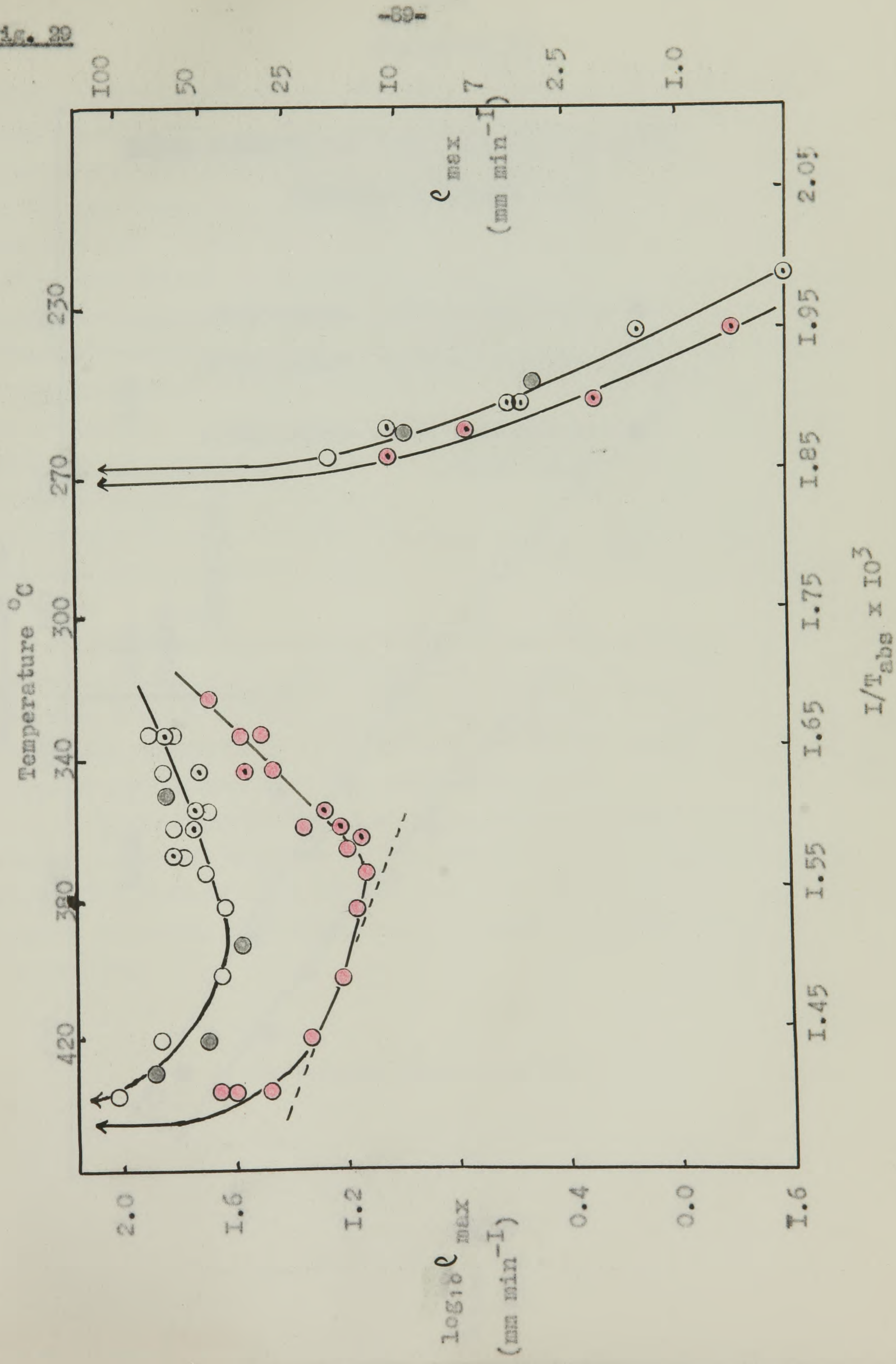
cyclopentane oxidation

Silica vessel

- - cyclopentane 40 mm oxygen 80 mm
- - cyclopentane 50 mm oxygen 110 mm
- ⊙ - peroxide added
- ⊗ - cyclopentane 50 mm oxygen 110 mm
pyrex vessel.

The broken line is taken from the results of McGowan and Tippet [55] for the oxidation of 40 mm cyclopentane and 80 mm oxygen over the temperature range shown.

Fig. 39



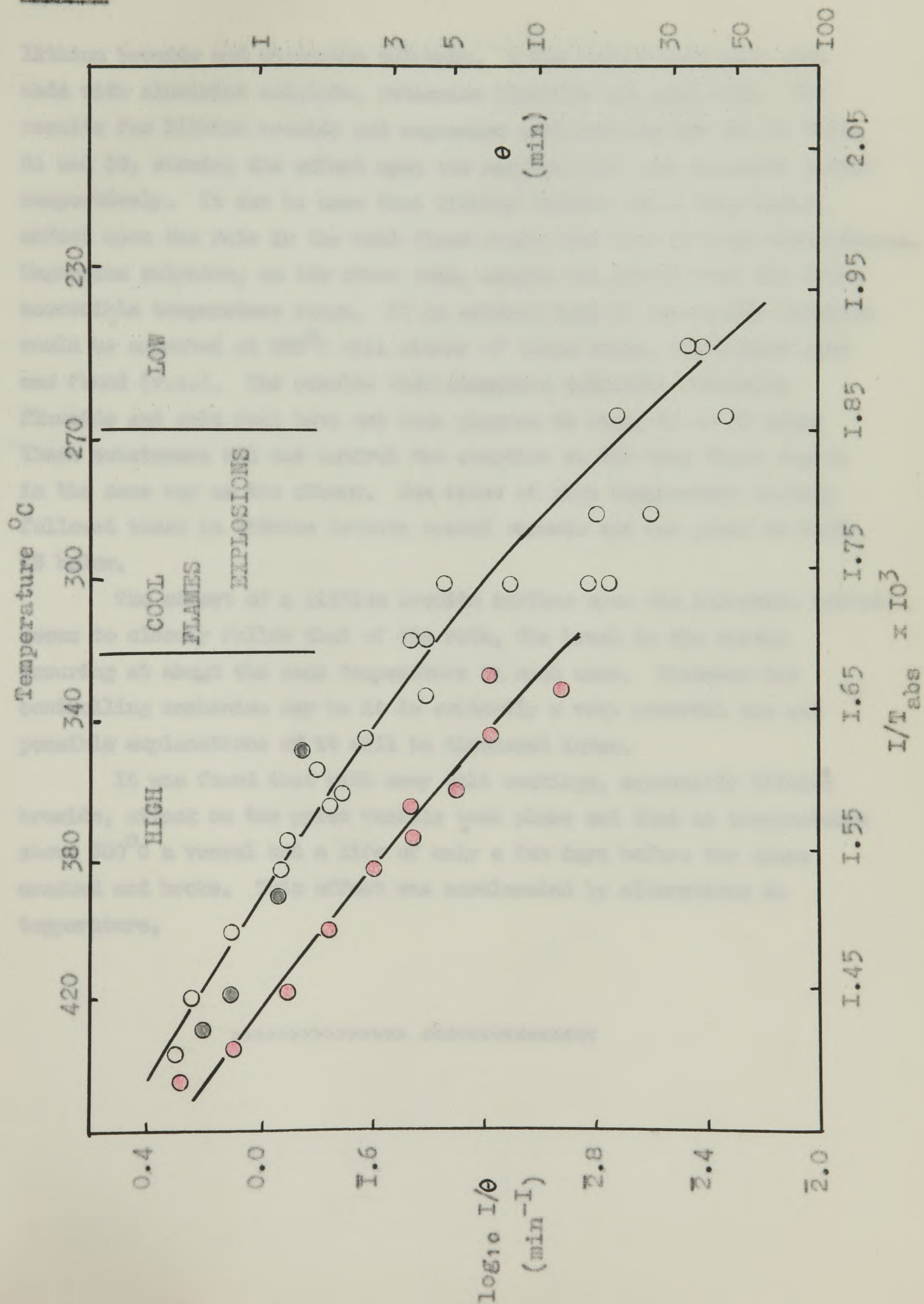
Key to Fig. 50

Effect of temperature upon the induction period
of cyclopentane oxidation

- - cyclopentane 40 mm oxygen 80 mm
- - cyclopentane 50 mm oxygen 110 mm
- - cyclopentane 40 mm oxygen 110 mm
pyrex vessel.

Fig. 30

191



Key to Fig. 31

Effect of lithium bromide and magnesium sulphate coated
vessels upon the maximum rate of oxidation of
cyclopentane

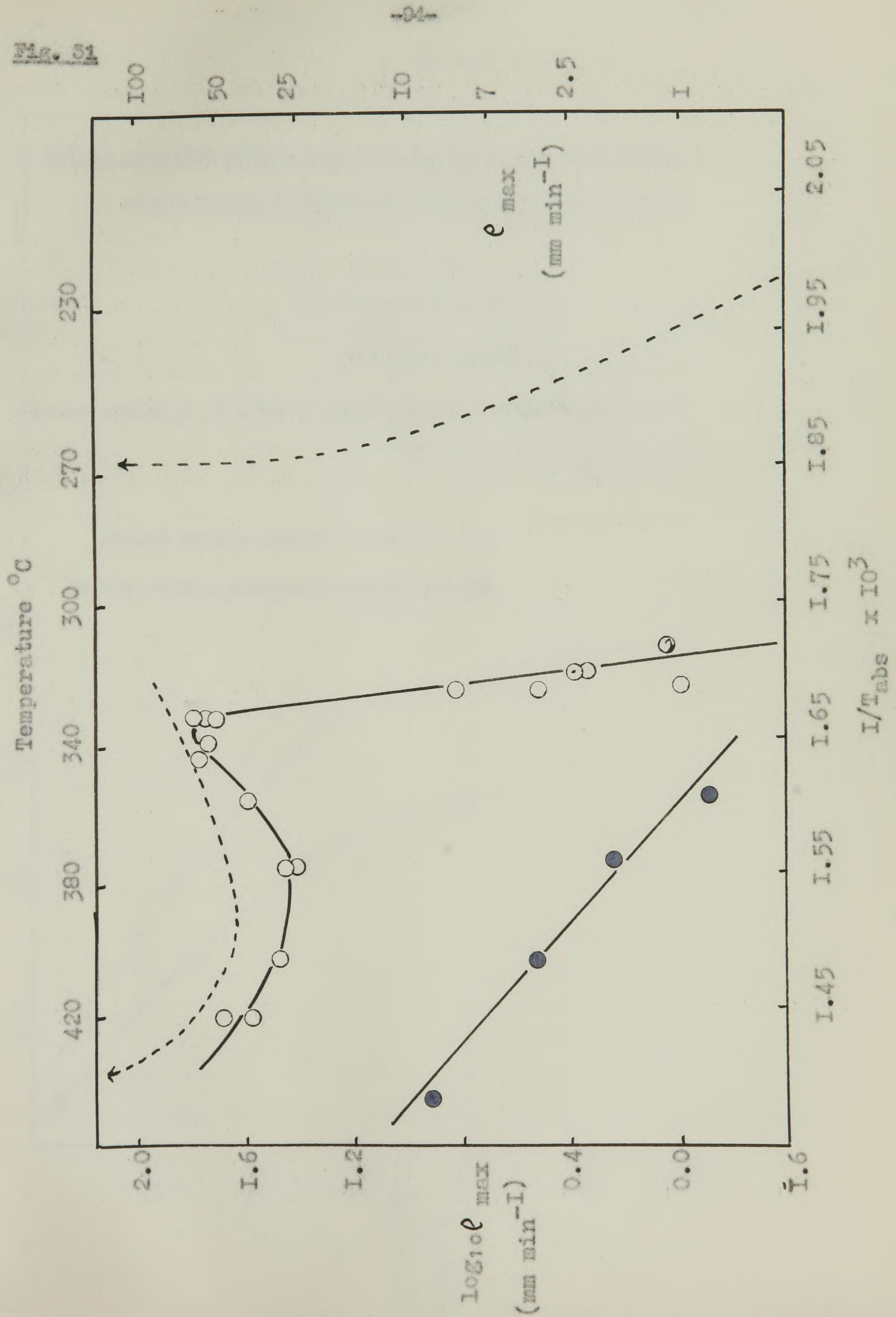
cyclopentane - 50 mm

oxygen - 110 mm

Broken lines show the rates in a silica vessel and are taken
from Fig. 29.

- - lithium bromide coated vessel
- - magnesium sulphate coated vessel
- ⊙ - peroxide added as an initiator

Fig. 51



Key to Fig. 52

Effect of lithium chloride and magnesium sulphate coated
vessels upon the induction period of cyclopentane

cyclopentane - 50 mm

oxygen - 110 mm

Broken line shows the induction periods in a silica vessel
and is taken from Fig. 50

- - lithium bromide coated vessel
- - magnesium sulphate coated vessel

Fig. 52

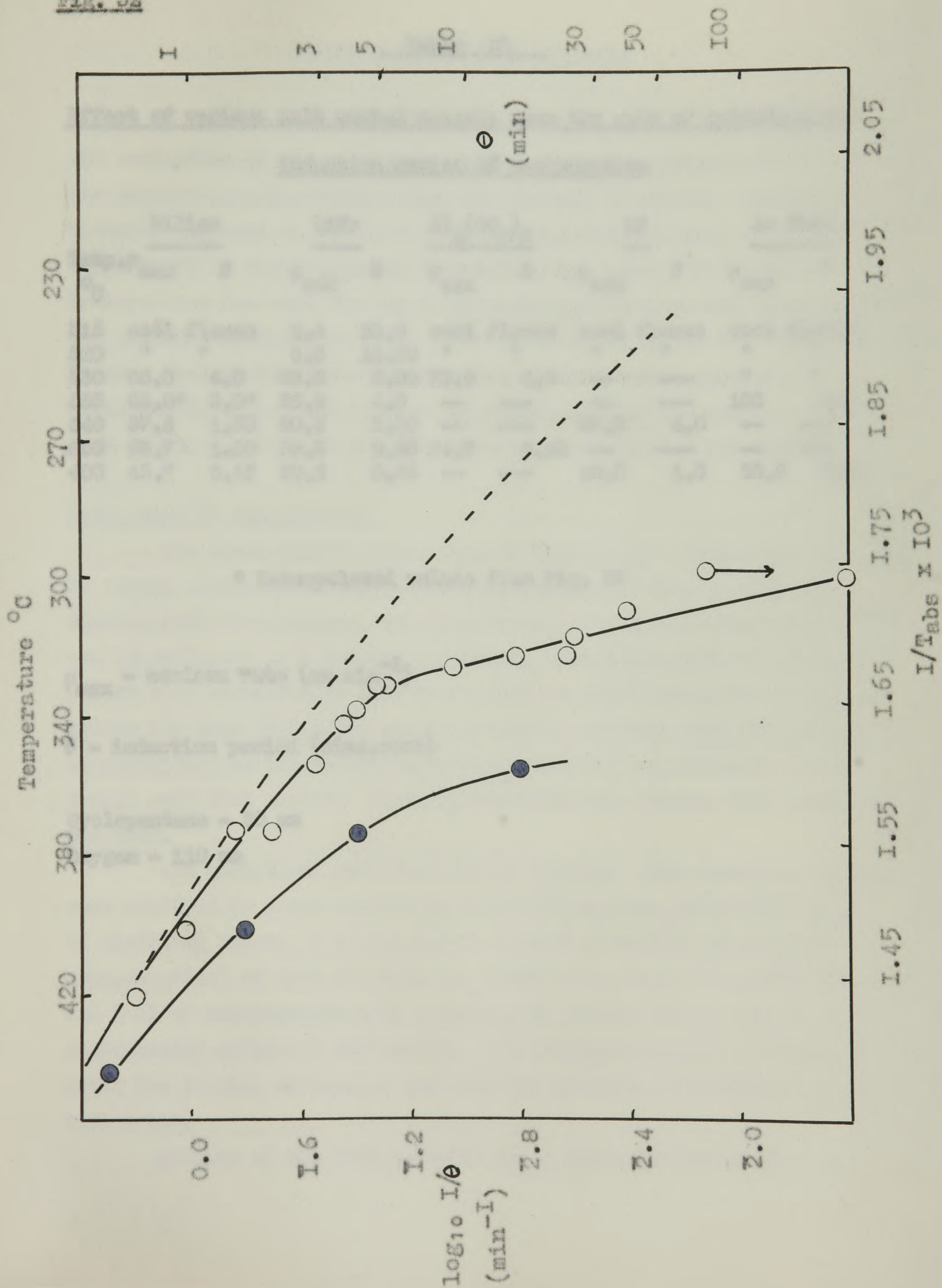


Table 18

Effect of various salt coated vessels upon the rate of oxidation and
induction period of cyclopentane

Temp. °C	<u>Silica</u>		<u>LiBr</u>		<u>Al₂(SO₄)₃</u>		<u>KF</u>		<u>Au foil</u>	
	$\rho_{\max}$	θ	$\rho_{\max}$	θ	$\rho_{\max}$	θ	$\rho_{\max}$	θ	$\rho_{\max}$	θ
515	cool flames		2.4	25.0	cool flames		cool flames		cool flames	
520	"	"	5.5	14.50	"	"	"	"	"	"
530	66.0	4.0	65.0	5.30	72.4	4.0	---	---	"	"
535	65.0*	5.0*	56.2	4.0	---	---	---	---	100	5.0
540	57.5	1.50	60.5	5.30	---	---	47.9	4.0	---	---
550	55.7	1.50	59.8	2.55	54.7	6.20	---	---	---	---
400	45.7	0.45	50.2	0.55	---	---	10.0	1.0	58.9	0.55

* Interpolated values from Fig. 29

$\rho_{\max}$ - maximum rate (mm min⁻¹)

θ - induction period (mins.secs)

Cyclopentane - 50 mm

Oxygen - 110 mm

Products and Product Analysis

A combination of techniques has been used for the detection and estimation of the reaction products. The mass spectrometric and gas chromatographic methods have been already mentioned. Chemical analysis was used to estimate peroxides and formaldehyde, neither of which could be satisfactorily analysed by the other two methods. Cyclopentane has been used as a representative hydrocarbon since it is the simplest member used which could be oxidised in the low temperature range. Cyclopropane, the first member of the series, requires a considerably higher temperature for oxidation than the others. Some mass spectrometric analysis has, however, been carried out with it.

Estimation of Formaldehyde

The Chromotropic Acid Method of Bricker and Johnson was used [65]. In strong mineral acid solution chromotropic acid forms a deep red complex with formaldehyde, and concentrations down to 5 microgram ml⁻¹ can be estimated on a spectrophotometer. The originators of the method report that acetaldehyde interferes with the development of the red colour but this difficulty can be overcome, provided that the acetaldehyde concentration is not too high, by using stronger solutions of chromotropic acid than normal. Since acetaldehyde was present this modification was used.

The analytical procedure was as follows. The reaction products were admitted to a gas pipette in the usual way and shaken with 10 ml of distilled water. 1 ml (or 0.5 ml according to the formaldehyde concentration) of this solution was placed in a 50 ml volumetric flask and 1 ml of chromotropic acid solution (15 gm in 50 ml) and 10 ml of concentrated sulphuric acid added. The flask was heated in boiling water for 50 min, allowed to cool and the contents were diluted to 50 ml with water.

Samples of the test solution and a blank were compared on a

"Unicam Spectrophotometer" at 5,700 Å. The method was calibrated with a water soluble trimer of formaldehyde, sym-trioxane, and the calibration curve was found to be linear over the experimental range.

Check experiments with sym-trioxane solutions and added acetaldehyde, showed that acetaldehyde, in the concentrations reached during the oxidations, did not interfere with the accuracy of the formaldehyde determinations.

Estimation of Peroxides

An iodometric method was used and no attempt was made to discriminate between different types of peroxide. The combustion gases were shaken with water in a gas pipette and about one gram of potassium iodide and five cc of 2N sulphuric acid added to this solution. Two drops of a 3% ammonium molybdate solution, to speed the reaction of alkyl hydrogen peroxides with acidified potassium iodide, and two drops of a 0.1N solution of ferrous ammonium sulphate, to catalyse the decomposition of dialkyl peroxides, were added [25]. The mixture was allowed to stand for thirty minutes at room temperature and the liberated iodine titrated with 0.01N sodium thiosulphate solution. The amount of acetaldehyde present did not interfere and blank experiments were always carried out upon the reagents.

Estimation of other Products and Results

Analyses for carbon monoxide, oxygen and hydrocarbon were carried out with a mass spectrometer, the other products to be mentioned were estimated by gas chromatography as described in the experimental section. Water was estimated by difference.

