# THE SLOW COMBUSTION OF CYCLOPROPANE

by

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# INTRODUCTION

The discovery of fire and combustion must rank with the wheel as one of the earliest and most far-reaching of all the discoveries made by man. Fire has always occupied a prominent place amongst the mysteries of the world and aroused the interest of the earliest philosophers. It was one of the four elements of the alchemists, and the study of its cause, nature and application became a matter of the greatest importance with the advent of the internal combustion engine. The slow combustion of hydrocarbons has been studied largely because of the facility of working at temperatures below the ignition point. New techniques have been developed and a unique field of research in chemistry has been revealed. The importance of slow combustion studies does not now rest so heavily on the application of the results to the technical combustion of fuels; rather do such studies reveal the application of the methods of kinetics to the elucidation of the mechanism of very complicated systems and in particular the results obtained may be used to provide some knowledge of bond dissociation energies in hydrocarbons.

The first exact knowledge of the chemistry of burning was mainly derived by the work of Davy and his comtemporaries which was designed to elucidate the causes of mine explosions. Though this work gave rise to no great theoretical developments it disclosed certain broad facts relating to the ignition of explosive mixtures, the influence of cold surfaces and narrow passages in the extinction of flames, the effect of rarefaction and dilution of explosive mixtures and permitted some conclusion to be drawn as to the relative combustibilities of gases and their explosive limits.

After Davy's death, there arose the mistaken dogma of selective combustion of hydrogen in hydrocarbon flames but this became untenable after the discovery, by Smithells and Ingle, of hydrogen in the interconal gases of aerated hydrocarbon flames. These workers indicated that the probable series of changes for methane might be represented by the equations

$$CH_4 + O_2 \longrightarrow CO + H_2O + H_2$$
$$CO + H_2O \longrightarrow CO_2 + H_2$$

In 1874 H.E. Armstrong (1) suggested that the oxidation by hydrocarbons proceeded by a mechanism involving the successive formation of hydroxy-compounds such as $CH_3OH$, $CH_2(OH)_2$, $CH(OH)_3$ which would be thermally unstable, leading to the production of simpler substances, mainly by thermal dehydration. Though Armstrong's theory lay untested for almost thirty years, it was to become a very great force in the study of hydrocarbon combustions.

About 1900, W.A. Bone began a series of classical researches, the results of which appeared to establish the hydroxylation theory as a working hypothesis. With various collaborators, Bone (2,3,4,5) studied slow and explosive combustion of methane, ethane, ethylene and acetylene. Two experimental techniques were employed. In the first the reaction mixture was heated in a sealed glass tube and the gases were analysed at various times. Secondly, flow experiments were conducted in which the gases were passed through a heated tube packed with porous porcelain and then into traps where soluble and condensible products were removed. Several important points were recognised. For example oxides of carbon, water, aldehydes and acids were found in the products but neither carbon or hydrogen was detected. Further it was observed that carbon dioxide was formed under conditions where the oxidation of carbon monoxide was inconceivable and that aldehydes appeared in the products before steam or carbon-oxides. Regarding these facts as explicable by the hydroxlyation theory, Bones's collaborators Newitt and Haffner, seeking more direct proof, studied the oxidation of methane at high pressures and noted the formation of large amounts of methyl alcohol. (6).

In the Bakerian Lecture, 1932, Professor Bone (7) summarised the state of knowledge at that time and discussed in some detail the nature of the initially formed oxygenated molecule. It is not the least remarkable feature of hydrocarbon oxidations that most of the products contain one atom of oxygen so that the mode of scission of the diatomic oxygen molecule is perhaps the key to the problem of combustion mechanism. Bone's hydroxylation theory involved the breakdown of oxygen molecules into atoms. A vastly different idea had been advanced by Callendar in 1927 (8). He proposed that the first intermediate product was formed by the incorporation of an oxygen molecule as a whole in the hydrocarbon molecule. Thus $R{-}H + O{=}O \rightarrow R{-}O{-}O{-}H$ or $R{-}O{-}O{-}R$. This principle of primary peroxide-formation received strong support from a work by Bennett and Mardles (9) who considered that the separation of oxygen molecules into atoms would lead to a profusion of electrons but who could detect little or no ionisation during the slow combustion of some hydrocarbons.

At that time Bone concluded that all the evidence was in favour of the hydroxylation theory and that the first intermediate was a monohydric alcohol. Thus e.g. $CH_4 + O_2 \rightarrow CH_3OH$ This conclusion was probably justified as Bone and his collaborators had accumulated so much evidence for that process, whereas the peroxidation theory was too young to have any firm backing at that time.

About 1927 - 1930, Semenov, working in Leningrad, developed the theory of chain reactions. On the basis of the kinetic theory of gases he was able to explain the phenomenum of chain reactions and calculated certain relationships which were found to operate in very many cases. Semenov (10) recognised the existence of two types of reaction chains - stationary or unbranched, and branching chains. An excellent example of a stationary chain is that operating in the photochemical synthesis of hydrogen chloride. The propagation steps are

$$Cl + H_2 \longrightarrow HCl + H$$
$$H + Cl_2 \longrightarrow HCl + Cl$$

Chains with branching are different in that one complete cycle of operations results in a nett increase in the number of active centres. It will be seen that in the case of a stationary chain, while each step results in the formation of a chain 'carrier' it also consumes one (e.g. $H + Cl_2 \rightarrow HCl + Cl$) and that although the chain length may be very great there is never any increase in the average number of chain carriers. In a branching-chain reaction, on the other hand, the number of chain carriers may increase freely. In the following general example A, $AB_2$, CB and AB are all active centres for reaction while the other species are normal stable molecules.

$$A^* + B_2 \longrightarrow AB_2^* \qquad (1)$$

$$AB_2^* + CA \longrightarrow AB_2C + A^* \qquad (2)$$

$$AB_2C \longrightarrow AB^* + CB^* \qquad (3)$$

The two reactions (1) and (2) constitute a normal stationary chain while reaction (3) represents branching of the chain. It need hardly be pointed out that even if AB were a stable molecule reaction (3) would still result in branching since there is an overall gain of one active body as a result of the cycle of operations $A^* + B_2 + AC \rightarrow A^* + AB + CB^*$. Calling the length of the primary (stationary) chain $\nu$, the probability of branching at any link $\delta$, and $\beta$ the probability of chain-breaking at any given link, Semenov has shown that the velocity of reaction at any time t is given by $\omega = \frac{n_o}{\delta-\beta}\left\{e^{\frac{(\delta-\beta)t}{\Delta\gamma}} - 1\right\}$ where $n_o$ is the number of initial active centres and $\Delta\gamma$ is the time necessary for the formation of one link in the chain i.e. the time for which an active centre created in the chain exists before entering the reaction. For large values of t the expression reduces to

$$\omega = Ae^{\phi t} \quad \text{where } A = \frac{n_o}{\delta-\beta}$$

$$\text{and} \quad \phi = \frac{\delta-\beta}{\Delta\gamma} = \frac{n_o}{A\Delta\gamma}$$

Assuming reasonable values for $\delta$, $\beta$ and $\Delta\gamma$ Semenov indicated that a reaction of this type would increase its velocity by e in times of the order of one second. However, many reactions are known where the time required for such an increase in velocity is of the order of several hours. To explain this phenomenum it is necessary to admit that $\Delta\gamma$ may be measured in minutes rather than in tenths of a second as was done in the first case. This is the basis of the rather special theory of the existence of chains with degenerate branching. This postulates the operation of a primary chain, not accompanied by branching, which leads to the formation of a relatively stable intermediate which, after a comparatively long time breaks down by non-radical reactions to form the final products of reaction. The intermediate may also be capable of a second reaction which incidentally creates further active centres, which, in turn, are able to start the chain of the primary reaction. Depending upon the stability of the intermediate, the degenerate branching may take place long after the perishing of the primary chain. The process may be represented thus:-

$A \longrightarrow M$ (formation of intermediate by the primary chain)

1. $M \xrightarrow{k_1} B$ (direct product formation)

2. $M \xrightarrow{k_2} B$ (formation of products with incidental creation of initial centres of $A \rightarrow M$ chains)

If the rate of generation of secondary chains (given by $\upsilon\delta_1$ where $\upsilon$ = primary chain-length and $\delta_1$ = probability that one molecule of the intermediate M will create a secondary chain) exceeds the rate at which the primary chains perish, then the consequent increase of the reaction velocity is given by

$$\omega(t) = \frac{n_0 \upsilon}{\delta_1 \upsilon - 1} \left\{ e^{\frac{(\delta_1 \upsilon - 1)t}{\theta}} - 1 \right\}$$

where $\theta$ is the time between the commencement of the primary chain and the beginning of the secondary chain. Since the time of development of each primary chain is very small, $\theta$ may be regarded as the life-time of the intermediate M. For high enough values of t the above rate relationship reduces to

$$\omega(t) = Ae^{\phi t} \text{ where } A = \frac{n_0 \upsilon}{\delta_1 \upsilon - 1} \text{ and } \phi = \frac{\delta_1 \upsilon - 1}{\theta} = \frac{n_0 \upsilon}{A\theta}$$

By a consideration of the significance of $\delta_1$ and $\theta$ the expression for the rate can be further simplified. If the velocity of processes 1. and 2. are given by $k_1(M)$ and $k_2(M)$

then $\delta_1$ = the probability that $M \longrightarrow B$ by process 2.

$$= \frac{k_2(M)}{k_1(M) + k_2 M} = \frac{k_2}{k_1 + k_2}$$

Also $\theta$ = the average life of the molecule M

$$= \frac{1}{\frac{1}{\theta_1} + \frac{1}{\theta_2}}$$

But $\frac{1}{\theta_1} = k_1$ and $\frac{1}{\theta_2} = k_2$

$$\therefore \quad \theta = \frac{1}{k_1 + k_2}$$

Thus

$$\frac{\delta_1 \nu - 1}{\theta} = \left( \frac{\nu k_2}{k_1 + k_2} - 1 \right) (k_1 + k_2)$$

$$= (\nu - 1) k_2 - k_1$$

Hence

$$\omega(t) = \frac{n_0 \nu (k_1 + k_2)}{(\nu - 1) k_2 - k_1} \cdot e^{\left[(\nu - 1) k_2 - k_1\right] t}$$

$$= \frac{n_0 \nu (k_1 + k_2)}{\phi} \cdot e^{\phi t} \quad \text{where } \phi = (\nu - 1) k_2 - k_1$$

The exponent $\phi$ has been described as the net-branching factor and is very important characteristic of a chain reaction with degenerate branching. It may be evaluated by measurement of the slope of the line obtained if the logarithm of the amount of change is plotted against time. Semonov analysed the results of several workers and demonstrated the linearity of this type of graph in the early stages of many reactions.

Not the least remarkable feature of this type of reaction is the extraordinary sensitivity of the reaction rate to the state of the walls of the vessel. Since there are two possibilities (homongeneous and heterogeneous) for each of the two reactions (1. and 2.) of M, there are, altogether, four cases to be considered

1. 1. homogeneous and 2. homogeneous
2. 1. homogeneous and 2. heterogeneous.
3. 1. heterogeneous and 2. homogeneous.
4. 1. heterogeneous and 2. heterogeneous.

Each of these four cases must be sub-divided according to whether the chains $A \rightarrow M$ are broken in the volume or on the walls. In each case where the primary chains are ruptured on the walls, $\upsilon = ad^2$ where d is the vessel diameter, and the rate is increased by increasing the vessel diameter; in the other case of primary chain rupture in the volume of the vessel, increase of the diameter leads to a decrease of the rate when reaction 2. is heterogeneous (cases 2. and 4. above), to an increase of the rate in case 3. and in case 1. increasing the vessel diameter does not affect the reaction velocity.

Apart from this extreme sensitivity of reaction velocity to the dimensions of the reaction vessel, the chain theory predicts several other characteristic properties, the existence of some of which in any particular case being considered as adequate demonstration of the operation of a chain mechanism. Among these are the existence of sharply defined explosion limits, the catalytic effect of traces of foreign substances, high quantum yields, the existence of an induction period and the operation of abnormal kinetic relationships and temperature dependences. Stimulated by the discovery (by Backstrom (11)) of the chain characteristics of the photo - and thermal - oxidation of benzaldehyde, Egerton (12) was led to subscribe to the peroxidation ideas proposed by Callendar (8); at the same time he advanced the idea that an energy chain operated. While studying the problem of knocking in internal combustion engines, Egerton found that one molecule of lead tetra-ethyl in 200,000 molecules of the fuel-air mixture was effective in the prevention of knock, which is, essentially, premature slow combustion of fuel This remarkably efficient inhibition was only explicable in terms of a chain reaction and the following scheme was suggested

$$RH^{*} + O_2^{*} \longrightarrow RO_2H^{*} \qquad (1)$$

$$RO_2H^{*} \longrightarrow RO_2H + \qquad (2)$$

$$RO_2H^{*} + RH \longrightarrow RO_2H + RH^{*} \qquad (3)$$

$$RO_2H^{*} + M \longrightarrow RO_2H + M^{*} \qquad (4)$$

$$RO_2H^{*} \longrightarrow R\,CHO^{*} + H_2O^{*} \qquad (5)$$

This energy chain explained the detectability of peroxides and aldehydes at an early stage in the reaction, the high efficiency of lead tetra-ethyl as an inhibitor and the luminescence often observed far below the ignition temperature.

The year 1935 saw the publication of two very important papers of a theoretical nature. The first, by Norrish (13), criticised the Bone hydroxylation theory on the grounds that it did not account for the kinetic evidence, the high efficiency of positive and negative catalysts, the inhibition due to increase of surface area, the effect of variation of the vessel diameter upon the ignition temperature, the existence of sharp kinetic limits of explosion and the difficulty of detection of alcohols in the early stages of the reaction. Norrish also criticised the Egerton energy-chain theory because of the difficulty of detection of peroxides during the induction period, the lack of effect on the induction period of addition of peroxides and because the addition of an inert gas did not result in deactivation. This latter effect would certainly be anticipated in the case of an energy-chain reaction. Reviewing the work of Hinshelwood (14), Egerton (12), Haber (15) and Semenov (10), Norrish concluded that a chain reaction was in operation and advanced his atom chain theory to account for the oxidation of methane.

Thus
$$O + CH_4 \longrightarrow CH_4O \xrightarrow{x} CH_3OH + x$$
$$CH_4O \longrightarrow CH_2 + H_2O$$
$$CH_2 + O_2 \longrightarrow CH_2O + O$$

This was the first theory of hydrocarbon combustion which involved the participation of hydrocarbon free radicals of short life, and the following year Norrish and Foord (16) reported the demonstration of a degenerate chain-branching mechanism in the oxidation of methane. Describing formaldehyde as the essential intermediate and using the atom chain to account for its formation, these authors postulated a mechanism, which, on the application of the stationary state method, led to the expression.

$$\frac{-d(CH_4)}{dt} = \frac{K(CH_4)\ (O_2)\ P.d}{S}$$

where P = total pressure, d = diameter of vessel, S = surface area. The experimental results had shown that the maximum rate of the reaction was, in fact, given by

$$= K(CH_4)\ (O_2)P$$

and that increase of the surface: volume ratio, by packing the vessel, reduced the rate and that increasing the vessel diameter increased the rate.

The second important paper of 1935 was by Ubbelohde (17) who dismissed the hydroxylation theory in favour of a chain mechanism for much the same reasons as Norrish. Arguing on the similarity between hydrocarbon oxidation and aldehyde oxidation and the fact that oxygen atoms are very unlikely to feature in the latter reactions, Ubbelohde critised Norrish's atom chain theory. Ubbelohde favoured the peroxide type of mechanism which leads to the production of hydroxyl radicals which, it was known, are plentiful in flames and to the early production of excited formaldehyde molecules. This is an important point because spectral studies showed that the chemiluminescence in cool flames was always due to excited formaldehyde, irrespective of the hydrocarbon which was oxidising. The principal reactions in Ubbelohde's scheme were

$$
\begin{aligned}
&\mathrm{RCH_2^{\cdot} + O_2} &&\longrightarrow &&\mathrm{RCH_2O_2^{\cdot}}\\
&\mathrm{RCH_2O_2^{\cdot} + RCH_3} &&\longrightarrow &&\mathrm{RCH_2O_2H + RCH_2^{\cdot}}\\
&\mathrm{RCH_2O_2H} &&\longrightarrow &&\mathrm{RCH_2O^{\cdot} + OH^{\cdot}}\\
&\mathrm{RCH_2O_2H} &&\longrightarrow &&\mathrm{RCHO + H_2O}\\
&\mathrm{RCH_2O^{\cdot} + O_2} &&\longrightarrow &&\mathrm{RO_2^{\cdot} + CH_2O}
\end{aligned}
$$

Thus the two major kinetic theories of the slow combustion of hydrocarbons were formulated. They are very different but it would be very untrue to say that there are two schools of thought since it is generally thought now that the peroxide-intermediate theory probably does apply to propane and higher paraffins at lower temperatures but not to methane and ethane, while the excellent work of Bolland and his colleagues (18) has demonstrated its operation in the case of the higher (liquid) olefines. On the other hand there seems to be ltttle doubt that formaldehyde is the effective intermediate in the slow combustion of methane and ethylene. This latter theory is clearly a descendent of the earlier hydroxylation theory.

Perhaps the most important contributor to the peroxide theory has been Sir Cyril Hinshelwood. He and his collaborators, notably Cullis, Partington and Mulcahy have made valuable studies of the slow combustion of many paraffin hydrocarbons and their simple derivatives (19). They have shown in these cases that an induction period is followed by the acceleration of the rate to a maximum, that the rate is largely independent of the initial pressure of oxygen and dependent upon the hydrocarbon pressure to about the second power, and that added inert gases have little or no effect upon the maximum reaction rate. They have carried out analyses of the products of reaction at various stages in its course finding that the peroxide content rose to a maximum in a manner parallel to the variation of rate and that formaldehyde was an early product of the reaction. The mechanism which they have suggested is given below.

$$RCH_3 + O_2 \rightarrow RCH_2^{\cdot} + HO_2^{\cdot} \qquad \text{initiation}$$

$$\left.\begin{array}{l} RCH_2^{\cdot} + O_2 \rightarrow RCH_2O_2^{\cdot} \\ RCH_2O_2^{\cdot} + RCH_3 \rightarrow RCH_2O_2H + RCH_2^{\cdot} \end{array}\right\} \quad \text{propagation}$$

$$\left.\begin{array}{l} RCH_2O_2H \rightarrow RCH_2O^{\cdot} + OH^{\cdot} \\ RCH_2O_2H \rightarrow RCHO + H_2O \end{array}\right\} \quad \begin{array}{l}\text{degenerate chain-}\\ \text{branching reactions}\end{array}$$

$$RCH_2O_2H + O_2 \rightarrow \text{inactive products}$$

$$RCH_2O^{\cdot} \rightarrow R^{\cdot} + CH_2O \qquad \text{degradation}$$

This scheme explains the observed kinetics $\rho_{max} \simeq p_{RCH_3}^{2}$ with no dependence upon the oxygen pressure unless this latter is small. The experimental dependence of rate upon initial pressures of reactants and additives is seen to be quite different from the rate expression for the methane oxidation. The above scheme of reactions is very attractive in that the reaction steps are all very simple and feasible: for instance the degradation of the alkoxyl radical to the next lower alkyl and formaldehyde requires only the shift of one electron. The observed energies of activation are all of the order of 35 kcals./mole which is a reasonable figure for the branching reaction $R-O-O-H \quad R-O^{\cdot} + {}^{\cdot}O-H$ The initiation reaction has been criticised on account of the unlikelihood of the existence of the $HO_2^{\cdot}$ radical. However, the existence of the $HO_2$ radical has been amply demonstrated (20.21.22). Norrish has opposed the theory expressing the view that the alkyl hydroperoxide does not fulfil all the requirements of the intermediate in a reaction with degenerate branching of the chains (23). He has shown that the essential intermediate must attain a pressure of several millimetres at the maximum rate to account for delayed branching and inclines to the view that aldehydes are responsible for the degenerate branching observed.

The formaldehyde-intermediate theory of Norrish was modified as a result of an investigation into the mechanism of oxidation of formaldehyde itself, by Axford and Norrish (24). Their mechanism for this reaction will be discussed later but it may be noted, at this stage, that the principal reactions suggested were

$$CH_2O + OH \longrightarrow H_2O + CO + H$$

$$H + O_2 + CH_2O \longrightarrow CO + H_2O + OH$$

the second reaction being regarded as a reaction of a highly energised $HO_2$ complex rather than as a ternary reaction. This suggested mechanism for the formaldehyde oxidation shifted the emphasis from $CH_2$ and O radicals to $CH_3$ and OH radicals in the methane reaction (25). Thus the propagation steps were written

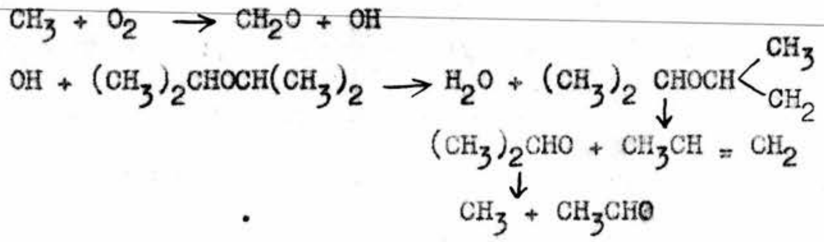
$$CH_4 + OH \longrightarrow CH_3 + H_2O$$

$$CH_3 + O_2 \longrightarrow CH_2O + OH$$

and the formaldehyde thus formed reacted as shown above.

Norrish has also suggested (23) that higher hydrocarbons are oxidised by a mechanism involving the production and reaction of aldehydes but it is now thought that the temperature of reaction influences the mechanism. Pease (26) observed (in the case of propane) a slackening of the reaction rate with increasing temperature and that the Arrhenius curve actually passed through a minimum at about 360°C. Mulcahy (27), discussing this important observation, has suggested that this indicates the extistence of two distinct regions of reaction high - and low - temperature and has pointed out that the pronounced structural effect on the rate of oxidation in the low-temperature region is not observed in the higher temperature range. Now this structural effect has been interpreted by Hinshelwood (28,29) in terms of the effect of the nature of the alkyl group in the decomposition of alkyl group in the decomposition alkyl hydroperoxides to alkoxyl and hydroxyl radicals. Consequently Mulcahy concluded that the high-temperature reaction was not peroxidic in character and that the slackening in reaction rate with increasing temperature above 300°C was due to the gradual disappearance of peroxides from the reaction mechanism. It would then appear that methane and ethylene being simplest members of homologeous series exhibit rather singular behaviour in that they show no "low temperature" oxidation at all. Walsh (30) attempted to synthesise the two theories to some extent and sought to explain the absence of a low temperature methane oxidation on the grounds that in this case the hydroperoxyl radical is too unstable to survive with the heat involved in its formation from methyl and oxygen. This conclusion was based, to some extent, on the results of Bates and co-workers (31, 32) who studied the photo-oxidation of methyl (from methyl iodide) and ethyl (from ethyl iodide). These workers concluded that in the latter case ethyl peroxyl was formed but that in the case of methyl, formaldehyde and hydroxyl were the products of the reaction $CH_3 + O_2$.

Walsh's theory of the high temperature mechanism of combustion is illustrated in his work on the combustion of di-isopropyl ether (30) at temperatures ranging from 360°C to 460°C (i.e. in the "high temperature" region). The radicals involved in his proposed mechanism included methyl, hydroxyl and hydrogen peroxyl, the chain propagation steps being

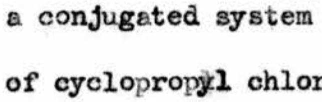


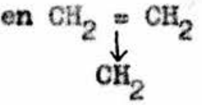
$$CH_3 + O_2 \rightarrow CH_2O + OH$$

$$OH + (CH_3)_2CHOCH(CH_3)_2 \rightarrow H_2O + (CH_3)_2\,CHOCH{<}{\begin{matrix}CH_3\\CH_2\end{matrix}}$$

$$\begin{array}{c}\downarrow\\(CH_3)_2CHO + CH_3CH = CH_2\\\downarrow\\CH_3 + CH_3CHO\end{array}$$

There has been very little work reported on the slow combustion of saturated cyclic hydrocarbons, although Chavanne and his co-workers have studied the products of oxidation of many substituted cyclohexanes and cyclopentanes (33). Levin (34) oxidised several alkyl cyclopentanes and cyclohexanes in a static system at 200°C and observed that an induction period was followed by a decrease of the pressure of some 10 m.ms. and eventually the pressure increased to a limiting value. Such a pressure decrease is very suggestive of primary peroxide formation and the products found by Chavanne also indicate the initial formation of an alkyl hydroperoxide. It would be quite unjustified to draw any more concrete conclusions from published work on the slow combustion of cycloparaffins.

Cyclopropane or trimethylene, is the simplest homocyclic compound and its structure has been the subject of some controversy in recent years. It is well known that while cyclobutane and higher homologues are not attacked by hydrogen bromide and yield substitution products with bromine, cyclopropane forms propyl bromide with HBr and is slowly attacked by bromine to form 1 : 3 dibromopropane. Walsh (35) has suggested that such addition reactions of cyclopropane are due to the unsaturated character of the C - C bonds. Arguing from the fact that the spectroscopic properties of compounds containing the  $CH_2 - CH - CH = CH-$ (with $CH_2$ below) grouping are properties characteristic of a conjugated system and from the fact that the dipole moment of cyclopropyl chloride is 0.3 D less than the values for isopropyl chloride and cyclopentyl chloride, Walsh proposed that the formula for cyclopropane should be written



$$\begin{array}{c} CH_2 = CH_2 \\ \downarrow \\ CH_2 \end{array}$$

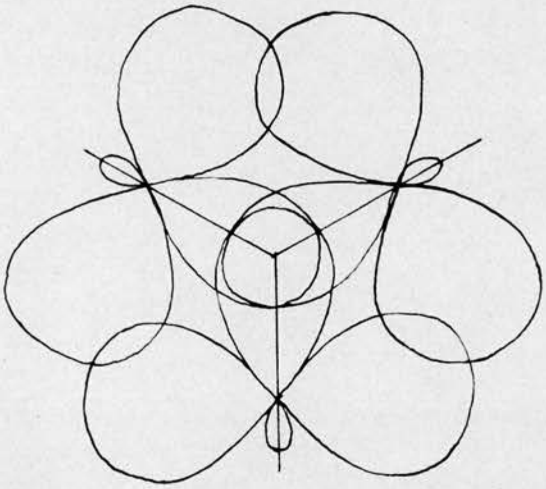
indicating the donation of electrons by the double bond to assist in the formation of a bond to the third methylene. The existence of $\pi$ electron dative bonds had been suggested earlier by Dewar (36) to account for some rearrangements of the hydrazobenzene → benzidine type and to explain some anomalies in aromatic substitution by cationoid reagents.

Robinson (37) objected to this proposal, pointing out that the formula drawn by Walsh did not possess the required symmetry and that to achieve symmetry by writing three identical canonical forms was to assign to cyclopropane its classical structure. In replying to this criticism Walsh (38) remarked that the hybrid visualised did differ from the classical structure in that the orbital hybridisation in the carbon atoms was trigonal rather than tetrahedral. A very important piece of evidence for $sp^2$ hybridisation is the low dipole moment of cyclopropyl chloride since a trigonal carbon atom has a higher electronegativity in its $sp^2$ valencies than has a tetrahedral carbon atom in its $sp^3$ valencies. Further evidence for the similarity between the C - C bonds in cyclopropane and ethylene is afforded by the determination of the angle HCH Bastiansen and Hassel as 118·2 ± 2 (i.e. greater than tetrahedral and almost trigonal)(39), by Linnett's calculation of the C - H stretching-force constant to be $5{\cdot}0 \times 10^5$ dynes/cm. (compared with $5{\cdot}1 \times 10^5$ dynes/cm. in ethylene and $4{\cdot}6 \times 10^5$dynes/cm.