In the first instance analyses were carried out upon the oxidation products of 150 mm cyclopentane and 110 mm oxygen, and the results are set out in Figs. 53 and 54. Since the induction periods are somewhat variable, samples were not withdrawn from the vessel at fixed times after the start of a run, but after fixed pressure increases. By reference

Key to Fig. 55

Principal products of cyclopentane oxidation

cyclopentane - 150 mm

250°C

Pyrex vessel

oxygen - 110 mm

● - oxygen gone

● - cyclopentane gone

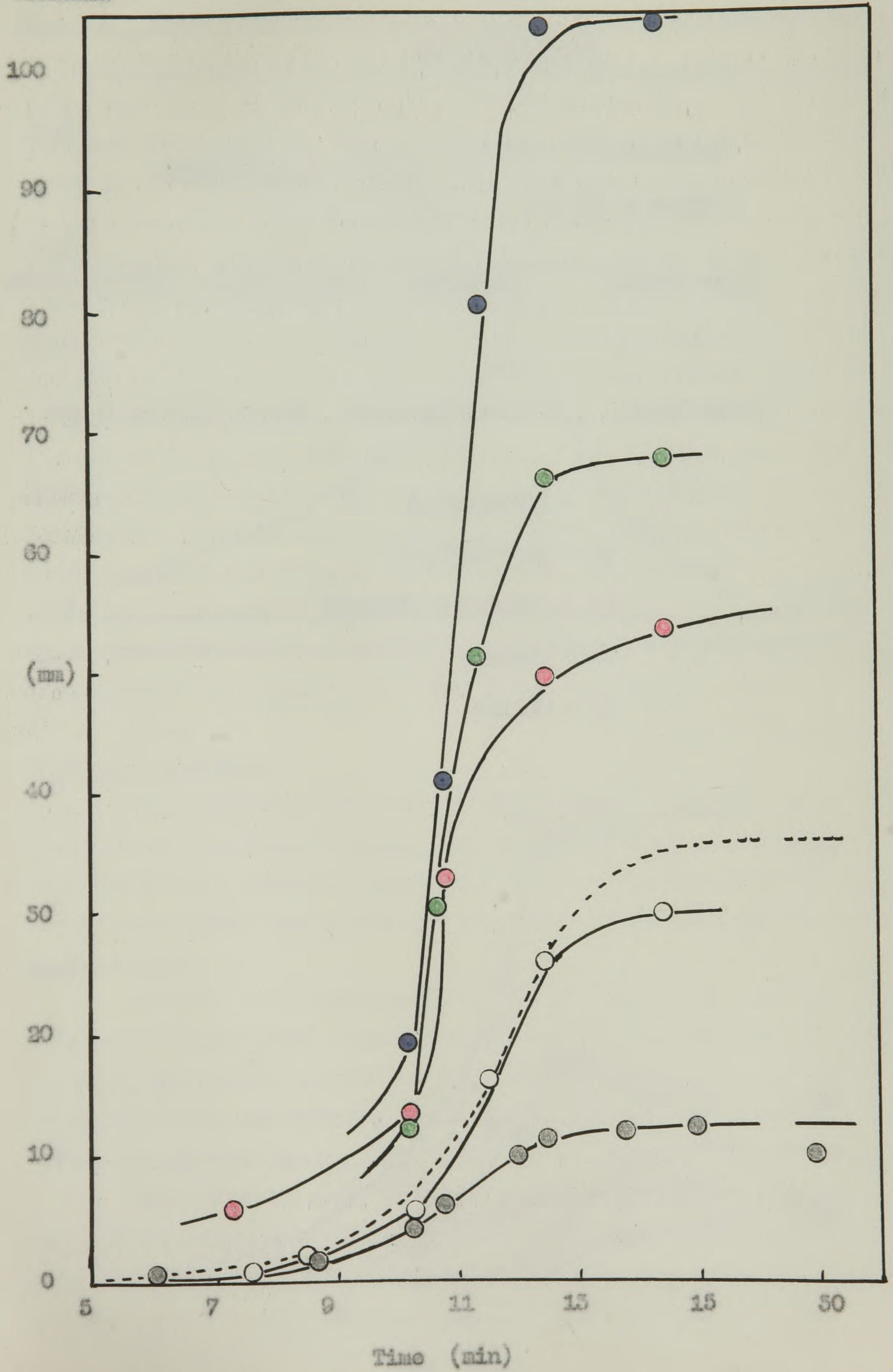
○ - carbon monoxide

● - carbon dioxide

● - water (by difference) $\pm \frac{1}{2}$

broken line - Δp

Fig. 55



Key to Fig. 54

cyclopentane - 150 mm

250°C Pyrex Vessel

oxygen - 110 mm

Upper Graph.

Peroxides

broken line - Δp /time curve.

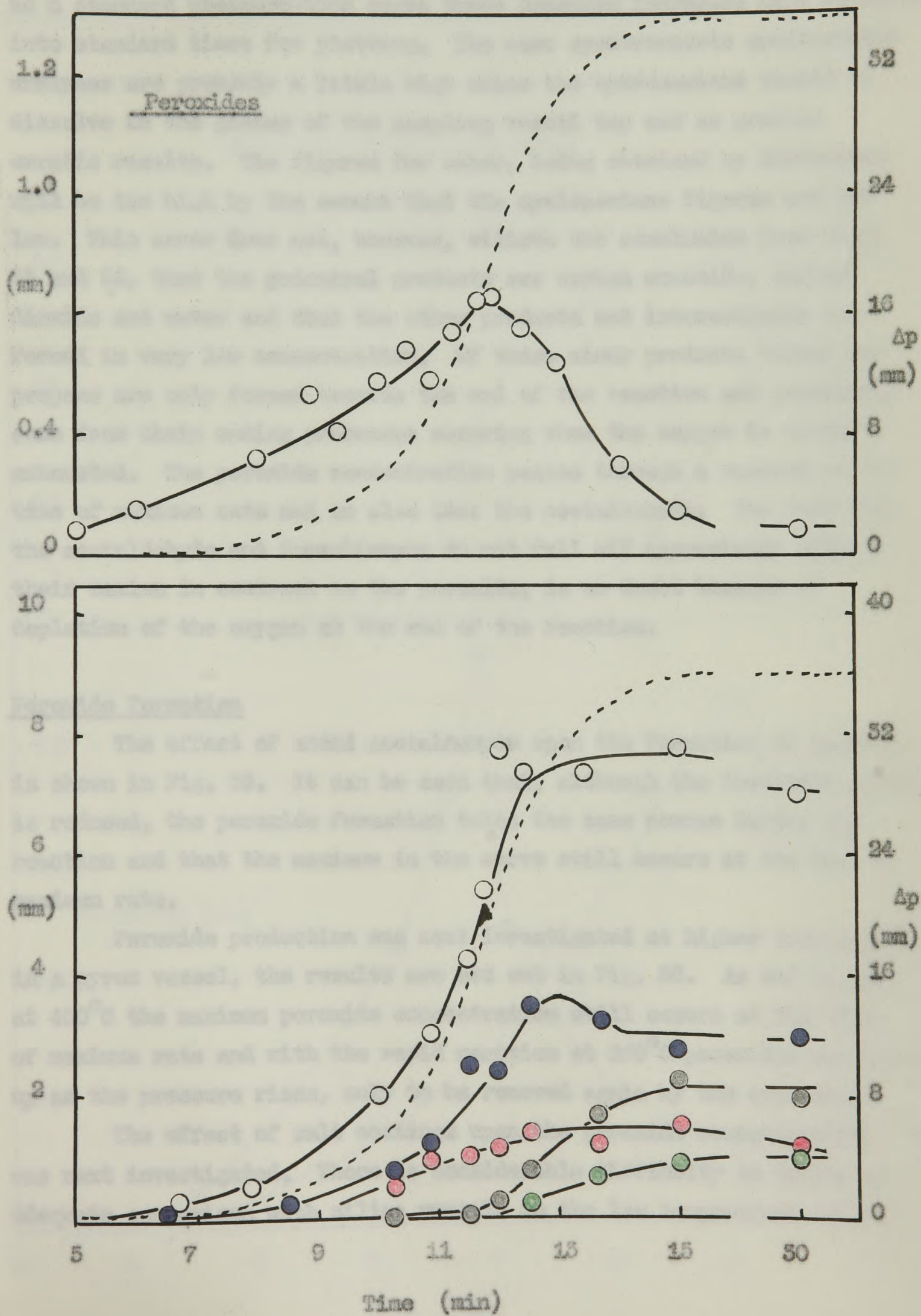
Lower Graph.

Other Products

Broken line as above.

- - formaldehyde
- - acetaldehyde
- - n-butyric aldehyde
- - propane
- - butene

Fig. 54. Minor products and intermediates of cyclopentane oxidation



to a standard pressure-time curve these pressure increases were converted into standard times for plotting. The mass spectrometric cyclopentane analyses are probably a little high since the hydrocarbons tended to dissolve in the grease of the sampling vessel tap and so produce erratic results. The figures for water, being obtained by difference, will be too high by the amount that the cyclopentane figures are too low. This error does not, however, vitiate the conclusion from Figs. 53 and 54, that the principal products are carbon monoxide, carbon dioxide and water and that the other products and intermediates are formed in very low concentration. Of these minor products butene and propane are only formed towards the end of the reaction and presumably come from chain ending processes occurring when the oxygen is almost exhausted. The peroxide concentration passes through a maximum at the time of maximum rate and so also does the acetaldehyde. The fact that the acetaldehyde and formaldehyde do not fall off appreciably after their maxima in contrast to the peroxide, is no doubt because of depletion of the oxygen at the end of the reaction.

Peroxide Formation

The effect of added acetaldehyde upon the formation of peroxide is shown in Fig. 55. It can be seen that, although the induction period is reduced, the peroxide formation takes the same course during the reaction and that the maximum in the curve still occurs at the time of maximum rate.

Peroxide production was next investigated at higher temperatures in a pyrex vessel, the results are set out in Fig. 56. As can be seen, at 400°C the maximum peroxide concentration still occurs at the time of maximum rate and with the rapid reaction at 360°C peroxides are built up as the pressure rises, only to be removed again by the explosion.

The effect of salt coatings upon the peroxide concentrations was next investigated. There is considerable difficulty in making an adequate comparison with silica vessels in the low temperature range

Fig. 55 Effect of acetaldehyde upon peroxide formation in a
cyclopentane - oxygen system, 250°C Pyrex vessel

Upper graph - Δp /time curves. Lower graph - peroxides.

● - 5 mm acetaldehyde added

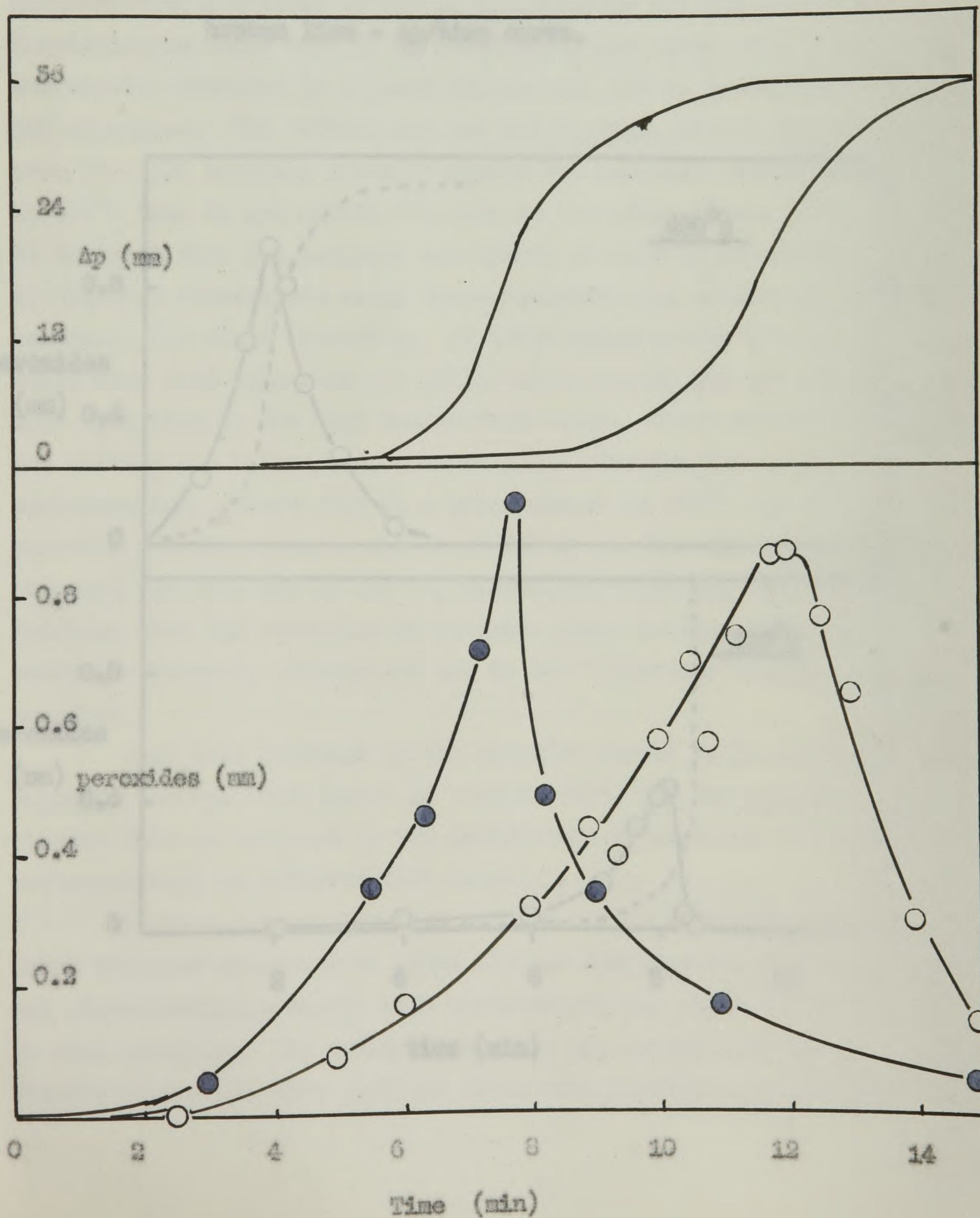


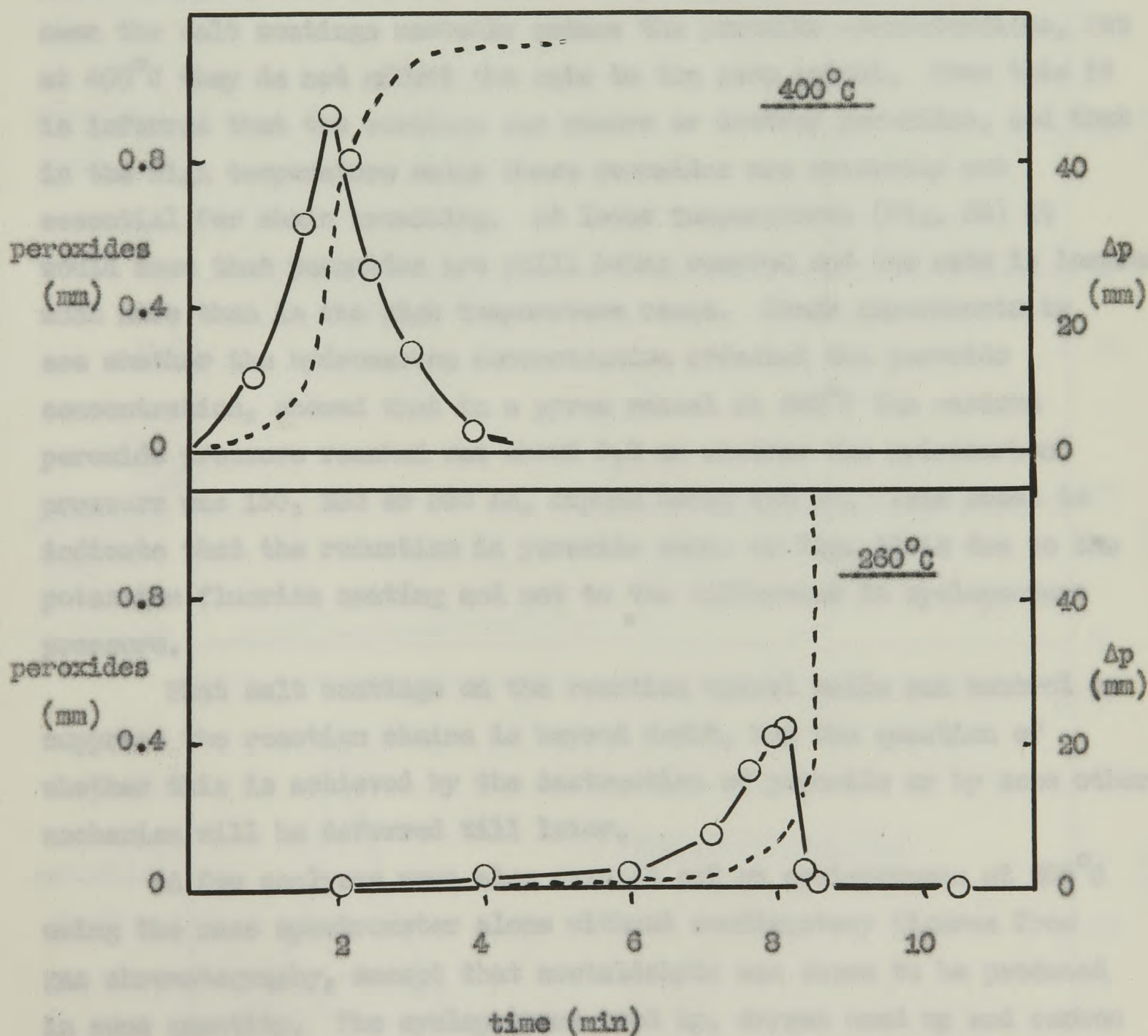
Fig. 36 Peroxide formation at two different temperatures

cyclopentane - 50 mm

pyrex vessel

oxygen - 110 mm

broken line - Δp /time curve.



since the more efficient salts completely suppress the reaction. Lithium bromide and potassium fluoride coatings could, however, be investigated in the high temperature range at 400°C , and compared with a clean pyrex surface (Fig. 57). At 250°C direct comparison was not possible. Peroxide concentrations in a potassium fluoride coated vessel were measured with a mixture of 350 mm cyclopentane and 110 mm oxygen, (acetaldehyde being used as an initiator), and these were compared with the results obtained in a pyrex vessel with 150 mm cyclopentane and 110 mm oxygen. The results are set out in Figs. 57 and 58. As can be seen the salt coatings markedly reduce the peroxide concentrations, but at 400°C they do not affect the rate to the same extent. From this it is inferred that the coatings can remove or destroy peroxides, and that in the high temperature range these peroxides are evidently not essential for chain branching. At lower temperatures (Fig. 58) it would seem that peroxides are still being removed and the rate is lowered much more than in the high temperature range. Check experiments to see whether the hydrocarbon concentration affected the peroxide concentration, showed that in a pyrex vessel at 250°C the maximum peroxide pressure reached was about 0.8 mm whether the hydrocarbon pressure was 150, 250 or 350 mm, oxygen being 110 mm. This seems to indicate that the reduction in peroxide shown in Fig. 58 is due to the potassium fluoride coating and not to the difference in cyclopentane pressure.

That salt coatings on the reaction vessel walls can control or suppress the reaction chains is beyond doubt, but the question of whether this is achieved by the destruction of peroxide or by some other mechanism will be deferred till later.

A few analyses were also carried out on cyclopropane at 285°C using the mass spectrometer alone without confirmatory figures from gas chromatography, except that acetaldehyde was shown to be produced in some quantity. The cyclopropane used up, oxygen used up and carbon dioxide formed all give straight lines when plotted against Δp as can

Fig. 57 Effect of different salt coatings upon peroxide formation

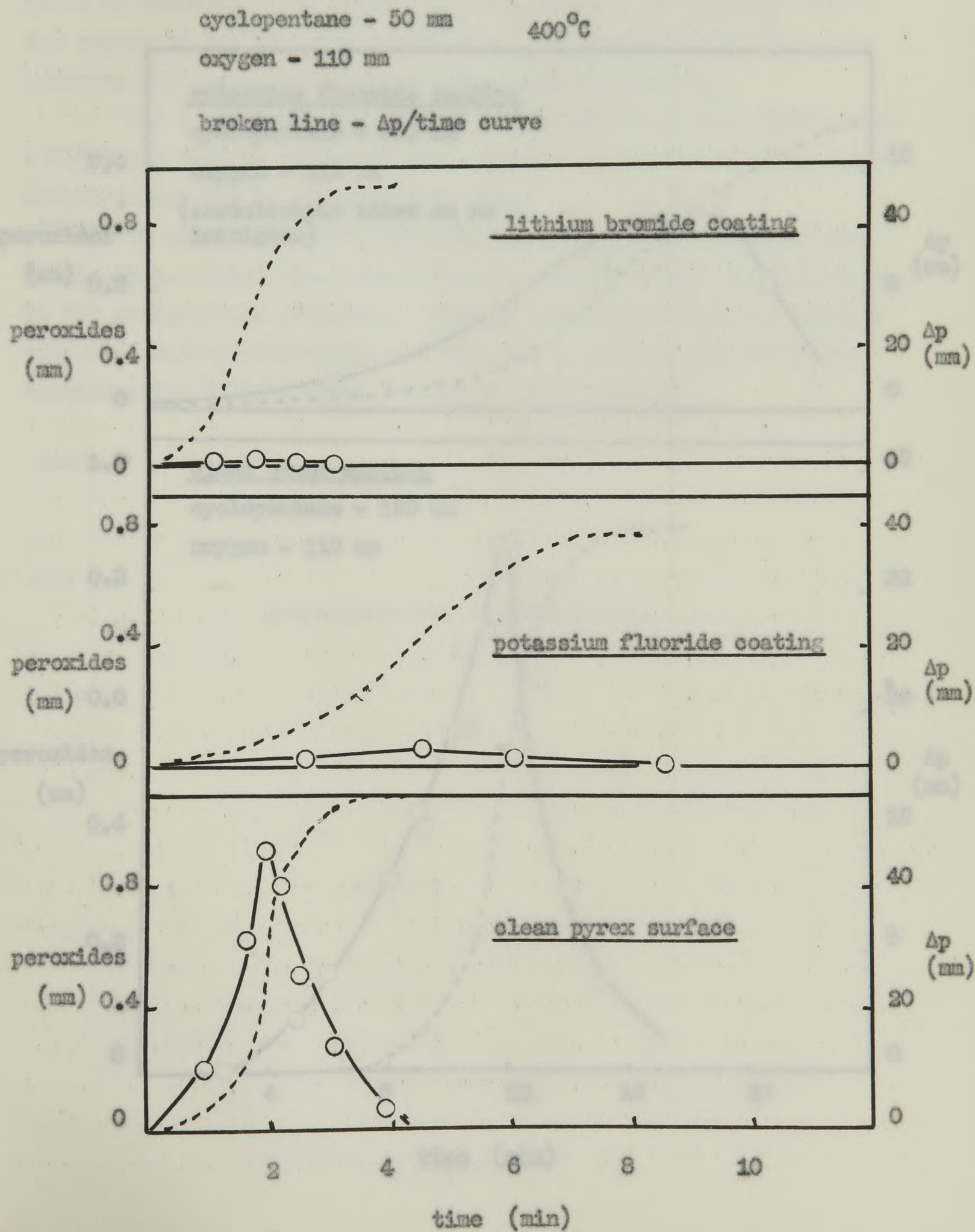


Fig. 38 Effect of a salt coating upon peroxide formation

broken line - Δp /time curve 250°C

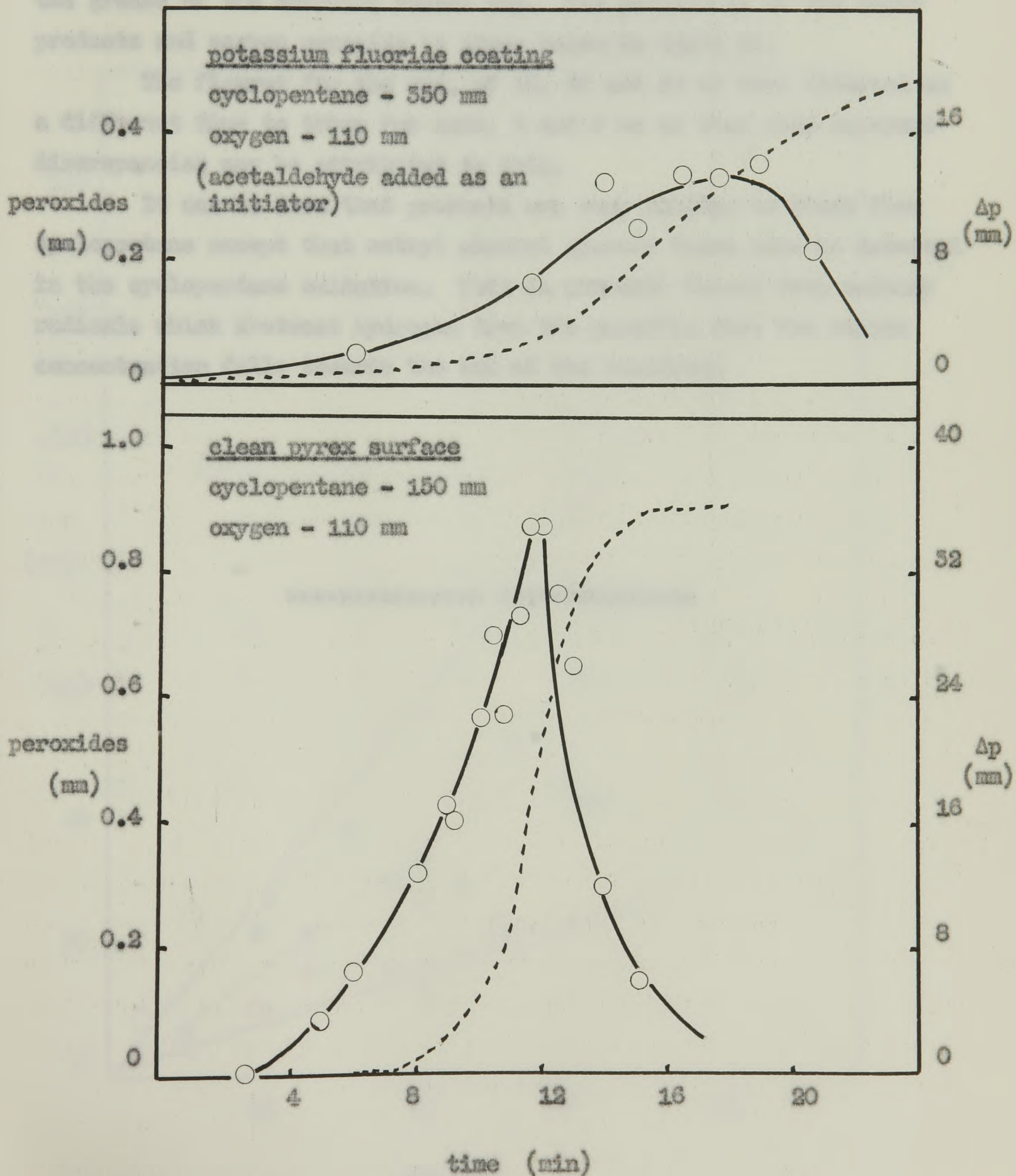


Fig. 59. Cyclopropane analyses

cyclopropane - 300 mm

oxygen - 110 mm

285°C

Silica vessel

● - cyclopropane gone

○ - oxygen gone

● - carbon dioxide

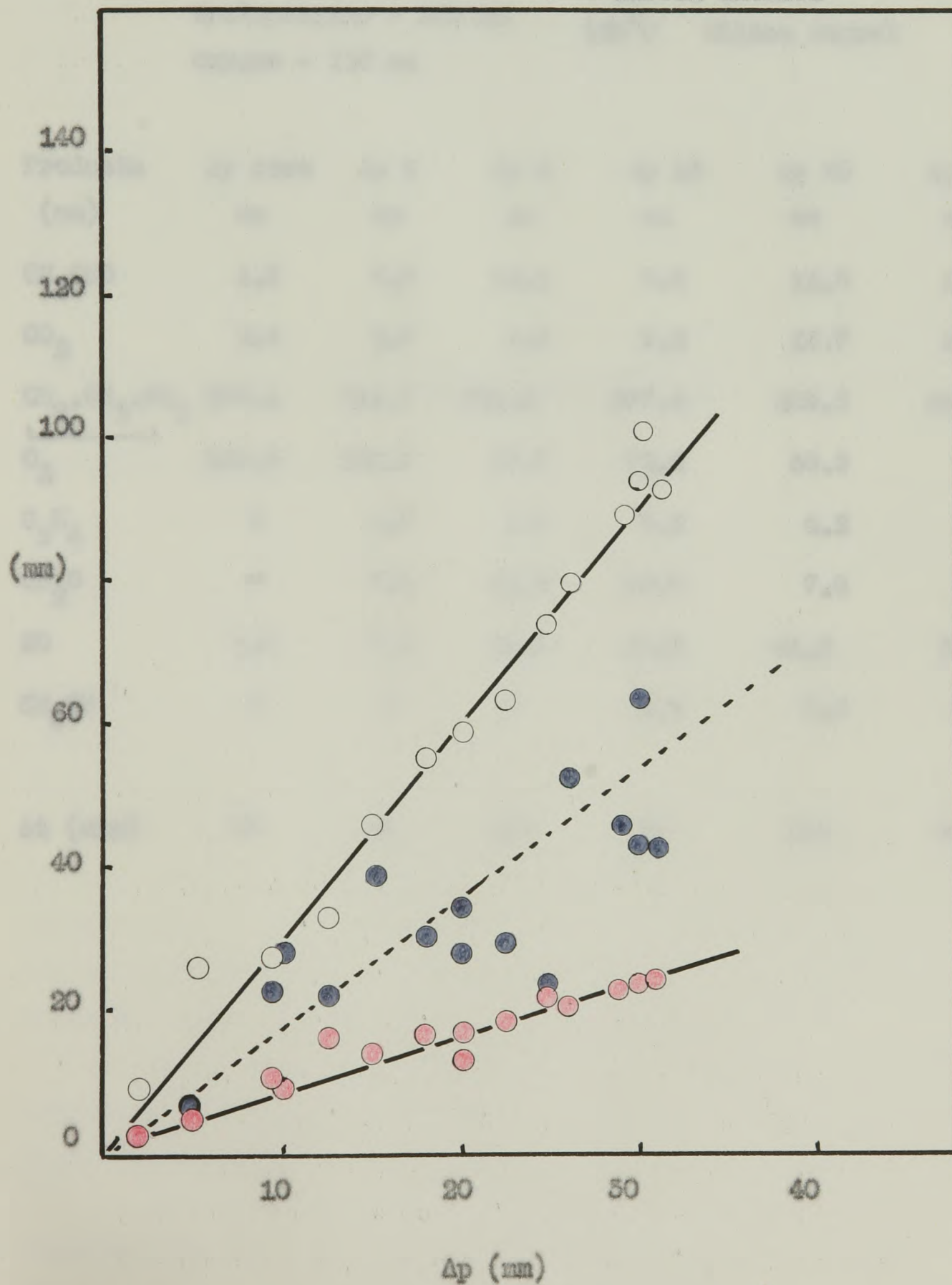


Table 19

Products of cyclopropane oxidation

(analysis by mass spectrometer)

cyclopropane - 500 mm 235°C Silica vessel
oxygen - 110 mm

Products (mm)	Ap zero mm	Ap 2 mm	Ap 5 mm	Ap 10 mm	Ap 20 mm	Ap 50 mm
CH_3CHO	1.5	8.8	14.1	9.5	11.8	11.9
CO_2	2.4	2.7	4.8	9.2	16.7	22.1
$\text{CH}_2\text{CH}_2\text{CH}_2$	505.1	514.7	501.5	277.4	269.6	261.1
O_2	114.4	104.7	85.7	72.2	56.5	9.6
C_2H_4	0	1.7	1.7	4.2	4.2	6.3
CH_2O	0	7.1	11.9	12.0	7.8	9.9
CO	1.9	7.0	14.3	18.5	41.9	57.8
CH_3OH	0	0	0	5.1	5.6	8.6
At (min)	87	99	110	90	115	94

Discussion

Inspection of the results shows that there is a good agreement between the prediction of eq. (1) and experiment. It is noted that the prediction of eq. (1) is in good agreement with the experimental results only when the initial concentration of the reactants is high. It is noted that the prediction of eq. (1) is in good agreement with the experimental results only when the initial concentration of the reactants is high. It is noted that the prediction of eq. (1) is in good agreement with the experimental results only when the initial concentration of the reactants is high.

The results obtained in the present study, and the previous indicated in the literature, are summarized in Table I.

DISCUSSION

Reaction Mechanism and Order of the Reaction

Various authors have proposed different mechanisms for the reaction and it will now be considered in greater detail in the next section.

A reaction scheme that might be proposed for the reaction is as follows: (1) $A \rightarrow B$, (2) $B \rightarrow C$, (3) $C \rightarrow D$, (4) $D \rightarrow E$, (5) $E \rightarrow F$, (6) $F \rightarrow G$, (7) $G \rightarrow H$, (8) $H \rightarrow I$, (9) $I \rightarrow J$, (10) $J \rightarrow K$, (11) $K \rightarrow L$, (12) $L \rightarrow M$, (13) $M \rightarrow N$, (14) $N \rightarrow O$, (15) $O \rightarrow P$, (16) $P \rightarrow Q$, (17) $Q \rightarrow R$, (18) $R \rightarrow S$, (19) $S \rightarrow T$, (20) $T \rightarrow U$, (21) $U \rightarrow V$, (22) $V \rightarrow W$, (23) $W \rightarrow X$, (24) $X \rightarrow Y$, (25) $Y \rightarrow Z$, (26) $Z \rightarrow A$. The reaction is first order with respect to A and second order with respect to B. The rate of reaction is independent of the concentration of C. The reaction is first order with respect to A and second order with respect to B. The rate of reaction is independent of the concentration of C.

It is generally considered that the proposed reaction scheme is a reasonable one and it is suggested that the reaction is first order with respect to A and second order with respect to B.

In a mixture of paraffin and oxygen there will be some initiating reaction to start the chain. There are a number of possibilities for

Discussion

Inspection of the results shows that there is a great similarity between the oxidation of cyclo and n-paraffins. It is indeed a tantalizing fact that many paraffinic, or substituted paraffinic, fuels show marked resemblances in their oxidation and at first sight it would seem to be an easy matter to discover what the kinetics of such oxidations are. It is only upon closer inspection that many subtle variations in behaviour are observed. Even so the general similarity between various systems seems to justify the hope that one day a unified theory may be developed which will explain all of the many diverse effects observed.

The results obtained in this investigation, and the problems indicated in the introduction will be discussed under several headings.

Slow Development and Course of the Reaction

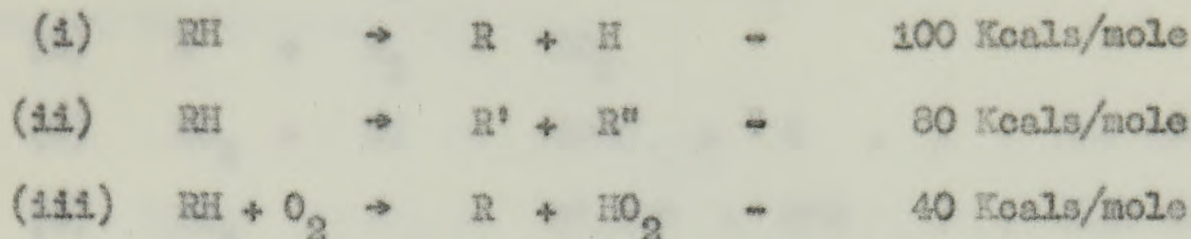
Various oxidation theories have been presented in the Introduction and it will now be convenient to consider what are the most likely reaction steps.

A reaction scheme must explain several key points, a) the induction period followed by a rapid rise in rate; b) the fact that the principal products of the reaction contain only one atom of oxygen, so that the oxygen-oxygen bond in O_2 must be broken during the oxidation; c) the mechanism for transition from one mode of oxidation to another as the temperature is raised; and d) the fact that the absolute contribution from the low temperature mechanism must actually decrease as the temperature is raised, and not merely become relatively less important than another which increases faster.

It is generally considered that the degenerate branching chain mechanism of Semenov [2] adequately explains the induction period and rapid rise in rate.

In a mixture of paraffin and oxygen there must be some initiating reaction to start the chains. There are a number of possibilities for

this, such as.

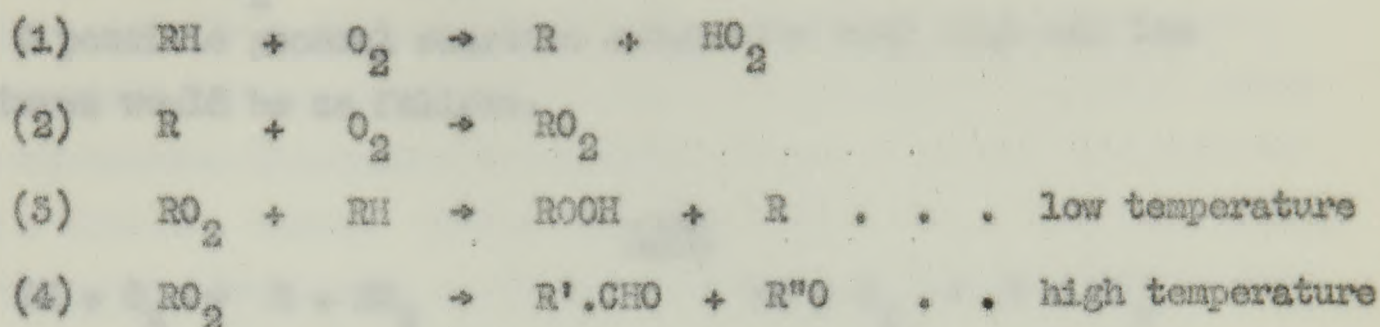


(The bond dissociation energies for reactions (i) and (ii) are approximations for hydrocarbons of from 2 to 4 carbon atoms and the activation energy of reaction (iii) is an approximation used by Semenov [64].)

On energetic grounds reaction (iii) would seem to be the most likely, since hydrocarbons oxidise in the low temperature range between 200°C and 300°C where little molecular dissociation is likely and initiation may be expected to proceed mainly through the step having the lowest activation energy.

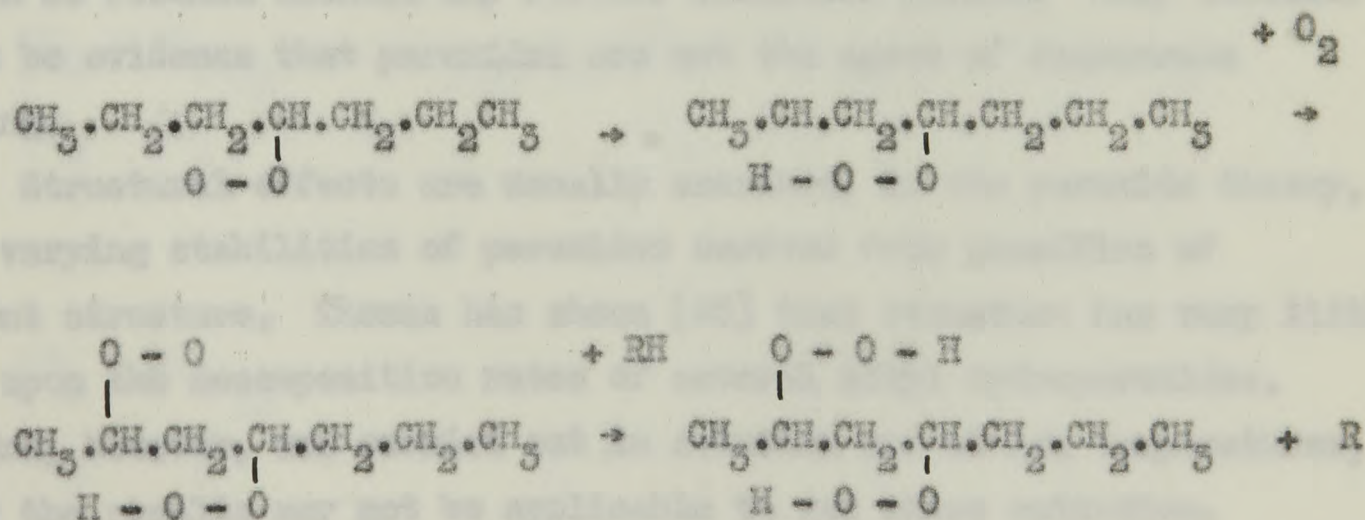
The probable fate of the alkyl radicals produced is to react with oxygen and give RO_2 radicals, rather than decomposing to olefin and lower alkyl radicals. The fate of the RO_2 radicals is open to some doubt, but when we consider the products of very low temperature oxidations, such as those in the liquid phase, and the fact that some change in mechanism must take place at higher temperatures around 300°C, then reasonable modes of reaction can be assumed.

Photo-oxidations in the liquid phase at room temperature give hydroperoxides as the main product [65], while at higher temperatures aldehydes begin to appear, and at about 300°C, in the case of the mercury-sensitized photo-oxidation of propane, Fok and Nalbandyan [65] detected only aldehydes and no peroxides. It would seem, therefore, that some peroxide forming mechanism gives way, as the temperature is raised, to an aldehyde forming one. This could be explained by the following sequence of reactions.



Reaction (4) replaces (3) as the temperature is raised and thus prevents the formation of peroxides. Aldehydes can be easily oxidised at the same temperatures as hydrocarbons [65]. In the low temperature region the hydroperoxide is probably the branching agent. This could split at the oxygen-oxygen bond as has already been suggested by Cullis and Hinshelwood [8], or be further oxidised before decomposition.

Tipper and Cartlidge [66] report that in the oxidation of n-heptane in a flow system at 250°C to 275°C dihydro peroxides and some trihydro peroxides, both alone and complexed with formaldehyde, were formed in larger concentrations than the monohydro peroxide. They do not say, however, whether these peroxides are formed by oxidation of the monohydro peroxide or isomerisation of the RO_2 radical and then oxidation, thus.

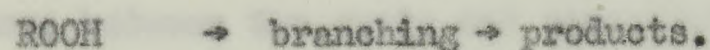


In the low temperature region both peroxides and aldehydes probably play a part in the branching reactions, and at higher temperatures the alkyl peroxides will not be formed owing to the increasingly rapid

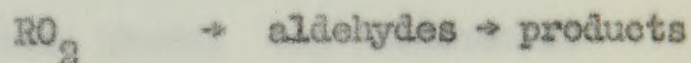
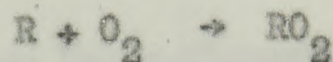
decomposition of RO_2 radicals.

A possible general reaction scheme for both high and low temperatures would be as follows.

LOW



HIGH



In the normal low temperature range of gas phase oxidations some contribution would be expected from the high temperature mechanism.

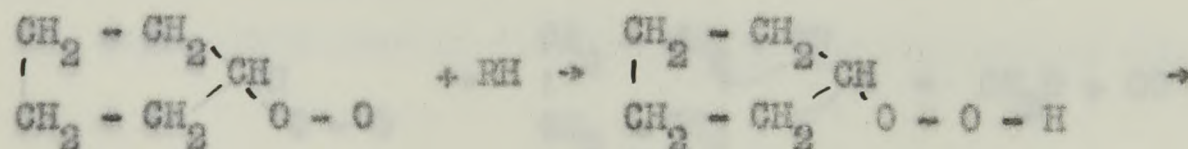
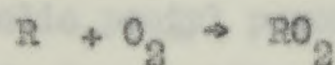
There is a certain amount of experimental evidence against the theory of a peroxide agent of degenerate branching. Shtern and Polyak [67] for propylene and Batten and Ridge [55] for isobutane and propylene showed that if the reacting mixture is withdrawn from the reaction vessel at the end of the induction period, the peroxides destroyed with mercury and the mixture replaced in the reaction vessel again, the reaction is resumed without any further induction period. They consider this to be evidence that peroxides are not the agent of degenerate branching.

Structural effects are usually ascribed, in the peroxide theory, to the varying stabilities of peroxides derived from paraffins of different structure. Thomas has shown [68] that structure has very little effect upon the decomposition rates of several alkyl hydroperoxides. This work, however, was carried out in solution and at low temperatures, so that the results may not be applicable to gas phase oxidation.

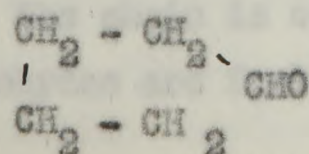
The cycloparaffins are probably oxidised, in the low temperature range, by a scheme very similar to that put forward by Cullis and Hinshelwood for the n-paraffins [8]. The rate-pressure relationship which they derive will not, however, fit all the experimental observations,

either for the cycloparaffins or, as now appears, for n-pentane itself. This can be seen from Figs. 5, 5, 12, 13, 14 and 15 where increasing oxygen pressure can cause a rise in rate to explosion, and where under certain conditions increasing hydrocarbon pressure causes the rate to rise to a limiting value. Cullis and Hinshelwood found that increasing oxygen pressure always gave a limiting rate and increasing hydrocarbon pressure a rate rising to explosion.

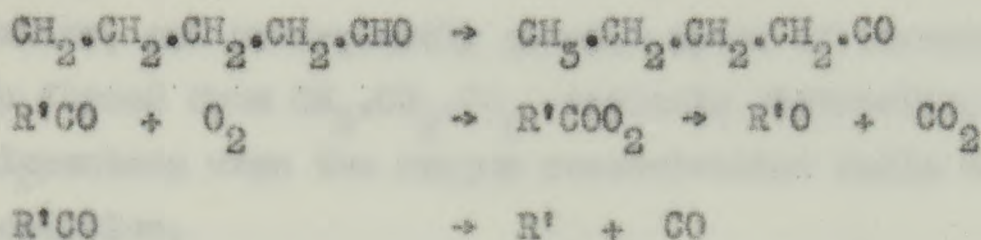
It will now be convenient to see how far cyclopentane could fit into an oxidation scheme such as that outlined above. One fundamental difference between the cyclo and open chain paraffins is that the breaking of the cycloparaffin ring at some stage of the oxidation leaves a structure with two hydrogen atoms less than the corresponding open chain compound. Nevertheless the kinetics appear to be similar. The low temperature oxidation could lead to a hydroperoxide as follows, the branching occurring while the ring was still intact.



The cyclic radical could then isomerise thus.