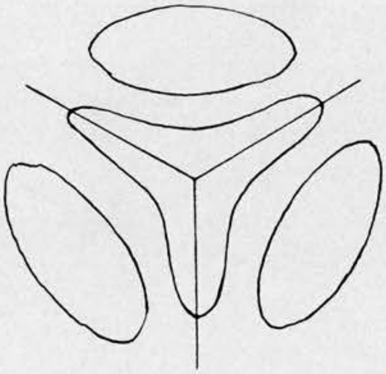
in a paraffinic methylene group)(40), and by the high value of the quenching cross-section of cyclopropane for cadmium resonance radiation (41).

Having discussed the likelihood of trigonal hybridisation, Walsh then considered the synthesis of the cyclopropane ring from three $CH_2$ groups whose C - H valencies were of the $sp^2$ type and whose planes were perpendicular to the carbon ring plane (42). Molecular orbitals are then formed by the overlap of (a) the 2p atomic orbitals lying in the plane of the ring and (b) the third $sp^2$ orbitals whose axes also lie in the plane of the ring. The overlap is shown in figure 1. and the probability pattern of the electrons in the resultant molecular orbitals is shown below it. Sugden (43) has reported a qualitative application of the non-localized molecular orbital theory to justify Walsh's conclusions as to the structure of cyclopropane.

In contrast to the usual comparitive reactivity of cyclopropane its thermal oxidation shows it to be in some respects a stable substance. Day and Pease (44) studying the slow combustion of several hydrocarbons of different types found that like methane and ethylene, but unlike paraffins in general, cyclopropane gave no cool flames (which are a fair indication of combustion by a peroxide intermediate mechanism at low temperatures). Furthermore, cyclopropane was found to oxidise more slowly than propane or propylene whose ignition temperatures were considerably lower than that of the cyclic hydrocarbon. These authors gave three rates of reaction measured at 370°C which showed that the rate was independent



ORBITAL OVERLAP IN CYCLOPROPANE



PROBABILITY PATTERN

of the initial oxygen pressure and strongly dependent upon the initial pressure of cyclopropane. They also noted that the addition of a little acetaldehyde to the reaction mixture produced a shortening of the induction period..

The slow combustion has been studied, therefore, by the static method, kinetically and analytically, in the temperature range 380° C to 430°C, with partial pressures of the reactants between 40 m.m. and 400 m.m.

# EXPERIMENTAL TECHNIQUE

## THE APPARATUS

The apparatus employed in this investigation was of a conventional type and is illustrated diagramatically in figure 2. It was constructed in Pyrex glass throughout and all taps and interchangeable joints were lubricated with Apiezon Grease L.

The reaction vessel was thoroughly washed with hot concentrated nitric acid to remove contaminating materials on the glass. It was then rinsed with tap water for several hours and finally distilled water before being sealed on to the apparatus. The reaction vessel was housed in a well-lagged furnace whose brass core was wound with nickel-chrome resistance wire. The resistance of the winding was 55 ohms and it was operated at a current of 2 amps. The imput voltage (110 volts) was supplied by a variac transformer.

Since pressure measurements were to be made with some accuracy, a considerable degree of temperature control was necessary. A Sunvic energy regulator was used to regulate the imput energy. It was found that when the mains voltage was steady the temperature of the reaction vessel could be kept constant ± 1°C with little difficulty.

Temperature measurements were made thermo-electrically. A Ferry-Bright-ray thermocouple was contructed and was calibrated by maintaining its cold junction at 0°C and measuring the thermal e.m.f.s. produced when its hot junction was placed in melting ice, condensing steam, condensing glycerol vapour, condensing sulphur vapour and cadmium, potassium dichromate and

APPARATUS

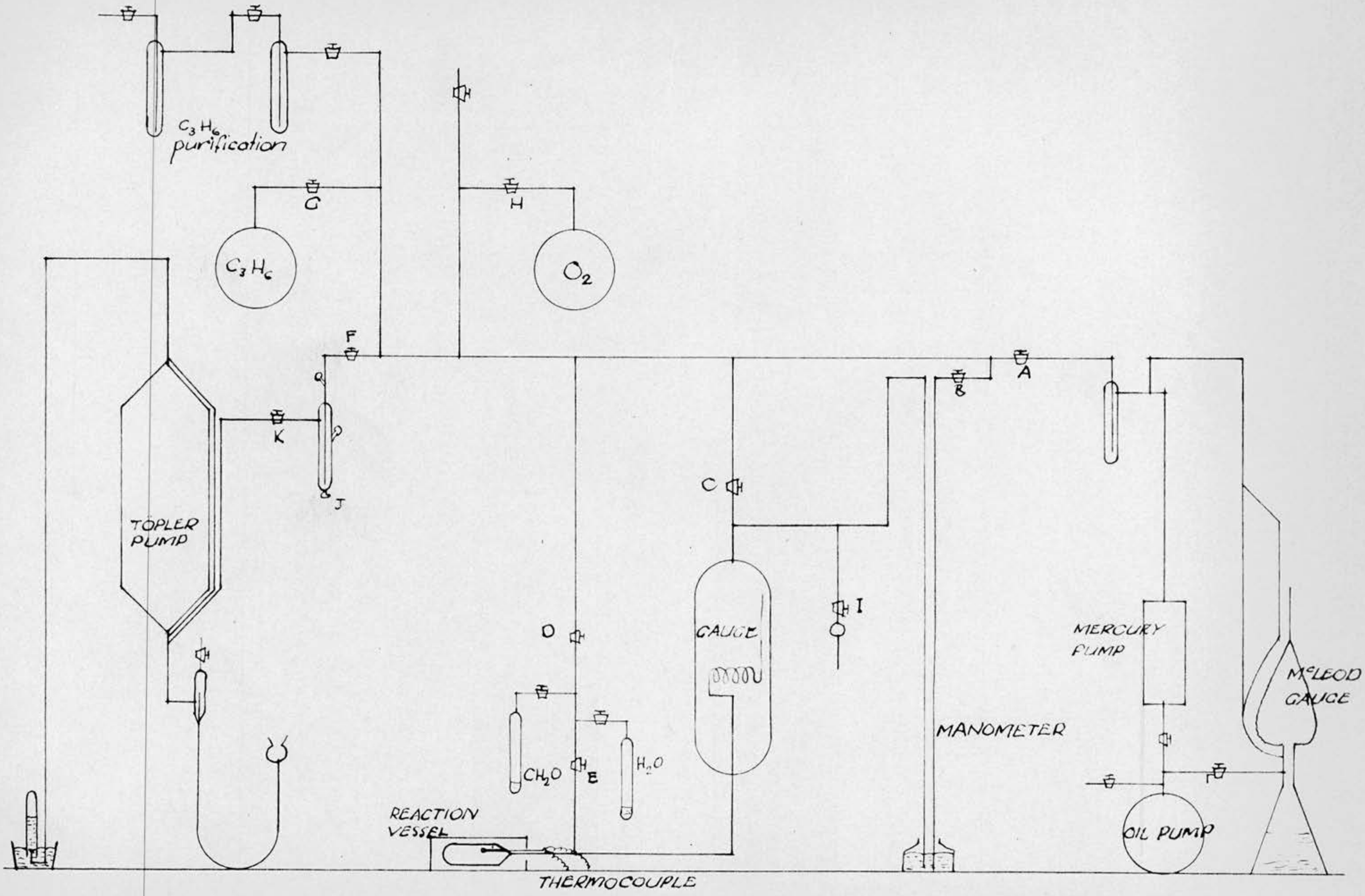


FIG. 2.

zinc at their respective melting points.

These e.m.f.s. were measured by means of a Cambridge potentiometer and a ballistic galvanometer. During reactions, experimental temperatures were measured by the same technique, the hot junction being kept inside the reaction vessel as shown (fig. 2).

The measurement of pressure in the kinetical study of gas reactions has aroused much interest and discussion. The direct use of a mercury manometer is impossible in free radical and other reactions due to the catalytic effect of metals. To overcome this difficulty many types of gauge have been devised. The Foord gauge has many advantages and one was used in conjunction with a mercury manometer in preliminary experiments. Its sensitivity, however, was unnecessarily high and its robustness, unfortunately, was not high enough.

A more robust and adequately-sensitive instrument is the spiral gauge (fig. 2). The construction of such a gauge has been described (45). A piece of glass-tubing (4 m.m. diameter) was drawn down so that its wall thickness was very small but without greatly affecting the internal diameter. This was suspended from the end of a slightly tapered brass rod which was rotated at a very slow speed so that the rod moved, slowly, horizontally while the glass tube remained vertical. The glass tube was heated indirectly by an iron plate which was, itself, heated by an oxy-coal gas flame.

In this way a delicate spiral of about eight turns was wound. This was sealed off at one end to which was affixed a thin glass pointer. The other end was sealed into an outer jacket and joined on to the apparatus as shown.

An optical system was arranged to give a ten-times magnification of pointer movement on a screen. The spiral gauge was used as a null-point instrument, the external pressure being adjusted by manipulation of taps C and I, and, at the null-point, pressures being read off on the mercury manometer. The spiral gauge was found to be very robust and the arrangement was found to be sensitive enough for all purposes.

The pumping system was not complex, consisting of a two-stage vertical, annular-jet type of mercury-vapour pump backed by a Hyvac rotary oil-pump. A McLeod gauge, which was joined to the evacuation line just before the liquid oxygen cooled trap, was employed for the measurement of pressure in the system during evacuation. It was found that the pressure could be reduced to $10^{-5}$ to $10^{-6}$ m.m. of mercury after much less than one hour's evacuation.

The removal of the products for analysis was affected by use of a Toepler (Antropoff) pump of conventional construction.

The gases used were taken from cylinders. The oxygen was drawn through a liquid-oxygen-cooled trap to remove condensible materials and was then allowed to leak into a two-litre bulb.

The cyclopropane was condensed in a trap cooled to -180°C by liquid oxygen. It was then distilled, the middle fraction being trapped in a second cold trap. The middle fraction of a second distillation was then allowed to leak into an evacuated five-litre reservoir.

Nitrogen was taken from a cylinder, was passed over heated copper to remove oxygen and finally through two traps cooled in liquid oxygen before being allowed to leak into the system.

Hydrogen was also taken from a cylinder and received exactly the same pretreatment as nitrogen.

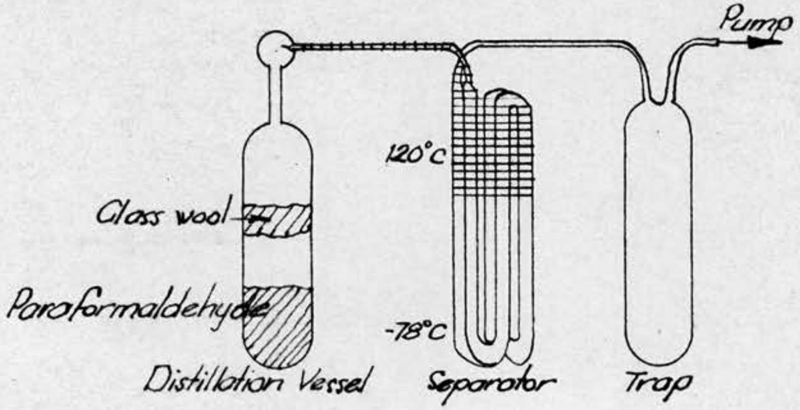
Pure liquid monomeric formaldehyde was prepared by the method of Spence and Wild (46). Paraformaldehyde, obtained by careful evaporation of a 40% aqueous solution of formaldehyde, was broken up and dried for two days over concentrated sulphuric acid in a vacuum desiccator. The product was then finely powdered and heated to 110°C in the distillation vessel of the apparatus (figure 3) which had been evacuated to $10^{-6}$ m.m of mercury pressure while the condensing vessels were heated. While the first fraction was distilling these vessels were heated in a blow-pipe flame to prevent the condensation of water there.

The trap was then cooled to -180°C and the tap to the pump was closed. As the distillation proceeded the oil-bath temperature was gradually raised to 120°C and when sufficient monomer had been collected, the oil-bath was removed and the trap was carefully sealed off. Alternate removal and replacement of the liquid oxygen container brought all the formaldehyde to the foot of the trap which was then sealed on to the line in position.

The function of the separator, a compact block of three U-tubes, was to alternately heat and cool the gases, whereby

FIGURE 3.

Apparatus for preparation of formaldehyde



water was removed completely. (Slightly wet formaldehyde polymerises readily).

For the experiments involving the addition of water, a trap was attached to the line containing freshly boiled distilled water. This was freed from dissolved air by alternate heating in a warm water bath and cooling to -180°C; the gases liberated on warming were pumped away.

It is obvious that a knowledge of the reaction volume (which includes the dead space of the capillary tube and the spiral of the gauge) is essential if an attempt is to be made to study the stoichiometry of the reaction.

The pressure of a certain amount of oxygen was measured in the reaction vessel at a noted temperature. The oxygen was then removed by Toepler pump and its volume was determined at room-temperature and pressure.

## GAS ANALYSIS

The apparatus employed is represented diagramatically in figure 4.

By way of tube B, the gases were drawn from the collecting tube A into the absorption tube C. The volume of the sample was measured by transferring it to the 10 m.l. burette D, closing tap J and adjusting the height of the reservoir E until the mercury levels in D and F were the same (with tap G open to the air) i.e. when the gas in D was at atmospheric pressure (less the saturated vapour pressure of water). A slow flow of water through the jacket ensured some constancy of temperature which was read off on a thermometer.

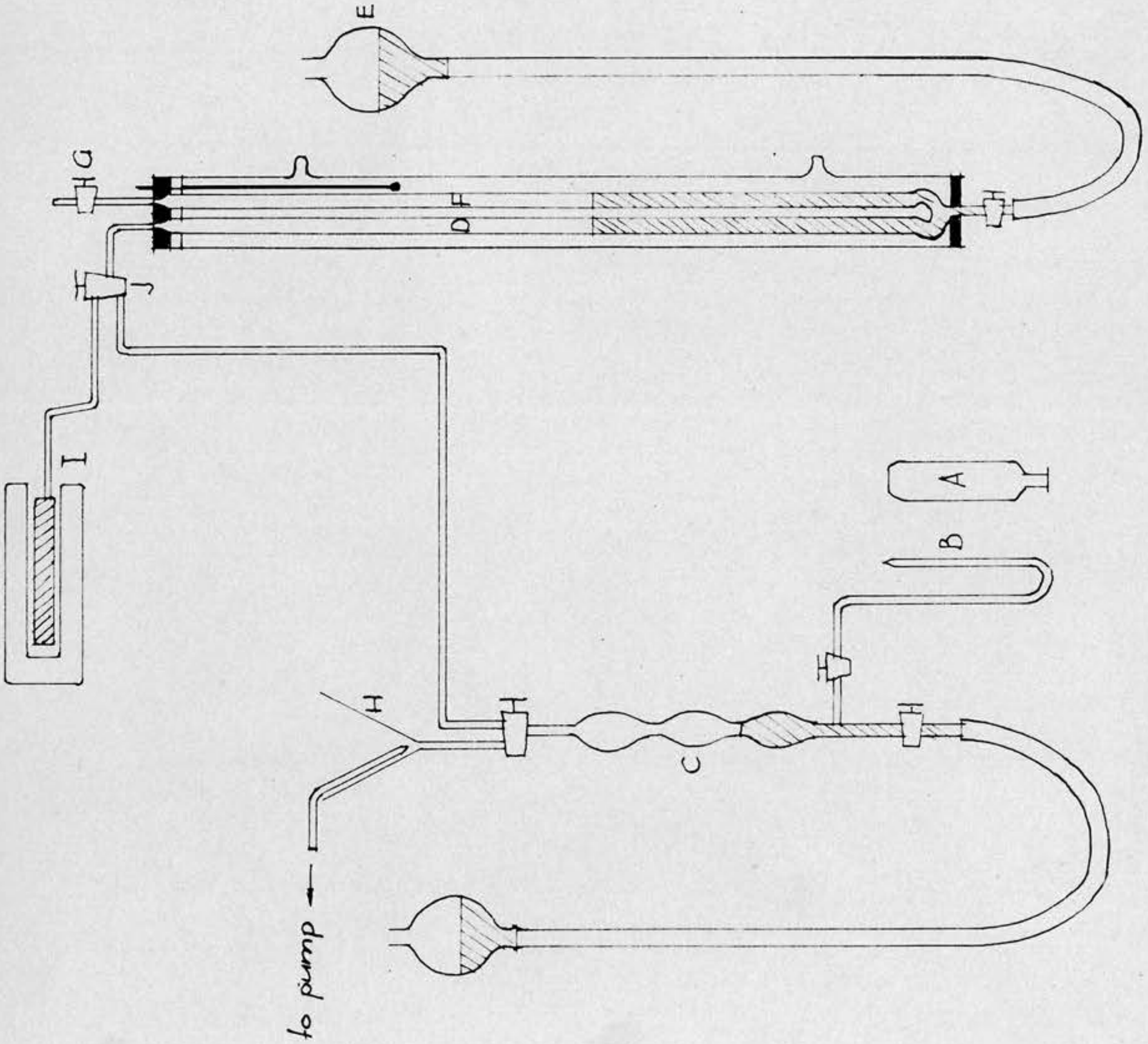
The sample was then transferred to C and some of the reagent required was drawn in from H. A few drops of mercury were added to form a seal between H and C. After absorption was complete the gas was pushed back to the burette D and the spent reagent was removed at H. Last traces of reagents were washed out first with dilute sulphuric acid, and finally with water.

I is a silica combustion tube containing copper oxide heated by a small furnace around it to 550°C. Before the beginning of an analysis it was evacuated by manipulation of the reservoir E. By a Toepler-like procedure gas was drawn from I into D. Tap J was then closed to I and the gas was pushed over to C and was eventually removed at H.

The reagents used for the various gases were as follows:-

FIG. 4

# GAS ANALYSIS APPARATUS



| Gas | Reagent |
|---|---|
| Carbon dioxide | 30% aqueous caustic potash |
| Oxygen | Alkaline pyrogallol. |
| Ethylene | Saturated bromine water. |
| Propylene | A solution of 57 g. mercuric sulphate in 200 gms. 22% sulphuric acid. |
| Cyclopropane | 87% sulphuric acid. |
| Acetylene | Alkaline potassium mercuri-iodide solution. |
| Carbon monoxide | 10% cuprous chloride in conc. HCl. |

Hydrogen and paraffin hydrocarbons were determined by combustion and nitrogen was obtained by difference. In actual practice some separation of the products was effected before analysis. The product gases were pumped through a trap cooled in liquid oxygen by the Toepler pump. The fraction, gaseous at this temperature was collected and analysed for carbon dioxide, oxygen, unsaturated hydrocarbons, cyclopropane, carbon monoxide, hydrogen, methane, and nitrogen. The trap was then allowed to warm up to -78°C, by replacing the liquid oxygen by acetone cooled with solid carbon dioxide. Incidentally, it was found that the addition of a few drops of paraffin oil to the acetone prevented excessive frothing when the carbon dioxide was added.

A second gas fraction was then pumped off and analysed for carbon dioxide and cyclopropane. The contents of the trap were then allowed to warm up to room temperature and air, dried by passage through a calcium chloride tube, was then admitted to the trap.

## Qualitative Examination of the Condensible Products.

The accumulated products from several experiments were examined qualitatively. It was dissolved in 20 mls. of water.

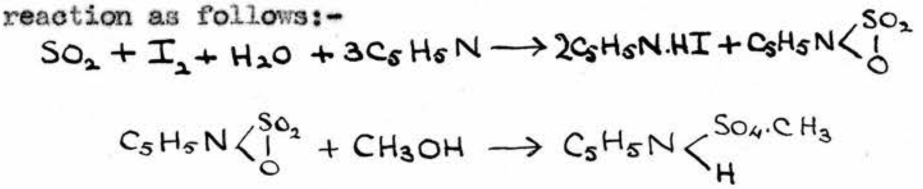
It had a characteristic odour and was slightly acid to litmus.

1. It was found that 1 ml. of the solution restored the colour to Schiff's Reagent, slowly and on standing.
2. The presence of formaldehyde was established by the production of a violet colour when 1 ml. of the solution was heated with a sulphuric acid solution of chromotropic acid (1:8-dihydroxynaphthalene - 3: 6 disulphonic acid).(47).
3. The absence of acetone was indicated by the failure of the sodium nitroprusside test.(48).
4. The acidity of the solution was only slight. 10 mls. of it required only 1 ml. of $\frac{N}{100}$ alkali for neutralisation. The neutral solution thus obtained was evaporated gently to about half bulk. A few drops of aqueous silver nitrate were added but no precipitate appeared. On further evaporation some silver was deposited by oxidation of aldehyde but no silver salts appeared.
5. One ml. of solution was tested for peroxides with a methanolic solution of ferrous thiocyanate.(49) There was no development of the ferric thiocyanate colour, thus indicating the absence of peroxides.
6. The presence of acrolein in the condensible products was suspected for some time. The failure of the σ-dianisidine reaction can not be said to be due to the masking effect of formaldehyde since the reagent is four hundred times more sensitive to acrylic aldehyde than formaldehyde and since the former aldehyde gives darker colours with the reagent than formaldehyde. (50).

7. The failure to obtain a trinitrobenzoyl derivative indicated the absence of a reasonable quantity of alcohols and various colorimetric tests were applied with negative results for other aldehydes. (51).

Determination of water formed in the reaction

There are many physical methods available for the determination of reasonably large quantities of water. Of the many attempts to determine small amounts chemically, by far the most successful is the Karl Fischer method which involves the following reactions between sulphur dioxide, iodine, pyridine, nethanol and water. Smith, Bryant and Mitchell (52) represented the reaction as follows:-



$$SO_2 + I_2 + H_2O + 3C_5H_5N \longrightarrow 2C_5H_5N.HI + C_5H_5N\Big\langle\begin{matrix}SO_2\\|\\O\end{matrix}$$

$$C_5H_5N\Big\langle\begin{matrix}SO_2\\|\\O\end{matrix} + CH_3OH \longrightarrow C_5H_5N\Big\langle\begin{matrix}SO_4.CH_3\\H\end{matrix}$$

The solution of sulphur dioxide, iodine and pyridine dissolved in dry methanol (the Karl Fischer reagent) is unstable, partly due to its extremely hygroscopic nature and partly due to the other reactions taking place even in the absence of water. For this reason it must be standardised against a standard solution of water before use.

The visual determination of the end-point (change from chromate-yellow to a yellow permanently tinged with the reddish-brown of free iodine) is uncertain. For this reason and also to prevent absorption of moisture during titration a commercial titration unit was used which was claimed to exclude moisture and which incorporated a sensitive micro-ammeter to measure conductance between two platinum electrodes immersed in the titration mixture which is stirred by a stream of dry nitrogen. At the beginning of the titration the meter registers about five scale divisions while the end-point was taken when the meter registered about eighty scale divisions for at least half a minute.

The Karl Fischer reagent was prepared according to the formula of Smith, Bryant and Mitchell.(52). A solution of 84.7 g. iodine and 269 mls. pyrdine in 667 mls. dry methanol was cooled in a slurry of ice. 64 g. of liquid sulphur dioxide was added slowly and with stirring. The solution was rapidly transferred to the storage bottle on the apparatus.

## Determination of Formaldehyde Formed in the Reaction

The amount of formaldehyde present in the condensible products was determined by a method similar to that of Bricker and Johnson (53).

100 mgms. ± 10 mgms. of chromotropic acid were weighed into a 30 mls. beaker and 1 ml. of solution of formaldehyde was added. 5 mls. of concentrated sulphuric acid were added slowly and with cooling and the solution was then heated for 30 minutes on a boiling water bath. The solution was then cooled and diluted to 50 mls. in a graduated flask. When the temperature fell to that of the room the volume was made up to exactly 50 mls. and the optical intensity of the solution was then compared with that of a reagent blank at 570 m.m.

In exactly the same way the optical intensity was measured of solutions obtained by treatment of 1 ml. of various standard solutions of formaldehyde. These were prepared by suitable dilution of a 32% formalin solution which was standardised by titration with iodine.

## Results

2.5 ccs. of the formalin solution were diluted to 500 ccs with distilled water. Two 25 mls. samples were pipetted into conical flasks where they were treated with 50 ccs. of 0.0955 N iodine introduced by pipette. The solutions were then treated with 10% caustic soda until a pale yellow colour developed and were allowed to stand for 15 minutes with occasional shaking. On acidifying with dilute hydrochloric acid, unchanged hypoidite was reliberated as iodine and this was then back titrated in the usual way with 0.0947 N thiosulphate.

Titrations: 21.53 mls. and 21.57 mls.

i.e. mean titration: 21.55 mls. 0.0947 N thio-sulphate.

Thus 25 mls. of the diluted formalin solution required

(50 - 21.55 x 0.0947) mls. of 0.0955 N iodine for oxidation

But 30 gms. $CH_2O$ = 2 li. N $I_2$

$\therefore$ Formaldehyde present in 25 mls. solution

= (50 - 21.55 x 0.0947) x 0.0955 x 0.00150 gms. ?

Hence 1 cc of this solution contains 0.00164 gms. of formaldehyde.

By suitable dilution of 10 mls. samples of this solution, solutions containing 8.9, 16.4, 32.8, 65.6, 82.0, 104.0 and 164.0

micrograms of formaldehyde/ml. were obtained. These provided satisfactory colorimetric standards and the data in table no. 1 illustrate the variation of extinction coefficient with changing formaldehyde concentration.

TABLE NO. 1.

| Conc. of Formaldehyde (Y/ml.) | Log. $\frac{I_0}{I}$ |
|---|---|
| 8·2 | 0;074 |
| 16;4 | 0·157 |
| 32·8 | 0·287 |
| 65·8 | 0·544 |
| 82·0 | 0·670 |
| 104·0 | 0·754 |
| 164·0 | 0·948 |

# EXPERIMENTAL RESULTS

## A TYPICAL EXPERIMENT

The apparatus was evacuated for one hour, so that the pressure in the system was $10^{-5}$ m.m. or below, as measured by the McLeod gauge. It was ensured that the temperature was constant at 678°A. The taps A, B, C, D, E and F were then closed and dry air was admitted through tap I to the gauge jacket until the manometer showed a pressure head of 177·4 m.m.

By opening tap G the connecting tubing was filled with cyclopropane. Tap G was then reclosed and by manipulation of taps D and E the hydrocarbon was cautiously admitted to the reaction vessel until the gauge-pointer's shadow returned to the null point on the screen. Tap A was then opened to remove all cyclopropane left in the connecting tubing.

Dry air was again admitted to the gauge jacket until the manometer registered a pressure of 328·8 m.m. and 151·4 m.m. of oxygen were allowed into the reaction vessel in a manner similar to that adopted in the case of hydrocarbon. The stop-watch was started just as the first of the oxygen entered the reaction vessel.

After all the residual oxygen in the tubing had been pumped away, the pressure in the gauge jacket was increased by admission of a little more air and the manometer readings were taken. When the pointer's shadow returned to the zero mark, the time was noted and the external gauge pressure was again altered. By this procedure, the rather cumbersome technique of altering the external pressure to balance the pointer movement was avoided.

The alterations of pressure were designed to give time intervals of between one minute and ninety seconds. When there was no further change of pressure and the final reading had been taken, taps D, E and F were opened and the products were pumped through the trap J as previously described. After the gas fractions had been collected and the trap J had warmed up to room temperature, dry air was admitted to it. 20 mls. of dry methanol were then pipetted into the trap which was then carefully removed and stoppered. Meanwhile the tap F was closed and the remainder of the apparatus was evacuated in readiness for the next experiment. The pressure-time record is given in table No. 2. The table also gives the values of the rates operative over the times between consecutive pressure readings. The times t'midway between these readings are also given. Another column in the table lists the logarithms of the pressure changes noted at each time.

Table No. 2

12. 2. 52 Evacuation time = 1 hour Run No. B.99 Temperature = 701°A

| Time (minutes) | PRESSURE READINGS Left limb. | Right limb. | Head | Pressure Change (Δp) | Log.₁₀ Δp | Rate m.m./mm | Time t' | Remarks. |
|---|---|---|---|---|---|---|---|---|
| - | 594·6 | 772·0 | 177·4 | - | - | - | - | 177·4 m.m. cyclopropane admitted. |
| 0 | 444·8 | 773·6 | 328·8 | - | - | - | - | 151·4 m.m. oxygen admitted. |
| 5·00 | 443·8 | 773·6 | 329·8 | 1·0 | 0·0000 | 0·20 | 2·50 | |
| 6·92 | 440·0 | 773·6 | 333·6 | 4·8 | 0·6812 | 1·98 | 5·96 | |
| 7·57 | 435·1 | 773·6 | 338·5 | 9·7 | 0·9868 | 7·54 | 7·25 | |
| 8·32 | 425·0 | 773·7 | 348·7 | 19·9 | 1·2989 | 13·60 | 7·95 | |
| 9·00 | 410·2 | 773·9 | 363·7 | 34·9 | 1·5428 | 21·95 | 8·67 | |
| 9·60 | 395·0 | 774·0 | 379·0 | 50·2 | 1·7007 | 25·50 | 9·30 | |
| 10·08 | 382·2 | 774·1 | 391·9 | 63·1 | 1·8000 | 26·69 | 9·85 | |
| 10·78 | 369·1 | 774·3 | 405·2 | 76·4 | 1·8831 | 19·00 | 10·43 | |
| 15·00 | 366·2 | 774·5 | 408·3 | 79·5 | 1·9004 | 0·73 | 13·05 | |

From the data in the table many important factors may be determined. The graph No. 1 illustrated the variation of with time. The curve is a smooth S-shaped one of the type normally found in free radical hydrocarbon oxidations, which are also characterised by a long induction period. The second graph (No. 2) illustrates the method of determination of the maximum rate. The rates (table No. 2) are plotted against time (t') and the curve shows the gradual increase of rate to a maximum after which it falls off again to zero.

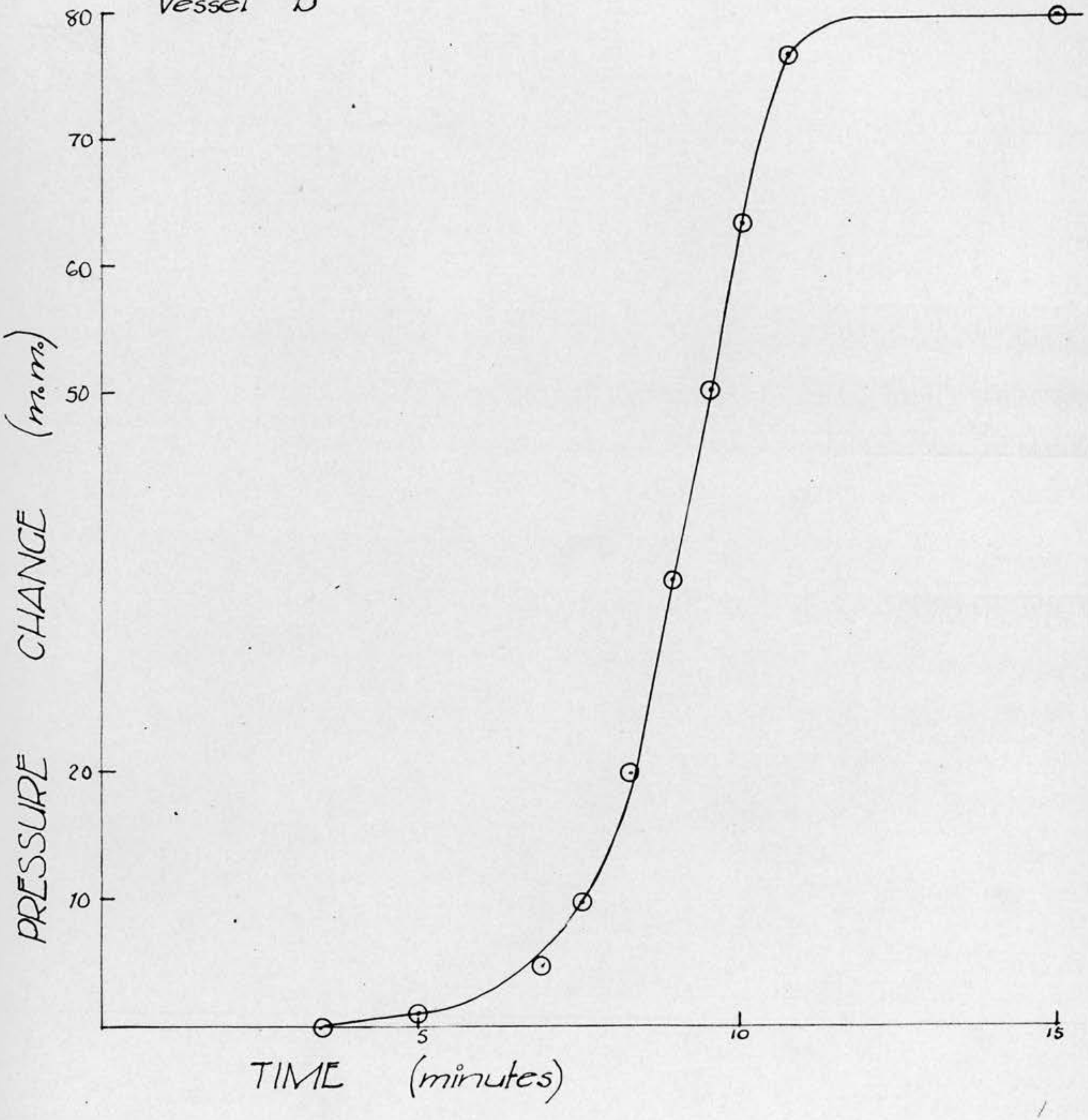
The application of the Semenov theory of degenerate branching chains to the reaction is justified by the graph (No. 3) of $\log_{10}\Delta p$ against time. This graph is linear over a very considerable period but begins to curve away some time before the attainment of maximum rate, and must be considered to be a better line than many which have appeared in the literature. The gradient of the line, if multiplied by 2.303 gives the net-branching factor $\phi$ but since this offers no particular advantage, future reference in this thesis to the net-branching factor A' actually means the gradient of the line relating $\log_{10}\Delta p$ and t i.e. $\frac{\phi}{2.303}$

It is to be concluded from the results obtained in this typical experiment that the rate of the reaction increased to a maximum value and that the early part of the reaction, at least, proceeded in accordance with the relationship $\Delta p = Ae^{\phi t}$. Furthermore the reaction was characterised by a long induction period. These are characteristic features of a chain reaction with

GRAPH No 1

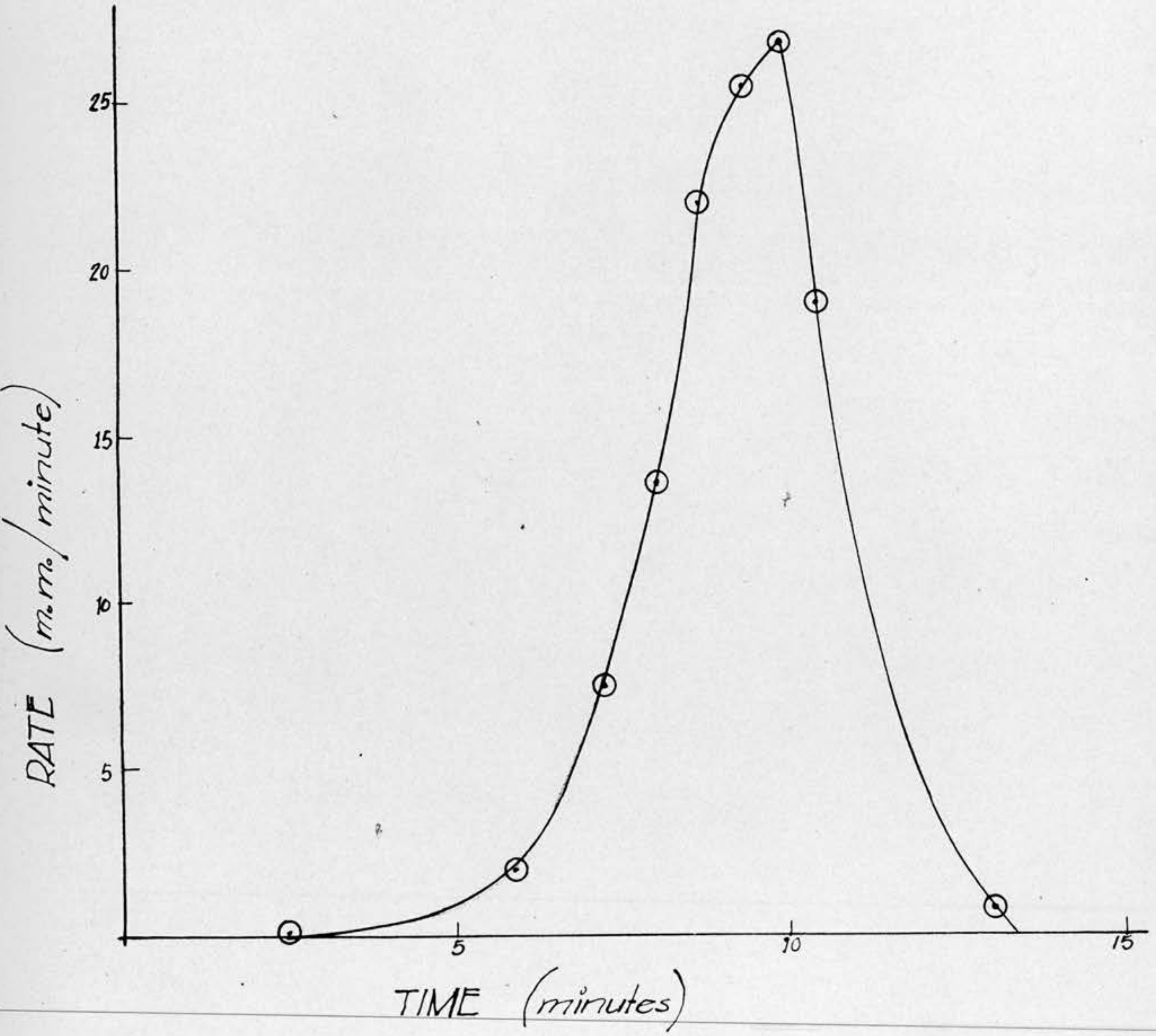
## Pressure - Time Curve (Run No B99)

$p_{C.P.}$ = 177·4 m.m.
$p_{O_2}$ = 151·4 m.m.
T = 701° A
Vessel B



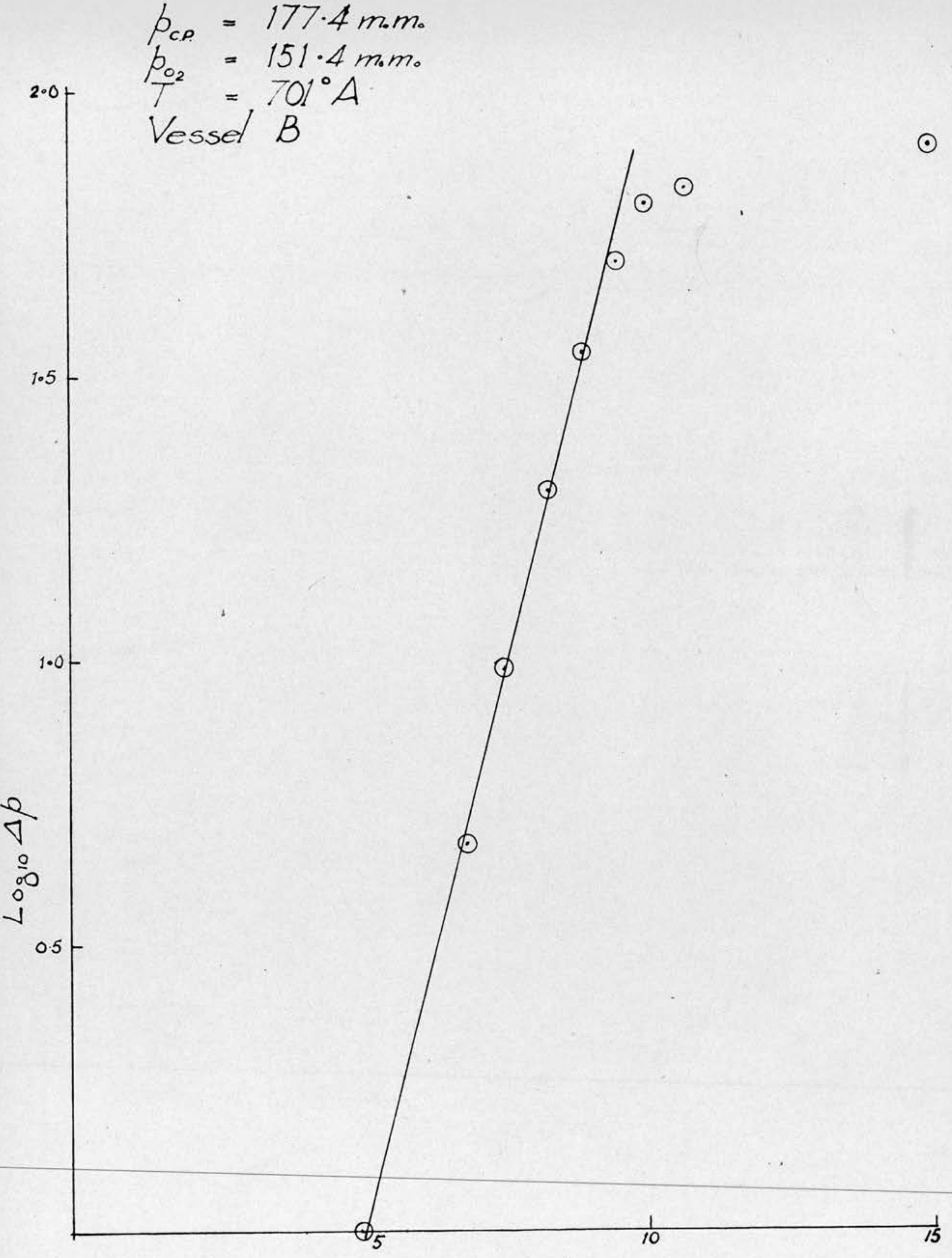
Rate - Time Curve (Run Nº B99)

$p_{C.P.}$ = 177·4 m.m.
$p_{O_2}$ = 151·4 m.m.
T = 701°A
Vessel B



GRAPH No 3

Determination of A′ (Run No B99)



$p_{C.P.}$ = 177·4 m.m.

$p_{O_2}$ = 151·4 m.m.

$T$ = 701°A

Vessel B

degenerate branching and in accordance with earlier work in the slow-combustion field the following parameters of the reaction were considered to be of importance - the maximum rate, $\rho_{max}$; the net-branching factor A'; the time elapsing before the occurrence of a pressure change of 1 millimetre, $\tau$; the time elapsing before the attainment of maximum rate, $\theta$; the pressure change occurring during the time $\theta$, $\Delta p_{max}$; and the total pressure change, $\Delta p_{\infty}$. The values of these parameters are given in table No. 3 which refers to the typical experiment just described.

TABLE NO. 3.

Results of a Typical Experiment

Run No. B.99

Initial pressure of cyclopropane ($p_{cp}$) = 177.4 m.m.

Initial pressure of oxygen ($p_{o_2}$) = 151.4 m.m.

Temperature = 701°A

$\rho_{max}$ = 26.8 m.m./minute

$A'$ = 0.394

$\tau$ = 5.0 mins

$\theta$ = 9.8 mins.

$\Delta p_{max}$ = 56 m.m.

$\Delta p_{\infty}$ = 79.5 m.m.

## Determination of the Reaction-vessel Volume

A volume of oxygen was admitted to the reaction vessel (by which is understood the vessel itself and the dead space up to the tap and up to the gauge) and when it came to thermal equilibrium, the gauge pointer was brought back to the zero mark and the external (balancing) pressure was read off on the manometer. The temperature of the vessel was noted. The oxygen was then removed by the Toepler pump and was collected over mercury. Its volume was measured in the usual way in the gas analysis apparatus; the mercury in the burette was moistened with water and the volume was corrected for the pressure of saturated water vapour.

Results

In the vessel, pressure of oxygen = 90·3 m.m.
Temperature of vessel = 682·5°A.
In the gas analysis burette, volume = 8·48 c.cs.
atmospheric pressure = 746·7 m.m.
saturated vapour pressure = 17·0 m.m.
temperature = 292·5°A.

Since the gas employed was oxygen the applicability of the gas laws is unquestionable. Hence the reaction volume is given by:-

$$V = \frac{729 \cdot 7 \times 8 \cdot 48 \times 682 \cdot 5}{90 \cdot 3 \times 292 \cdot 5} \text{ c.cs.}$$

i.e. reaction volume = 159·9 c.cs.

A second determination showed the volume to be 159·1 c.cs. and so the true volume was taken to be 159·5 c.cs. (i.e. the mean of two results).

Typical Gas Analysis:- (Run no. E54).

First fraction (permanent gases)

Total volume = 16·45 ccs. Barometric pressure = 741·5 m.m.
Temperature = 10·5°C. S.V.P. at 10·5°C = 9·5 m.m.

Vol. of sample = 9·51 ccs.

Vol. less $O_2$ = 4·21 ccs. Vol of $O_2$ in sample = 5·30 ccs. Pressure of $O_2$ in vessel = 100·6 m.m.

Vol. less $C_3H_6$ = 4·19 ccs. Vol. of $C_3H_6$ in sample = 0·02 ccs. Pressure of $C_3H_6$ in vessel = 0·2 m.m.

Vol. less CO = 0·23 ccs. Vol. of CO in sample = 3·96 ccs. Pressure of CO in vessel = 75·1 m.m.

Vol. after combustion Vol. of $H_2$ in sample = 0·08 ccs. Pressure of $H_2$ in vessel = 1·5 m.m.

= 0·15 ccs. Vol. of $CH_4$ in sample = 0·03 ccs. Pressure of $CH_4$ in vessel = 0·7 m.m.

Vol. less $CO_2$ = 0·12 ccs. Vol. of $N_2$ in sample = 0·12 ccs. Pressure of $N_2$ in vessel = 2·4 m.m.

Second fraction (non-permanent gases)

Total volume = 16·32 ccs. Barometric pressure = 741·5 m.m. Temperature = 10·5°C.
S.V.P. at 10·5°C = 9·5 m.m.

Vol. of sample = 9·31 ccs.

Vol. less $C_3H_6$ = 0·38 ccs. Vol. of $C_3H_6$ in sample = 8·93 ccs. Pressure of $C_3H_6$ in vessel = 171·9 m.m.

Vol. less $CO_2$ = 0·00 ccs. Vol. of $CO_2$ in sample = 0·38 ccs. Pressure of $CO_2$ in vessel = 7·3 m.m.

Analysis of gaseous products (as pressures in vessel E at 678°A)

$C_3H_6$ = 172·1 m.m.
$O_2$ = 100·6 m.m.
CO = 75·1 m.m.
$CO_2$ = 7·3 m.m.
$H_2$ = 1·5 m.m.
$CH_4$ = 0·7 m.m.
$N_2$ = 2·4 m.m.

Typical analysis for water :- (Run no. E8)

The contents of the trap were treated with 25·0 mls. of methanol and two 10 mls. samples were titrated with the Karl Fischer reagent. Two 10 mls. samples of the methanol used were also titrated with the reagent, as were two 10 mls. samples of the standard water solution containing 1 g. of water per litre of the same methanol.

## Results

Titration of 10 mls. of methanol. Titres = 3·60 mls. and 3·62 mls. = 3·61 mls.

Titration of 10 mls. of standard solution. Titres = 8·61 mls. and 8·61 mls.

Titration of 10 mls. of unknown solution. Titres = 5·80 mls. and 5·83 mls.

99·9 mls. of methanol = 36·06 mls. of Karl Fischer reagent

So 0·1 g. $H_2O$ = 86·1 mls. — 36·1 mls. = 50·0 mls. reagent

i.e. 1 ml. reagent = 0·0020 g. $H_2O$

Now 25 mls. of methanol = 2·5 x 3·61 mls. Karl Fischer reagent

$H_2O$ in the trap = 2·5 x (5·82 — 3·61) mls. reagent

= 2·5 x 2·21 x 0·0020 g. $H_2O$

$$= 2{\cdot}5 \times 2{\cdot}21 \times 0{\cdot}0020 \times \frac{22400}{18} \text{ ccs. steam at N.T.P.}$$

= 13·75 ccs. steam at N.T.P.

# KINETICS

## THE EFFECT OF THE SURFACE

A characteristic of reactions involving chains with degenerate branching, which may be explained in the light of the Semenov analysis is the extraordinary sensitivity of the reaction rate and more markedly the induction period to the state of the walls of the vessel. Several different reaction vessels were employed in this investigation and, although the differences in their surface and volume dimensions were small they gave different results for the same experiment. Table No. 4 gives the measured parameters for five vessels for the reaction of 200 m.m. of cyclopropane with 200 m.m. of oxygen at 405°C (678°A). The table also includes details of surface and volume measurements.

Table No. 4.

Initial $p_{cp} = p_{o_2} = 200$ m.m. $T = 678^\circ A.$

| Vessel | Surface Area | Volume ccs. | $f_{max}$ | $A'$ | $\gamma$ | $\theta$ | $\Delta p_{max}$ | $\Delta p_\infty$ |
|---|---|---|---|---|---|---|---|---|
| A | 190 | 197 | 5·9 | 0·122 | 31 | 45 | 53·1 | 100·8 |
| B | 172 | 159 | 10·4 | 0·163 | 15 | 20 | 55·7 | 100·0 |
| C | 188 | 180 | 9·1 | 0·165 | 28 | 38 | 52·4 | 99·6 |
| D | 166 | 151 | 11·2 | 0·240 | 18 | 27 | 51·0 | 99·2 |
| E | 160 | 145 | 6·3 | 0·115 | 23 | 37 | 58·1 | 100·0 |

It will be seen that the rates in vessels A and E are of the same order while those in the other three vessels are also comparable with each other. Apart from the smaller volumes of vessels A and E, there seems to be little distinction between them and the other three. It is possible, of course, that some slight difference in the nature of the glass accounts for the results in table No. 4. Kinetical experiments were carried out in vessels A, B and D (mainly in B) and the form of the kinetical characteristics of the reaction was found to be unaltered by change of vessel, although the absolute values of the parameters varied between the three vessels.

The behaviour of the vessels during the ageing process is also worthy of comment. Vessels C, D and E required the performance of only a few (about 6) experiments before steady state conditions were attained. In vessels A and B, on the other hand, the rate gradually increased becoming steady after some twenty experiments. It was also noted that the induction periods in the first three experiments were roughly the same as the final (steady state) value of θ but during the intervening experiments θ rose to a maximum. In the case of the maximum rate, however, the trend was slow and continuous from 3·7 in the first to 9·7 in the nineteenth experiment. The results of these nineteen experiments are given in table No. 5.

Table No. 5.
Ageing on a new vessel.

Initial $p_{cp}$ = 200 m.m. $p_{O_2}$ = 110 m.m.
T = 678 °A. Vessel B

| Run No. | $\rho_{max}$ | θ |
|---|---|---|
| B 1 | 3·7 | 33 |
| B 2 | 4·5 | 25 |
| B 3 | 4·5 | 26 |
| B 4 | 5·6 | 45 |
| B 5 | 5·6 | 49 |
| B 6 | 6·1 | 34 |
| B 7 | 6·0 | 50 |
| B 8 | 6·5 | 63 |
| B 9 | 7·7 | 43 |
| B10 | 8·0 | 48 |
| B11 | 9·0 | 42 |
| B12 | 9·2 | 40 |
| B13 | 9·4 | 37 |
| B14 | 9·8 | 24 |
| B15 | 9·4 | 36 |
| B16 | 9·6 | 29 |
| B17 | 9·5 | 39 |
| B18 | 9·8 | 23 |
| B19 | 9·7 | 23 |

Even after the attainment of a steady state the reproducibility of results could be drastically changed. For example if the vessel was allowed to cool down without admitting air to it and was then reheated, the ensuing experiments yielded low results for the maximum rate and high values for the induction period. Gradually these parameters returned to their normal value as is shown in table No. 6.

Table No. 6.

Experiments performed after cooling of the vessel

Initial $p_{cp}$ = 200 m.m. $p_{O_2}$ = 110 m.m.
T = 678°A. Vessel B

| Run No. | $\rho_{max}$ | $\theta$ |
|---|---|---|
| B 128 | 5·7 | 70 |
| B 129 | 6·3 | 51 |
| B 130 | 6·9 | 34 |
| B 131 | 7·2 | 30 |
| B 132 | 7·9 | 27 |
| B 133 | 8·9 | 25 |
| B 134 | 9·7 | 22 |
| B 135 | 9·7 | 23 |

It will be observed that the cooling of the vessel only reduced the rate by some 35% and that only eight experiments were needed for the reattainment of equilibrium conditions. ( $\rho_{max} = 9.7$ , $\theta = 23.$ ). In this connection it will also be noted that the trend in $\theta$ is continuous in table no. 6 from 70 minutes in experiment No. 128 to 23 in No. 135. Another effect of great importance was that obtained by the admission of air to the hot vessel. This manifested itself in the production of lower rates and shorter induction periods which, however, soon returned to normal.

Apart from these considerations the state of surface of the vessels seemed sometimes to change in some way very suddenly and in contrast with those effects above, the change, on occasion, was irreversible. Two examples, each of a different nature, will suffice to illustrate the point. In vessel D during a series of experiments to determine the effect of variation of initial oxygen pressure upon the reaction, results consistent with expectation were obtained. These included an experiment with 300 m.m. of oxygen and 100 m.m. of cyclopropane at 701°A (run No. D 14). When some time later, the same run was repeated during the study of the effect of variation of initial hydrocarbon pressure (run No. D 21), different results were obtained for the reaction parameters. These latter results, however, were consistent with the other values obtained in the study of the variation of initial cyclopropane pressure. The results are given in table No. 7.

Table No. 7.

Initial $p_{cp}$ = 100 m.m.   $p_{O_2}$ = 300 m.m.

T = 701°A   Vessel D

| Run No. | $\rho_{max}$ | $A'$ | $\theta$ |
|---|---|---|---|
| D 14 | 7·6 | 0·27 | 12 |
| D 21 | 8·6 | 0·183 | 18 |

The second example of this sudden change occurred in vessel B. During the running - in of this vessel the steady state induction period for a mixture of 200 m.m. cyclopropane and 110 m.m. oxygen at 678°A was 23 minutes (table No. 5). During the study of variation of oxygen pressure with initial hydrocarbon pressure 200 m.m., results were obtained with which to be consistent an induction period of 59 minutes would be required for that experiment. No change had taken place in the maximum rate, however, which was 9·7 m.m. per minute in each case. The change in $\theta$ with no accompanying change in rate became even more remarkable when, a very considerable time later, during the experiments on the effect of cooling of the vessel (table No. 6) there was a return (in the steady state) to the value of 23 minutes for the induction period.

Mr. W. N. Broatch obtained some very interesting results in experiments designed to determine the effect of changes of surface upon the reaction parameters. He compared these characteristics for the reaction of 200 m.m. of each gas in a cylindrical pyrex vessel with those obtained in a second vessel of identical geometry packed with pyrex capillary tubing so that its surface to volume ratio was 11·7 times that of the unpacked vessel. The changes which occurred are tabulated below.

Table No. 8.

Comparison of results in packed and unpacked vessels.