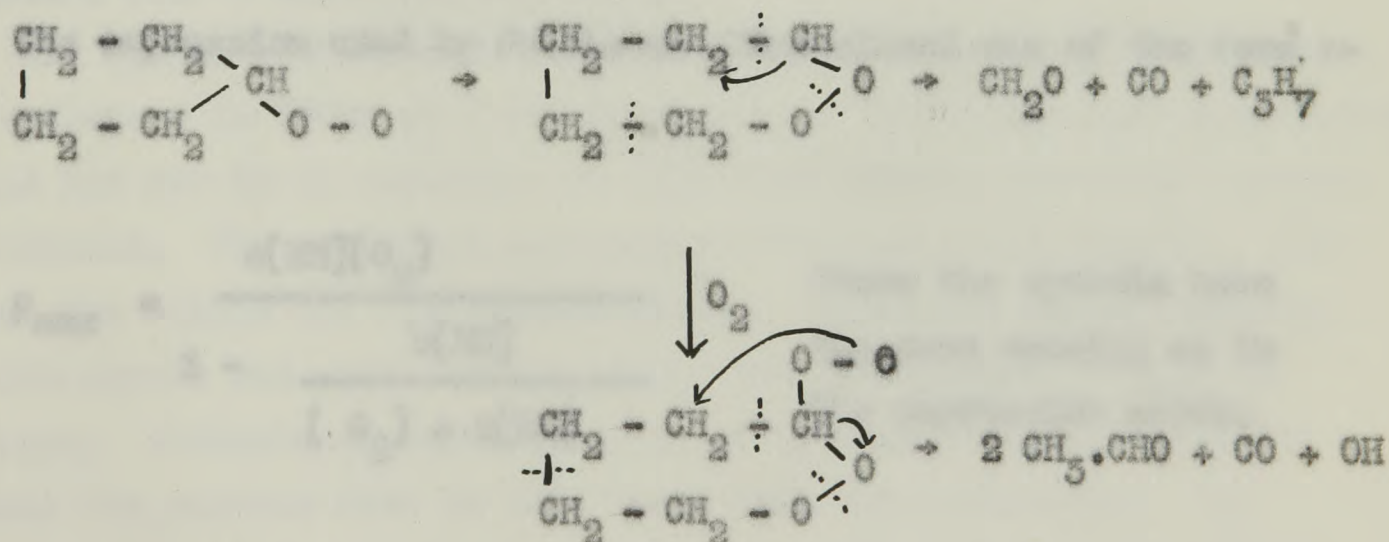
The open chain radical could then either react with more paraffin to give an aldehyde and an alkyl radical or, by further isomerisation and oxidation, give carbon dioxide and a RO radical. By decomposition a lower alkyl radical and carbon monoxide can also be obtained.



where R' is $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$

The ring having been broken, the open chain alkyl radicals could react as in the scheme put forward by Cullis and Hinshelwood [8] and described in the Introduction.

The high temperature oxidation may proceed by a scheme such as that put forward by McGowan and Tipper [55] in which it is considered that cyclic pentyl peroxy radicals are formed which either decompose or are further oxidised thus.



The chain is continued by the alkyl and hydroxy radicals while the aldehydes are further oxidised.

The aldehydes found analytically in the low temperature range can be accounted for by the decomposition of the RO radicals produced together with some contribution from the high temperature reaction mechanism. The fact that smaller amounts of the higher than of the lower aldehydes are found may be merely a result of their greater ease of oxidation, and consequently greater speed of removal. Propane is probably formed from $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2$ radicals abstracting hydrogen from the cyclopentane when the oxygen concentration falls towards the end of the reaction.

The significance of the experimental rate-pressure curves will be considered later. The curves were found to be given by a simple empirical expression of the form :-

$$p_{\max} = \frac{c}{1 - \frac{[\text{RH}][\text{O}_2]}{a[\text{RH}] + b[\text{O}_2]}}$$

Where a, b and c are constants. $[\text{RH}]$, $[\text{O}_2]$ the initial pressures of hydrocarbon and oxygen. $p_{\max}$ is the maximum rate.

The expression used by Cullis and Hinshelwood was of the form :-

$$p_{\max} = \frac{c[\text{RH}][\text{O}_2]}{1 - \frac{b[\text{RH}]}{[\text{O}_2] + c[\text{RH}]}}$$

Where the symbols have the same meaning as in the expression above.

It will be seen that the expression now found differs from this in so far as an oxygen concentration term has been added to the denominator, and the concentration terms in the numerator, which represent the initiation reaction, have been omitted.

With suitable constants the empirical expression gives results which are compared with the experimental results for cyclopentane in Fig. 40. The detailed fit is not very good but the one expression is seen to be useful in so far as it reproduces the general shapes of all four curves.

In complex branching chain systems of this kind, there are several complexities to be taken into account. Self-heating may occur at high rates and distort the form of the curves. At the point of maximum rate there may have been sufficient reactant consumption to affect their form also. As has been seen in the results section and in Figs. 3, 5, 12, 15, 14 and 15, in the oxidation of several hydrocarbons there is a limiting pressure either of hydrocarbon or of oxygen above which increase in the pressure of the other reactant causes a rapid rise in rate to explosion. Below this critical pressure of the one reactant the rate attains a limiting value with increase in the pressure of the other reactant. Thus under certain conditions the rate becomes independent of the concentration of either hydrocarbon or oxygen. The change from one type of behaviour to the other is gradual, and there is an intermediate region where the rate is linearly proportional to the concentration of one reactant over a wide pressure range.

The question now arises how far the observed type of behaviour can be explained in terms of a simple theory of the Cullis and Hinshelwood type, and how far it is necessary to take into account the complications just mentioned. The empirical expression now found would require, over and above the Cullis and Hinshelwood scheme, additional chain branching steps with oxygen and chain ending steps with hydrocarbon as well as with oxygen. Attempts at formulating a set of steady state equations to express the maximum rate on this basis were not successful. The addition of extra steps to the Cullis and Hinshelwood scheme resulted in equations which were of a very complex nature, and it was considered that the over simplification of these to make a solution possible would have given a meaningless result.

Key to Fig. 40

Full lines - experimental curves

250°C

broken lines - calculated curves

The curves have been calculated from the expression:-

$$P_{\max} = \frac{c}{1 - \frac{[RH][O_2]}{a[RH] + b[O_2]}}$$

Where $[RH]$ and $[O_2]$ are the concentrations of cyclopentane and oxygen. a, b and c are constants

$$a = 152.9$$

$$b = 43.6$$

$$c = 3.5559$$

A cyclopentane 200 mm oxygen varied

A'

B

" 40 mm " "

B'

C

oxygen 200 mm cyclopentane varied

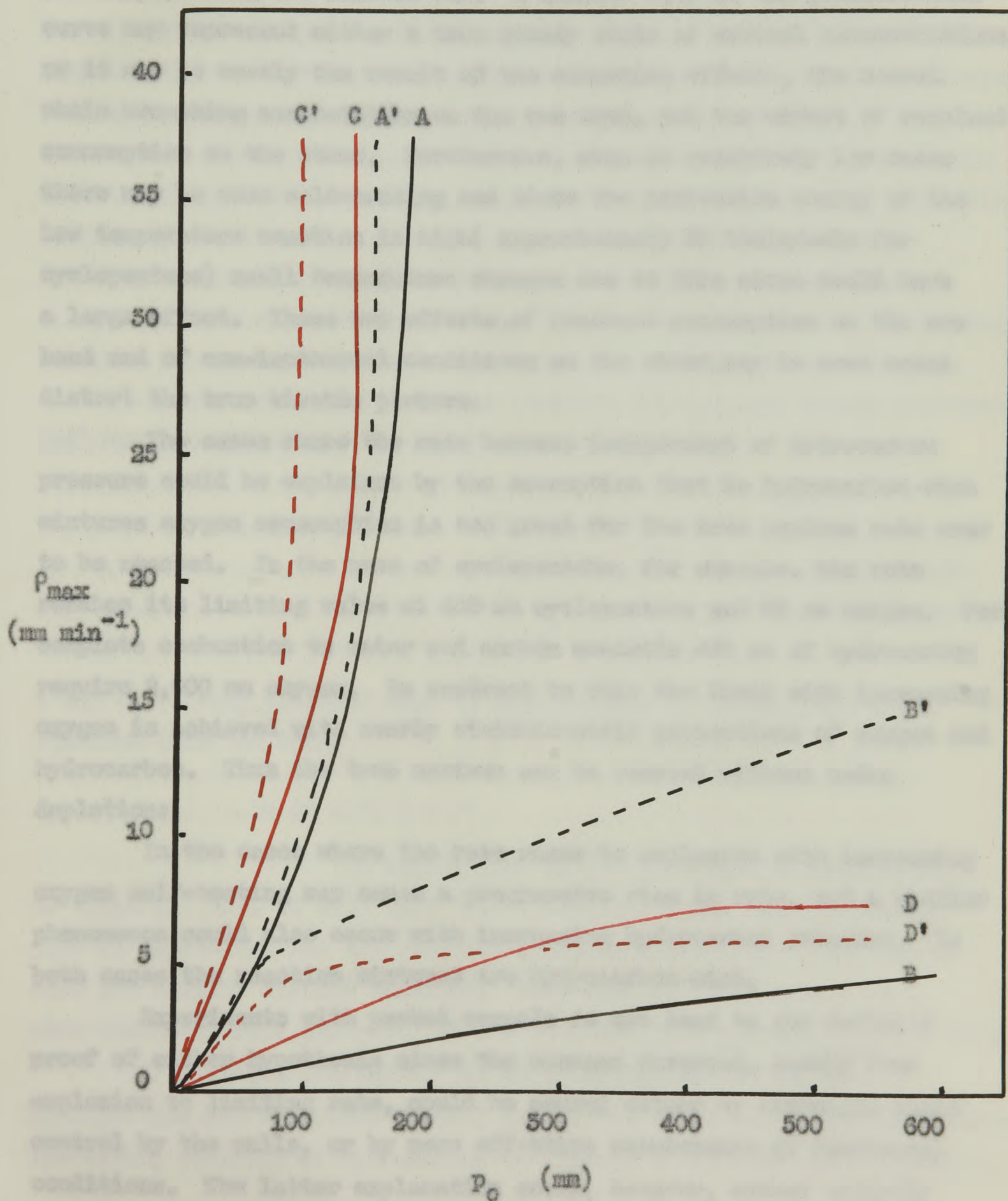
C'

D

" 60 mm " "

D'

Fig. 40 Experimental and calculated curves for the variation in maximum rate of oxidation of cyclopentane with the pressures of the reacting gases



The differences between the behaviour now observed and that found in a more limited range by Cullis and Hinshelwood could be accounted for if the complications arising from reactant consumption and self-heating are allowed for. A maximum rate in the pressure-time curve may represent either a true steady state of radical concentrations or it may be merely the result of two competing effects, the normal chain branching acceleration on the one hand, and the effect of reactant consumption on the other. Furthermore, even at relatively low rates there may be some self-heating and since the activation energy of the low temperature reaction is high (approximately 60 Kcals/mole for cyclopentane) small temperature changes due to this cause could have a large effect. These two effects, of reactant consumption on the one hand and of non-isothermal conditions on the other, may in some cases distort the true kinetic picture.

The cases where the rate becomes independent of hydrocarbon pressure could be explained by the assumption that in hydrocarbon-rich mixtures oxygen consumption is too great for the true maximum rate ever to be reached. In the case of cyclopentane, for example, the rate reaches its limiting value at 400 mm cyclopentane and 60 mm oxygen. For complete combustion to water and carbon monoxide 400 mm of hydrocarbon require 2,000 mm oxygen. In contrast to this the limit with increasing oxygen is achieved with nearly stoichiometric proportions of oxygen and hydrocarbon. Thus the true maximum can be reached without undue depletions.

In the cases where the rate rises to explosion with increasing oxygen self-heating may cause a progressive rise in rate, and a similar phenomenon could also occur with increasing hydrocarbon pressure. In both cases the reaction mixtures are hydrocarbon-rich.

Experiments with packed vessels do not lead to any definite proof of either hypothesis since the changes observed, namely from explosion to limiting rate, could be caused either by increased chain control by the walls, or by more effective maintenance of isothermal conditions. The latter explanation seems, however, rather unlikely

since rates as high as 65 mm min^{-1} (tending to a limiting value) have been measured in packed vessels while in unpacked vessels rates as low as 10 mm min^{-1} with cyclopentane and 4 mm min^{-1} with cycloheptane give place to explosion with quite small further increases of reactant pressure.

Cycloheptane (Fig.12) gives some evidence for the view that the rise in rate to explosion is inherently "kinetic" and not "non-isothermal". Only a 10 mm increase in cycloheptane pressure from 30 mm to 40 mm is required to change the form of the rate-pressure curve from that giving a limiting rate to that showing an increase to explosion. The explosion occurs with hydrocarbon-rich mixtures, while the limiting rate is transferred from the hydrocarbon-rich to the oxygen-rich mixtures.

Further evidence is given by consideration of the "net branching factors" for cyclopentane and n-pentane under different conditions.

In the early stages of the reaction the pressure change observed follows, approximately, the simple law.

$$\Delta p = Ae^{\phi t}$$

Where A and ϕ are constants.

ϕ is called the net branching factor and is a measure of the rate of acceleration of the reaction.

ϕ can be readily obtained from Δp measurements by putting the above equation into the form,

$$\ln \Delta p = \ln A + \phi t$$

so that a plot of $\ln \Delta p/t$ gives a straight line of slope ϕ . This is only true over a limited range. As the maximum rate is approached and the reactant concentrations fall, ϕ approaches zero and finally becomes negative. Some authors think that ϕ is a more characteristic parameter of the reaction than either p_{max} or θ [75].

If ϕ values are calculated from the Δp /time curves for cyclopentane and n-pentane (Figs 3 and 5) and these values plotted against increasing pressure of hydrocarbon or oxygen, it is seen that increasing

rate causes an increase in ϕ . In the case of n-pentane where increasing oxygen pressure gives a limiting rate, ϕ becomes constant also. In all other cases, however, where limiting rates are obtained with increasing reactant pressure, ϕ continues to increase (Figs. 41, 42, 43 and 44). Thus it could be argued that in the case of n-pentane the limit observed with increase in oxygen is of kinetic significance. With both cyclopentane and n-pentane increasing hydrocarbon pressure causes no fall off from linearity of the $\phi/[RH]$ plots and this suggests that the limiting rate observed may be caused by reactant consumption. In the case of cyclopentane (Fig. 44) the rate has not really reached its limit at the highest oxygen pressure and ϕ is still increasing. Furthermore the mixture would become very hydrocarbon deficient if the curve were projected any further. This case is then rather ambiguous.

To sum up, it seems that the limit to the rate reached with increasing oxygen pressure is kinetically significant. The limit reached with increasing hydrocarbon pressure, however, may be due to consumption of reactant which makes the true maximum rate unobservable. The rise in rate to explosion which occurs with increase in both oxygen and hydrocarbon pressure is probably of kinetic significance although it may be caused by self-heating.

Effect of Structure

The structural effects in the cycloparaffin series are very similar to those with the open chain paraffins where methyl groups strongly decrease the rate. The rates for a number of cycloparaffins and methyl cycloparaffins have already been given in Table 5. The structural effects are usually explained, in the peroxide theory, in terms of the stabilizing influence of the methyl groups on the decomposition of the intermediate peroxide. In the expression for the maximum rate which Cullis and Hinshelwood derived and which can be abridged to the form

Fig. 41 Comparison of maximum rate and net branching factor of

n-pentane oxidation

250°C

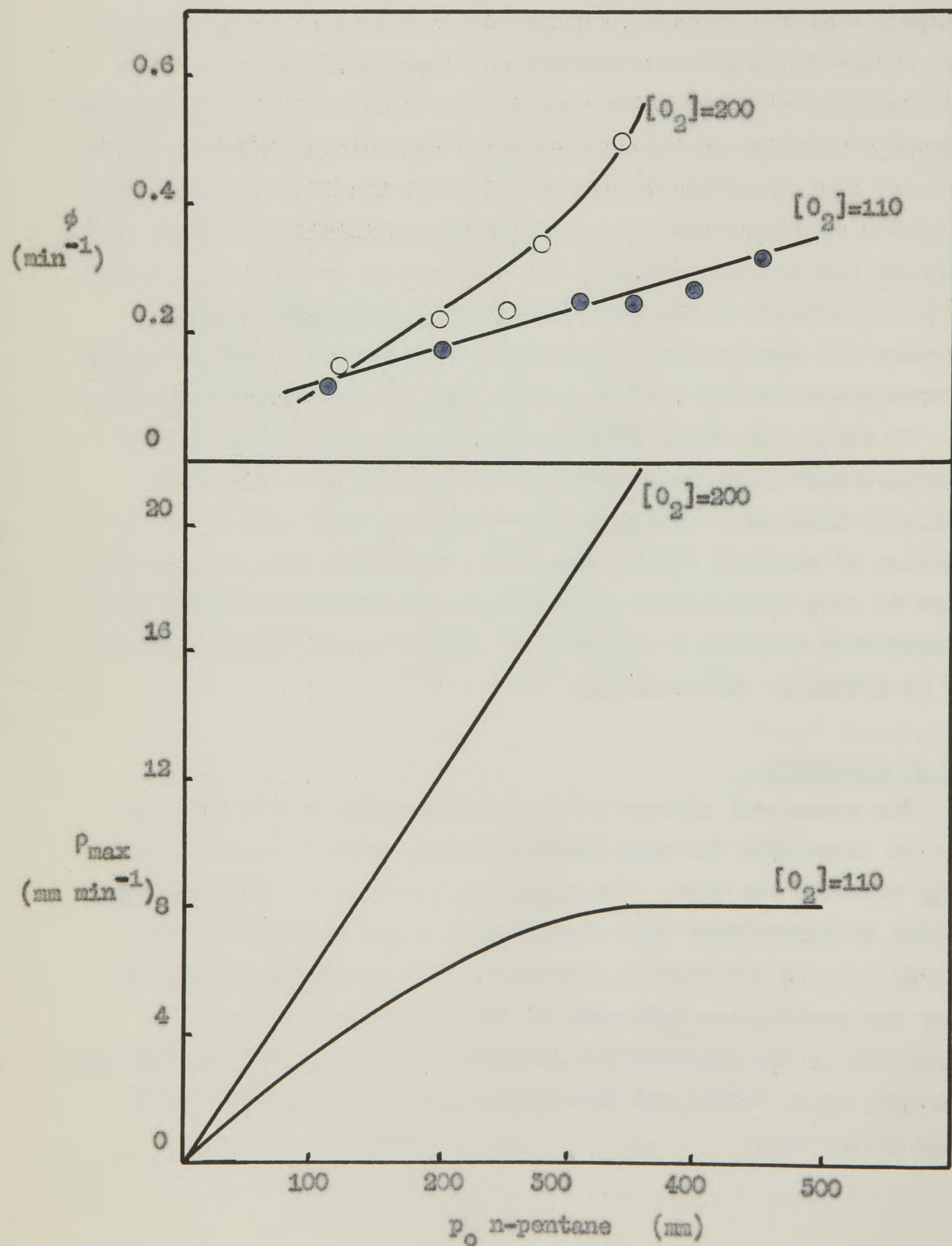


Fig. 42 Comparison of maximum rate and net branching factor of

n-pentane oxidation

250°C

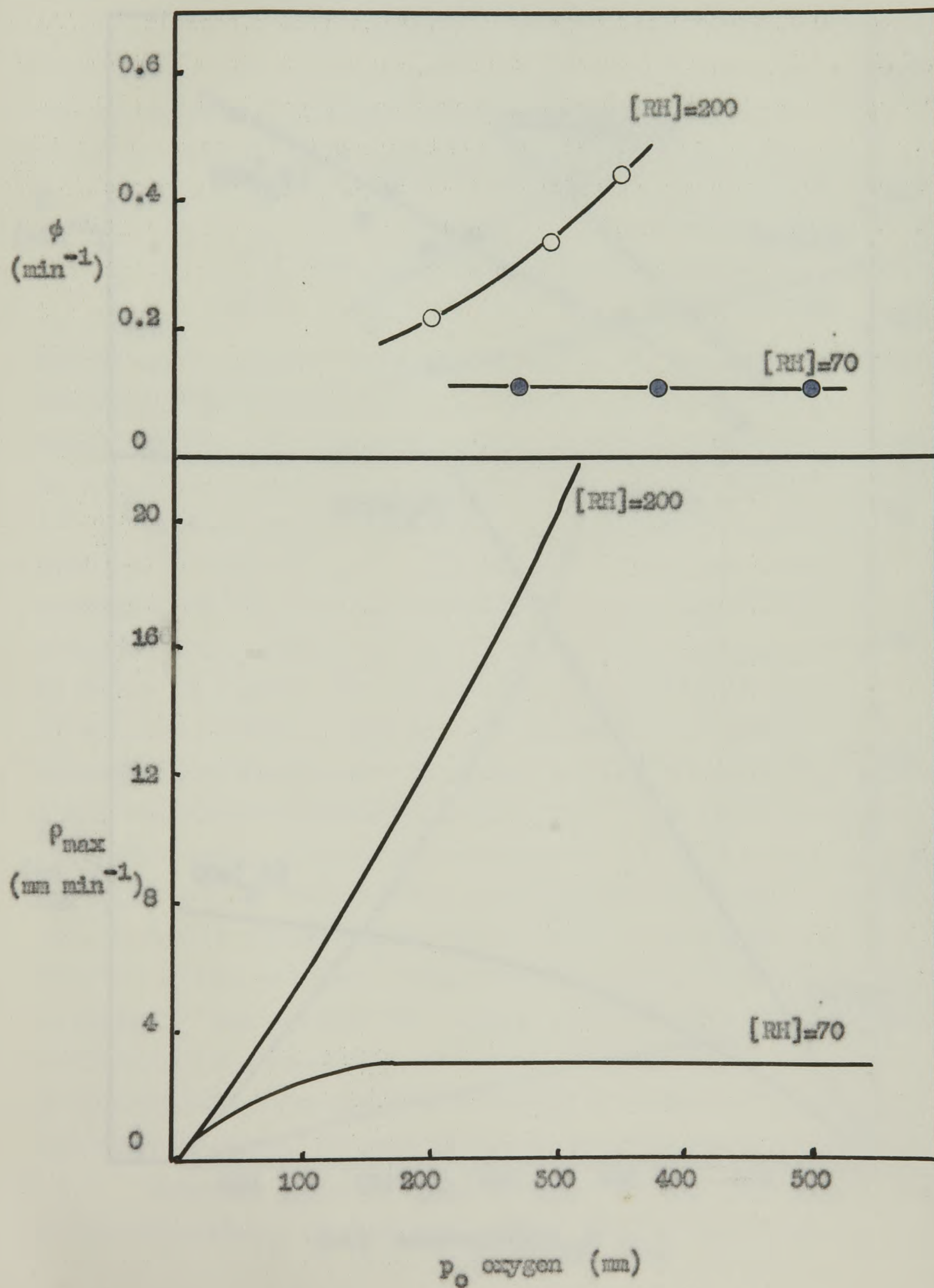


Fig. 45 Comparison of maximum rate and net branching factor of
cyclopentane oxidation 250°C