Initial $p_{cp}$ = 200 m.m. = Initial $p_{o_2}$

| Vessel | $\rho_{max}$ | $A'$ | $\Upsilon$ | $\theta$ | $\Delta p_{max}$ | $\Delta p_{\infty}$ |
|---|---|---|---|---|---|---|
| Packed vessel | 0·86 | 0·008 | 283 | 349 | 56·3 | 80 |
| Unpacked vessel | 8·1 | 0·078 | 35 | 51·0 | 55·5 | 103 |

## THE DEPENDENCE OF THE MAXIMUM RATE UPON CONDITIONS.

### 1. Dependence Upon Initial Oxygen Pressure

A series of experiments was performed at 678°A (405°C) with a fixed cyclopropane pressure of 178 m.m. and with varying amounts of oxygen over the range 50 - 200 m.m. Other similar series of experiments were then performed at the same temperature with the fixed initial cyclopropane pressures 200 m.m., 250 m.m. and 300 m.m. respectively. The results are shown in tables Nos. 9, 10, 11, 12 and on the graph (No. 4)

Table No. 9

Initial $p_{cp}$ = 178 m.m. T = 678°A
Vessel B

| Run No. | $p_{O_2}$ (m.m.) | $\rho_{max}$ |
|---|---|---|
| B 43 | 50·0 | 3·0 |
| B 42 | 89·7 | 5·9 |
| B 44 | 101·0 | 6·7 |
| B 39 | 108·4 | 7·6 |
| B 41 | 149·4 | 7·8 |
| B 49 | 200·9 | 8·0 |

Table No. 10

Initial $p_{cp}$ = 200 m.m. T = 678°A
Vessel B

| Run No. | $p_{O_2}$ | $\rho_{max}$ |
|---|---|---|
| B 24 | 50·0 | 4·4 |
| B 26 | 70·0 | 6·3 |
| B 25 | 100·5 | 8·9 |
| B 27 | 130·0 | 10·3 |
| B 30 | 199·8 | 10·4 |
| B 28 | 248·7 | 10·2 |

Table No. 11

Initial $p_{cp}$ = 250 m.m. T = 678°A
Vessel B

| Run No. | $p_{O_2}$ | $\rho_{max}$ |
|---|---|---|
| B 35 | 48·3 | 5·4 |
| B 34 | 94·5 | 11·4 |
| B 33 | 109·8 | 12·7 |
| B 38 | 124·7 | 13·9 |
| B 32 | 134·8 | 16·0 |
| B 31 | 180·0 | 16·7 |
| B 36 | 198·8 | 16·2 |
| B 37 | 250·0 | 16·4 |

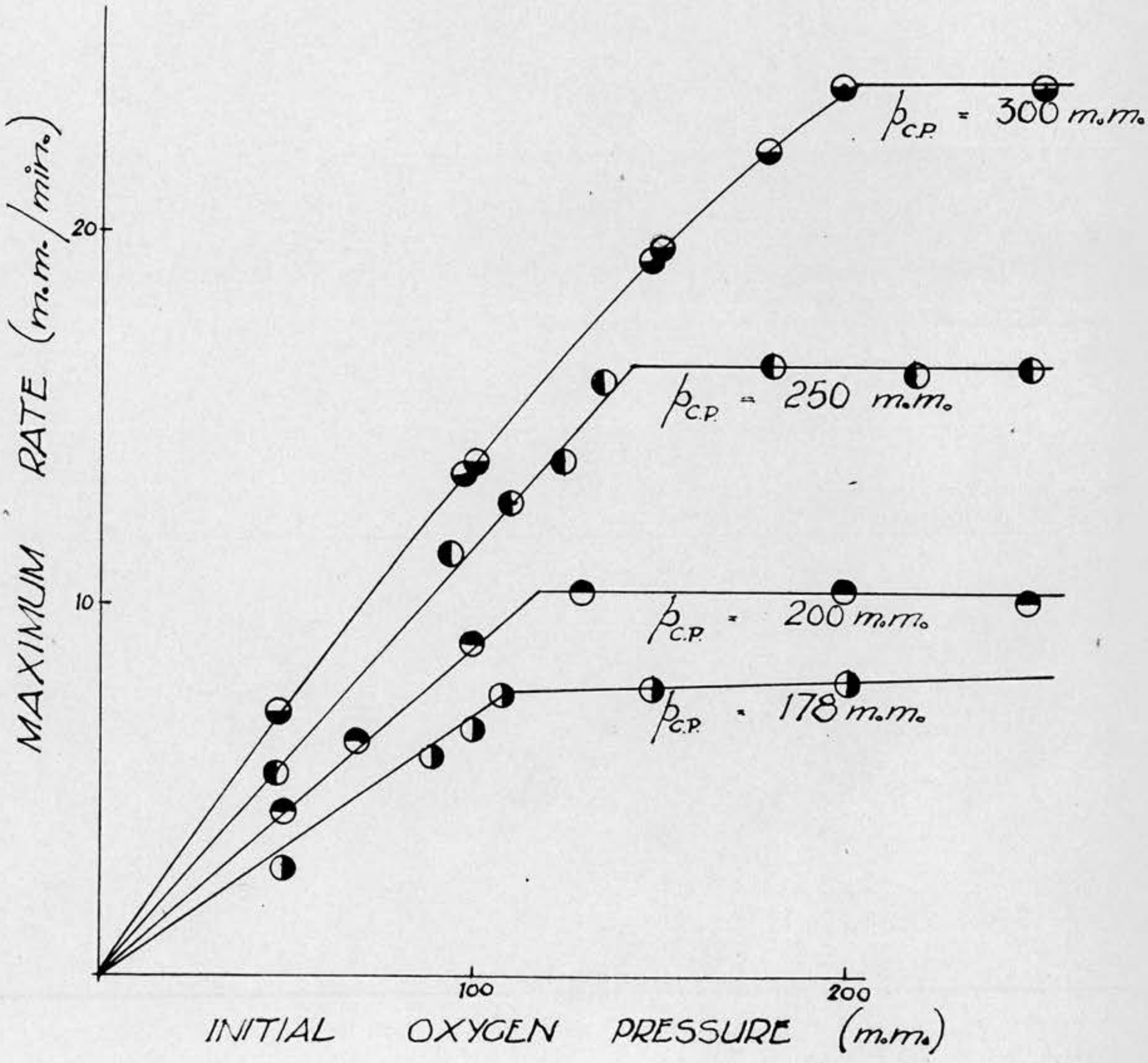
Table No. 12

Initial $p_{cp}$ = 300 m.m. T = 678°A
Vessel B

| Run No. | $p_{O_2}$ | $\rho_{max}$ |
|---|---|---|
| B 67 | 49·5 | 7·2 |
| B 62 | 97·4 | 13·6 |
| B 68 | 101·7 | 13·9 |
| B 70 | 147·2 | 19·4 |
| B 71 | 149·7 | 19·6 |
| B 72 | 178·3 | 22·3 |
| B 64 | 198·0 | 24·0 |
| B 66 | 252·7 | 24·0 |

It will be clearly seen that there are two distinct regions on each curve. There is, at lower oxygen pressures,

# Variation of Initial Oxygen Pressure at 678°A (Vessel B)



an apparently linear dependence of the maximum rate which changes to an independence at higher pressures of oxygen. The transition from dependence to independence is seen to be fairly critical at lower cyclopropane pressures, whereas with 300 m.m. of hydrocarbon, the linear relationship obtains only at lower oxygen pressures the change to independence being much more gradual.

It is also evident that the "critical oxygen pressure" increased with the increase of initial hydrocarbon pressure. Table No. 13 shows the quantitative influence of the latter upon the critical oxygen pressure which has been found by extrapolation of the early linear part of each graph to cut the line of oxygen independence. Graph (No. 5) demonstrates the relation existing between critical oxygen pressure and initial cyclopropane pressure. Furthermore table No. 14 illustrates the dependence of the gradient of the early (linear) part of each graph upon the initial hydrocarbon pressure. These results are plotted upon the same graph (No. 5).

TABLE NO. 13

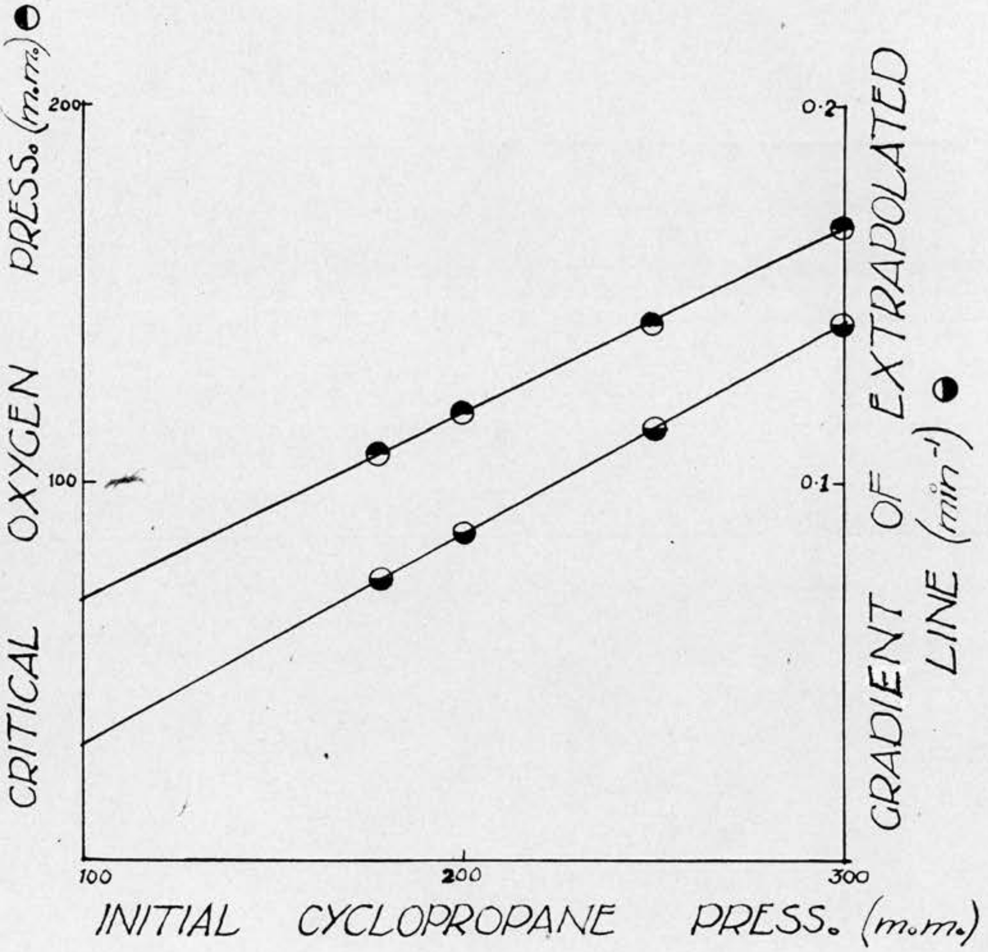
| $p_{cp}$ | Extrapolated $p_{O_2}$ | $\frac{p_{cp}}{\text{Extrapolated } p_{O_2}}$ |
|---|---|---|
| 178 | 108 | 1·65 |
| 200 | 118 | 1·70 |
| 250 | 143 | 1·75 |
| 300 | 168 | 1·78 |

TABLE NO. 14

| $p_{cp}$ | Gradient of extrapolated line | $\frac{p_{cp}}{\text{gradient}}$ |
|---|---|---|
| 178 | 0·0741 | 2402 |
| 200 | 0·0873 | 2291 |
| 250 | 0·1140 | 2191 |
| 300 | 0·1429 | 2100 |

Now, in the region wherein $\rho_{max}$ depends upon the initial oxygen pressure, the gradient of the line and hence the rate at

GRAPH Nº5


CRITICAL OXYGEN PRESS. (m.m.) ◐
200
100
0·2
0·1
GRADIENT OF EXTRAPOLATED LINE (min⁻¹) ◐
100
200
300
INITIAL CYCLOPROPANE PRESS. (m.m.)

any oxygen pressure, below the critical pressure, depends also upon initial cyclopropane pressure, i.e. Rate $\propto p_{cp} \cdot p_{O_2}$. Above the critical oxygen pressure, however, the maximum rate is independent of oxygen pressure but, being given by the product of the gradient of the line and the critical oxygen pressure, is proportional to the square of the initial hydrocarbon pressure i.e. Rate $\propto p_{cp}^{2}\, p_{O_2}^{0}$. Thus the two distinct regions of oxygen pressure dependence appear to indicate two totally different regions of order viz. Rate $= k_1 p_{cp} \cdot p_{O_2}$ below the critical oxygen pressure and Rate $= k_2 p_{cp}^{2}\, p_{O_2}^{0}$ above the critical oxygen pressure.

The dependence of rate upon initial oxygen pressures was determined for an initial cyclopropane pressure of 250 m.m. at a temperature of 651°A (378°C). The results are given in table No. 15 and graph (No. 6) shows the dependence of the maximum rate upon initial oxygen pressure for 250 m.m. of hydrocarbon both at 651°A and at 678°A.

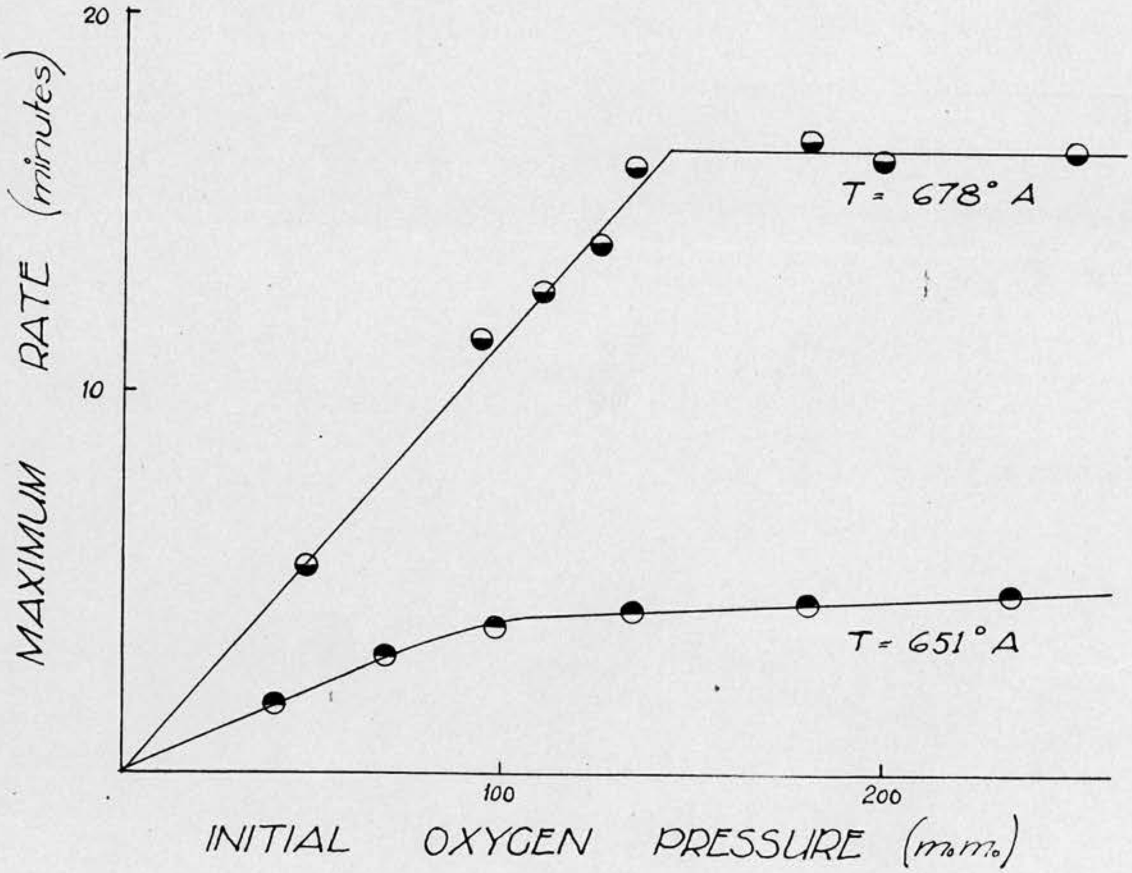
Table No. 15

Initial $p_{cp}$ = 250 m.m. $T = 651^{\circ}$A Vessel B

| Run No. | $p_{O_2}$ | $\rho_{max}$ |
|---|---|---|
| B 95 | 40·0 | 1·8 |
| B 94 | 69·9 | 3·1 |
| B 93 | 99·0 | 3·8 |
| B 92 | 134·2 | 4·2 |
| B 91 | 180·4 | 4·4 |
| B 90 | 233·7 | 4·7 |

In principle, the graphs are the same but both the gradients of the lines representing low oxygen pressure dependence, and the critical oxygen pressures are vastly different in the two

Variation of Initial Oxygen Pressure ($p_{C.P.}$ = 250 m.m.)
Vessel B



cases. The transition from dependence to independence is probably much more gradual at the lower temperature and it will be clearly seen that the kinetics Rate $\propto p_{cp} \cdot p_{o_2}$ are operative over a considerably shorter oxygen pressure range at 651°A.

The oxygen-pressure dependence was redetermined for an initial cyclopropane pressure of 178 m.m. at 701°A. As might have been anticipated from the temperature effect observed above, the kinetics Rate $\propto p_{cp} \cdot p_{o_2}$ operate over a very large range of oxygen pressures in this case. Results are given in table No. 16 and graph No. 7 illustrates the change of the curve (rate against initial oxygen pressure) for a fixed cyclopropane pressure of 178 m.m. at 701°A and 678°A.

Table No. 16

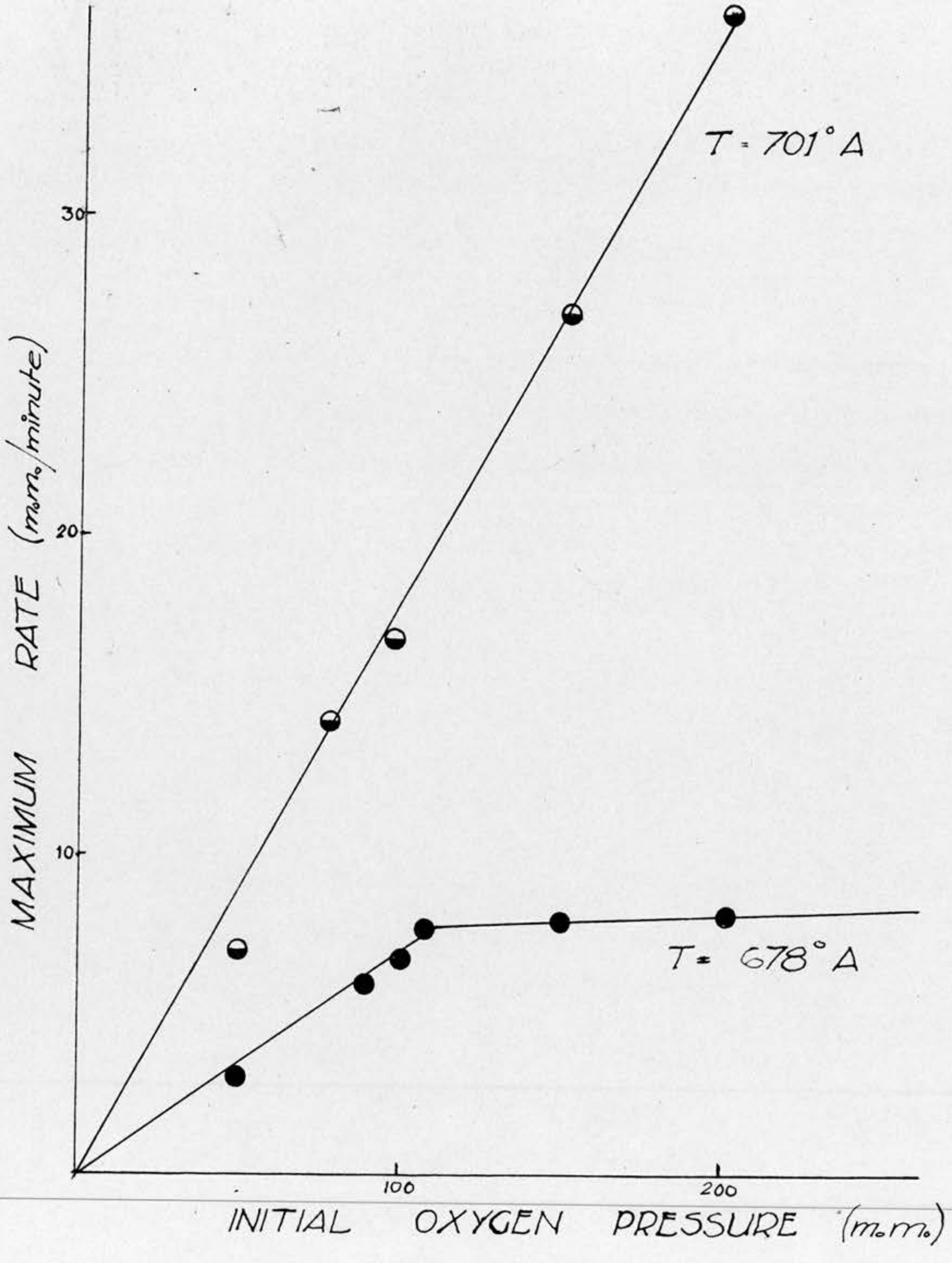
Initial $p_{cp}$ = 178 m.m.    T = 701°A  Vessel B

| Run No. | $p_{o_2}$ | $\rho_{max}$ |
|---|---|---|
| B 97 | 50·7 | 6·9 |
| B106 | 78·8 | 14·0 |
| B 98 | 98·6 | 16·6 |
| B 99 | 151·4 | 26·7 |
| B100 | 200·3 | 36 |

The experiments described so far were all performed in the second reaction vessel B and it is interesting to study the effect of change of vessel upon the oxygen dependence of the maximum rate of reaction. Table No. 17 lists the results obtained at 678°A with 200 m.m. of cyclopropane and varying amounts of oxygen. The graph No. 8 shows two lines, one relating to each vessel, for 200 m.m. of hydrocarbon at 678°A. It will be seen that, apart from differences in the absolute

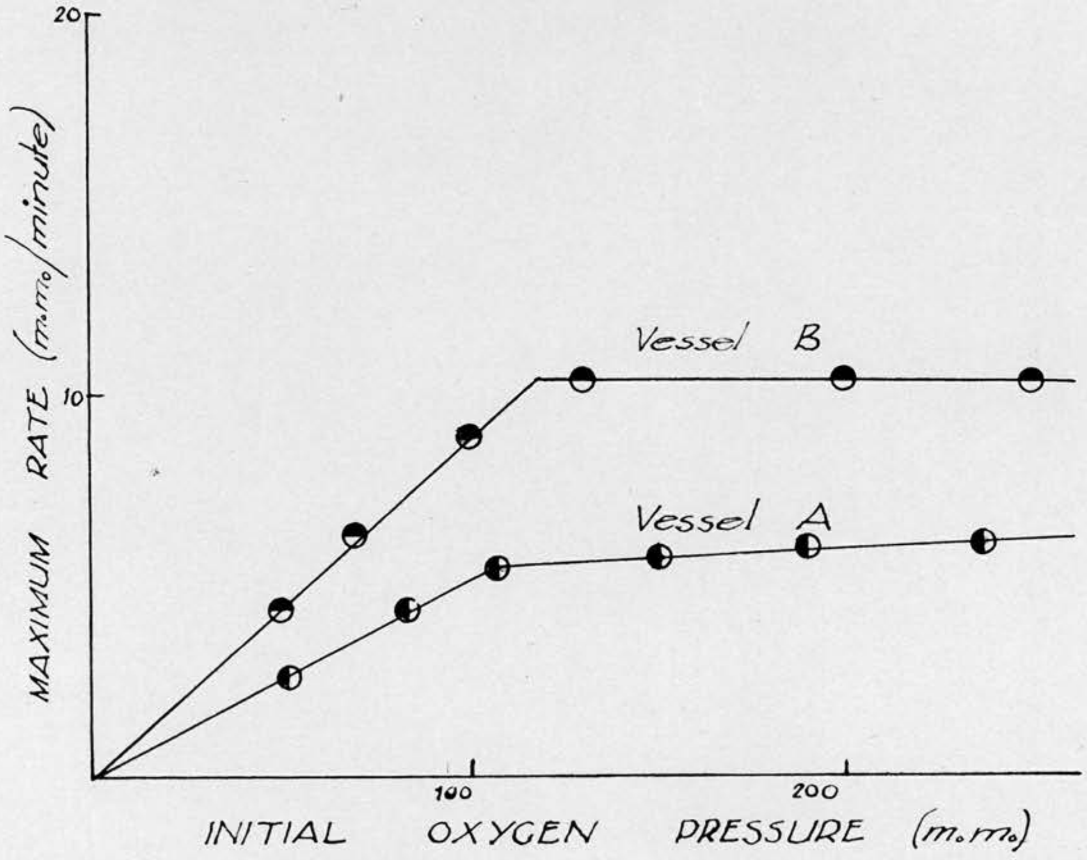
GRAPH Nº 7

Variation of Initial Oxygen Pressure
($p_{C.P.}$ - 178 m.m.)



GRAPH No8

# Variation of Initial Oxygen Pressure ($p_{C.P.}$ = 200 m.m.; T = 678°A)



values of the rates, the kinetical characteristics are the same in the two cases, although the critical oxygen pressure is somewhat higher in the second vessel (B)

Table No. 17

Initial $p_{cp}$ = 200 m.m. $T = 678^\circ A$ Vessel A

| Run No. | $p_{O_2}$ | $\rho_{max}$ |
|---|---|---|
| A 41 | 52·1 | 2·6 |
| A 42 | 84·7 | 4·3 |
| A 37 | 106·5 | 5·5 |
| A 40 | 150·9 | 5·7 |
| A 38 | 189·8 | 5·9 |
| A 39 | 234·8 | 6·1 |

Table No. 18 and graph No. 9 illustrate the maximum rate-initial oxygen pressure relationship in vessel D at 701°A with an initial hydrocarbon pressure of 100 m.m. Once again, the kinetical behaviour is seen to be the same as in other cases, there existing a region of linear dependence which is followed by an independence.

Table No. 18

Initial $p_{cp}$ = 100 m.m. $T = 701^\circ A$ Vessel D

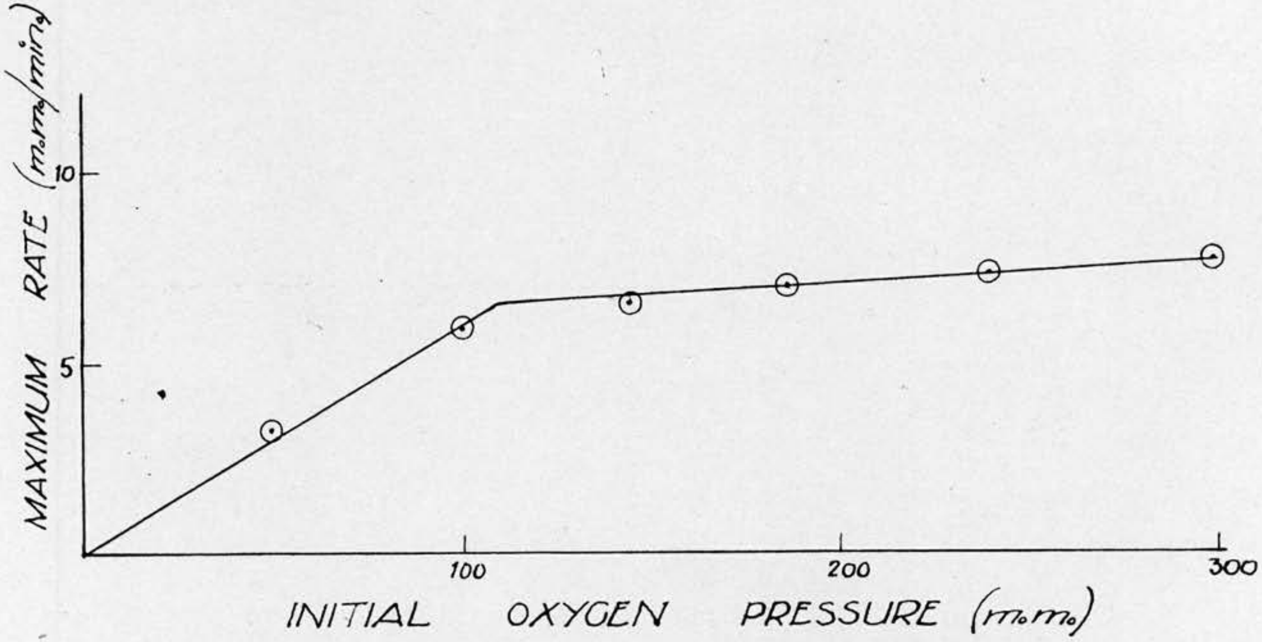
| Run No. | $p_{O_2}$ | $\rho_{max}$ |
|---|---|---|
| D 18 | 49·0 | 3·2 |
| D 13 | 100·5 | 5·9 |
| D 17 | 144·5 | 6·5 |
| D 15 | 186·3 | 6·9 |
| D 16 | 240·0 | 7·3 |
| D 14 | 298·8 | 7·6 |

## 2. Dependence Upon Initial Cyclopropane Pressure

The proved existence of two regions of oxygen dependence and the prediction (from critical oxygen pressures) of two

GRAPH N° 9

Variation of Initial Oxygen Pressure ($p_{CP}$ = 100 m.m. : T = 701°A)
Vessel D.



regions of cyclopropane dependence necessitated care in selection of conditions for study of the effect of variation of initial hydrocarbon pressure upon the maximum rate. The knowledge gained of the critical oxygen pressures and their dependence upon initial cyclopropane pressure and temperature facilitated the study of dependence of the rate upon the hydrocarbon pressure in the different regions.

A series of experiments was carried out at 678°A with initial oxygen pressure of 200 m.m. and cyclopropane pressures in the range 150 m.m. to 300 m.m. In other words it was ascertained that for each cyclopropane pressure employed, 200 m.m. of oxygen was above the critical oxygen pressure. The results are given in table No. 19 and are plotted on graph No. 10.

Table No. 19

Initial $p_{O_2}$ = 200 m.m. T = 678°A Vessel B

| Run No. | $p_{cp}$ | $\rho_{max}$ | $p_{cp}^2$ |
|---|---|---|---|
| B 21 | 152·0 | 5·9 | 23100 |
| B 23 | 159·0 | 6·4 | 25280 |
| B 49 | 177·9 | 8·0 | 31650 |
| B 20 | 200·0 | 10·4 | 40000 |
| B 36 | 249·7 | 16·3 | 62350 |
| B 64 | 300·0 | 24·0 | 90000 |

Another series of experiments was carried out at the same temperature (678°A) with initial oxygen pressure of 70 m.m. the hydrocarbon pressures varying over the range 150 m.m. to 400 m.m. i.e. every cyclopropane pressure was so high that 70 m.m. of oxygen fell below the critical oxygen pressure. The results are given in table No. 20 and are plotted on the same graph No. 10.

GRAPH Nº 10

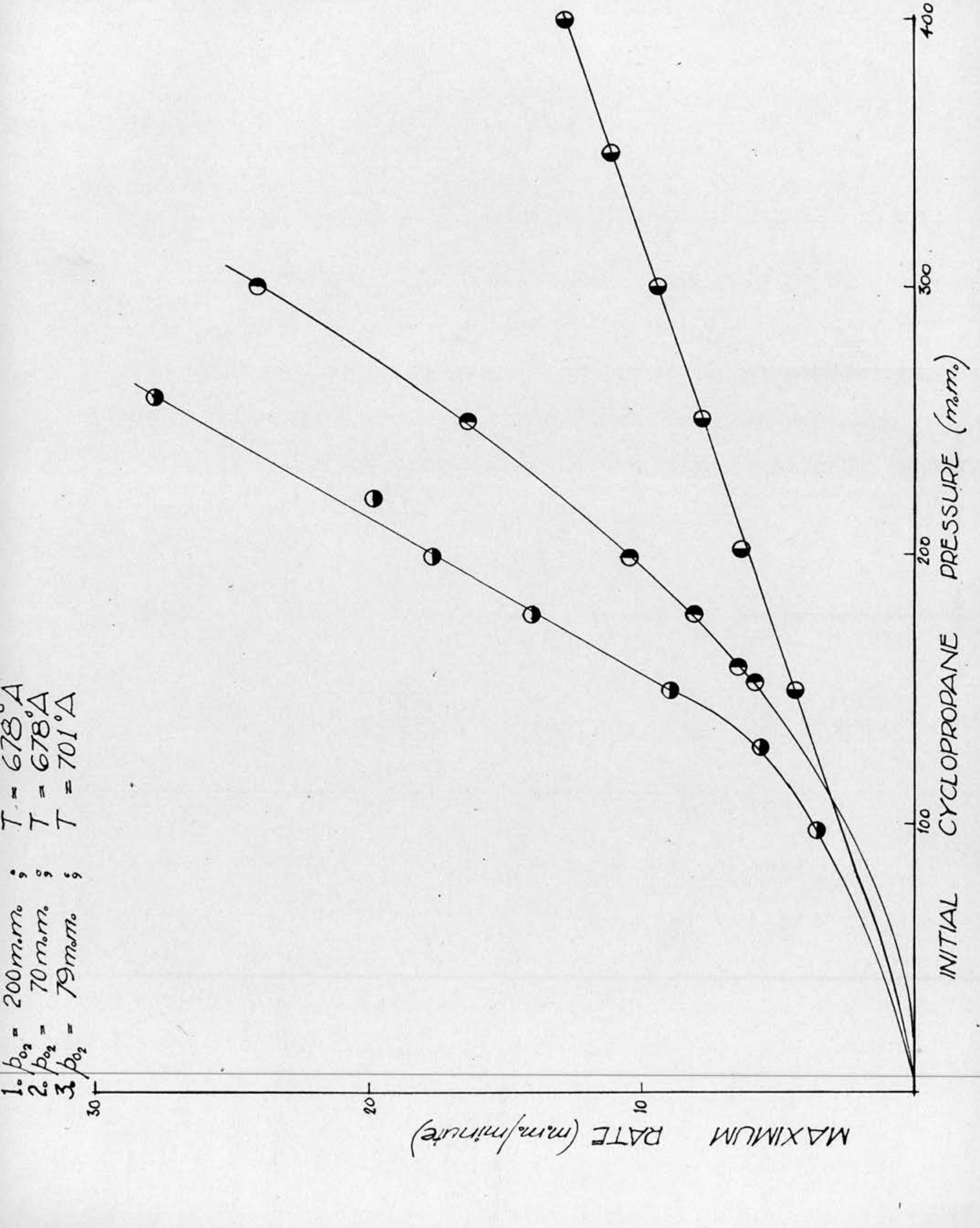

1. $p_{O_2}$ = 200 m.m. ; T = 678 °A
2. $p_{O_2}$ = 70 m.m. ; T = 678 °A
3. $p_{O_2}$ = 79 m.m. ; T = 701 °A
MAXIMUM RATE (m.m./minute)
30
20
10
INITIAL CYCLOPROPANE PRESSURE (m.m.)
100
200
300
400

Table No. 20

Initial $p_{O_2}$ = 70 m.m.  T = 678°A  Vessel B

| Run No. | $p_{cp}$ | $\rho_{max}$ |
|---|---|---|
| B 74 | 150·0 | 4·3 |
| B 78 | 202·5 | 6·3 |
| B 77 | 252·0 | 7·7 |
| B 73 | 300·0 | 9·3 |
| B 76 | 350·0 | 11·0 |
| B 75 | 400·0 | 12·7 |

The third curve on the graph was obtained by plotting maximum rate against initial cyclopropane pressure for several experiments at 701°A with an initial pressure of 79 m.m. in every case. The results are given in detail in table No. 21.

Table No. 21

Initial $p_{O_2}$ = 79 m.m.  T = 701°A  Vessel B

| Run No. | $p_{cp}$ | $\rho_{max}$ | $p_{cp}^2$ |
|---|---|---|---|
| B 108 | 99·2 | 3·6 | 9840 |
| B 107 | 128·5 | 5·6 | 16510 |
| B 117 | 150·0 | 9·0 | |
| B 106 | 177·8 | 14·0 | |
| B 116 | 198·7 | 17·6 | |
| B 115 | 221·2 | 19·8 | |
| B 114 | 258·8 | 27·8 | |

The graphs clearly demonstrate the verification of the prediction of the existence of the two regions of dependence of rate upon cyclopropane pressure. Thus it is evident that, at 678°A, with oxygen pressures below the critical, the rate is proportional to the cyclopropane pressure. With oxygen pressures above the critical, at 678°A, the dependence is obviously greater than linear and the linearity of the plot of rate against the square of the initial cyclopropane pressure shows the index of dependence to be two (graph No. 13). Hence there is complete justification, now, for expressing the rate in terms of initial pressures in the following form:-

Rate $\propto p_{cp} \cdot p_{O_2}$ if $p_{O_2} <$ critical oxygen pressure
Rate $\propto p_{cp}^2 \cdot p_{O_2}^0$ if $p_{O_2} >$ critical oxygen pressure

It is instructive to observe that in this second case, the graph indicates that the linear relationship must be replaced by the dependence when the hydrocarbon pressure falls to about 120 m.m. by which time, of course, the condition $p_{O_2}$ less than the critical oxygen pressure no longer holds since the critical oxygen pressure for a cyclopropane pressure of 120 m.m. would be expected to be about 70 m.m.

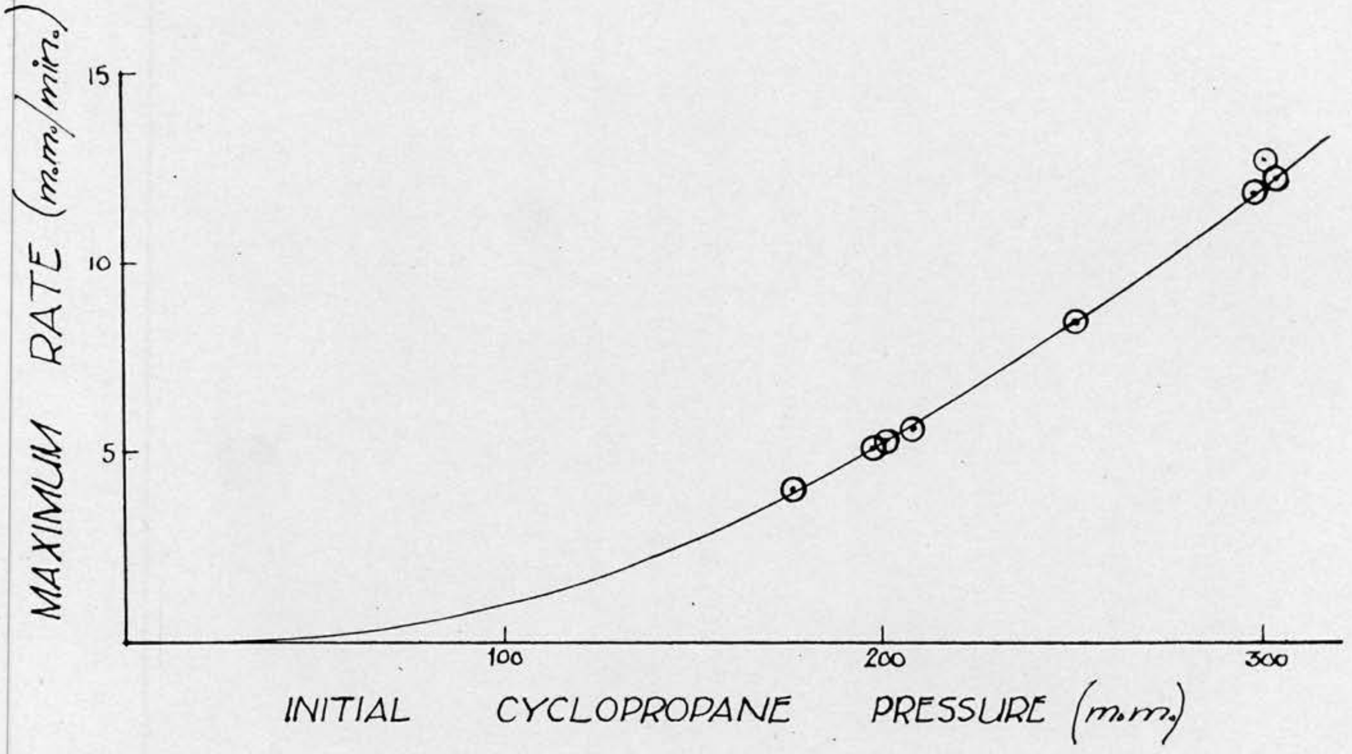
The third graph on the paper, referring to the experiments at 701°A with 79 m.m. of oxygen, clearly shows the change of mechanism at about 130 m.m. of cyclopropane. Above that pressure the relationship is obviously a linear one. Below 130 m.m. of cyclopropane, however, the relationship is more complex and the graph of maximum rate against the square of the hydrocarbon pressure for lower pressures shown on graph No. 13 reveals that the dependence is again a square one.

The experiments so far described were all performed in the second reaction vessel (B) but apart from the lower absolute values of the rates observed in vessel (A) the kinetical characteristics were found to be identical. Table No. 22 lists rates measured in the latter vessel at 678°A with an initial oxygen pressure of 150 m.m. (higher than the critical oxygen pressures for the cyclopropane pressures employed). The results are plotted on graph No. 11 and the square dependence is

GRAPH N° 11

Variation of Initial Cyclopropane Pressure (Vessel A)

$p_{O_2}$ = 150 m.m.; T = 678°A



proved on graph No. 13.

Table No. 22.

Initial $p_{O_2}$ = 150 m.m. T = 678°A Vessel A

| Run No. | $p_{cp}$. | $\rho_{max}$ | $p_{cp}^2$ |
|---|---|---|---|
| A 35 | 176·3 | 4·1 | 31070 |
| A 25 | 199·1 | 5·1 | 39650 |
| A 23 | 201·8 | 5·3 | 40720 |
| A 14 | 208·0 | 5·6 | 43270 |
| A 33 | 250·5 | 8·4 | 62750 |
| A 28 | 299·0 | 11·9 | 89430 |
| A 32 | 302·2 | 12·6 | 91330 |
| A 30 | 304·0 | 12·2 | 92380 |

Since all these experiments were carried out with a stoichiometric excess of cyclopropane, a series of experiments with 300 m.m. of oxygen and varying quantities of hydrocarbon over the range of 80 m.m. to 130 m.m. was performed at 701°A in vessel D. The results are detailed in table No. 23 and the figures are plotted on graph No. 12. This is a graph of the form Rate $\propto p_{cp}^2$.

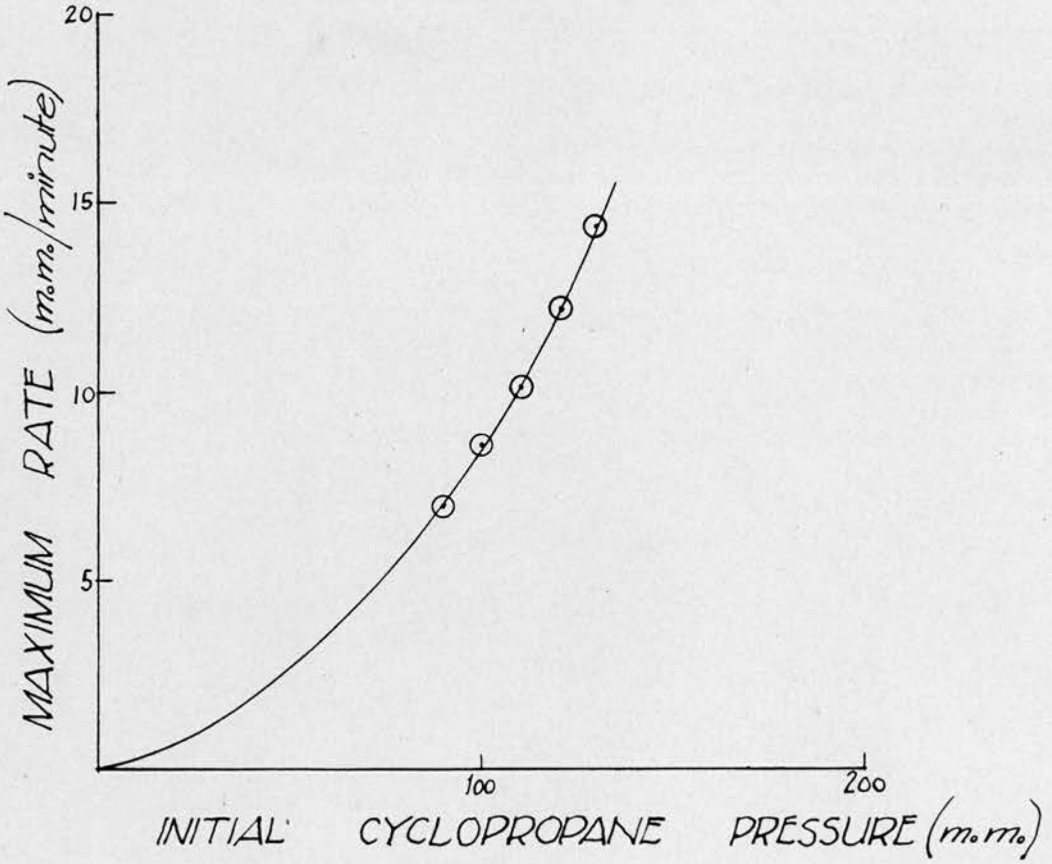
Table No. 23

Initial $p_{O_2}$ = 300 m.m. T = 701°A Vessel D

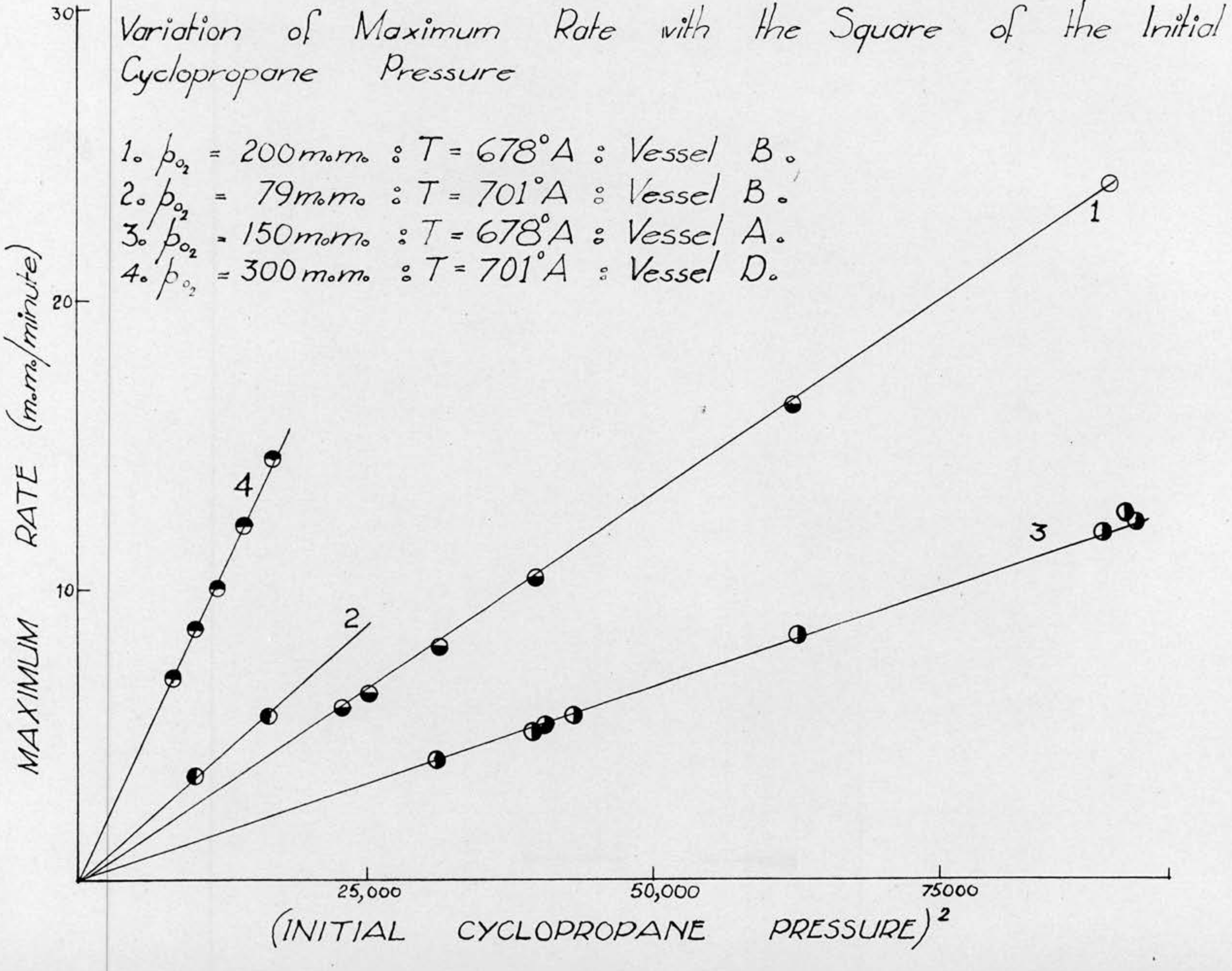
| Run No. | $p_{cp}$ | $\rho_{max}$ | $p_{cp}^2$. |
|---|---|---|---|
| D 26 | 90 | 7·0 | 8100 |
| D 21 | 100·0 | 8·6 | 10000 |
| D 20 | 110·2 | 10·0 | 12150 |
| D 22 | 120·0 | 12·2 | 14400 |
| D 24 | 130·0 | 14·4 | 16900 |

Graph No. 13 shows the linear relation between maximum rate and the square of the initial hydrocarbon pressures. It refers to the experiments listed in tables Nos. 19, 22 and 23 and to the experiments in table No. 21 at lower hydrocarbon pressure.

Variation of Initial Cyclopropane Pressure (Vessel D)
$p_{O_2} = 300$ m.m. ; $T = 701°A$



GRAPH N°13



Variation of Maximum Rate with the Square of the Initial Cyclopropane Pressure

### 3. Dependence Upon the Temperature

The effect of temperature changes upon the maximum rate of an autocatalytic chain reaction is in principle the same as the influence of temperature change upon the rate of more simple reactions. In the latter case, however, the dependence of rate upon temperature has a very important significance. The well-known expression due to Arrhenius is found to apply.

$$k = Ae^{\frac{-E}{RT}}$$

where k = the specific rate constant

R = the gas constant

T = the absolute temperature

A and E are constants over small temperature ranges, A being practically independent of temperature and E an energy term, the activation energy of the reaction.

In the case of a chain reaction, the Arrhenius relation is usually obeyed but the "activation energy" is then of complex significance being a function of the activation energies of all the elementary reactions in the chain.

By taking logarithms of the Arrhenius expressions we obtain:-

$$\text{Log } k = \log A - \frac{E}{RT}$$

Thus by plotting log k, or what is equivalent, log maximum rate against the reciprocal of the absolute temperature, a straight line of gradient $\frac{-E}{R}$ should be obtained.

In the case in point two different series of experiments were performed to investigate the influence of temperature upon the maximum rate. In the first series, the rate of reaction of a mixture of 250 m.m. cyclopropane and 70 m.m. of oxygen was measured at various temperatures over the range 651°A - 705°A. The results are given in table No. 24. In the second series of experiments the mixture employed consisted of 178 m.m. of cyclopropane and 200 m.m. of oxygen while the temperatures ranged from 660°A - 701°A. These results are given in table No. 25. Two Arrhenius plots are drawn on the graph No. 14.

TABLE NO. 24

Initial $p_{cp}$ = 250 m.m. $p_{O_2}$ = 70 m.m.

Vessel B

| Run No. | T | $\frac{10^3}{T}$ | $\rho_{max}$ | $\log_{10}\rho_{max}$ |
|---|---|---|---|---|
| B 89 | 651 | 1·536 | 3·3 | 0·5185 |
| B 88 | 658 | 1·520 | 4·4 | 0·6435 |
| B 87 | 665 | 1·504 | 4·9 | 0·6902 |
| B 86 | 671 | 1·490 | 6·2 | 0·7924 |
| B 77 | 678 | 1·475 | 7·7 | 0·8865 |
| B 83 | 683 | 1·464 | 9·2 | 0·9638 |
| B 80 | 689 | 1·451 | 11·6 | 1·0645 |
| B 81 | 697 | 1·435 | 15·2 | 1·1818 |
| B 84 | 702 | 1·425 | 19·7 | 1·2945 |

TABLE NO. 25

Initial $p_{cp}$ = 178 m.m. $p_{O_2}$ = 200 m.m.

Vessel B

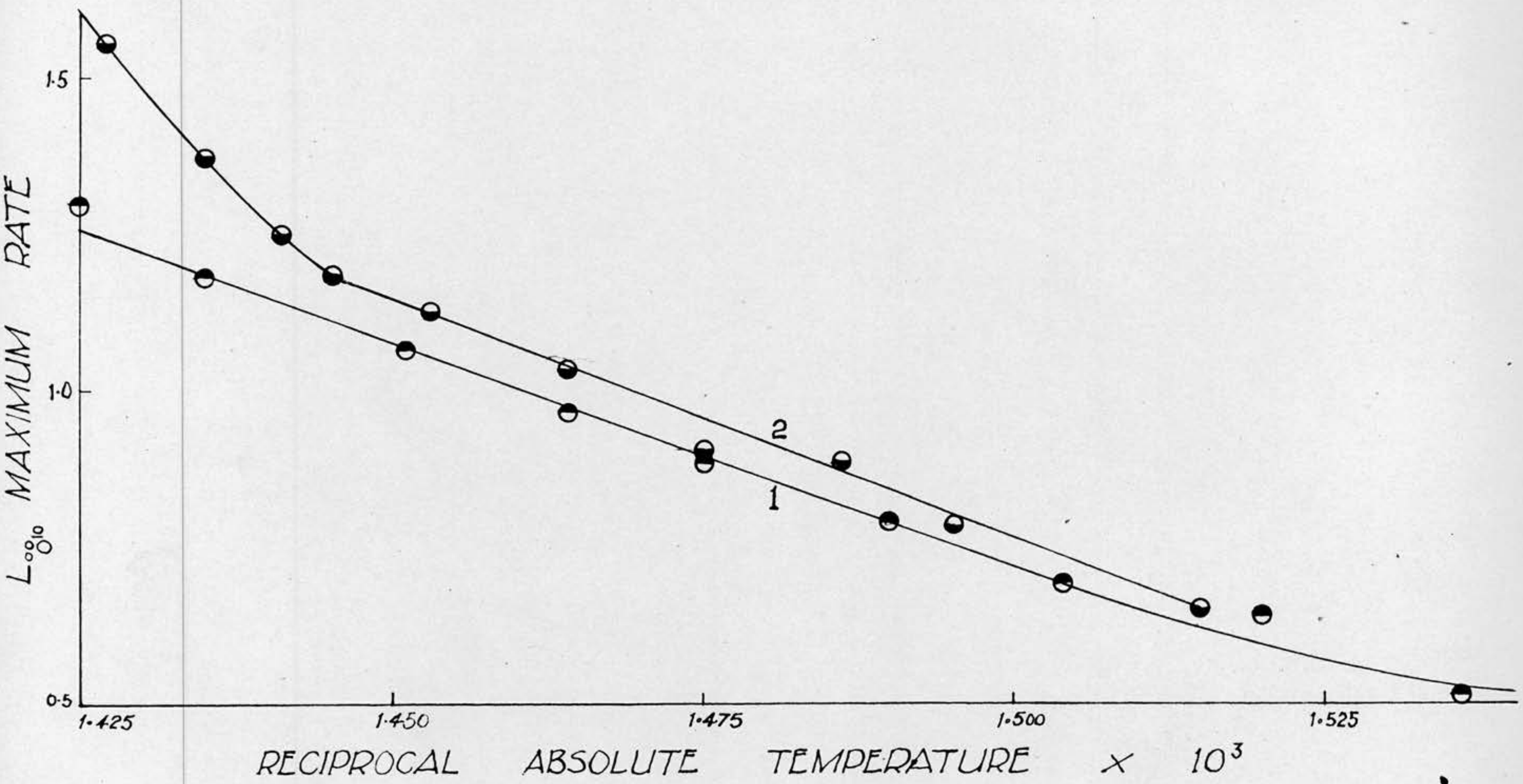
| Run No. | T | $\frac{10^3}{T}$ | $\rho_{max}$ | $\log_{10}\rho_{max}$ |
|---|---|---|---|---|
| B 56 | 660 | 1·515 | 4·5 | 0·6532 |
| B 57 | 669 | 1·495 | 6·1 | 0·7853 |
| B 58 | 673 | 1·486 | 7·7 | 0·8865 |
| B 49 | 678 | 1·475 | 8·0 | 0·9031 |
| B 48 | 683 | 1·464 | 10·7 | 1·0294 |
| B 50 | 688 | 1·453 | 13·4 | 1·1271 |
| B 52 | 692 | 1·445 | 15·2 | 1·1818 |
| B 51 | 694 | 1·441 | 17·8 | 1·2504 |
| B 47 | 697 | 1·435 | 23·7 | 1·3747 |
| B100 | 701 | 1·427 | 36 | 1·5563 |

It has already been demonstrated that there are two very distinct types of kinetic behaviour characteristic of the slow combustion of cyclopropane and that the proportion of oxygen in the reacting mixture and the temperature are two important factors which decide which of the two rate expressions Rate $\propto p_{cp}.p_{O_2}$ or Rate $\propto p_{cp}^2$ is operative. Thus the curvature over part of the activation energy plots is hardly unexpected. The significance of the curvature will be discussed in some detail

GRAPH No.14

# Effect of Change of Temperature upon Maximum Rate (Vessel B)

1. $p_{C.P.} = 250$ m.m.; $p_{O_2} = 70$ m.m.
2. $p_{C.P.} = 178$ m.m.; $p_{O_2} = 200$ m.m.



later.