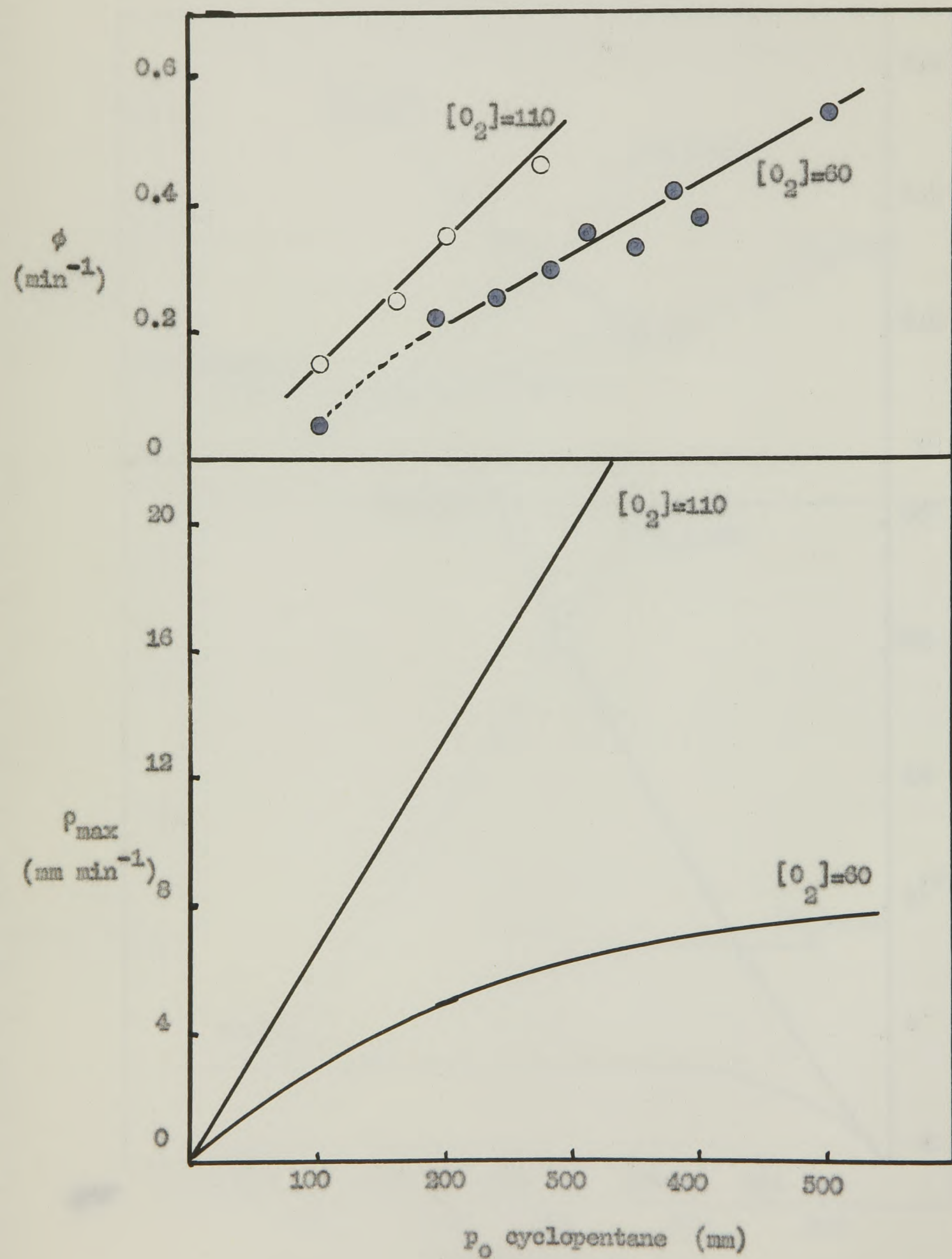
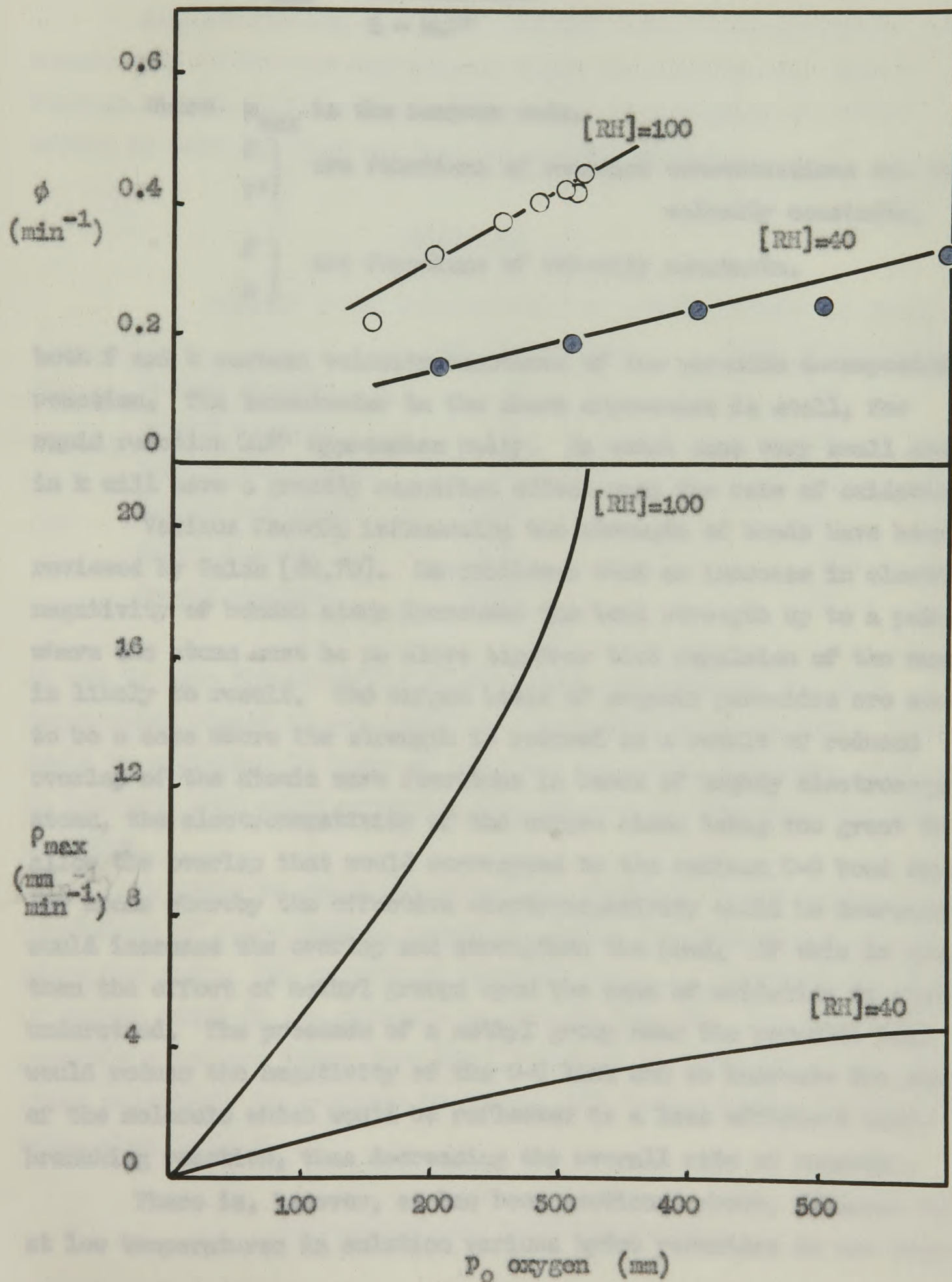


Fig. 44 Comparison of maximum rate and net branching factor of
cyclopentane oxidation 250°C



$$p_{\max} = \frac{f \cdot F}{1 - k \cdot F'}$$

Where $p_{\max}$ is the maximum rate.

F
 F' } are functions of reactant concentrations and various velocity constants.

f
 k } are functions of velocity constants.

both f and k contain velocity constants of the peroxide decomposition reaction. The denominator in the above expression is small, for rapid reaction $k \cdot F'$ approaches unity. In which case very small changes in k will have a greatly magnified effect upon the rate of oxidation.

Various factors influencing the strength of bonds have been reviewed by Walsh [69,70]. He considers that an increase in electronegativity of bonded atoms increases the bond strength up to a point where the atoms must be so close together that repulsion of the nuclei is likely to result. The oxygen bonds of organic peroxides are considered to be a case where the strength is reduced as a result of reduced overlap of the atomic wave functions in bonds of highly electronegative atoms, the electronegativity of the oxygen atoms being too great to allow the overlap that would correspond to the maximum O-O bond strength. Any means whereby the effective electronegativity could be decreased would increase the overlap and strengthen the bond. If this is true, then the effect of methyl groups upon the ease of oxidation is readily understood. The presence of a methyl group near the peroxide bond would reduce the negativity of the O-O link and so increase the stability of the molecule which would be reflected in a less efficient chain branching reaction, thus decreasing the overall rate of reaction.

There is, however, as has been mentioned above, evidence that at low temperatures in solution various hydro peroxides do not decompose

Key to Fig. 45

All rates adjusted to n-hexane and cyclohexane as unity.

- - n-paraffins
- - cycloparaffins
- - substituted cycloparaffins
 - a - methyl cyclopentane
 - b - methyl cyclohexane
 - c - 1:4 dimethyl cyclohexane
 - d - 1:3:5 trimethyl cyclohexane
 - e - 1:1:3 trimethyl cyclopentane

Fig. 45 Effect of structure upon hydrocarbon oxidation

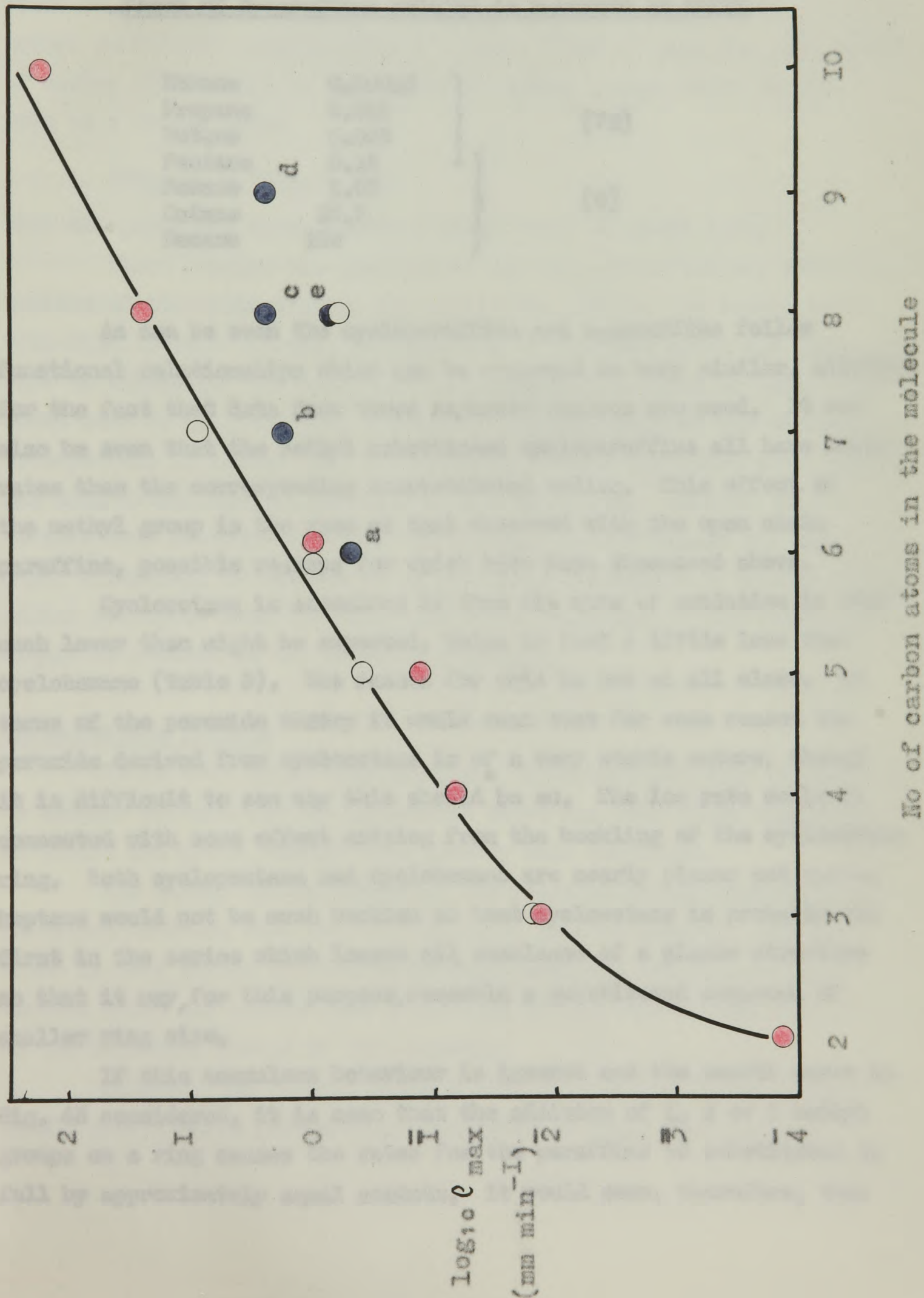


Table 21

Rates of n-paraffins related to n-hexane as unity

Ethane	0.00015	}	[72]
Propane	0.015		
Butane	0.065		
Pentane	0.15		
Hexane	1.00	}	[8]
Octane	26.7		
Decane	184		

As can be seen the cycloparaffins and n-paraffins follow functional relationships which can be regarded as very similar, allowing for the fact that data from three separate sources are used. It can also be seen that the methyl substituted cycloparaffins all have lower rates than the corresponding unsubstituted bodies. This effect of the methyl group is the same as that observed with the open chain paraffins, possible reasons for which have been discussed above.

Cyclooctane is anomalous in that its rate of oxidation is very much lower than might be expected, being in fact a little less than cyclohexane (Table 5). The reason for this is not at all clear. In terms of the peroxide theory it would mean that for some reason the peroxide derived from cyclooctane is of a very stable nature, though it is difficult to see why this should be so. The low rate could be connected with some effect arising from the buckling of the cyclooctane ring. Both cyclopentane and cyclohexane are nearly planar and cycloheptane would not be much buckled so that cyclooctane is probably the first in the series which loses all semblance of a planar structure so that it may, for this purpose, resemble a substituted compound of smaller ring size.

If this anomalous behaviour is ignored and the smooth curve in Fig. 45 considered, it is seen that the addition of 1, 2 or 3 methyl groups on a ring causes the rates for the paraffins so substituted to fall by approximately equal amounts. It would seem, therefore, that

the effect of methyl groups upon the rate of cycloparaffin oxidation is additive. Thus if the methyl group is assigned an antagonistic value of α and if the rate of oxidation of a cycloparaffin is R and of a methyl substituted cycloparaffin R^* (where R and R^* have the same number of carbon atoms) then if the number of methyl groups added on the ring is x we may write

$$\log_{10} R^* = \log_{10} R - \alpha x$$

With the paraffins investigated α has a value of about 0.5 .

There remains the question of the comparison between corresponding members of the cycloparaffin and n-paraffin series. As can be seen from Figs. 5 to 8 although cyclopentane is oxidised about 2.5 times as fast as n-pentane, its induction period is 2 to 5 times as long. This would seem to indicate that although the development of the chains in cyclopentane is slower than in n-pentane, once a branching chain reaction has been established it proceeds at a higher rate. Whether this is because some inherent stability of the ring system delays the onset of rapid branching, or because of the possible production of easily oxidised higher aldehydes when the ring breaks, as suggested in the scheme above, cannot be decided on the evidence available.

Heterogeneous Effects

It is well known that gas phase oxidations are very susceptible to surface effects and the incidental short and long range variations in silica and pyrex vessels have already been mentioned.

The effect of the nature of the reaction vessel surface on the oxidation kinetics will now be considered in more detail. Although there is very little difference between pyrex and silica surfaces various salts and metals have a profound effect both on the rate and on the induction period of the reaction.

Although ~~the~~ general reasons why, in such reactions, surface should play a large part are not difficult to give, more precise

identification of the individual reaction steps leading to inhibition or acceleration is difficult.

The length of the induction period depends both on the rate at which the reaction chains are initiated and on the acceleration. Only the earliest stages of the reaction are determined by the rate of the initiating process itself. A change in the catalytic action of the surface could either facilitate or retard the initial production of radicals. As the chains develop, the walls of the vessel may take up radicals or free atoms and so terminate chains (and this with varying efficiency), and the removal of a branching intermediate will effectively retard the reaction.

It has been known for some years that potassium chloride has an effect upon the kinetics of propane oxidation. Pease and his co-workers [74,75,76,77] oxidising propane in a flow system at temperatures between 325°C and 400°C found that coating the reaction tube with KCl reduced the yield of peroxides almost to zero, without other effect on the reaction. Static experiments, on the other hand, at 270°C to 280°C with a KCl coated pyrex reaction vessel showed a greatly lengthened induction period.

Similar results have been obtained more recently by Egerton, Minkoff and Solooja [78] and also by Walsh [79] who have studied the effect of surfaces in the oxidation of methane at about 500°C. Among other points, Walsh divides the surfaces into three types according to their effect on the rate of oxidation. These are :-

- i) Acidic : silicic acid, boric acid, phosphoric acid,
germanium dioxide.
- ii) Salts in general and metallic oxides.
- iii) Metals.

The rates in vessels having the above types of surfaces fell in the order i) > ii) > iii), the third type, metals having the slowest rate.

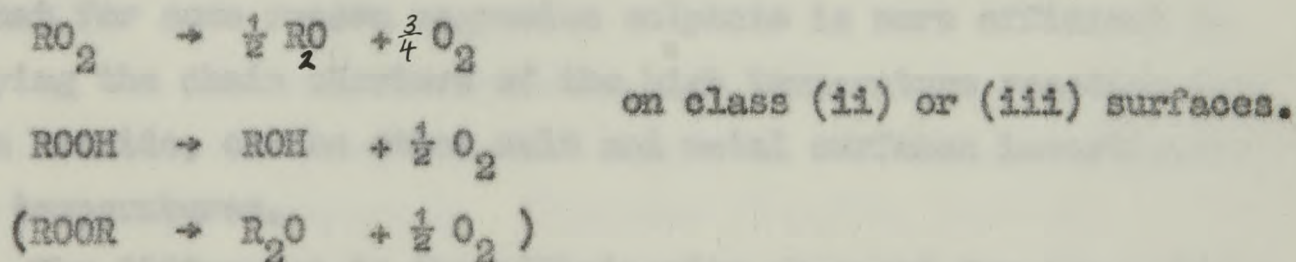
The activity is ascribed to the destruction of HO_2 radicals and

H_2O_2 molecules on the surface according to the scheme below.

<u>Type of Surface</u>			
	(i)	(ii)	(iii)
HO_2	Either preserved or $\text{HO}_2 \rightarrow (\text{HO}_2)_{\text{abs}} \rightarrow \text{H}^+$ $\frac{1}{2} \text{H}_2\text{O}_2 + \frac{1}{2} \text{O}_2$	$\text{HO}_2 \xrightarrow{e} \frac{1}{2} \text{H}_2\text{O} + \frac{3}{4} \text{O}_2$ Diffusion controlled	Same as (ii)
H_2O_2	Preserved	$\text{H}_2\text{O}_2 \xrightarrow{e} \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$ Not diffusion controlled	Diffusion controlled

The activity is supposed to be due to the ability of the surfaces to donate electrons to the adsorbed radical and so facilitate its decomposition.

If this is the correct interpretation of such effects at high temperature it is interesting to consider the analogy of a possible low temperature inhibition caused by the removal of RO_2 and ROOH (or ROOR).



At first sight this is not very promising since the ether or alcohol produced is very easily oxidised. During their oxidation, however, peroxides or peroxy radicals would be formed and these could again be destroyed. If the processes given above for RO_2 and ROOH removal are very rapid, then chain branching due to the peroxide could be delayed for a considerable time.

The results of the present investigation show that a wide variety of salts lengthen the induction period of cyclopentane oxidation considerably. Since it is not necessary to coat the whole inside of the reaction vessel with salt but only to introduce a layer on the bottom of it (LiBr and LiCl), and since gold, platinum and silver were also active in the form of wire or foil, the effect is more probably due to the destruction of a branching intermediate than to the suppression of an initiation reaction on the surface. For the same reason the destruction of a labile peroxide intermediate is perhaps more likely than that of a transient peroxy radical.

Inhibition by the destruction of an intermediate hydroperoxide would explain the fall in efficiency as the temperature is raised and the reaction proceeds more and more through RO_2 radical decomposition. It would also explain the fall in rate observed in the salt-coated vessels.

The rate is hardly affected at high temperatures by a coating of lithium bromide (Fig. 51) but at lower temperatures where the peroxide branching mechanism might be expected to operate, a very marked fall is observed. Magnesium sulphate, on the other hand, lowers the rate over the whole accessible temperature range. If we accept the explanation given above for radical and peroxide removal, this would mean that for some reason magnesium sulphate is more efficient in destroying the chain carriers of the high temperature reaction than lithium bromide, or the other salt and metal surfaces investigated at higher temperatures.

The difference in the efficiencies observed for the various salts may be the result of a number of conflicting factors. If Walsh's explanation of HO_2 and H_2O_2 destruction and the analogous explanation in terms of RO_2 and $ROOH$ is correct, then it might be expected that the efficiency of the salts would lie in the order of their ability to donate electrons. Some such order is indeed observable and although other factors must clearly play a part, this electronic effect is

probably the most important single influence. It should be mentioned that there was no observable order of efficiencies in relation to crystal structure.

Some surfaces lose their activity with use, and in the case of silver wire the activity lost during a number of reactions could be completely restored by wiping the wire clean with cotton wool. The platinum wire required rather more drastic treatment to restore its activity but it would seem possible that the covering of the surface layer with carbon or reaction products of high molecular weight can cause the loss of efficiency observed.