Meanwhile, it may be noted that the curvature occurs at the high temperature end of the line referring to the oxygen-rich mixture and at the low temperature end of the other graph. The overall activation energies calculated from the slopes of the straight portions are approximately the same, 34·1 and 35·0 respectively. It is interesting to note that Mr. Broatch determined the activation energy of the reaction as 35·2 kcal /mole in the packed vessel already described.

## 4. The effect of Added Nitrogen

In the slow combustion of cyclopropane, the existence of two distinct types of kinetic behaviour necessitated the study of a possible inert gas effect on each case. A series of experiments was performed with 200 m.m. each of cyclopropane and oxygen at 678°A i.e. in a region where the kinetical relation Rate $\propto p_{cp}^2 \cdot p_{O_2}$ was known to operate. The results given in table No. 26 show that the reaction rate was independent of total pressure, at least at moderate pressures, a result which was hardly unexpected in view of the fact that under these conditions increase of the oxygen pressure had no effect upon the rate.

A second series of experiments was carried out; this time at 701°A with 178 m.m. of hydrocarbon and 79 m.m. of oxygen i.e. where the kinetical expression Rate $\propto p_{cp} \cdot p_{O_2}$ was known to hold. The results given in table No. 27 again show the absence of an inert gas effect.

Table No. 26

Initial $p_{cp}$ = 200 m.m. $p_{O_2}$ = 200 m.m.

T = 678°A Vessel B

| Run No. | $p_{N_2}$ | $\rho_{max}$ |
|---|---|---|
| B 122 | - | 10·4 |
| B 121 | 50·0 | 10·4 |
| B 120 | 98·4 | 10·4 |

Table No. 27

Initial $p_{cp}$ = 178 m.m. $p_{O_2}$ = 79 m.m.

T = 701°A Vessel B

| Run No. | $p_{N_2}$ | $\rho_{max}$ |
|---|---|---|
| B 106 | - | 14·0 |
| B 103 | 50·3 | 14·0 |
| B 104 | 99·6 | 14·0 |

Using the packed vessel already described, Mr. W. N. Broatch studied the effect of the addition of 100 m.m. of nitrogen to a mixture of 200 m.m. each of cyclopropane and oxygen, at 696°A. The maximum rate was 1·4 m.m./minute with or without the addition of nitrogen.

## 5. The Effect of Added Hydrogen

It has been previously observed that molecular hydrogen inhibits hydrocarbon oxidation markedly (54). It may be pointed out that the molecular velocity of hydrogen is $\sqrt{14}$ x the molecular velocity of nitrogen and that consequently hydrogen molecules suffer collisions (perhaps deactivating a chain carrier) some four times as frequently as nitrogen. The specific effect of hydrogen upon pseudo-unimolecular reactions has been discussed by Hinshelwood (55). It appears that the effect is not due entirely to the greater velocity of hydrogen since helium has no similar effect though, of course, the five degrees of freedom of the hydrogen molecule, as compared with the three of the helium molecule, must facilitate the transfer of energy.

Ubbelohde (56) believes the process of inhibition by hydrogen in hydrocarbon oxidation to be due to the deactivation of the $RO_2^*$ radicals (i.e. Those endowed with excess energy).

$$\text{Thus } RO_2^* + H_2 \longrightarrow RO_2 + H_2^*$$

Such a transfer of internal to translational energy would lead to inhibition of the reaction. Prettre, on the other hand, considers the retardation to be a surface effect (57).

In the present work, the effect of added hydrogen was studied in reaction vessel D at 678°A with 200 m.m. each of cyclopropane and oxygen. The results are given in table No. 28

TABLE NO. 28

| Run No. | Pretreatment | $p_{H_2}$ | $P_{max}$ |
|---|---|---|---|
| D 3 | One hour's evacuation | - | 11·2 |
| D 4 | One hour's evacuation | 50 | 9·8 |
| D 5 | 50 m.m. of products of run No. D4 (incl. 5 m.m. $H_2$) left in the heated vessel for 37 hours<br>One hour's evacuation | - | 8·5 |
| D 6 | One hour's evacuation | - | 8·6 |
| D 7 | One hour's evacuation | - | 8·9 |
| D 8 | 50 m.m. of products of run No. D7 (no. $H_2$) left in the hot vessel for 67 hours<br>One hour's evacuation | - | 11·2 |
| D 9 | 50 m.m. of hydrogen placed in the hot vessel for 40 minutes followed by one hour's evacuation | - | 8·6 |
| D 10 | Seven hour's evacuation | - | 9·4 |

From these results it can be seen that the hydrogen effect is not merely a gas effect and is due in large part to a change in the surface of the vessel. The results indicate that normally the reaction walls are coated with some substance formed in the reaction, that is removed by hydrogen but is not replaced (since long evacuation has little effect) by any hydrogenous substance.

## THE DEPENDENCE OF THE NET BRANCHING FACTOR UPON CONDITIONS

### 1. Dependence upon Initial Oxygen Pressure

The experiments which yielded this information have been described already and it only remains to indicate the results. In general, the net-branching factor varied with initial oxygen pressure in a manner analagous to the maximum rate. Tables Nos. 29, 30, 31 and 32 give details of experiments performed at 678°A in reaction vessel B with 178, 200, 250 and 300 m.m. of cyclopropane respectively. The results of these four series of experiments are plotted on graph No. 15.

TABLE NO. 29

Initial $p_{cp}$ = 178 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | A′ |
|---|---|---|
| B 43 | 50·0 | 0·095 |
| B 42 | 89·7 | 0·128 |
| B 44 | 101·0 | 0·145 |
| B 39 | 108·4 | 0·180 |
| B 41 | 149·4 | 0·170 |
| B 49 | 200·9 | 0·160 |

TABLE NO. 30

Initial $p_{cp}$ = 200 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | A′ |
|---|---|---|
| B 24 | 50·0 | 0·070 |
| B 26 | 70·0 | 0·100 |
| B 25 | 100·5 | 0·145 |
| B 27 | 130·0 | 0·160 |
| B 30 | 199·8 | 0·163 |
| B 28 | 248·7 | 0·165 |

TABLE NO. 31

Initial $p_{cp}$ = 250 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | A′ |
|---|---|---|
| B 35 | 48·3 | 0·145 |
| B 34 | 94·5 | 0·251 |
| B 33 | 109·8 | 0·210 |
| B 38 | 124·7 | 0·225 |
| B 32 | 134·8 | 0·240 |
| B 31 | 180·0 | 0·250 |
| B 36 | 198·8 | 0·250 |
| B 37 | 250·0 | 0·250 |

TABLE NO. 32

Initial $p_{cp}$ = 300 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | A′ |
|---|---|---|
| B 67 | 49·5 | 0·191 |
| B 62 | 97·4 | 0·274 |
| B 68 | 101·7 | |
| B 70 | 147·2 | 0·310 |
| B 71 | 149·7 | 0·320 |
| B 72 | 178·3 | 0·367 |
| B 64 | 198·0 | 0·370 |
| B 66 | 252·7 | 0·370 |

Variation of Initial Oxygen Pressure at 678°A
(Vessel B)

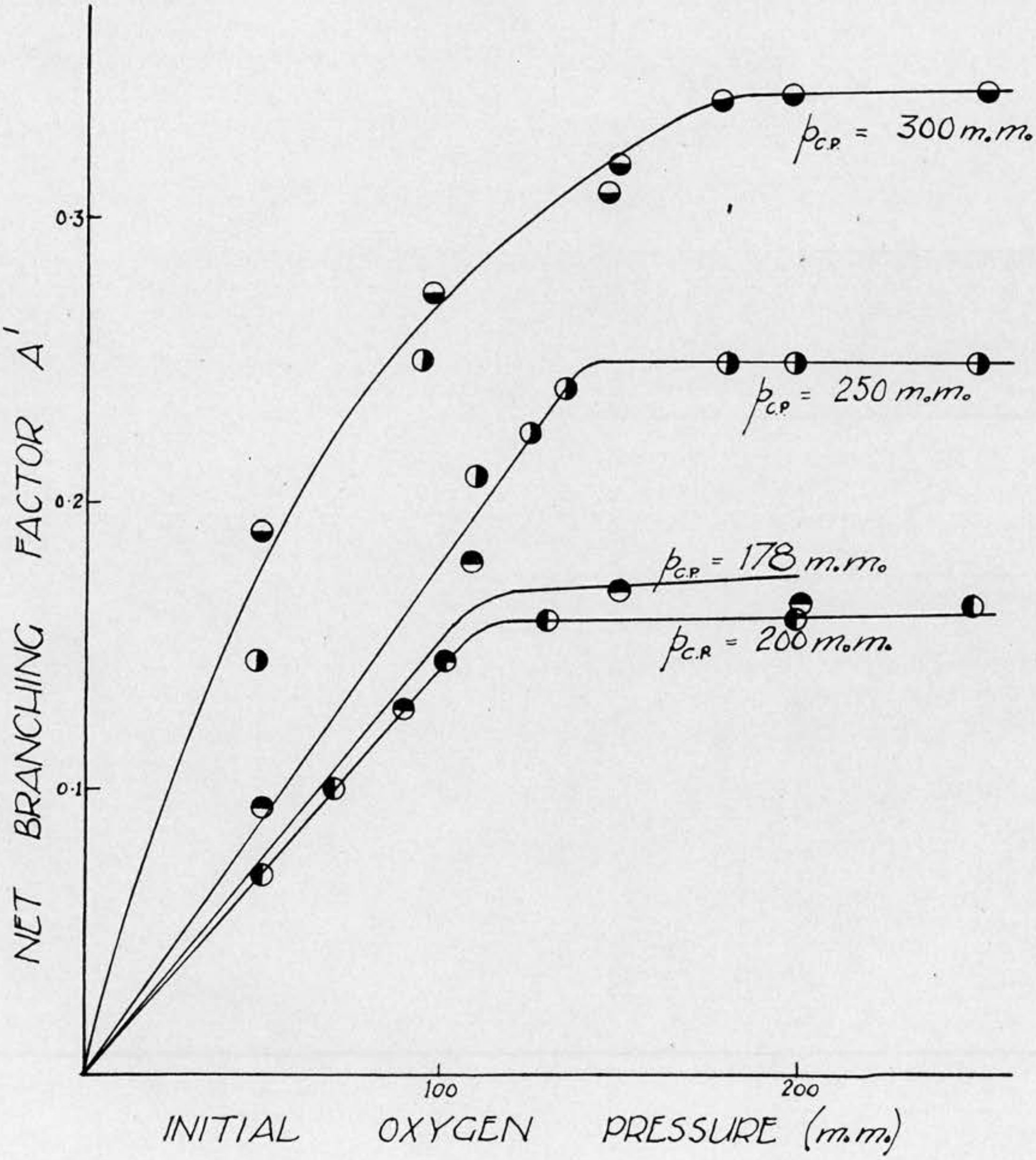


Table No. 33 and graph No. 16 illustrate the variation of the net-branching factor with change of oxygen pressure at 651° A the initial cyclopropane pressure being again 250 m.m. The graph also shows for comparison, the corresponding curve for 250 m.m. of hydrocarbon at 678° A.

Table No. 33

Initial $p_{cp}$ = 250 m.m. T = 651° A Vessel B

| Run No. | $p_{O_2}$ | A′ |
|---|---|---|
| B 95 | 40·0 | 0·080 |
| B 94 | 69·9 | 0·085 |
| B 93 | 99·0 | 0·086 |
| B 92 | 134·2 | 0·101 |
| B 91 | 180·4 | 0·108 |
| B 90 | 233·7 | 0·104 |

Table No. 34 gives the details of experiments with 178 m.m. cyclopropane at 701° A and graph No. 17 illustrates the influence of temperature upon the net-branching factor-initial oxygen pressure curve for 178 m.m. of hydrocarbon. The next table of results (No. 35) gives the data for experiments carried out in the first reaction vessel (A) at 678° A with 200 m.m. of cyclopropane and with varying amounts of oxygen. The graph (No. 18) compares the corresponding curves for the two vessels.

TABLE NO. 34

Initial $p_{cp}$ = 178 m.m. T = 701° A

Vessel B

| Run No. | $p_{O_2}$ | A′ |
|---|---|---|
| B 97 | 50·7 | 0·286 |
| B106 | 78·8 | 0·343 |
| B 98 | 98·6 | 0·403 |
| B 99 | 151·4 | 0·386 |
| B100 | 200·3 | 0·387 |

TABLE NO. 35

Initial $p_{cp}$ = 200 m.m. T = 678° A

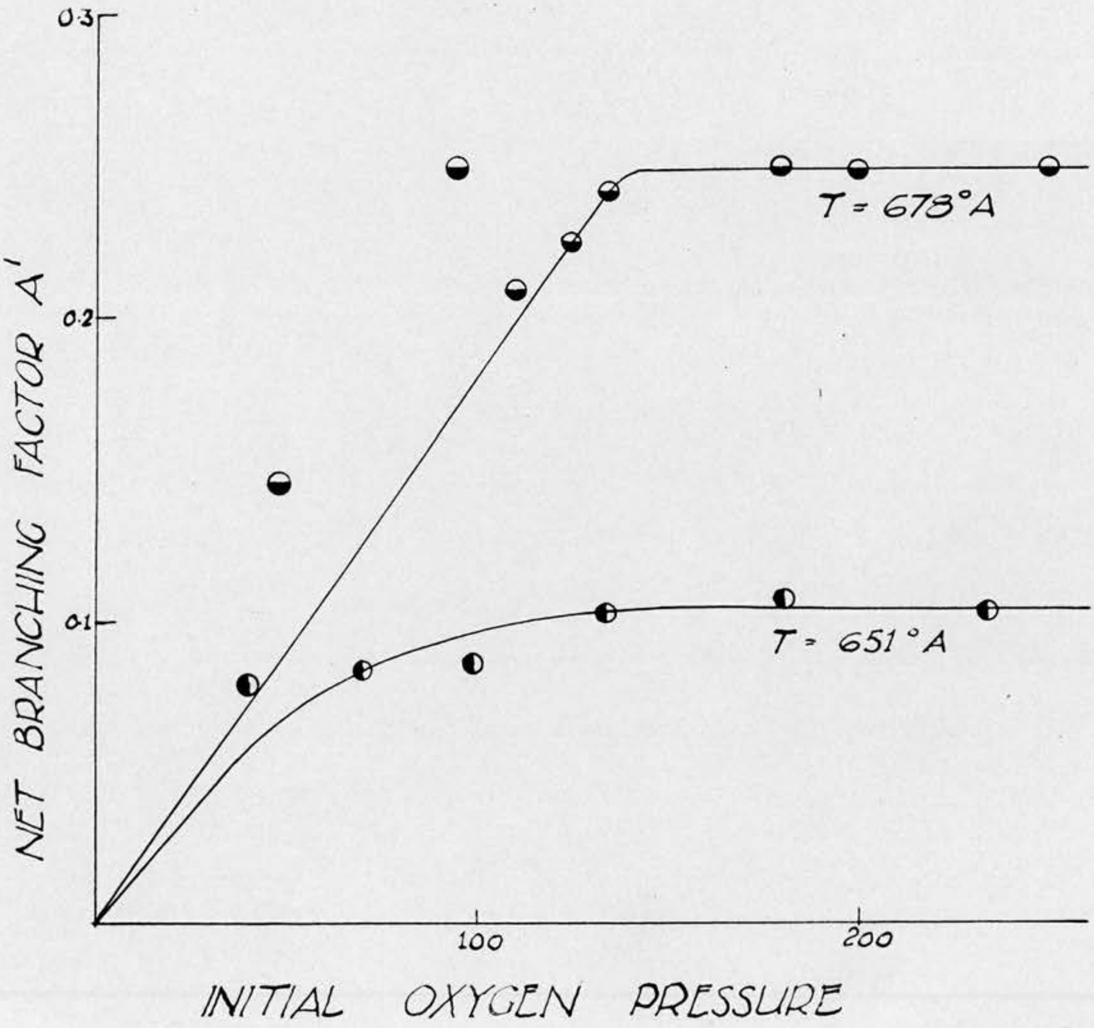
Vessel A

| Run No. | $p_{O_2}$ | A′ |
|---|---|---|
| A 41 | 52·1 | 0·077 |
| A 42 | 84·7 | 0·095 |
| A 37 | 106·5 | 0·100 |
| A 40 | 150·9 | 0·117 |
| A 38 | 189·8 | 0·122 |
| A 39 | 234·8 | 0·115 |

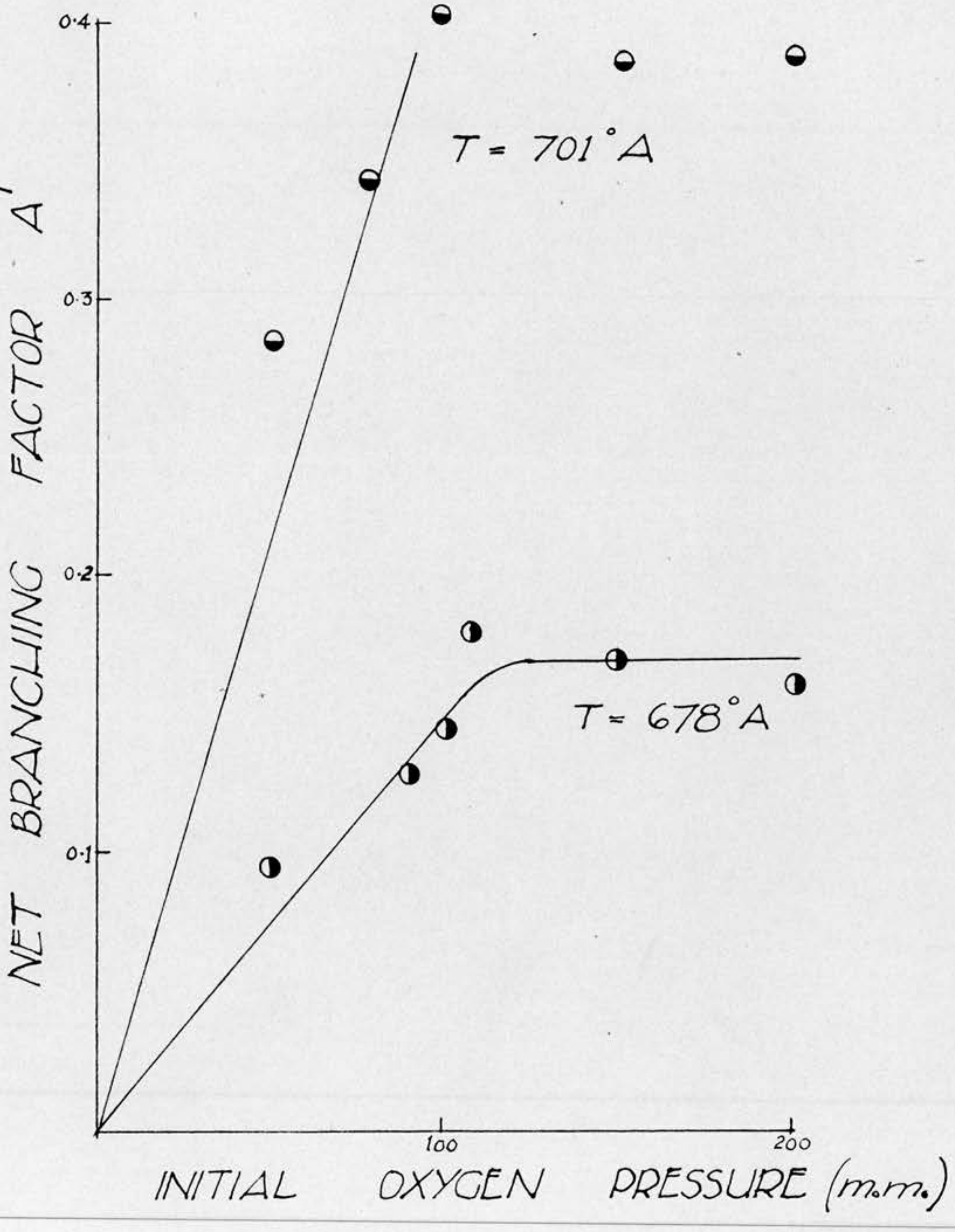
GRAPH Nº16

Variation of Initial Oxygen Pressure (Vessel B)

$p_{C.V.}$ = 250 m.m.



Variation of Initial Oxygen Pressure (Vessel B)
$p_{C.P.} = 178$ m.m.



GRAPH Nº 18

Variation of Initial Oxygen Pressure
($p_{C.P.}$ = 200 m.m.; T = 678°A)

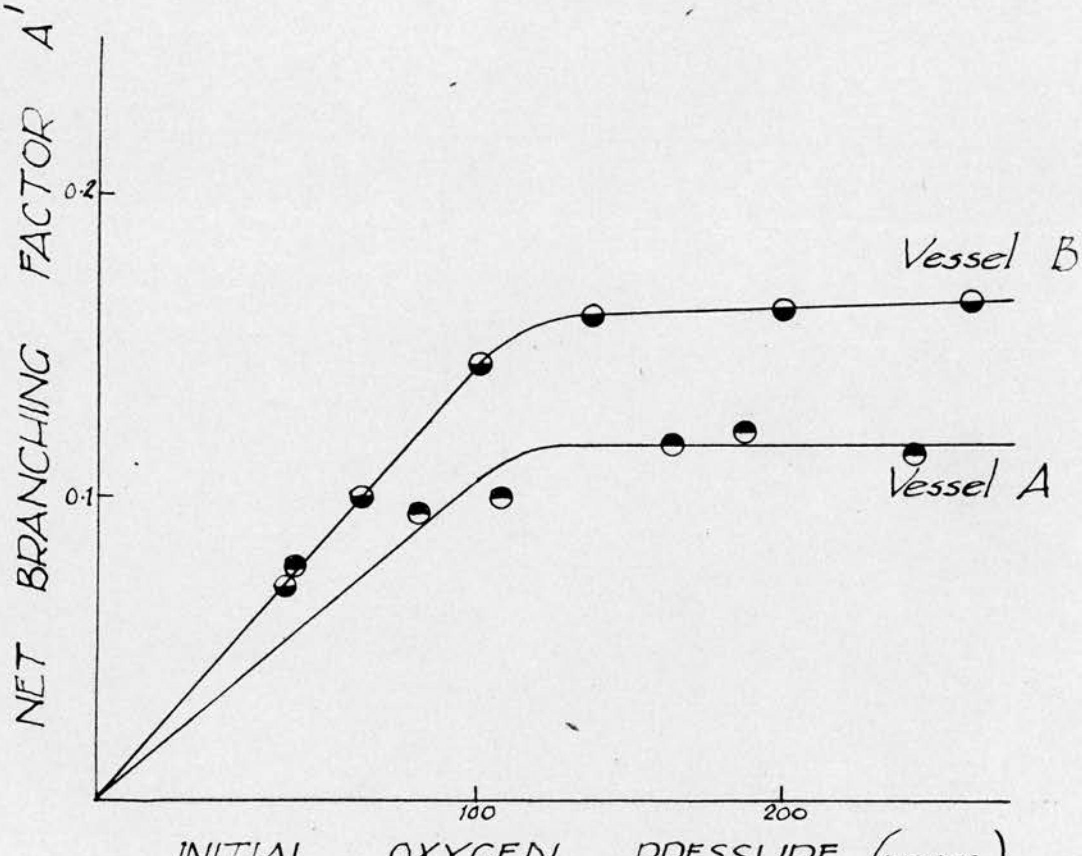


Table No. 36 contains the results of the experiments carried out in vessel D at 701°A. The initial hydrocarbon pressure in each experiment was 100 m.m. and the oxygen pressures ranged between 49 and 300 m.m. The graph (No. 19) again demonstrates that the kinetic behaviour is largely independent of the vessel, although the actual values of the parameters may vary considerably from vessel to vessel.

Table No. 36

Initial $p_{cp}$ = 100 m.m. T = 701°A Vessel D

| Run No. | $p_{O_2}$ | A′ |
|---|---|---|
| D 18 | 49·0 | 0·16 |
| D 13 | 100·5 | 0·19 |
| D 17 | 144·5 | 0·24 |
| D 15 | 186·3 | 0·25 |
| D 16 | 240·0 | 0·24 |
| D 14 | 298·8 | 0·27 |

2. Dependence Upon Initial Cyclopropane Pressure

Tables No. 37, 38 and 39 give the details of experiments carried out at 678°A, 678°A and 701°A with 200 m.m., 70 m.m. and 79 m.m. of oxygen respectively. The three series are represented on the graph (No. 20).