Further evidence that it is the peroxides themselves which are destroyed by the salt surfaces is given by the analytical results for the total peroxide concentration found during the course of reactions carried out in salt-coated and in uncoated vessels (Figs 37,38). In a lithium bromide coated vessel at 400°C the peroxide concentration is almost zero throughout the reaction, although there is very little change in rate. The same is true for potassium fluoride coated vessels, though in this case the rate is somewhat depressed, probably as a result of the destruction of high temperature chain carriers such as HO_2 or RO_2 . The peroxide present at 400°C is almost certainly hydrogen peroxide since other evidence suggests that alkyl peroxides are not formed above about 350°C .

In the low temperature range, at 250°C , lithium bromide could not be used for these experiments because it completely suppresses the reaction at this temperature. Potassium fluoride, however, could be used (Fig. 38) and in its presence peroxide concentrations were found to be reduced by about one half, and the rate also to be greatly reduced.

At 400°C the potassium fluoride coating in the reaction vessel lowers the rate by a factor of 4.6 and the peroxide nearly to zero. At 250°C it lowers the rate by a factor of 12.5 while halving the peroxide concentration. The results with lithium bromide at 400°C suggest that peroxides are not essential for the development of the reaction chains

in the high temperature region. It would seem therefore that in the low temperature oxidation mechanism not only do the salt coatings exert their effect through the destruction of peroxides (and possibly of other radicals as well), but also that a peroxide intermediate must play an important part in the kinetics.

Homogeneous Additions

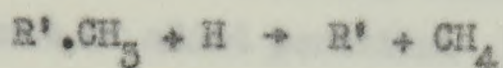
The effect of various homogeneous additions on the oxidation of cycloparaffins will now be considered. As might be expected the additions which have no effect on the rate and induction period are found to be substances which are probably stable under the conditions of the experiment. Materials, on the other hand, which either decompose to give radicals, or can be attacked during the reaction to give radicals, usually have some effect.

Of the materials which had an accelerating effect upon the rate the mode of action of the higher aldehydes is fairly straightforward. They are easily oxidised, at the temperature of the experiments, in a chain manner and it is evident that these chains can initiate the main reaction. The greater efficiency of the aldehydes observed in the oxidation of cyclopropane is probably a result of the higher temperature at which the experiments were carried out, since the initiator itself will be more rapidly oxidised giving a corresponding increase in the rate of radical production. Since the addition increases the total aldehyde concentration during the reaction, and oxidation of any aldehyde can lead to chain propagation, it is evident that the rate of reaction might be expected to increase with increasing aldehyde addition, as is found experimentally.

Formaldehyde has a rather more complex effect on the induction period than do the higher aldehydes. It may either retard or accelerate the initial stages of the reaction. The inhibition may be caused by a mechanism such as that proposed by Cullis [25]. He considers that reaction of formaldehyde with alkyl radicals results in chains of lower activity.



Cullis suggests that the hydrogen atom reacts with more paraffin to produce an alkyl radical which is of lower carbon content than the original fuel, and which is considered to be less reactive.



On the other hand, reaction with oxygen would continue the chains in a branching manner,



or the formaldehyde itself could be oxidised.

It is the balance of such competing reactions which, presumably, causes the variety of effects found when formaldehyde is added to different systems of paraffin and oxygen.

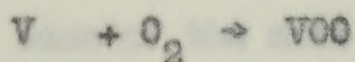
Ditertiary butylperoxide, being very unstable at the temperature of the experiments, will, on being admitted to the reaction vessel, produce a burst of methyl radicals which can initiate reaction chains.

In a salt-coated vessel, where the induction periods are very long, the addition of peroxide as an initiator seems to be an "all or none" process (Fig. 28), in contrast to acetaldehyde addition where the induction period can be steadily reduced by increasing amounts of aldehyde. A possible explanation of these effects will be considered.

The end of the induction period can be regarded as the time at which a minimum concentration of branching intermediate has been built up so that the reaction chains begin to accelerate rapidly. If the oxidation of acetaldehyde is much slower than the decomposition of ditertiary butylperoxide at the temperature of the experiments, then with added acetaldehyde a slow accumulation of intermediate, derived from the aldehyde oxidation, is superimposed on that produced by the usual reaction chains. Thus a progressive fall in the induction period might be expected on adding increasingly larger amounts of aldehyde.

Ditertiary butylperoxide, on the other hand, produces a very rapid burst of radicals in its decomposition, since its half-life at the temperature of the experiments is of the order of 0.8 sec. Its final decomposition products, acetone and ethane, are more or less inactive. The radicals produced will quickly give rise to some concentration of some branching intermediate by initiating chains, the number of which increases with the amount of added peroxide. This rapidly produced concentration of intermediate may be high enough to give rapid chain branching, in which case the induction period will be nearly zero. It may, however, not be sufficient for this, in which case, being a highly labile substance, it decays faster than it can autocatalytically generate a high concentration of itself.

The diminution of the induction period observed after ditertiary butylperoxide has been left in the vessel for many times its half-life before the admission of hydrocarbon and oxygen, is presumably caused by some surface activation. The most obvious cause of this is that radicals have been adsorbed on the vessel walls. If radicals of almost any type are adsorbed on the walls they will facilitate the initiation of chains in the gas phase. Thus if V is an adsorbed radical, possible reactions would be



the alkyl radical starting chains in the gas phase in the normal way. Such a mechanism agrees with the observations that the rates in such "activated" vessels are unaffected.

The effect of di- and triethylamine on the rate of oxidation and induction period of cyclopentane can be explained in terms of the formation of acetaldehyde during their oxidation [30]. This accounts for the fact that the effect both upon the rate and induction period is similar to that observed with added acetaldehyde. Ethylamine and ammonia, not having acetaldehyde as an oxidation product under the

conditions of the experiment, have no effect on cyclopentane oxidation.

Bromine probably exerts its effect on cyclopentane oxidation through the formation of hydrogen bromide by radical attack. Hydrogen bromide is known to be very efficient in catalysing hydrocarbon oxidations [81] and allowing them to proceed at temperatures a hundred degrees below those normally necessary for reaction. This is believed to occur through some such mechanism as.



An increase in the rate of the initiating reaction would both reduce the induction period and increase the rate. Neither hydrogen chloride nor hydrogen iodide react in this way quite so easily as hydrogen bromide does, which may account for the inactivity of chlorine and iodine in the oxidation of cyclopentane.

Those substances which have no effect on the reaction, such as ammonia, carbon tetrachloride, carbon tetrafluoride and so on, are presumably not attacked by either the reactants or the radicals present under the prevailing conditions.

Some of the most interesting results in this investigation are those relating to the effect of surfaces on the course of the oxidations. It has been seen that a wide variety of surfaces exert a most marked effect in prolonging the induction period, in some cases almost indefinitely, and in reducing the maximum rate of reaction. The action of such surfaces is probably connected with the destruction of active peroxide intermediates. Although the chains by which reaction is propagated are almost certainly initiated on the vessel walls, the prevention of this initiation does not seem to be the method of action of the inhibitors. Therefore the control of ignition by salts would be expected to be most effective when the salt is widely distributed through the gas. In view of the practical importance of the control

APPENDIX A

Table 11: For Figure 3 and 4

Variation of Induction Time and Induction Period with pressure of cyclopentane and isopentane at different liquid temperatures.

120°C		Silicon Vessel		
P_0 Cyclopentane (mm)	P_0 Isopentane (mm)	P_{ind} (mm $\times 10^{-2}$)	t_{ind} (seconds)	t_{ind} (min $\times 10^{-2}$)
100.0	60.0	5.7	20.0	0.333
112.5	60.0	6.0	21.0	0.350
125.0	60.0	6.3	22.0	0.367
137.5	60.0	6.6	23.0	0.383
150.0	60.0	6.9	24.0	0.400
162.5	60.0	7.2	25.0	0.417
175.0	60.0	7.5	26.0	0.433
187.5	60.0	7.8	27.0	0.450
200.0	60.0	8.1	28.0	0.467
212.5	60.0	8.4	29.0	0.483
225.0	60.0	8.7	30.0	0.500
237.5	60.0	9.0	31.0	0.517
250.0	60.0	9.3	32.0	0.533
262.5	60.0	9.6	33.0	0.550
275.0	60.0	9.9	34.0	0.567
287.5	60.0	10.2	35.0	0.583
300.0	60.0	10.5	36.0	0.600
312.5	60.0	10.8	37.0	0.617
325.0	60.0	11.1	38.0	0.633
337.5	60.0	11.4	39.0	0.650
350.0	60.0	11.7	40.0	0.667
362.5	60.0	12.0	41.0	0.683
375.0	60.0	12.3	42.0	0.700
387.5	60.0	12.6	43.0	0.717
400.0	60.0	12.9	44.0	0.733
412.5	60.0	13.2	45.0	0.750
425.0	60.0	13.5	46.0	0.767
437.5	60.0	13.8	47.0	0.783
450.0	60.0	14.1	48.0	0.800
462.5	60.0	14.4	49.0	0.817
475.0	60.0	14.7	50.0	0.833
487.5	60.0	15.0	51.0	0.850
500.0	60.0	15.3	52.0	0.867
512.5	60.0	15.6	53.0	0.883
525.0	60.0	15.9	54.0	0.900
537.5	60.0	16.2	55.0	0.917
550.0	60.0	16.5	56.0	0.933
562.5	60.0	16.8	57.0	0.950
575.0	60.0	17.1	58.0	0.967
587.5	60.0	17.4	59.0	0.983
600.0	60.0	17.7	60.0	1.000
612.5	60.0	18.0	61.0	1.017
625.0	60.0	18.3	62.0	1.033
637.5	60.0	18.6	63.0	1.050
650.0	60.0	18.9	64.0	1.067
662.5	60.0	19.2	65.0	1.083
675.0	60.0	19.5	66.0	1.100
687.5	60.0	19.8	67.0	1.117
700.0	60.0	20.1	68.0	1.133
712.5	60.0	20.4	69.0	1.150
725.0	60.0	20.7	70.0	1.167
737.5	60.0	21.0	71.0	1.183
750.0	60.0	21.3	72.0	1.200
762.5	60.0	21.6	73.0	1.217
775.0	60.0	21.9	74.0	1.233
787.5	60.0	22.2	75.0	1.250
800.0	60.0	22.5	76.0	1.267
812.5	60.0	22.8	77.0	1.283
825.0	60.0	23.1	78.0	1.300
837.5	60.0	23.4	79.0	1.317
850.0	60.0	23.7	80.0	1.333
862.5	60.0	24.0	81.0	1.350
875.0	60.0	24.3	82.0	1.367
887.5	60.0	24.6	83.0	1.383
900.0	60.0	24.9	84.0	1.400
912.5	60.0	25.2	85.0	1.417
925.0	60.0	25.5	86.0	1.433
937.5	60.0	25.8	87.0	1.450
950.0	60.0	26.1	88.0	1.467
962.5	60.0	26.4	89.0	1.483
975.0	60.0	26.7	90.0	1.500
987.5	60.0	27.0	91.0	1.517
1000.0	60.0	27.3	92.0	1.533
1012.5	60.0	27.6	93.0	1.550
1025.0	60.0	27.9	94.0	1.567
1037.5	60.0	28.2	95.0	1.583
1050.0	60.0	28.5	96.0	1.600
1062.5	60.0	28.8	97.0	1.617
1075.0	60.0	29.1	98.0	1.633
1087.5	60.0	29.4	99.0	1.650
1100.0	60.0	29.7	100.0	1.667
1112.5	60.0	30.0	101.0	1.683
1125.0	60.0	30.3	102.0	1.700
1137.5	60.0	30.6	103.0	1.717
1150.0	60.0	30.9	104.0	1.733
1162.5	60.0	31.2	105.0	1.750
1175.0	60.0	31.5	106.0	1.767
1187.5	60.0	31.8	107.0	1.783
1200.0	60.0	32.1	108.0	1.800
1212.5	60.0	32.4	109.0	1.817
1225.0	60.0	32.7	110.0	1.833
1237.5	60.0	33.0	111.0	1.850
1250.0	60.0	33.3	112.0	1.867
1262.5	60.0	33.6	113.0	1.883
1275.0	60.0	33.9	114.0	1.900
1287.5	60.0	34.2	115.0	1.917
1300.0	60.0	34.5	116.0	1.933
1312.5	60.0	34.8	117.0	1.950
1325.0	60.0	35.1	118.0	1.967
1337.5	60.0	35.4	119.0	1.983
1350.0	60.0	35.7	120.0	2.000
1362.5	60.0	36.0	121.0	2.017
1375.0	60.0	36.3	122.0	2.033
1387.5	60.0	36.6	123.0	2.050
1400.0	60.0	36.9	124.0	2.067
1412.5	60.0	37.2	125.0	2.083
1425.0	60.0	37.5	126.0	2.100
1437.5	60.0	37.8	127.0	2.117
1450.0	60.0	38.1	128.0	2.133
1462.5	60.0	38.4	129.0	2.150
1475.0	60.0	38.7	130.0	2.167
1487.5	60.0	39.0	131.0	2.183
1500.0	60.0	39.3	132.0	2.200
1512.5	60.0	39.6	133.0	2.217
1525.0	60.0	39.9	134.0	2.233
1537.5	60.0	40.2	135.0	2.250
1550.0	60.0	40.5	136.0	2.267
1562.5	60.0	40.8	137.0	2.283
1575.0	60.0	41.1	138.0	2.300
1587.5	60.0	41.4	139.0	2.317
1600.0	60.0	41.7	140.0	2.333
1612.5	60.0	42.0	141.0	2.350
1625.0	60.0	42.3	142.0	2.367
1637.5	60.0	42.6	143.0	2.383
1650.0	60.0	42.9	144.0	2.400
1662.5	60.0	43.2	145.0	2.417
1675.0	60.0	43.5	146.0	2.433
1687.5	60.0	43.8	147.0	2.450
1700.0	60.0	44.1	148.0	2.467
1712.5	60.0	44.4	149.0	2.483
1725.0	60.0	44.7	150.0	2.500
1737.5	60.0	45.0	151.0	2.517
1750.0	60.0	45.3	152.0	2.533
1762.5	60.0	45.6	153.0	2.550
1775.0	60.0	45.9	154.0	2.567
1787.5	60.0	46.2	155.0	2.583
1800.0	60.0	46.5	156.0	2.600
1812.5	60.0	46.8	157.0	2.617
1825.0	60.0	47.1	158.0	2.633
1837.5	60.0	47.4	159.0	2.650
1850.0	60.0	47.7	160.0	2.667
1862.5	60.0	48.0	161.0	2.683
1875.0	60.0	48.3	162.0	2.700
1887.5	60.0	48.6	163.0	2.717
1900.0	60.0	48.9	164.0	2.733
1912.5	60.0	49.2	165.0	2.750
1925.0	60.0	49.5	166.0	2.767
1937.5	60.0	49.8	167.0	2.783
1950.0	60.0	50.1	168.0	2.800
1962.5	60.0	50.4	169.0	2.817
1975.0	60.0	50.7	170.0	2.833
1987.5	60.0	51.0	171.0	2.850
2000.0	60.0	51.3	172.0	2.867
2012.5	60.0	51.6	173.0	2.883
2025.0	60.0	51.9	174.0	2.900
2037.5	60.0	52.2	175.0	2.917
2050.0	60.0	52.5	176.0	2.933
2062.5	60.0	52.8	177.0	2.950
2075.0	60.0	53.1	178.0	2.967
2087.5	60.0	53.4	179.0	2.983
2100.0	60.0	53.7	180.0	3.000
2112.5	60.0	54.0	181.0	3.017
2125.0	60.0	54.3	182.0	3.033
2137.5	60.0	54.6	183.0	3.050
2150.0	60.0	54.9	184.0	3.067
2162.5	60.0	55.2	185.0	3.083
2175.0	60.0	55.5	186.0	3.100
2187.5	60.0	55.8	187.0	3.117
2200.0	60.0	56.1	188.0	3.133
2212.5	60.0	56.4	189.0	3.150
2225.0	60.0	56.7	190.0	3.167
2237.5	60.0	57.0	191.0	3.183
2250.0	60.0	57.3	192.0	3.200
2262.5	60.0	57.6	193.0	3.217
2275.0	60.0	57.9	194.0	3.233
2287.5	60.0	58.2	195.0	3.250
2300.0	60.0	58.5	196.0	3.267
2312.5	60.0	58.8	197.0	3.283
2325.0	60.0	59.1	198.0	3.300
2337.5	60.0	59.4	199.0	3.317
2350.0	60.0	59.7	200.0	3.333
2362.5	60.0	60.0	201.0	3.350
2375.0	60.0	60.3	202.0	3.367
2387.5	60.0	60.6	203.0	3.383
2400.0	60.0	60.9	204.0	3.400
2412.5	60.0	61.2	205.0	3.417
2425.0	60.0	61.5	206.0	3.433
2437.5	60.0	61.8	207.0	3.450
2450.0	60.0	62.1	208.0	3.467
2462.5	60.0	62.4	209.0	3.483
2475.0	60.0	62.7	210.0	3.500
2487.5	60.0	63.0	211.0	3.517
2500.0	60.0	63.3	212.0	3.533
2512.5	60.0	63.6	213.0	3.550
2525.0	60.0	63.9	214.0	3.567
2537.5	60.0	64.2	215.0	3.583
2550.0	60.0	64.5	216.0	3.600
2562.5	60.0	64.8	217.0	3.617
2575.0	60.0	65.1	218.0	3.633
2587.5	60.0	65.4	219.0	3.650
2600.0	60.0	65.7	220.0	3.667
2612.5	60.0	66.0	221.0	3.683
2625.0	60.0	66.3	222.0	3.700
2637.5	60.0	66.6	223.0	3.717
2650.0	60.0	66.9	224.0	3.733
2662.5	60.0	67.2	225.0	3.750
2675.0	60.0	67.5	226.0	3.767
2687.5	60.0	67.8	227.0	3.783
2700.0	60.0	68.1	228.0	3.800
2712.5	60.0	68.4	229.0	3.817
2725.0	60.0	68.7	230.0	3.833
2737.5	60.0	69.0	231.0	3.850
2750.0	60.0	69.3	232.0	3.867
2762.5	60.0	69.6	233.0	3.883
2775.0	60.0	69.9	234.0	3.900
2787.5	60.0	70.2	235.0	3.917
2800.0	60.0	70.5	236.0	3.933
2812.5	60.0	70.8	237.0	3.950
2825.0	60.0	71.1	238.0	3.967
2837.5	60.0	71.4	239.0	3.983
2850.0	60.0	71.7	240.0	4.000
2862.5	60.0	72.0	241.0	4.017
2875.0	60.0	72.3	242.0	4.033
2887.5	60.0	72.6	243.0	4.050
2900.0	60.0	72.9	244.0	4.067
2912.5				

Appendix ATable (1) for Figs. 3 and 4

Variation of Maximum Rate and Induction Period with pressure of cyclopentane and n-pentane at different Oxygen Pressures.

250°C Silica Vessel.				
p_{O} Cyclopentane (mm)	p_{O} Oxygen (mm)	ρ_{max} (mm min ⁻¹)	θ (mins.secs)	$1/\theta$ (min ⁻¹)
100.0	60.9	2.7	34.50	0.029
192.5	60.6	4.8	13.50	0.074
241.9	61.6	6.1	9.50	0.105
281.5	62.5	5.2	9.20	0.106
307.5	58.8	6.5	7.50	0.135
353.6	60.9	6.6	6.45	0.148
390.9	61.7	7.0	5.50	0.182
402.5	56.4	6.7	5.45	0.174
452.1	61.0	6.8	5.0	0.200
500.5	59.8	7.5	4.10	0.242
104.5	111.8	7.6	23.0	0.043
157.2	111.0	9.5	11.0	0.091
202.8	111.1	15.2	8.40	0.115
274.2	109.6	19.4	6.0	0.167
297.7	111.0	20.0	6.10	0.125
357.1	109.1	23.5	5.40	0.176
402.1	111.5	29.5	5.0	0.200
455.4	110.0	30.5	4.10	0.242
491.2	111.4	31.5 - 55.6	4.20	0.238
101.8	202.7	14.5	16.0	0.062
102.2	203.8	16.9	13.50	0.074
107.5	202.2	14.8	17.50	0.057
121.2	202.7	18.2	25.0	0.044
131.2	202.5	Explosion	16.0	0.062
137.0	199.1	"	13.50	0.074
149.5	200.2	"	10.0	0.100
199.2	201.8	"	7.20	0.155

Table (1) Cont.

p_o n-pentane (mm)	p_o Oxygen (mm)	β_{max} (mm min ⁻¹)	θ (mins.secs)	$1/\theta$ (min ⁻¹)
113.0	112.2	5.5	8.30	0.180
202.5	110.0	6.0	4.0	0.250
306.5	110.2	7.2	2.40	0.372
552.5	111.0	7.7	1.50	0.540
597.5	109.8	7.9	1.40	0.600
455.0	112.9	7.9	1.20	0.700
121.7	203.6	6.2	5.25	0.292
202.5	201.8	12.4	2.0	0.500
252.5	201.5	16.0	1.55	0.650
280.5	198.8	17.1	1.50	0.670
344.0	200.0	18.2	1.0	1.000
558.8	205.0	Explosion	1.0	1.000
568.0	199.5	22.0	0.50	1.200
581.0	196.0	29.4	0.50	1.200
503.5	203.5	12.0	.	.
301.1	203.0	14.5	.	.
38.0	202.0	15.6	.	.
301.9	207.5	17.5	.	.
375.1	211.0	24.5	.	.
300.5	212.5	25.5	.	.
303.5	240.7	Explosion	.	.
42.5	202.5	1.5	.	.
41.5	212.0	5.0	.	.
42.1	403.5	5.5	.	.
41.5	420.5	4.5	.	.
42.5	503.0	4.5	.	.
.	.	.	.	.
.	.	.	.	.
178.5	200.5	13.5	2.5	0.280
202.5	201.5	17.5	2.10	0.390
204.0	207.5	Explosion	2.5	0.280
150.5	200.5	5.5	5.5	0.180
73.5	200.5	5.5	5.50	0.180
71.7	207.5	7.5	5.50	0.180

Table (ii) for Figs. 5 and 6

Variation of Maximum Rate and Induction Period with pressure of Oxygen at different cyclopentane and n-pentane Pressures.