TABLE NO. 37

Initial $p_{O_2}$ = 200 m.m. T = 678°A

Vessel B

| Run No. | $p_{cp}$ | A′ | $p_{cp}^2$ |
|---|---|---|---|
| B 21 | 152·0 | 0·080 | 23100 |
| B 23 | 159·0 | 0·090 | 25280 |
| B 49 | 177·9 | 0·160 | 31650 |
| B 20 | 200·0 | 0·163 | 40000 |
| B 36 | 249·7 | 0·250 | 62350 |
| B 64 | 300·0 | 0·370 | 90000 |

TABLE NO. 38

Initial $p_{O_2}$ = 70 m.m. T = 678°A

Vessel B

| Run No. | $p_{cp}$ | A′ |
|---|---|---|
| B 74 | 150·0 | 0·108 |
| B 78 | 202·5 | 0·137 |
| B 77 | 252·0 | 0·193 |
| B 73 | 300·0 | 0·238 |
| B 76 | 350·0 | 0·250 |
| B 75 | 400·0 | 0·340 |

GRAPH Nº 19

Variation of Initial Oxygen Pressure (Vessel D)

$p_{C.P.} = 100$ m.m. : $T = 701$°A

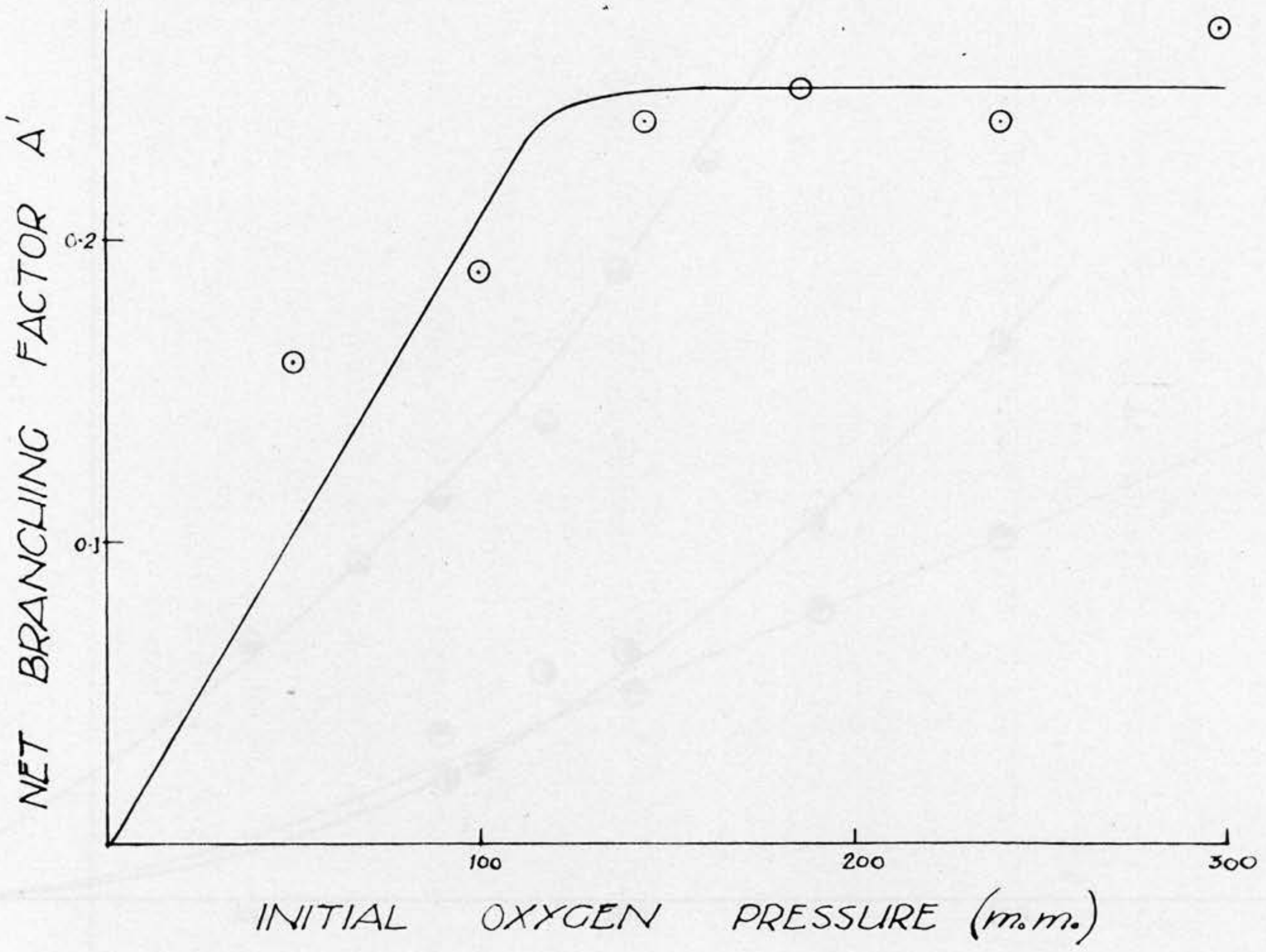


Table No. 39

Initial $p_{O_2}$ = 79 m.m. T = 701°A

Vessel B

| Run No. | $p_{cp}$ | A′ |
|---|---|---|
| B 108 | 99·2 | 0·170 |
| B 107 | 128·5 | 0·221 |
| B 117 | 150·0 | 0·264 |
| B 106 | 177·8 | 0·316 |
| B 116 | 198·7 | 0·415 |
| B 115 | 221·2 | 0·490 |
| B 114 | 258·8 | 0·650 |

Table No. 40 gives results obtained in the vessel A with 150 m.m. $O_2$ at 678°A and the graph (No. 21) illustrates the dependence of A' upon $p_{cp}$ . The other figure on the graph relates to the results in table No. 41 obtained in vessel D by varying the cyclopropane pressure at 701°A with a stoichiometric excess (300 m.m.) of oxygen.

TABLE NO. 40

Initial $p_{O_2}$ = 150 m.m. T = 678°A

Vessel A

| Run No. | $p_{cp}$ | A′ | $p_{cp}^2$ |
|---|---|---|---|
| A 35 | 176·3 | 0·077 | 31070 |
| A 25 | 199·1 | 0·100 | 39650 |
| A 23 | 201·8 | 0·105 | 40720 |
| A 14 | 208·0 | 0·112 | 43270 |
| A 33 | 250·5 | 0·166 | 62750 |
| A 28 | 299·0 | 0·218 | 89430 |
| A 32 | 302·2 | 0·226 | 91330 |
| A 30 | 304·0 | 0·223 | 92380 |

TABLE NO. 41

Initial $p_{O_2}$ = 300 m.m. T = 701°A

Vessel D

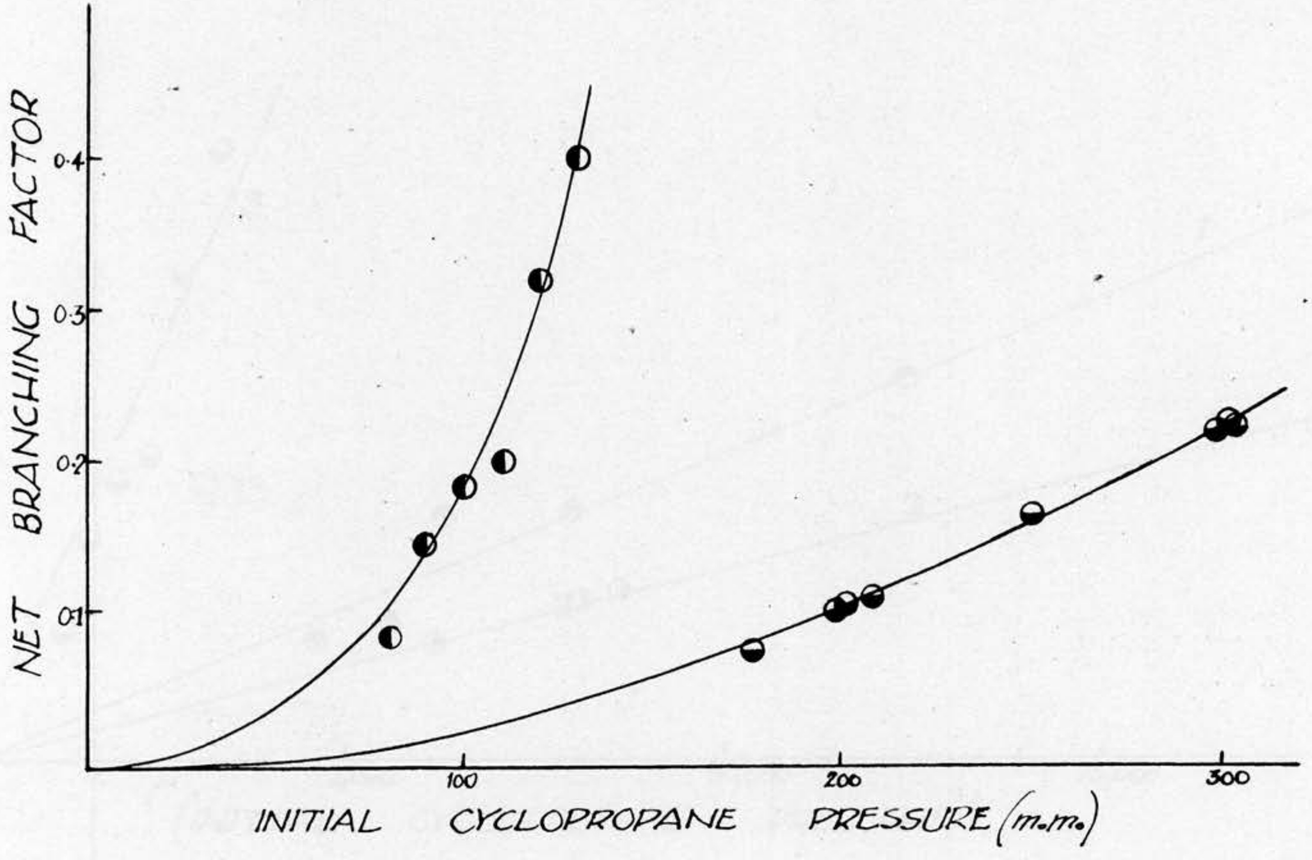
| Run No. | $p_{cp}$ | A′ | $p_{cp}^2$ |
|---|---|---|---|
| D 25 | 80·0 | 0·085 | 6400 |
| D 26 | 90·0 | 0·145 | 8100 |
| D 21 | 100·0 | 0·183 | 10000 |
| D 20 | 110·2 | 0·200 | 12150 |
| D 22 | 120·0 | 0·320 | 14400 |
| D 24 | 130·0 | 0·400 | 16900 |

Two types of dependence will be recognised, a linear dependence and a higher dependence. That this second dependence was a square one was shown by the straight-line graph of A' against the square of the initial cyclopropane pressures (graph No. 22) shown in tables No. 37, 40 and 41.

GRAPH Nº 21

Variation of Initial Cyclopropane Pressure

1. $p_{O_2}$ = 150 m.m. ; T = 678°A (Vessel A)
2. $p_{O_2}$ = 300 m.m. ; T = 701°A (Vessel D)



## 3. Dependence Upon the Temperature

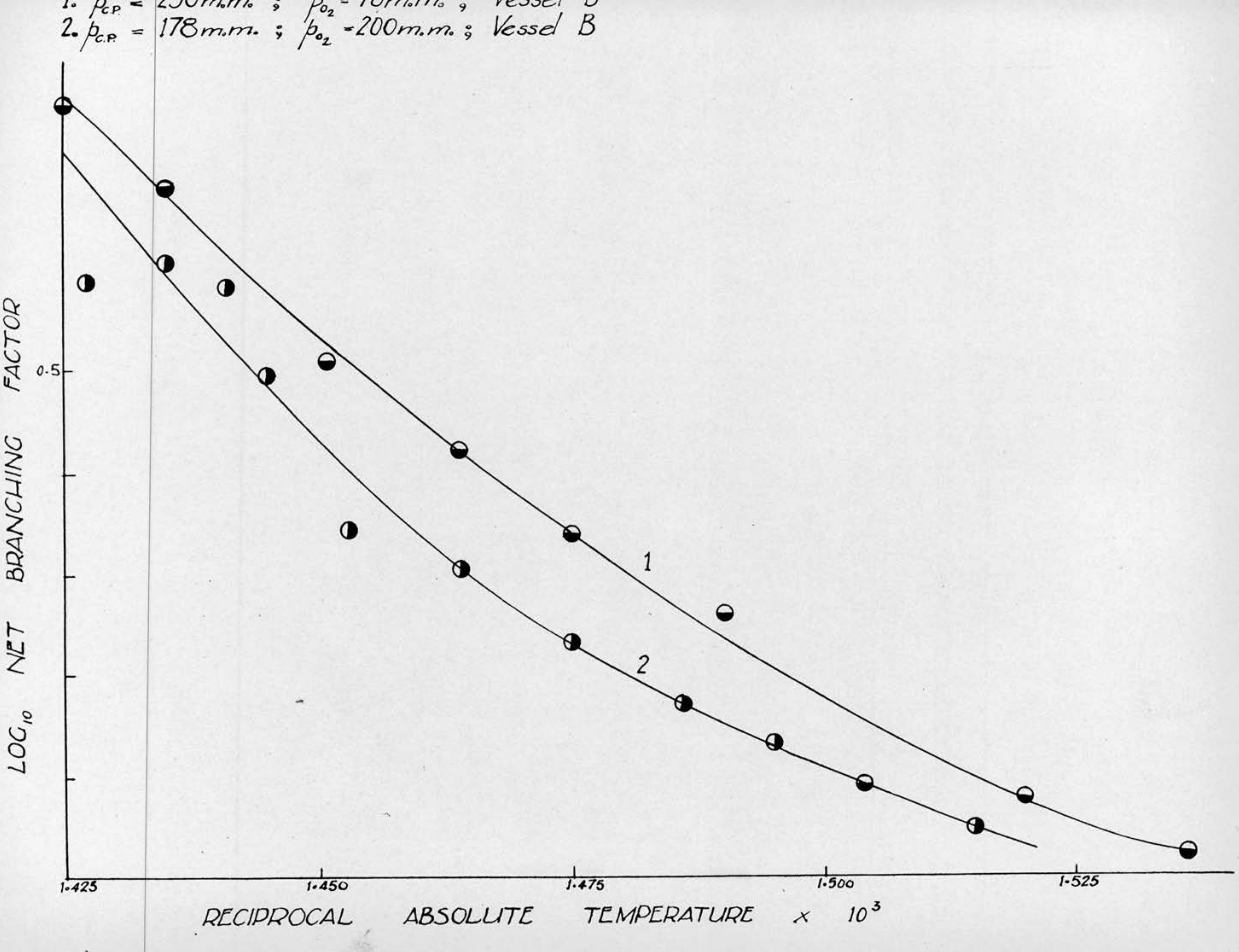
Experiments designed to elucidate the temperature dependence of the reaction have been already described in the section dealing with maximum rates. Two distinct series of experiments were performed and the net-branching factors have been calculated and are tabulated in tables Nos. 42 and 43, the former relating to experiments at different temperatures with a mixture of 250 m.m. cyclopropane and 70 m.m. of oxygen and the latter referring to the reaction of a mixture of 178 m.m. of hydrocarbon and 200 m.m. of oxygen at various temperatures over the range 651°A - 705°A. Graph No. 23 illustrates the variation of log A' with reciprocal absolute temperature for the two series.

Table No. 42

Initial $p_{cp}$ = 250 m.m. $p_{O_2}$ = 70 m.m.

Vessel B

| Run No. | $T$ | $\frac{10^3}{T}$ | $A'$ | $\log_{10} A'$ |
|---|---|---|---|---|
| B 89 | 651 | 1·536 | 0·105 | 0·0212 |
| B 88 | 658 | 1·520 | 0·120 | 0·0792 |
| B 87 | 665 | 1·504 | 0·123 | 0·0899 |
| B 86 | 671 | 1·490 | 0·181 | 0·2577 |
| B 77 | 678 | 1·475 | 0·216 | 0·3345 |
| B 83 | 683 | 1·464 | 0·263 | 0·4200 |
| B 80 | 689 | 1·451 | 0·320 | 0·5051 |
| B 81 | 697 | 1·435 | 0·477 | 0·6785 |
| B 84 | 702 | 1·425 | 0·576 | 0·7604 |


1. $p_{C.P.}$ = 250 m.m. ; $p_{O_2}$ = [illegible] m.m. ; Vessel B
2. $p_{C.P.}$ = 178 m.m. ; $p_{O_2}$ = 200 m.m. ; Vessel B
LOG$_{10}$ NET BRANCHING FACTOR
0.5
1
2
1.425
1.450
1.475
1.500
1.525
RECIPROCAL ABSOLUTE TEMPERATURE × $10^3$

GRAPH No. 23

Table No. 43

Initial $p_{cp}$ = 178 m.m. $p_{O_2}$ = 200 m.m.

Vessel B

| Run No. | T | $\frac{10^3}{T}$ | A' | $\log_{10} A'$ |
|---|---|---|---|---|
| B 56 | 660 | 1·515 | 0·112 | 0·0492 |
| B 57 | 669 | 1·495 | 0·135 | 0·1303 |
| B 58 | 673 | 1·486 | 0·147 | 0·1673 |
| B 49 | 678 | 1·475 | 0·170 | 0·2304 |
| B 48 | 683 | 1·464 | 0·200 | 0·3010 |
| B 50 | 688 | 1·453 | 0·220 | 0·3424 |
| B 52 | 692 | 1·445 | 0·310 | 0·4914 |
| B 51 | 694 | 1·441 | 0·380 | 0·5798 |
| B 47 | 697 | 1·435 | 0·404 | 0·6064 |
| B100 | 701 | 1·427 | 0·387 | 0·5877 |

The graphs closely resemble the log maximum rate against reciprocal absolute temperature plots and the activation energies calculated from the slopes of their straight portions are 35·0 kcals. and about 35 kcals. respectively, the considerable curvature (or perhaps scatter) in the latter case making selection of a best line difficult.

## 4. Effect of added Nitrogen

Experiments previously described yielded some information as to the effect of nitrogen upon the net-branching factor. The results are given in table No. 44 referring to experiments with 200 m.m. of each gas at 678°A (Rate $\propto p_{cp}^2$ ) and in table No. 45 referring to experiments at 701°A with 178 m.m. cyclopropane and 79 m.m. of oxygen (Rate $\propto p_{cp} \cdot p_{O_2}$ ). It will be seen that the net-branching factor was unaffected by dilution of the reaction mixture with nitrogen.

TABLE NO. 44.

Initial $p_{cp}$ = 200 m.m. $p_{O_2}$ = 200 m.m.

T = 678°A Vessel B

| Run No. | $p_{N_2}$ | A' |
|---|---|---|
| B 122 | - | 0·163 |
| B 121 | 50·0 | 0·160 |
| B 120 | 98·4 | 0·165 |

TABLE NO. 45

Initial $p_{cp}$ = 178 m.m. $p_{O_2}$ = 79 m.m.

T = 701°A Vessel B

| Run No. | $p_{N_2}$ | A' |
|---|---|---|
| B 106 | - | 0·343 |
| B 103 | 50·3 | 0·350 |
| B 104 | 99·6 | 0·350 |

## 5. Effect of added Hydrogen

Table No. 46 illustrates the results of the study made on the effect of added hydrogen upon the net-branching factor. While it will be noted that the pretreatment of the vessel with hydrogen and the addition of hydrogen to the system led to the lowest values of A' very little can be concluded from the results as there is not such a distinct trend as was observed in the case of the maximum rates.

TABLE NO. 46

| Run No. | Pretreatment | $p_{H_2}$ | A' |
|---|---|---|---|
| D 3 | One hour's evacuation | - | 0·24 |
| D 4 | One hour's evacuation | 50 | 0·20 |
| D 5 | 50 m.m. of products of run No. D4 (incl. 50 m.m. $H_2$) left in the hot vessel for 37 hours<br>One hour's evacuation | - | 0·18 |
| D 6 | One hour's evacuation | - | 0·22 |
| D 7 | One hour's evacuation | - | 0·22 |
| D 8 | 50 m.m. of products of run No. D7 (No. $H_2$) left in the hot vessel for 67 hours<br>One hour's evacuation | - | 0·24 |
| D 9 | 50 m.m. of $H_2$ heated in the vessel for 40 minutes<br>One hour's evacuation | - | 0·23 |
| D 10 | Seven hour's evacuation | - | 0·20 |

In these experiments it was noted that the graphs of log against time showed more curvature than usual when hydrogen was presnnt. This gradual decrease of A' as the experiment proceeded made it necessary to consider the initial part of the graph only in the determination of A'.

## THE DEPENDENCE OF THE INDUCTION PERIOD UPON CONDITIONS

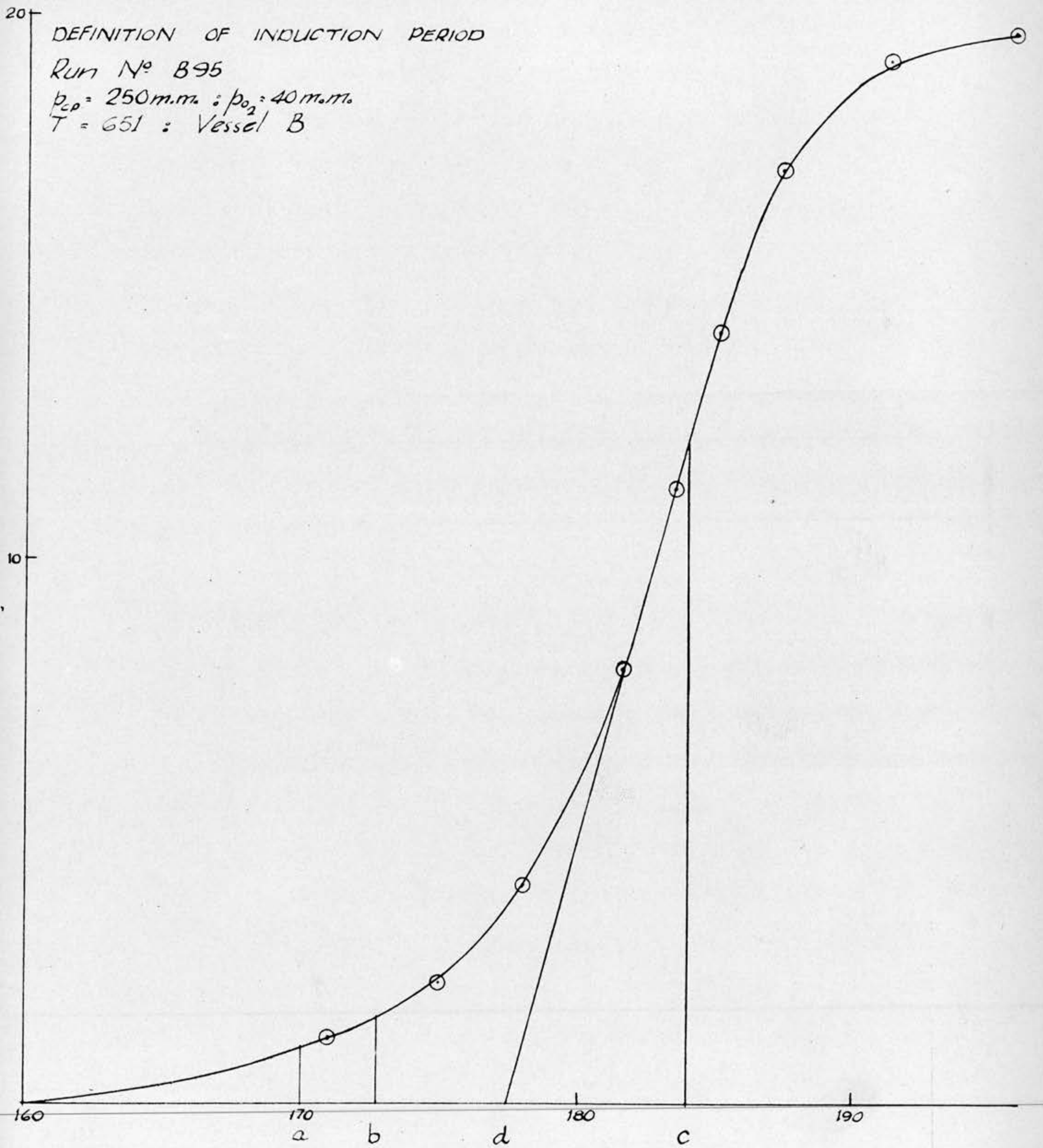
The definition and method of measurement of that remarkable feature of hydrocarbon oxidation -the induction period - requires a little discussion. The term induction period has been used to describe several distinct factors. These are (a) the time taken until the first measureable pressure change occurs, (b) the time taken until the rate reaches a certain small speed (say 0·5 m.m. per minute), (c) the time taken for the attainment of the maximum rate and (d) the time measured by the extrapolation of the tangent to the $\Delta p$-$t$ curve at the maximum rate back to the time axis. These are illustrated on the graph (No. 24).

In the present work the initial time ($t_o$) has been taken as the time of addition of the oxygen to the cyclopropane in the reaction. It will be seen later that so long as the time between admission of hydrocarbon and $t_o$ is small there is no danger of pyrolysis except at very high temperatures so that the description of $t_o$ as time of admission of oxygen is justified.

It can easily be shown that the two extremes of induction period definition (a) and (c) above are sufficiently equivalent to make their separate study unnecessary. This is clearly shown on the graph (No. 31) where the reciprocals of $\theta$ and $\Upsilon$ have been plotted against reciprocal temperature on the same paper.

In general, therefore, induction period has been taken as the time elapsing between the admission of oxygen to the vessel and the attainment of maximum rate.

It has been found that no high degree of reproducibility


20
10
DEFINITION OF INDUCTION PERIOD
Run Nº B95
$p_{cp}$ = 250 m.m. : $p_{O_2}$ : 40 m.m.
T = 651 : Vessel B
160
170
180
190
a
b
d
c
Time (mins.)

has been obtained in the study of induction periods. As earlier suggested, the state of the surface has a very pronounced effect upon the period of induction. With this limitation in mind, however, certain conclusions have been drawn with regard to the variation of induction period with change of conditions.

## 1. Dependence Upon Initial Oxygen Pressure

The induction periods and their reciprocals are detailed in tables Nos. 47, 48, 49 and 50 for the variation of initial oxygen with 178, 200, 250 and 300 m.m. of cyclopropane respectively at 678°A in vessel B. The results are shown on graph No. 25. Table No. 51 shows the variation of reciprocal induction period with change of initial oxygen pressure at 651°A (initial hydrocarbon pressure = 250 m.m.). The graph (No. 26) shows the relationship between $\frac{1}{\theta}$ and $p_{O_2}$ at 651°A and 678°A for $p_{cp}$ = 250 m.m.