250°C Silica Vessel.

p_o Cyclopentane (mm)	p_o Oxygen (mm)	ρ_{max} (mm min ⁻¹)	θ (mins.secs.)	$1/\theta$ (min ⁻¹)
203.8	80.2	7.5	Peroxide Added	
201.1	104.9	12.2	"	"
202.2	100.0	11.6	8.45	0.114
201.4	120.0	10.4	Peroxide Added	
205.8	130.9	22.0	"	"
209.2	137.3	22.3	8.40	0.115
199.5	159.9	25.8	9.0	0.111
200.1	177.8	Explosion	9.30	0.105
99.4	150.2	7.5	Peroxide Added	
101.202.2	202.8	12.0	"	"
101.1	251.0	14.5	"	"
99.0	281.0	15.6	"	"
101.8	297.8	17.8	"	"
101.1	311.0	24.4	"	"
100.5	312.4	23.6	"	"
102.3	340.7	Explosion	"	"
41.4	202.9	1.8	"	"
41.8	315.0	3.0	"	"
42.1	406.9	3.6	"	"
41.0	495.5	4.0	"	"
40.0	599.0	4.6	"	"
p_o n-pentane (mm)				
199.5	199.2	13.5	2.0	0.500
202.5	291.5	19.2	1.10	0.880
204.0	347.5	Explosion	1.0	1.000
70.870.8	272.6	3.0	5.0	0.200
72.3	380.2	3.5	5.50	0.285
71.7	497.5	2.5	2.50	0.358

Table (iii) for Figs. 7 and 8

Maximum Rates and Induction Periods of Various Hydrocarbons as a function of Hydrocarbon Pressure. Oxygen Pressure 110 mm

p _o methyl- cyclopentane (mm)	250°C		Silica Vessel	
	p _o Oxygen (mm)	p _{max} (mm min ⁻¹)	θ (mins.secs)	1/θ (min ⁻¹)
100.6	110.6	5.8	16.45	0.060
116.4	109.6	7.3	13.30	0.074
141.8	109.5	8.7	10.30	0.095
160.2	108.8	9.2	8.15	0.121
172.0	109.8	9.8	8.0	0.125
182.7	111.5	9.9	8.50	0.113
188.5	111.7	10.7	7.20	0.136
208.8	100.6	12.2	6.20	0.158
228.2	110.6	14.0	5.0	0.200
222.5	110.6	15.7	6.30	0.154
239.9	110.5	18.8	5.30	0.182
242.0	111.2	21.5	5.20	0.185
p _o Cyclohexane				
(mm)				
62.4	110.7	7.5	36.25	0.028
77.1	109.0	8.5	19.15	0.051
84.2	111.7	9.5	18.0	0.056
89.7	110.0	9.8	16.30	0.061
107.9	115.2	11.5	14.30	0.069
115.1	109.8	11.0	9.0	0.111
121.6	111.2	12.5	10.0	0.100
152.6	111.4	15.1	9.25	0.107
157.4	110.8	25.5	5.15	0.190

Table (iii) Cont.

p ₀ methyl- cyclohexane (mm)	p ₀ Oxygen (mm)	p _{max} (mm min ⁻¹)	θ (mins.secs)	1/θ (min ⁻¹)
30.5	111.0	5.8	65.50	0.015
35.5	111.5	5.1	19.50	0.051
39.6	112.1	6.4	16.40	0.060
45.0	110.5	7.6	16.20	0.061
51.0	109.6	8.8	14.50	0.069
50.2	109.1	9.4	11.40	0.085
54.4	110.1	9.5	15.40	0.064
59.4	109.4	11.2	12.5	0.082
65.3	110.6	11.1	14.15	0.070
69.4	110.9	12.4	10.0	0.100
60.5	111.6	12.5	10.40	0.094
70.5	109.2	15.2	10.0	0.100
76.8	111.6	Explosion	10.0	0.100
p ₀ 1:4 dimethyl- cyclohexane				
15.9	110.2	1.4	-	-
19.8	110.8	2.1	35.50	0.030
24.2	110.2	3.5	12.50	0.080
29.5	110.0	4.9	10.20	0.096
34.7	110.0	6.4	9.10	0.109
40.1	111.1	8.1	10.40	0.094
41.7	111.2	8.5	8.20	0.121
45.8	110.7	9.2	8.50	0.118
47.4	111.2	10.4	8.5	0.122
51.1	110.5	11.8	7.45	0.130
53.7	110.7	12.6	8.50	0.118
54.6	111.2	Explosion	6.50	0.147

Table (iii) Cont.

p 1:5:5 tri- methyl cyclo hexane. (mm)	p _O Oxygen (mm)	p _{max} (mm min ⁻¹)	θ (mins.secs)	1/θ (min ⁻¹)
15.1	110.1	1.5	11.0	0.091
19.9	109.3	2.5	9.30	0.105
24.8	111.7	3.4	9.0	0.111
29.0	112.5	4.8	8.50	0.118
29.7	112.7	4.5	8.0	0.125
35.5	111.4	5.4	9.30	0.105
36.3	111.2	5.7	8.40	0.115
40.2	112.5	6.7	8.40	0.115
40.4	112.3	6.9	8.0	0.125
43.5	110.0	9.2	7.20	0.135
47.2	111.5	9.5	6.30	0.154
44.4	109.2	10.6	6.10	0.162
49.6	112.0	11.2	6.30	0.154
48.4	111.7	12.0	6.30	0.154
47.6	109.1	12.4	5.50	0.182
50.3	113.5	Explosion	6.0	0.166
51.4	113.4	"	6.10	0.164
61.5	112.2	"	5.0	0.200

* Extrapolated data from least square graphs.

Table (iv) for Fig. 9

Variation of Maximum Rate and Induction Period with Pressure of Cyclopropane. Oxygen pressure 110 mm.

235°C Silica Vessel

p_{O} Cyclopropane (mm)	p_{O} Oxygen (mm)	p_{max} (mm min ⁻¹)	θ (mins.secs)	$1/\theta$ (min ⁻¹)
233.3	111.1	8.7	97.0	0.0103
275.5	112.5	10.3	78.50	0.0127
302.3	112.7	11.0	87.30	0.0114
303.6	112.4	11.8	77.0	0.0130
351.0	111.8	13.3	58.40	0.0170
381.0	113.8	14.4	64.40	0.0155
401.2	112.8	15.7	64.20	0.0156
451.7	109.7	17.5	62.10	0.0161

Table (v) for Fig. 10

Maximum Rate and Induction Period of Cyclopropane at Various Temperatures. Cyclopropane 500 mm Oxygen 110 mm . Silica Vessel.

Temperature °C	$1/T \times 10^3$ °Abs	p_{max} (mm min ⁻¹)	$\log_{10} p_{\text{max}}$ (mm min ⁻¹)	θ (mins.secs)	$\log_{10} 1/\theta$ (min ⁻¹)
500	1.745	40.7	1.61	59	2.415
500	1.745	33.1	1.52	50	2.505
292	1.770	22.4	1.35	47	2.520
292	1.770	21.4	1.33	53	2.275
285	1.792	11.8	1.07	78	2.110
285	1.792	11.0	1.04	82	2.085
* 250	1.192	0.63	1.800	316	3.500*

* Extrapolated data from least mean squares. *

Table (vi) for Fig. 11

Rate of Oxidation of Cyclooctane. Oxygen 110mm 250°C Silica Vessel

p_{O} Cyclooctane (mm)	p_{O} Oxygen (mm)	ρ_{max} (mm min ⁻¹)	θ (mins.secs)
21.6	108.9	1.0	15.0
23.5	108.5	1.7	15.4
25.6	113.3	1.7	12.0
29.8	112.9	2.5	11.15
32.0	112.0	2.0	-
59.0	111.0	2.2	2.0
20.7	107.8	5.5	0.30
32.5	115.1	4.2	-
51.1	115.1	2.4	9.15
23.3	111.2	2.3	4.10
29.6	109.9	1.8	4.20
25.8	110.3	1.7	1.0
54.8	110.2	2.4	9.45
27.2	109.6	2.5	8.15
34.9	111.9	2.0	-

Table (vii) for Fig. 12 and 13

Maximum Rate of Cycloheptane at Various Oxygen and Hydrocarbon Pressures. 245°C Silica Vessel.

Cycloheptane showed no induction period at this temperature.

p_{O} Cycloheptane (mm)	p_{O} Oxygen (mm)	ρ_{max} (mm min ⁻¹)
30.0	122.8	2.1
30.7	204.4	2.0
30.7	515.5	1.8
40.0	42.8	1.4
40.3	62.2	2.0
40.0	62.6	2.5
40.4	84.6	2.6
40.7	98.5	3.4
40.2	102.2	2.8

Table (vii) Cont.

p_o Cycloheptane (mm)	p_o Oxygen (mm)	P_{max} (mm min ⁻¹)
40.7	98.5	5.4
59.9	102.5	Explosion
40.7	125.5	"
35.5	60.0	1.6
48.1	61.0	2.7
64.6	62.1	5.0
67.7	60.8	2.7
51.6	90.1	2.8
80.8	90.2	3.6
27.7	110.0	2.4
43.2	115.5	3.5
49.5	115.8	4.5
55.8	112.8	5.8
60.5	108.8	6.4
69.5	111.5	Explosion

Table (viii) for Figs. 14, 15 and 16

Variation of Maximum Rate and Induction Period of 1:1:5 trimethyl-cyclopentane with Hydrocarbon and Oxygen Pressure. 250°C Silica Vessel.

p_o 1:1:5 trimethyl cyclopentane. (mm)	p_o Oxygen (mm)	P_{max} (mm min ⁻¹)	θ (mins.secs)	$1/\theta$ (min ⁻¹)
29.6	374.9	3.9	8.0	0.125
30.0	230.5	3.3	11.0	0.091
99.8	100.1	6.7	5.50	0.171
100.2	150.5	15.5	5.30	0.182
99.2	215.6	Explosion	4.30	0.222
51.0	70.0	2.0	14.0	0.071
110.6	71.5	5.6	-	-
123.5	70.4	5.1	6.20	0.158
30.9	113.4	2.0	15.0	0.067
35.8	112.1	3.5	9.10	0.110

Table (viii) Cont.

p_{O} 1:1:5 trimethyl p_{O} Oxygen cyclopentane	p_{max}	θ	$1/\theta$
(mm)	(mm min ⁻¹)	(mins.secs)	(min ⁻¹)
40.4	110.9	3.7	11.15
49.0	110.6	5.6	7.50
58.8	109.4	6.6	7.20
69.9	108.7	8.0	6.0
77.2	110.3	7.8	5.50
80.5	111.3	6.3	7.40
83.0	111.1	9.5	5.10
91.1	111.5	7.6	6.0
96.9	109.6	10.3	4.5
98.2	110.3	7.8	5.50
100.4	111.2	8.6	5.10
105.0	111.0	7.4	5.55
112.0	115.6	11.5	4.50
119.5	109.6	10.3	4.50
122.5	109.2	10.8	4.50
139.0	112.5	14.4	3.20
144.8	109.1	10.9	5.50
157.1	112.4	15.0	5.20
179.0	110.8	21.6	2.40

Table (ix) for Fig. 17

Variation of Maximum Rate of Cyclopentane with Oxygen Pressure in

Packed Vessels.

250°C Silica Vessels.

4.6 Fold Vessel

p_{O} Cyclopentane	p_{O} Oxygen	p_{max}	θ	$1/\theta$
(mm)	(mm)	(mm min ⁻¹)	(mins.secs)	(min ⁻¹)
203.0	111.1	15.2	12.15	0.082
201.5	113.5	16.0	Peroxide Added	
299.6	110.5	18.5	8.0	0.125
357.0	113.0	20.5	6.0	0.167
400.8	112.9	22.0	4.45	0.210
446.0	113.6	22.0	4.40	0.215

Table (ix) Cont.

p_o Cyclopentane (mm)	p_o Oxygen (mm)	ρ_{max} (mm min ⁻¹)	θ (mins.secs)	$1/\theta$ (min ⁻¹)
153.5	201.0	28.0	16.0	0.063
201.5	199.7	34.5	11.0	0.091
199.5	208.2	34.0	Peroxide Added	
245.2	200.2	35.5	8.40	0.116
299.0	199.0	39.0	6.30	0.154
360.0	200.0	41.0	5.30	0.182
429.0	194.5	42.0	4.40	0.215
200.6	304.2	48.0	Peroxide Added	
300.0	297.0	60.0	"	"
346.0	299.0	64.0	"	"

6.5 Fold Vessel

200.0	200.0	23.5	"	"
336.5	203.2	30.0	8.15	0.121
443.0	198.0	33.5	5.45	0.174

Table (x) for Fig. 18

Variation of Cyclopentane Rate in Packed Vessels. 250°C Silica Vessels.

p_o Cyclopentane (mm)	p_o Oxygen (mm)	ρ_{max} (mm min ⁻¹)	θ (mins.secs)	$1/\theta$ (min ⁻¹)
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6.5 Fold Vessel

200.0	200.1	23.5	Peroxide Added	
200.1	300.4	33.5	"	"
201.1	351.2	35.0	"	"
201.9	402.2	35.0	"	"

4.6 Fold Vessel

201.5	113.5	16.0	"	"
201.4	153.4	23.6	"	"
199.5	208.2	34.0	"	"
200.6	304.2	48.0	"	"
200.2	376.3	56.0	"	"
200.5	456.0	Violent Explosion		"

Table (xi) for Fig. 22

Effect of Various Amines and Ammonia upon the Oxidation of
Cyclopentane.

Cyclopentane - 550 mm		250°C	Silica Vessel	
Oxygen - 110 mm				
Triethylamine added (mm)	$\rho_{\max}$ (mm min ⁻¹)	θ (mins.secs)	$1/\theta$ (min ⁻¹)	
nil	-	5.30	0.182	
1.6	52.0	3.55	0.288	
4.5	very fast	2.0	0.500	
6.0	" "	1.40	0.600	
9.0	" "	1.0	1.000	
9.6	" "	1.05	0.927	
11.0	" "	1.20	0.700	
22.6	Explosion	0.35	1.172	
Diethylamine				
(mm)				
nil	-	5.0	0.200	
5.2	-	4.20	0.238	
10.5	very fast	4.0	0.250	
12.0	approx. 60.0	3.30	0.286	
Ethylamine				
(mm)				
nil	24.0	6.0	0.166	
nil	-	6.0	0.125	
7.0	-	5.45	0.174	
14.0	36.0	7.30	0.135	
20.0	-	6.45	0.148	
25.2	51.0	6.30	0.154	
Ammonia				
(mm)				
nil	50.0	6.0	0.166	
5.9	-	5.20	0.187	
15.8	-	7.0	0.143	
17.2	47.0	5.50	0.182	
28.9	51.4	5.0	0.200	

Table (xii) for Fig 23

Effect of Inert Gases upon the Oxidation of Cyclopentane

Cyclopentane - 200 mm

250°C Silica Vessel

Oxygen - 110 mm

Nitrogen added (mm)	$\rho_{\max}$ (mm min ⁻¹)	θ (mins.secs)	$1/\theta$ (min ⁻¹)
nil	16.7	7.40	0.130
nil	15.0	8.30	0.118
nil	14.0	9.30	0.105
nil	14.4	8.0	0.125
100.0	16.0	8.0	0.125
200.5	15.2	6.30	0.154
301.5	15.9	5.30	0.181
346.1	14.8	6.0	0.167

Carbon dioxide

(mm)

nil	16.2	9.30	0.105
54.0	14.0	9.0	0.111
252.5	14.8	7.30	0.133
360.7	14.4	6.45	0.148

Table (xiii) for Fig. 24

Effect of Nitrogen upon the Explosion Limit of Cyclopentane

Oxygen - 150 mm 250°C Silica Vessel

P_0 Cyclopentane (mm)	Nitrogen added (mm)	$\rho_{\max}$ (mm min ⁻¹)	θ (mins.secs)	$1/\theta$ (min ⁻¹)
100.1	nil	12.0	20.0	0.050
121.5	302.0	13.8	15.0	0.067
123.2	nil	13.9	15.0	0.067
132.0	299.1	14.5	14.0	0.071
129.5	nil	17.0	18.0	0.056
141.0	298.0	16.2	15.0	0.067
141.0	nil	18.1	15.0	0.077

Table (xiii) Cont.

P ₀ Cyclopentane (mm)	Nitrogen added (mm)	p_{max} (mm min ⁻¹)	θ (mins.secs)	$1/\theta$ (min ⁻¹)
150.5	nil	19.5	11.50	0.087
155.0	302.0	23.2	12.0	0.083
166.0	300.0	22.0	10.0	0.100
171.0	302.5	Explosion	11.50	0.087
172.0	nil	"	10.0	0.100
173.0	301.0	"	7.50	0.133
171.0	nil	"	11.50	0.087

Table (xiv) for Fig. 25

Effect of Various Salts upon the Induction Period of Cyclopentane

Cyclopentane - 350 mm Oxygen - 110 mm

Salt Coating	Temperature °C	$1/T_{abs} \times 10^5$	θ (mins.secs)	$\log_{10} 1/\theta$ (min ⁻¹)
Nil	235	1.969	12.0	2.96
(Clean Pyrex)	240	1.949	9.0	1.05
	250	1.912	4.0	1.40
	251	1.908	4.15	1.57
	260	1.876	2.0	1.70
	260	1.876	2.15	1.68
Potassium	250	1.912	720	3.14
Chloride	260	1.876	55	2.28
First Coat.	265	1.859	53	2.28
	270	1.842	15	2.82
	275	1.825	8	1.10
	280	1.808	3	1.47
	285	1.792	0.40	0.17
Second Coat.	265	1.859	40	2.40
	270	1.842	27	2.57
	275	1.825	7.50	1.17
	280	1.808	1.40	1.78
Third Coat.	250	1.912	551	3.26
	270	1.842	31	2.51

Table (xiv) Cont.

Salt Coating	Temperature °C	$1/T_{\text{abs}} \times 10^5$	θ (mins.secs)	$\log_{10} 1/\theta$ (mins ⁻¹)
Potassium Iodide	250	1.912	220	3.66
	255	1.894	41	2.59
	255	1.894	19	2.72
	260	1.876	25	2.60
	265	1.859	3.15	1.50
	270	1.842	5.50	1.46
	275	1.825	2.0	1.70
Potassium Bromide	250	1.912	660	3.18
First Coat	270	1.842	9	1.05
Second Coat	258.5	1.885	255	3.63
Lithium Chloride	255	1.894	140	3.85
	260	1.876	50	2.30
	265	1.859	36	2.44
	270	1.842	5.50	1.26
	275	1.825	2.15	1.65
Lithium Chloride	260	1.876	30	2.51
Loose in Vessel				
Lithium Bromide	255	1.894	> 1120	< 4.95
	265	1.859	207	3.684
	275	1.825	58	2.42
	285	1.792	2.30 + 1.0	1.45 - 1.82
Lithium Bromide	270	1.842	75	2.12
Loose in Vessel	280	1.808	11	1.98
Lithium Iodide	265	1.859	> 135	< 5.86
	275	1.825	> 50	< 2.30
	285	1.792	5 + 2	1.15 - 1.45
Potassium Sulphate	250	1.912	> 1080	< 4.99
	260	1.876	28	2.55
	260	1.876	15	2.80

Table (xiv) Cont.

Salt Coating	Temperature °C	$1/T_{\text{abs}} \times 10^5$	θ (mins.secs)	$\log_{10} 1/\theta$ (min ⁻¹)
Magnesium Chloride	260	1.876	> 480	< 5.51
	270	1.842	270	5.56
	280	1.808	50	3.51
	285	1.792	10	1.00
Caesium Chloride	270	1.842	120	5.91
	275	1.825	6	1.21
	280	1.808	1	0.00
Magnesium Sulphate	255	1.894	150	5.82
	260	1.876	33	2.48
	265	1.859	20	2.70
	270	1.842	4	1.40
Aluminium Sulphate	264	1.862	75	2.12
	270	1.842	22	2.65
	275	1.825	5	1.47
Potassium Fluoride	250	1.912	25	2.60
	255	1.894	14	1.85
	260	1.876	9	1.05
	270	1.842	5	1.50
<u>Metals</u>				
Silver Wire	250	1.912	> 190	< 3.75
	255	1.894	> 100	< 2.00
	260	1.876	> 90	< 2.05
	265	1.859	7.50	1.12
	270	1.842	8	1.10
	275	1.825	1.50	1.84
Gold Foil	255	1.894	> 25 < 54	2.48 - 2.60
	265	1.859	5.50	1.26
	275	1.825	2.0	1.70
Platinum Wire	270	1.842	> 60	< 2.22
	275	1.825	150	2.90
	275	1.825	90	2.08
	280	1.808	18	1.76
	285	1.792	20	1.70
	290	1.776	6	1.21

Table (xiv) Cont.

Cyclohexane - 80 mm Oxygen - 110 mm				
Salt Coating	Temperature °C	$1/T_{\text{abs}} \times 10^5$	θ (mins.secs)	$\log_{10} 1/\theta$ (min ⁻¹)
Potassium	250	1.912	> 1740	< 4.74
Chloride	255	1.894	> 720	< 5.14
	260	1.876	36	2.44
	270	1.842	13.30	2.87
	270	1.842	6.0	1.22
	280	1.808	1.0	0.00

Table (xv) for Fig. 26

Effect of Salts and Metals upon Cyclopentane Oxidation

Oxygen - 110 mm 2-5 mm ditertiary butylperoxide added.

Salt or Metal	p_o Cyclopentane (mm)	p_{max} (mm min ⁻¹)
Potassium	506.0	2.4
Fluoride	555.1	3.0
	409.5	3.4
Potassium	201.4	2.5
Iodide	239.2	4.8
	287.0	4.0
	510.9	4.4
	515.3	3.2
	356.0	4.0
	382.5	5.8
	392.5	7.4
Lithium	218.2	6.0
Chloride	323.5	4.0
	338.7	8.3
	361.1	8.0
	382.0	6.6
	449.2	10.2
Silver Wire	302.2	10.0
	337.0	14.2
	350.8	14.0

Table (xvi) for Fig 27

Effect of Lithium Chloride upon Cyclopentane Oxidation at
various Oxygen Pressures. 250°C Oxygen - 200 mm
2-5 mm ditertiary butylperoxide added.

p ₀ Cyclopentane (mm)	$\rho_{\max}$ (mm min ⁻¹)
196.5	6.5
252.5	11.6
298.0	15.8
355.0	Explosion
403.5	"

The data for the other curves
is taken from Tables i and xv

Table (xvii) for Fig. 28

Effect of Acetaldehyde and ditertiary butylperoxide upon the Induction
Period of Cyclopentane in a Potassium Chloride Coated Vessel. 250°C

Cyclopentane - 500 mm Oxygen - 110 mm

Acetaldehyde added (mm)	θ (mins.secs)	ditertiary butylperoxide added (mm)	θ (mins.secs)
nil	> 60	nil	> 60
1.5	19	0.1	> 60
2.2	11	0.15	14
3.5	12	0.175	> 60
5.8	8.50	0.24	4
9.0	5.50	0.25	5
11.0	5.0	0.5	4
14.2	5.50	0.5	2.30
		1.1	5
		1.1	2

Table (xviii) for Figs. 29 and 30

Effect of Temperature upon the Rate and Induction Period of

Cyclopentane Oxidation. Cyclopentane - 40 mm Silica Vessel
Oxygen - 80 mm

Temperature °C	$1/T_{\text{abs}} \times 10^3$	ρ_{max} (mm min ⁻¹)	$\log_{10} \rho_{\text{max}}$ (mm min ⁻¹)	θ (mins.secs)	$\log_{10} 1/\theta$ (min ⁻¹)
240	1.950	0.62	1.79	peroxide added	
250	1.912	2.00	0.03	"	"
260	1.876	6.0	0.78	"	"
265	1.859	12.8	1.06	"	"
270	1.842	Explosion		"	"
270	1.842	"		"	"
300	1.745	Cool Flames		"	"
320	1.686	47.0	1.67	6.50	1.18
330	1.658	40.0	1.60	12.0	2.92
330	1.658	38.0	1.58	peroxide added	
340	1.631	38.0	1.58	"	"
340	1.631	29.5	1.47	6.50	1.18
350	1.605	18.6	1.27	peroxide added	
355	1.592	16.6	1.22	"	"
355	1.592	22.4	1.35	5.0	1.30
358	1.585	14.5	1.16	peroxide added	
360	1.580	15.9	1.20	3.35	1.45
370	1.555	15.5	1.13	5.35	1.45
380	1.531	14.8	1.17	2.50	1.60
400	1.486	16.6	1.22	1.45	1.76
420	1.445	21.4	1.33	1.15	1.90
440	1.403	30.2	1.48	0.50	0.09
440	1.403	39.8	1.60	0.50	0.09
440	1.403	45.7	1.60	-	-
450	1.383	Explosion		0.50	0.30

Table (xviii) Cont.

Cyclopentane - 50 mm Oxygen - 110 mm

Temperature °C	$1/T_{\text{abs}} \times 10^5$	p_{max} (mm min ⁻¹)	$\log_{10} p_{\text{max}}$ (mm min ⁻¹)	θ (mins.secs)	$\log_{10} 1/\theta$ (min ⁻¹)
230	1.988	0.4	1.60	peroxide added	
240	1.950	1.4	0.15	"	"
250	1.912	3.5	0.54	"	"
250	1.912	4.0	0.60	"	"
260	1.876	10.7	1.05	19.0	2.72
265	1.859	17.8	1.25	19.0	2.72
265	1.859	Explosion		peroxide added	
285	1.792	Cool flames		16.15	2.79
285	1.792	"	"	25.0	2.60
300	1.745	"	"	4.25	1.35
300	1.745	"	"	7.55	1.10
300	1.745	"	"	15.10	2.82
300	1.745	"	"	17.0	2.77
315	1.701	"	"	5.50	1.45
315	1.701	"	"	4.0	1.40
315	1.701	"	"	12.50	2.90
330	1.658	72.4	1.86	peroxide added	
330	1.658	79.4	1.90	"	"
330	1.658	66.0	1.82	4.0	1.40
340	1.631	69.2	1.84	2.20	1.65
340	1.631	55.7	1.75	peroxide added	
350	1.605	57.5	1.76	1.30	1.82
350	1.605	55.7	1.75	peroxide added	
355	1.592	55.0	1.74	"	"
355	1.592	64.6	1.81	2.0	1.70
360	1.580	61.7	1.79	1.45	1.75
360	1.580	63.1	1.80	peroxide added	
370	1.555	50.1	1.70	1.15	1.90
380	1.531	44.7	1.65	1.10	1.95
400	1.486	45.7	1.66	0.45	0.15
420	1.443	75.9	1.88	0.55	0.25
440	1.403	107	2.03	0.50	0.50
440	1.403	Explosion		0.50	0.50

Pyrex Vessel Table (xviii) Cont.

Temperature °C	$1/T_{\text{abs}} \times 10^3$	ρ_{max} (mm min ⁻¹)	$\log_{10} \rho_{\text{max}}$ (mm min ⁻¹)	θ (mins.secs)	$\log_{10} 1/\theta$ (min ⁻¹)
246.5	1.925	5.5	0.52	peroxide added	
260	1.876	10.5	1.02	"	"
265	1.859	Explosion		"	"
345	1.618	69.2	1.84	1.25	1.85
390	1.508	57.2	1.57	1.10	1.95
420	1.445	51.5	1.71	0.50	0.08
430	1.422	81.5	1.91	0.40	0.17

Table (xix) for Figs. 51 and 52

Effect of Temperature upon the Rate and Induction Period of Cyclopentane in Vessels Coated with Lithium Bromide and Magnesium Sulphate.

Cyclopentane - 50 mm Oxygen - 110 mm

Lithium Bromide Coated Vessel

Temperature °C	$1/T_{\text{abs}} \times 10^3$	ρ_{max} (mm min ⁻¹)	$\log_{10} \rho_{\text{max}}$ (mm min ⁻¹)	θ (mins.secs)	$\log_{10} 1/\theta$ (min ⁻¹)
500	1.745	-	-	> 75	< 2.13
500	1.745	-	-	530	2.48
510	1.715	1.1	0.05	40	2.40
515	1.701	2.4	0.58	peroxide added	
515	1.701	2.5	0.57	25	2.60
520	1.686	1.0	0.00	23	2.64
520	1.686	5.5	0.52	14.50	2.84
520	1.686	6.6	0.82	-	-
550	1.658	52.5	1.72	4.50	1.52
550	1.658	65.1	1.80	5.50	1.26
550	1.658	57.5	1.76	4.50	1.52
555	1.645	56.2	1.75	4.0	1.40
560	1.651	60.5	1.78	3.50	1.45
550	1.605	59.8	1.60	2.55	1.55
570	1.555	26.2	1.45	2.05	1.68
570	1.555	27.5	1.44	1.50	1.82
400	1.486	50.2	1.48	0.55	0.04
420	1.445	57.2	1.57	0.55	0.24
420	1.445	49.0	1.69	-	-

Magnesium Sulphate Coated Vessel

550	1.605	0.8	1.90	15.50	2.80
370	1.555	1.8	0.25	4.0	1.40
400	1.486	5.5	0.55	1.50	1.82
450	1.385	8.2	0.92	0.55	0.24

Table (xx) for Fig. 53

Principal Products of Cyclopentane Oxidation.

Pyrex Vessel		Cyclopentane - 150 mm		250°C		
		Oxygen - 110 mm				
Time (mins)	Carbon dioxide (mm)	Carbon monoxide (mm)	Water* (mm)	Oxygen gone (mm)	Cyclopentane* gone (mm)	Ap (mm)
6	0.2	-	-	-	-	-
7.15	-	1.2	-	-	6.0	0.7
8.50	-	2.5	-	-	-	2.0
8.45	1.5	-	-	-	-	2.2
10.15	5.9	5.5	25	19.0	15	6.2
10.45	6.0	-	62	41	55	9.5
11.30	-	16.4	103	82	-	17.0
12.0	10.0	-	-	-	-	22.5
12.30	11.5	26.0	152	105	50	28.0
13.45	12.0	-	-	-	-	34.5
14.30	-	50.0	156	108	54	36.0
15.0	12.5	-	-	-	-	36.0

Table (xxi) for Fig. 54

Minor Products of Cyclopentane Oxidation

Pyrex Vessel		Cyclopentane - 150 mm		250°C		
		Oxygen - 110 mm				
Time (min)	HCHO (mm)	CH ₃ CHO (mm)	CH ₃ CH ₂ CH ₂ CHO (mm)	CH ₃ CH ₂ CH ₂ CHO (mm)	CH ₃ CH ₂ CH ₃ (mm)	Ap (mm)
6.30	-	0.1	0	0	0	-
6.40	0.5	-	-	-	-	0.5
7.50	0.5	-	-	-	-	1.0
8.30	-	0.55	-	-	-	2.0
10.0	2.0	-	-	-	-	5.0
10.15	-	0.65	0	0.5	0	6.2
10.50	5.0	1.15	0	0.95	0	10.0
11.30	4.25	2.60	0.05	1.0	0	17.0
11.45	5.4	-	-	-	-	20.0
12.0	7.75	2.5	0.2	1.1	-	22.6
12.30	7.4	3.5	0.75	1.4	0.6	23.0
13.15	7.4	-	-	-	-	32.5
13.40	-	5.25	1.9	1.2	0.7	34.0
15.0	7.75	2.8	2.25	1.4	0.9	36.0
30.0	7.0	3.1	2.0	1.2	1.0	36.0

Table (xxii) for Fig. 55

Peroxide Concentration in Cyclopentane Oxidation. With and without added Acetaldehyde. Cyclopentane - 150 mm Oxygen - 110 mm 250°C

Time (mins)	<u>No Acetaldehyde</u>		<u>+ 5mm Acetaldehyde</u>	
	Peroxides (mm)	Δp (mm)	Peroxides (mm)	Δp (mm)
2.50	0	0	-	-
3.0	-	-	0.05	0
5.0	0.09	0.2	-	-
5.50	-	-	0.34	1.0
6.0	0.16	0.3	-	-
6.30	-	-	0.47	3.0
7.15	-	-	0.72	9.6
7.45	-	-	0.98	20.0
8.0	0.32	0.9	-	-
8.50	-	-	0.48	27.1
9.0	0.55	2.0	0.35	30.0
9.50	0.40	3.2	-	-
10.0	0.58	4.6	-	-
10.50	0.70	6.9	-	-
11.0	0.58	10.0	1.6	33.6
11.15	0.74	13.2	-	-
12.0	0.88	19.0	-	-
12.0	0.86	19.0	-	-
12.30	0.76	25.5	-	-
13.0	0.65	30.0	-	-
14.0	0.30	34.3	-	-
15.0	0.15	38.0	0.05	35.0
30.0	0.09	36.0	-	-

Table (xxiii) for Fig. 56

Peroxide Concentrations at Two Different Temperatures in the Oxidation of Cyclopentane in a Pyrex Vessel. Cyclopentane - 50 mm Oxygen - 110 mm

<u>400°C</u>			<u>260°C</u>		
Time (min secs)	Peroxides (mm)	Δp (mm)	Time (min secs)	Peroxides (mm)	Δp (mm)
0.50	0.2	2.0	2.0	0.0	0.5
1.30	0.62	9.2	4.0	0.02	0.7
1.50	0.91	25.6	6.0	0.05	0.9
2.05	0.79	42.0	7.10	0.15	1.2
2.20	0.5	50.0	8.0	0.42	6.0
3.0	0.28	56.0	8.05	0.43	8.0
3.50	0.07	57.0	8.25	0.02	74.0
			8.50	0.01	74.0
			10.30	0.0	74.0

Table (xxiv) for Fig. 57

Effect of Salt Coatings upon Peroxide Concentrations in the Oxidation of Cyclopentane. Cyclopentane - 50 mm Oxygen - 110 mm 400°C

(For Pyrex Vessel see Table xxiii above.)

<u>Lithium Bromide</u>			<u>Potassium Fluoride</u>		
Time (mins secs)	Peroxides (mm)	Δp (mm)	Time (minssecs)	Peroxides (mm)	Δp (mm)
1.0	0.01	9.0	2.50	0.04	7.0
1.40	0.02	27.5	4.50	0.09	22.0
2.25	0.02	42.0	6.0	0.04	34.0
3.0	0.0	45.5	8.30	0.0	58.5

Table (xxv) for Fig. 38

Effect of Salt Coatings upon Peroxide Concentrations in the Oxidation of Cyclopentane. Oxygen 110 mm 250°C

Potassium Fluoride
Cyclopentane 350 mm

Pyrex Glass
Cyclopentane 150 mm

Time (mins.secs)	Peroxides (mm)	Δp (mm)	Time (mins.secs)	Peroxides (mm)	Δp (mm)
6	0.04	0.5			
11.59	0.16	5.0			
14.0	0.54	8.0			
15.10	0.24	8.0			
16.50	0.55	10.8			
17.40	0.54	12.7			
19.0	0.56	14.6			
20.50	0.21	17.0			
55.0	0.0	19.5			

See Table (xxii) above.

Table (xxvi) for Fig. 39

Cyclopropane Analysis at 285°C

Δp (mm)	Oxygen gone (mm)	Cyclopropane gone (mm)	Carbon dioxide (mm)
0	0	0	2.4
2	8.1	0	2.7
5	26.2	4.6	4.8
9.5	27.6	22.0	10.8
10.0	40.8	27.9	9.2
12.5	31.9	21.7	16.4
14.3	45.9	33.5	15.8
18.0	54.9	29.9	16.5
20.0	56.7	35.7	16.7
20.0	58.9	27.6	17.9
22.5	63.2	29.7	18.7
25.0	73.6	21.7	21.4
26.4	79.9	52.5	20.1
30.0	102.8	42.4	22.1
30.5	94.2	65.8	23.9

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There are many interesting problems associated with the thermal oxidation of hydrocarbons. The relationship between rate and structure is remarkable, the temperature dependence is anomalous and the kinetics are both complex and not fully understood. There is often a long induction period associated with the development of branching chains, during which time intermediates, such as peroxides and aldehydes, are built up in small quantity. The reaction is also very much subject to the influence of small homogeneous and heterogeneous additions. This means that not only can ignition be promoted, but by suitable means delayed or prevented, a subject of very great practical importance.

The objective of the work here described has been to investigate the gas phase oxidation of a series of cycloparaffins and to compare the kinetics with similar open chain systems. Particular reference has been made to the problems of the rate-structure relationship and the effect of surfaces, both on the induction period and on the rate. The systems studied for this purpose have been a series of cycloparaffins from cyclopropane to cyclooctane, excluding cyclobutane but including various methyl substituted cyclopentanes and hexanes. The more detailed study of the kinetics and of the relevant inhibition phenomena has been restricted to cyclopentane, n-pentane being used to provide comparison with the open chain paraffins.

The work was carried out in a conventional static apparatus at pressures from 100 to 700 mm Hg, reaction vessels being of pyrex or silica. The course of the reaction was followed by pressure increase, measured on a mercury manometer. Product analysis by mass spectrometer, gas chromatography and chemical methods showed that pressure changes were a good measure of the extent of the reaction. Oxidation reactions in the gas phase have an anomalous temperature dependence resulting in "high" and "low" temperature regions of reaction. Most of the present investigation has been carried out in the low temperature range, below 500°C, with a little comparative work done at higher temperatures.

It was first considered desirable to make some comparison of n-pentane and cyclopentane, since the oxidation of the normal paraffins has already been investigated, and the comparison would show how far results could be regarded as general. These experiments were carried out at 250°C , with variation of both the hydrocarbon and oxygen pressures. In general the kinetics of the two paraffins are very similar. The reciprocal induction period was in all cases linearly proportional to the pressure of hydrocarbon or oxygen, the dependence being a little steeper with increasing hydrocarbon pressure than oxygen pressure. The dependence upon reactant pressure of the rate was found to be more complex. There is a limiting pressure of either hydrocarbon or oxygen above which increase in the pressure of the other reactant causes a rapid rise in rate to explosion. Below this critical pressure the rate attains a limiting value with increase either in oxygen or in hydrocarbon. Thus under certain conditions the rate becomes independent of the concentration of one reactant. The change from one type of behaviour to the other is gradual, and there is a region where the rate is linearly proportional to the concentration of one reactant over a wide pressure range. This type of behaviour was observed with several hydrocarbons. It had been previously supposed that with n-pentane the rate attained a limiting value with increase of oxygen, but it now appears that this is not always so.

The comparison of a series of cycloparaffins was made at 250°C (except cyclopropane which was investigated at a higher temperature). The rate increases with the size of the ring, in the same way as it does in the open chain paraffins with length of the chain. The only anomaly observed was with cyclooctane, which oxidised at a rate between cyclopentane and cyclohexane. Methyl groups on the ring, as in branched open chain paraffins, progressively lower the rate.

The effect of increasing the surface to volume ratio of the reaction vessel, was investigated. Fourfold and sixfold increases lengthened the induction period by a small amount and decreased the

rate, besides raising the limiting pressures mentioned above. Much higher pressures were attained before the rate accelerated to explosion, and in some cases a limiting rate replaced an explosion.

The result of various small homogeneous additions was next investigated. Peroxides, aldehydes and some halogens all shorten the induction period and in most cases increase the rate. This is thought to be due to the rapid production of radicals which initiate the main reaction. Isopropyl halides had little or no effect on the induction period or rate, aniline, carbon tetrachloride and carbon tetrafluoride had none. Inert gases in the form of nitrogen and carbon dioxide had no effect, even in large amounts.

Experimental evidence suggests that the initiation reaction may take place largely on the surface of the containing vessel. In order to try and utilize this fact for the suppression of the reaction, various surface treatments were investigated. These consisted in coating the inside of the reaction vessel with a thick layer of various salts, deposited from an aqueous solution. Those used were a series of alkali halides and some salts of di- and tri- valent metals. In the first instance experiments on the length of the induction period were carried out between 250°C and 290°C. All the salts caused a large increase in the induction period (θ) and Arrhenius plots of $\log 1/\theta$ against $1/T_{\text{abs}}$ gave straight lines. The magnitude of this effect was large, induction periods being increased by up to a thousandfold. Some investigations were made on the rate of reaction at 250°C and on account of the length of the induction period at this temperature, a trace of ditertiary butylperoxide was used as an initiator. Only a few of the less efficient salts gave a measurable rate, which was from 10% to 50% of the normal value. The others gave no measurable pressure increase, even with large amounts of initiator. It was further discovered that in the case of at least two salts, a few grams of the loose salt in a clean pyrex vessel had the same inhibiting effect as coating the whole interior of the vessel. This type of inhibition is not confined to

salts, since silver wire, platinum wire and gold foil also inhibit the reaction.

The temperature coefficient of the reaction was next investigated with cyclopentane in both salt-coated and uncoated vessels, and is anomalous. Two sections of smooth reaction are separated by a temperature region of cool flames and explosion. On raising the temperature the rate first increases and then gives way to explosion: this is succeeded by cool flames which as the high temperature region is approached give way to a smooth reaction with a negative temperature dependence. Eventually this becomes positive again and the rate finally rises to explosion. The whole process occurs over a temperature range of about 250°C . The induction periods show no anomalous behaviour, and give one Arrhenius plot through both high and low temperature regions with no break in the cool flame portion. Similar experiments were carried out with salt-coated vessels. With lithium bromide the rate in the high temperature region was little affected, but at lower temperatures where cool flames might be expected, a very marked reduction in rate was noticed. Magnesium sulphate caused a large reduction in rate in the high temperature region.

The principal reaction products were carbon monoxide and water with some carbon dioxide, others being in very low concentrations. Other products and intermediates detected were formaldehyde, acetaldehyde, n-butyric aldehyde, butene and an unidentified peroxide or peroxides. The concentration of the principal products followed the rate of pressure rise closely. The peroxide concentration (determined by an iodometric method) passed through a well defined maximum at the time of maximum rate. In the cool flame and explosion region the peroxide concentration rose with the pressure increase and immediately after the explosion fell back to a lower value. In salt-coated vessels the peroxide concentration was most markedly reduced, both at low and high temperatures.

The interpretation of these results will now be considered. The kinetics of the cycloparaffins seem to be analogous to those of the

n-paraffin series. The reactants can apparently both start and end chains, since under certain conditions the rate can become independent of the concentration of one reactant, and even be depressed with increasing oxygen pressure. The general shape of the rate/pressure curves can be given by a simple empirical expression of the form :-

$$p_{\max} = \frac{c}{1 - \frac{[RH][O_2]}{a[RH] + b[O_2]}}$$

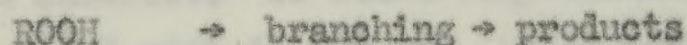
Where a, b and c are constants.

[RH], [O₂] the initial pressures of hydrocarbon and oxygen.

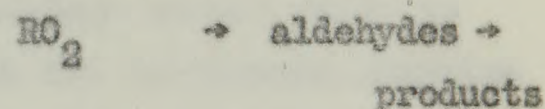
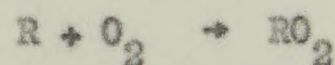
p_{max} is the maximum rate.

It is suggested that the progressive change in mode of reaction from low to high temperature occurs through the increased rate of decomposition of RO₂ radicals thus :-

Low



High



The cool flames are probably formed by the decomposition of the peroxide. The peroxide found experimentally at high temperatures is possibly hydrogen peroxide and not an organic peroxide. The peroxide postulated at low temperature may well be a cyclic one and the cyclic peroxy radicals of the high temperature mechanism would split to give one free radical and probably an aldehyde. The fact that the ring has to be broken means that there is a fundamental difference from the n-paraffins at some stage, although the resulting kinetics seem to be

the same. The anomalous form of the temperature coefficient is typical of the oxidation of higher hydrocarbons and shows that two separate mechanisms must exist, one showing a decrease in rate as the temperature is increased over a certain range.

The structural effects in the cycloparaffins are again very similar to those in the n-paraffin series, methyl groups strongly decreasing the rate. This is probably due, either to the stabilizing influence they have on a peroxide intermediate, or to the production of some more stable intermediate from the easily attacked tertiary carbon atoms.

Increase in the surface/volume ratio of the reaction vessel indicates that chain ending on the walls can control the reaction to a large extent. The addition of almost any material which can produce free radicals under the conditions of the experiment, (e.g. aldehyde or peroxide) reduces the length of the induction period and in large amounts raises the rate. Evidently there are many free radicals capable of initiating the chain and if these are produced over a period of time, as in the oxidation of an added aldehyde, their concentration can become large enough to upset the kinetic balance of the reaction and so raise the total rate.

The effect of a salt coating on the reaction vessel walls is of great interest. It seems very unlikely that the initiation reaction is interfered with in any way, since both metal wires and loose salt are as efficient as a complete coating. The inhibition must occur through the destruction of an intermediate, possibly a peroxide, since this has a half life time longer than that of the transient free radicals. Salt and metal surfaces might, however, destroy small radicals of the type HO_2 . Peroxide removal would explain the fact that the efficiency falls off as the temperature is raised towards the high temperature region.

The analytical results having shown that the rate of pressure