TABLE NO. 47

Initial $p_{cp}$ = 178 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| B 43 | 50·0 | 150 | 0·667 |
| B 42 | 89·7 | 93 | 1·075 |
| B 44 | 101·0 | 82 | 1·220 |
| B 39 | 108·4 | 76 | 1·316 |
| B 41 | 149·4 | 48 | 2·083 |
| B 49 | 200·9 | 35·5 | 3·817 |

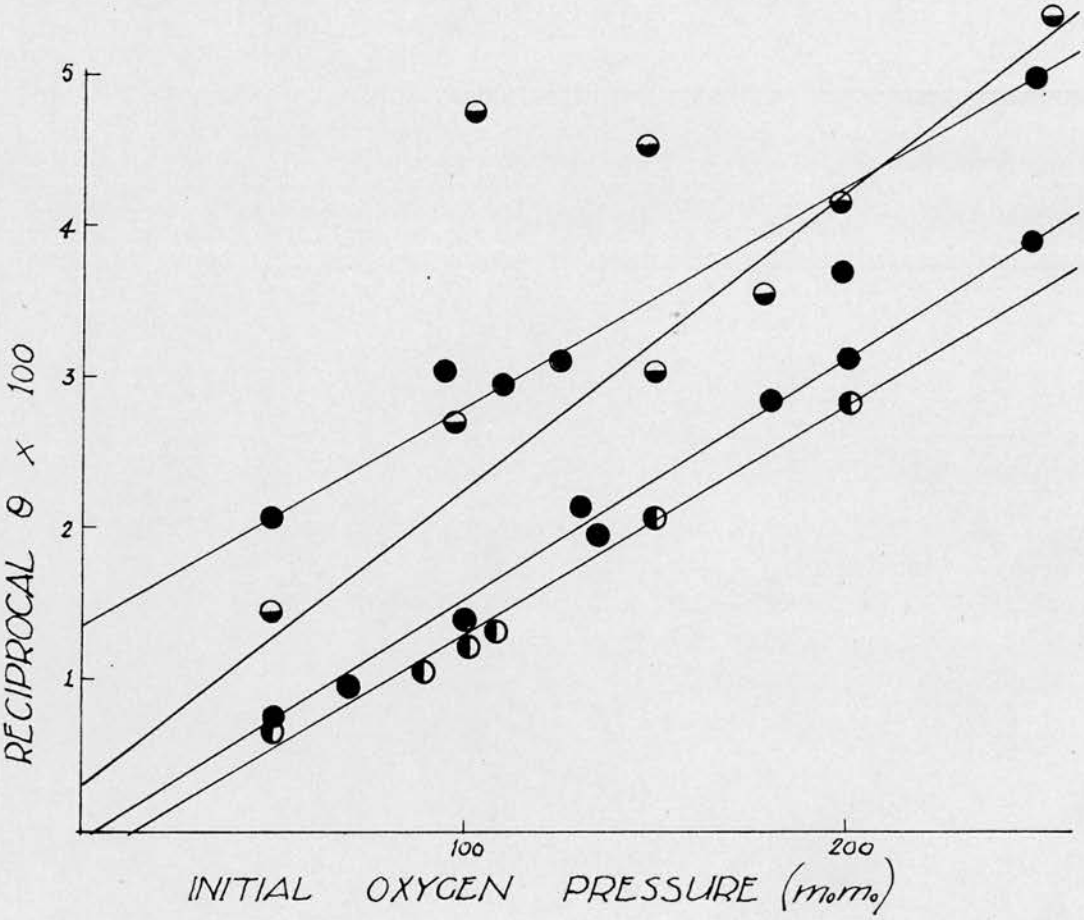
TABLE NO. 48

Initial $p_{cp}$ = 200 m.m. T = 678°A

Vessel B

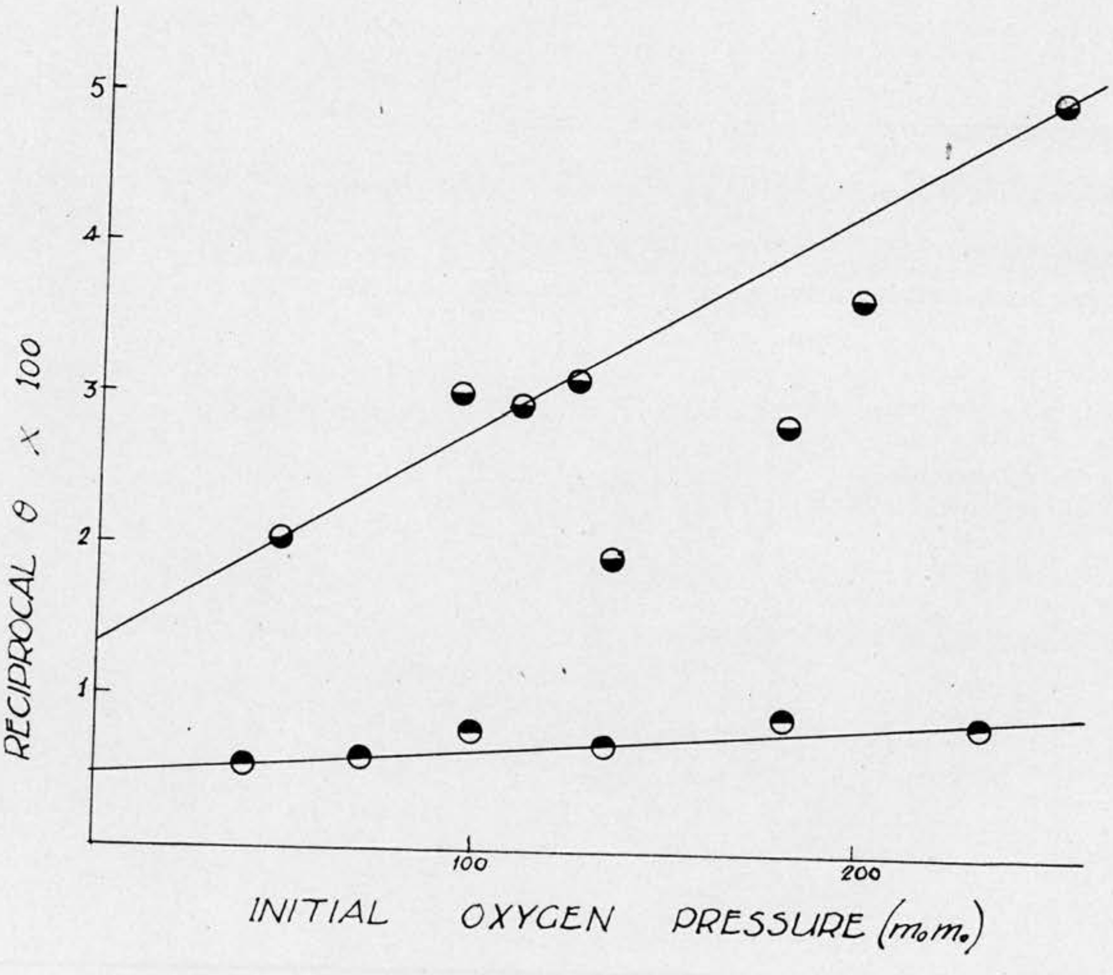
| Run No. | $p_{O_2}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| B 24 | 50·0 | 142 | 0·704 |
| B 26 | 70·0 | 105 | 0·952 |
| B 25 | 100·5 | 71 | 1·41 |
| B 27 | 130·0 | 47 | 2·13 |
| B 30 | 199·8 | 32 | 3·125 |
| B 28 | 248·7 | 25·2 | 3·922 |

# Variation of Initial Oxygen Pressure (Vessel B)



Variation of Initial Oxygen Pressure ($p_{C.P.}$ = 250 m.m.; Vessel B)

1. T = 678°A
2. T = 651°A



### TABLE NO. 49

Initial $p_{cp}$ = 250 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| B 35 | 48·3 | 48·5 | 2·062 |
| B 34 | 94·5 | 33 | 3·030 |
| B 33 | 109·8 | 34 | 2·941 |
| B 38 | 124·7 | 32 | 3·125 |
| B 32 | 134·8 | 51 | 1·961 |
| B 31 | 180·0 | 35 | 2·857 |
| B 36 | 198·8 | 27 | 3·704 |
| B 37 | 250·0 | 20 | 5·000 |

### TABLE NO. 50

Initial $p_{cp}$ = 300 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| B 67 | 49·5 | 68 | 1·471 |
| B 62 | 97·4 | 37 | 2·703 |
| B 68 | 101·7 | 21 | 4·762 |
| B 70 | 147·2 | 22 | 4·545 |
| B 71 | 149·7 | 33 | 3·030 |
| B 72 | 178·3 | 28 | 3·571 |
| B 64 | 198·0 | 24 | 4·167 |
| B 66 | 252·7 | 18·5 | 5·405 |

### TABLE NO. 51

Initial $p_{cp}$ = 250 m.m. T = 651°A

Vessel B

| Run No. | $p_{O_2}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| B 95 | 40·0 | 184·5 | 0·545 |
| B 94 | 69·9 | 160·0 | 0·625 |
| B 93 | 99·0 | 127·5 | 0·791 |
| B 92 | 134·2 | 140·5 | 0·712 |
| B 91 | 180·4 | 109·0 | 0·917 |
| B 90 | 233·7 | 114·0 | 0·877 |

Table No. 52 lists the induction times observed at 701°A with 178 m.m. cyclopropane and varying amounts of oxygen and the graph (No. 27) shows the relationship for $p_{cp}$ = 178 m.m. at 678°A and 701°A

### TABLE NO. 52

Initial $p_{cp}$ = 178 m.m. T = 701°A

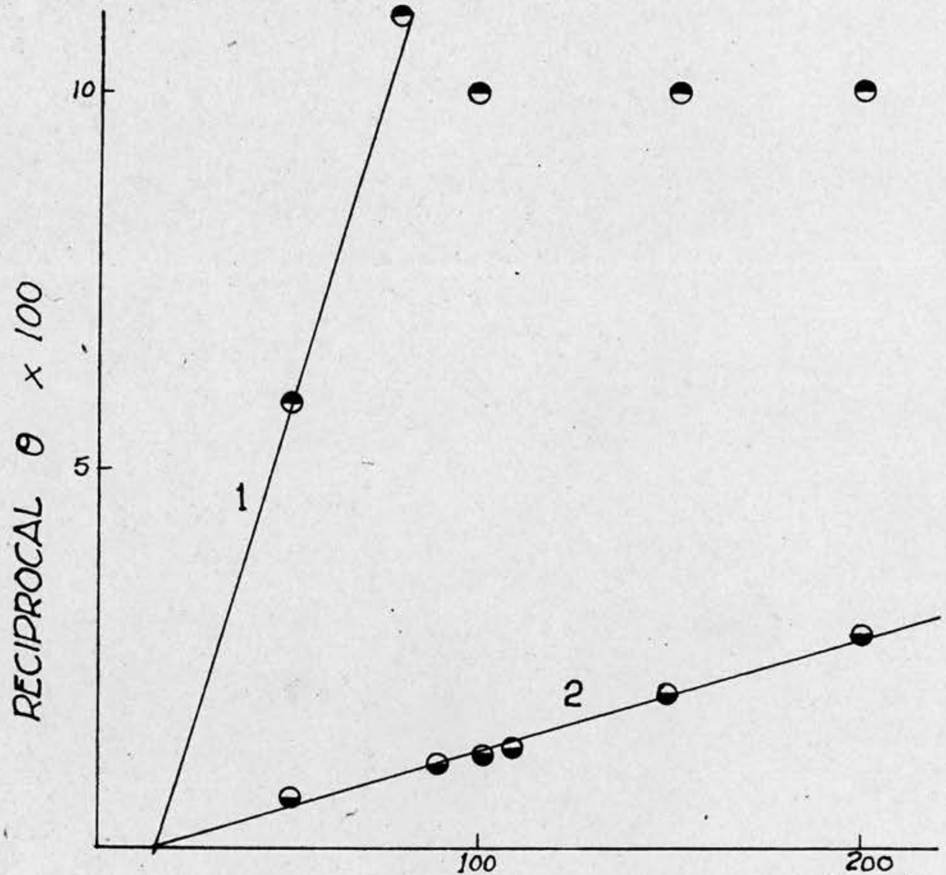
Vessel B

| Run No. | $p_{O_2}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| B 97 | 50·7 | 17 | 5·882 |
| B106 | 78·8 | 9·5 | 10·53 |
| B 98 | 98·6 | 10 | 10·0 |
| B 99 | 151·4 | 10 | 10·0 |
| B100 | 200·3 | 10 | 10·0 |

GRAPH Nº 27

Variation of Initial Oxygen Pressure
($p_{C.P.}$ = 178 m.m. ; Vessel B)

1. T = 701 °A
2. T = 678 °A



The data in table No. 53 and on the graph No. 28 refer to experiments in vessel A using 200 m.m. of cyclopropane and varying amounts of oxygen at 678°A, while table No. 54 lists details of experiments in vessel D with 100 m.m. of cyclopropane at 701°A. The figures in table No. 54 are also plotted on the graph (No. 28)

TABLE NO. 53

Initial $p_{cp}$ = 200 m.m. T = 678° A

Vessel A

| Run No. | $p_{O_2}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| A 41 | 52·1 | 92 | 1·087 |
| A 42 | 84·7 | 52 | 1·923 |
| A 37 | 106·5 | 55 | 1·818 |
| A 40 | 150·9 | 54 | 1·852 |
| A 38 | 189·8 | 48 | 2·083 |
| A 39 | 234·8 | 42 | 2·381 |

TABLE NO. 54

Initial $p_{cp}$ = 100 m.m. T = 701° A

Vessel D

| Run No. | $p_{O_2}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| D 18 | 49·0 | 33 | 3·030 |
| D 13 | 100·5 | 40 | 2·500 |
| D 17 | 144·5 | 18 | 5·556 |
| D 15 | 186·3 | 18 | 5·556 |
| D 16 | 240·0 | 18 | 5·556 |
| D 14 | 298·8 | 12 | 8·333 |

It is very difficult to make definite conclusions from these results. Recognising that some of the induction periods observed were obviously not consistent with the others in the same series the graphs are still not very satisfactory. The data in tables Nos. 47 and 48 provides strong evidence for the existence of some linear relationship between initial oxygen pressure and reciprocal induction period. Apart from the figures in table No. 52, most of the other results could be said to show some semblance of such a dependence, and it is probably justified to conclude that, in general, the induction period decreased more or less regularly when the initial pressure of oxygen was increased.

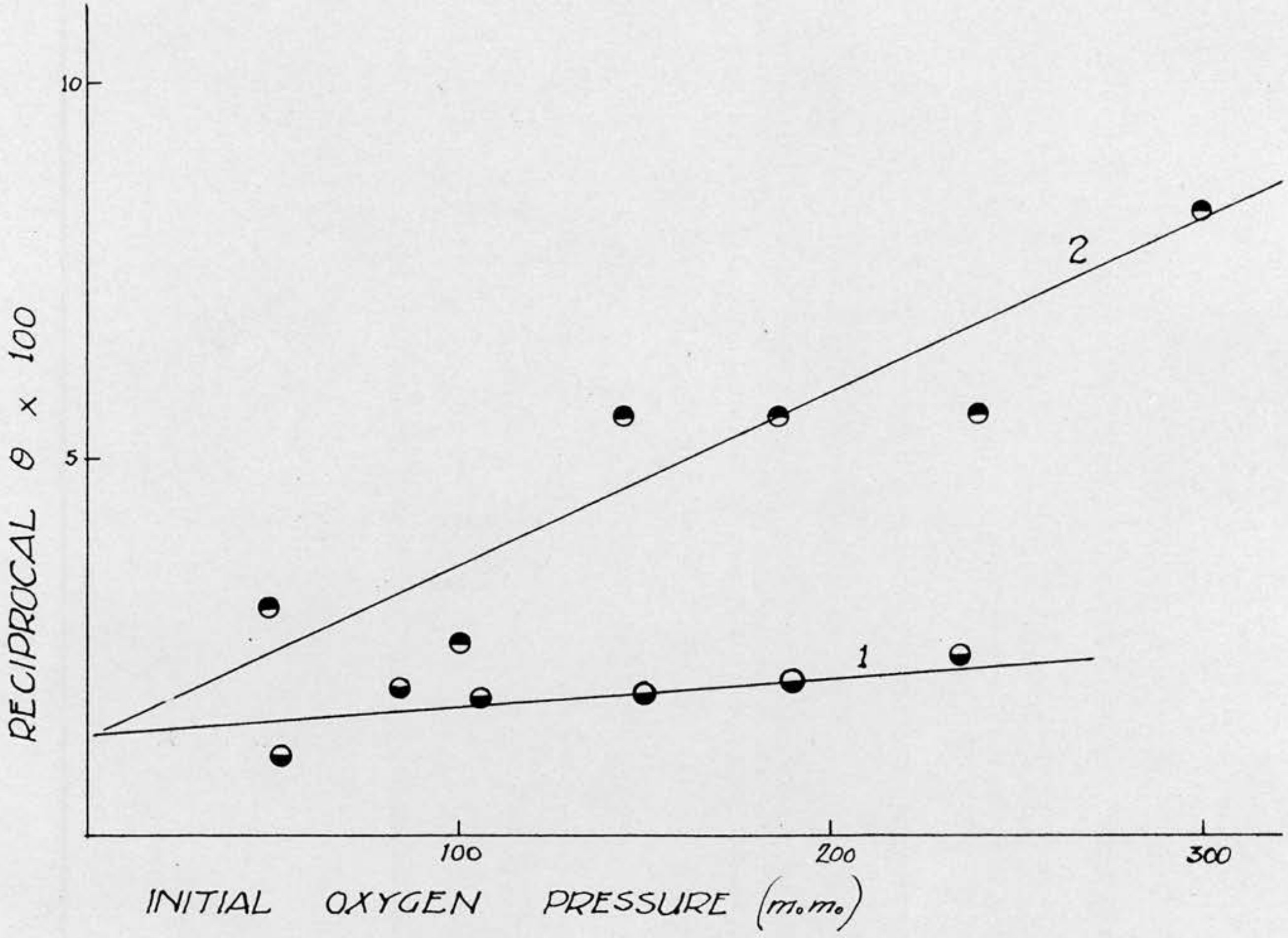
## 2. Dependence Upon Initial Cyclopropane Pressure

Tables Nos. 55, 56 and 57 give the details of experiments

GRAPH Nº 28

Variation of Initial Oxygen Pressure

1. $p_{C.P.}$ = 200 m.m. ; T = 678°A; Vessel A
2. $p_{C.P.}$ = 100 m.m. ; T = 701°A; Vessel D



carried out at temperatures 678°A, 678°A, and 701°A respectively with 200 m.m., 70 m.m. and 79 m.m. of oxygen respectively. The three series are represented on the Graph No. 29.

### TABLE NO. 55

Initial $p_{O_2}$ = 200 m.m. T = 678°A

Vessel B

| Run No. | $p_{CP}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| B 21 | 152·0 | 38 | 2·632 |
| B 23 | 159·0 | 42 | 2·381 |
| B 49 | 177·9 | 35·5 | 2·817 |
| B 20 | 200·0 | 32 | 3·125 |
| B 36 | 249·7 | 27 | 3·704 |
| B 64 | 300·0 | 24 | 4·167 |

### TABLE NO. 56

Initial $p_{O_2}$ = 70 m.m. T = 678°A

Vessel B

| Run No. | $p_{CP}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| B 74 | 150·0 | 57 | 1·75 |
| B 78 | 202·5 | 49·5 | 2·04 |
| B 77 | 252·0 | 30 | 3·33 |
| B 73 | 300·0 | 22 | 4·56 |
| B 76 | 350·0 | 19 | 5·26 |
| B 75 | 400·0 | 16 | 6·25 |

### TABLE NO. 57

Initial $p_{O_2}$ = 79 m.m. T = 701°A

Vessel B

| Run No. | $p_{CP}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| B 108 | 99·2 | 49 | 2·041 |
| B 107 | 128·5 | 33 | 3·030 |
| B 117 | 150·0 | 12 | 8·333 |
| B 106 | 177·8 | 9 | 11·111 |
| B 116 | 198·7 | 8 | 12·5 |
| B 115 | 221·2 | 7·5 | 13·33 |
| B 114 | 258·8 | 5 | 20·0 |

The results obtained with 150 m.m. of oxygen at 678°A in vessel A are given in table No. 58 and the graph No. 30 was constructed from these results.

GRAPH No 29

# Variation of Initial Cyclopropane Pressure

1. $p_{O_2}$ = 200 m.m. ; T = 678°A Vessel B
2. $p_{O_2}$ = 70 m.m. ; T = 678°A Vessel B
3. $p^{i}_{O_2}$ = 79 m.m. ; T = 701°A Vessel B

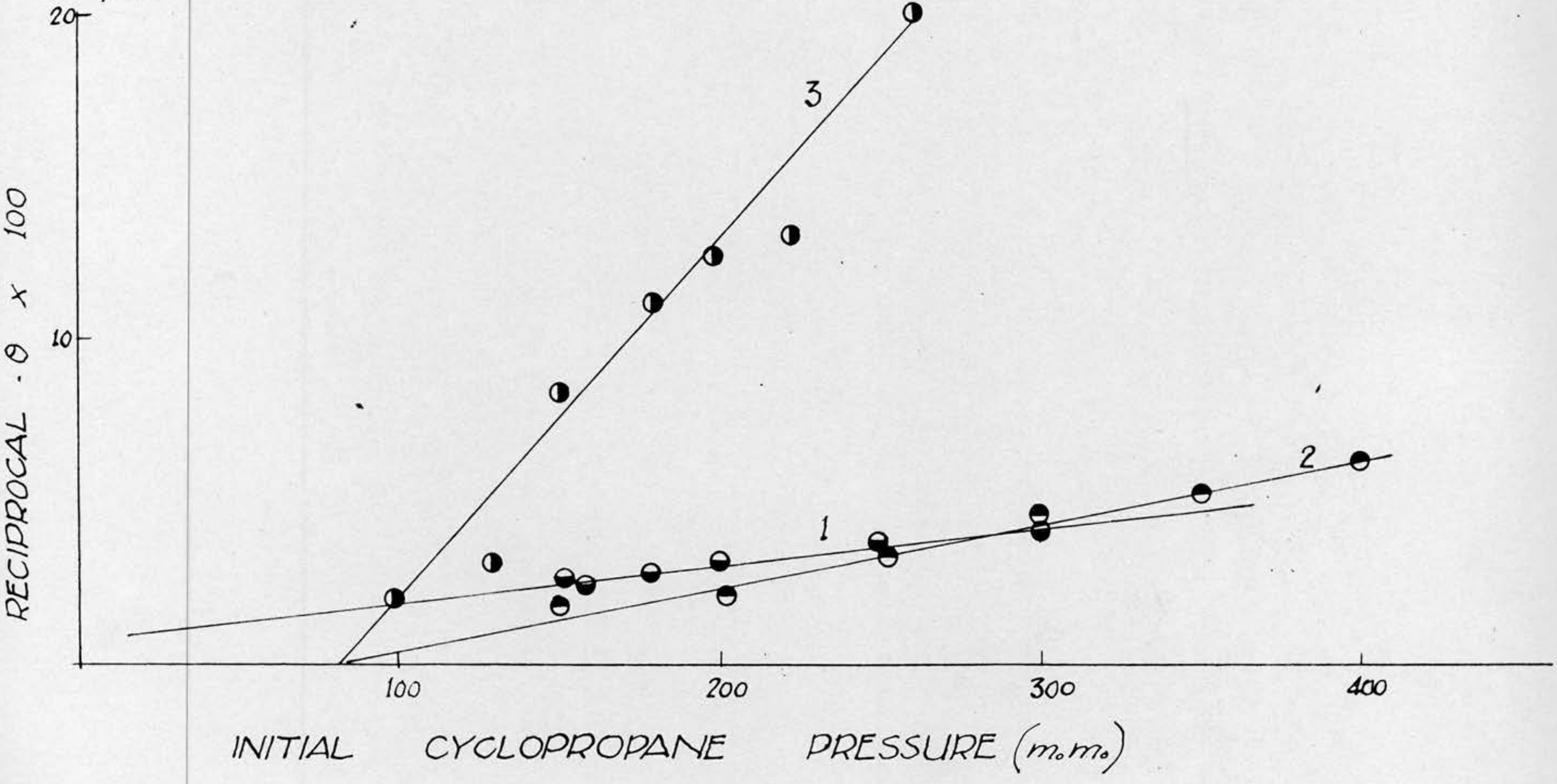


Table No. 58

Initial $p_{O_2}$ = 150 m.m. T = 678°A

Vessel A

| Run No. | $p_{cp}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| A 35 | 176·3 | 68 | 1·471 |
| A 25 | 199·1 | 54 | 1·852 |
| A 23 | 201·8 | 52 | 1·923 |
| A 14 | 208·0 | 48 | 2·083 |
| A 33 | 250·5 | 33 | 3·030 |
| A 28 | 299·0 | 29 | 3·448 |
| A 32 | 302·2 | 26 | 3·846 |
| A 30 | 304·0 | 25 | 4·000 |

The series of experiments already described using vessel D and a stoichiometric excess of oxygen at 701°A yielded the data in table No. 59. These data are also plotted on graph (No. 30).

Table No. 59

Initial $p_{O_2}$ = 300 m.m. T = 701°A

Vessel D

| Run No. | $p_{cp}$ | $\theta$ | $\frac{100}{\theta}$ |
|---|---|---|---|
| D 25 | 80·0 | 28·5 | 3·509 |
| D 26 | 90·0 | 22 | 4·545 |
| D 21 | 100·0 | 18 | 5·556 |
| D 20 | 110·2 | 20 | 5·000 |
| D 22 | 120·0 | 14·5 | 6·897 |
| D 24 | 130·0 | 13 | 7·692 |

We may conclude from a study of these results that the reciprocal induction period was directly proportional to the initial pressure of cyclopropane.

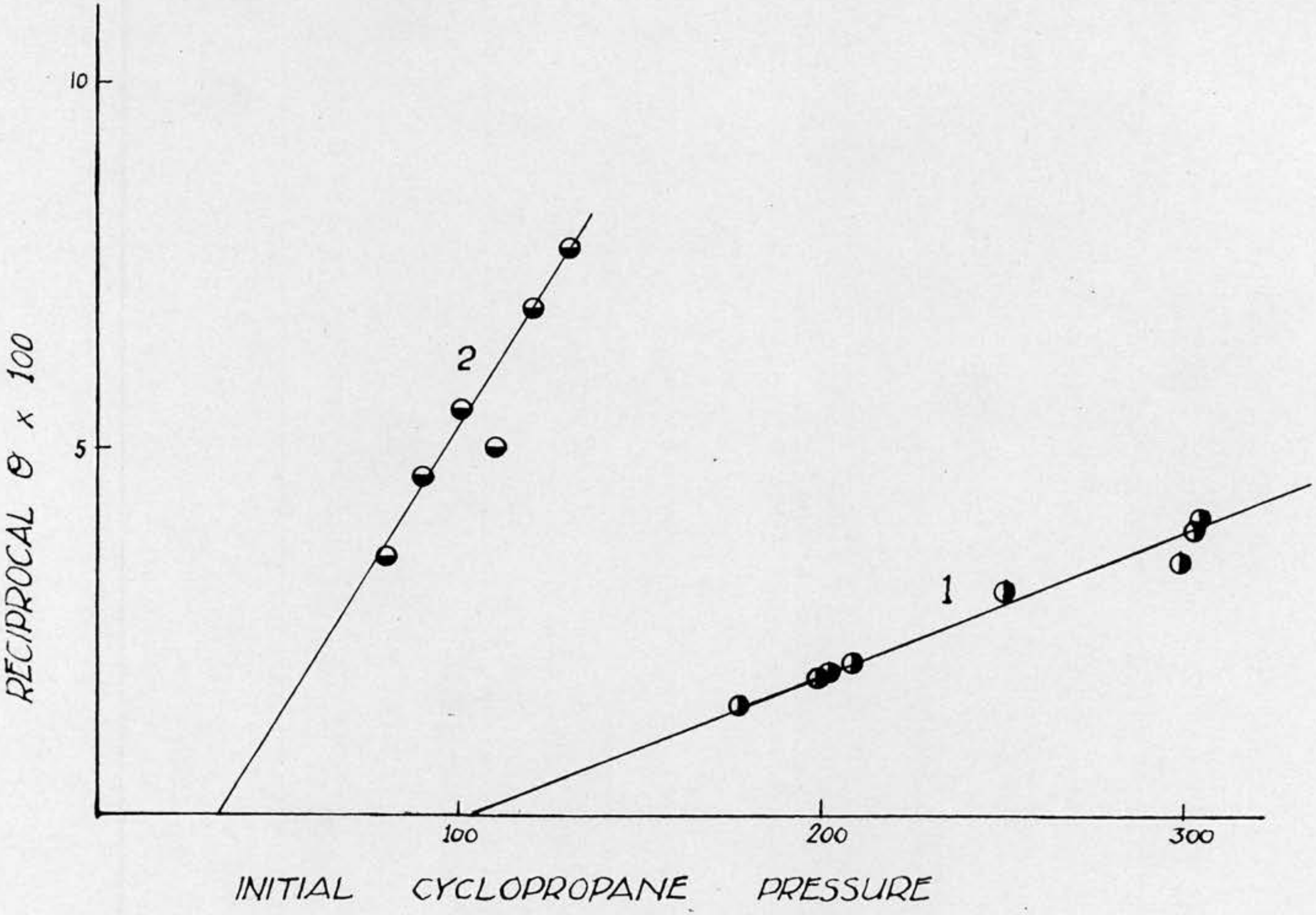
### 3. Dependence Upon the Temperature

Two series of experiments have been described in the previous sections which were designed to illustrate the temperature coefficient of the reaction. During these experiments data were collected referring to the variation of induction period with temperature. Table No. 60 contains the details of

GRAPH No 30

Variation of Initial Cyclopropane Pressure

1. $p_{O_2}$ = 150 m.m. ; T = 678°A (Vessel A)
2. $p_{O_2}$ = 300 m.m. ; T = 701°A (Vessel D)



experiments with 250 m.m. of hydrocarbon and 70 m.m. of oxygen while table No. 61 lists the figures obtained using a mixture of 178 m.m. of cyclopropane and 200 m.m. of oxygen at various temperatures. The former table also gives the values of $\gamma$ obtained. The graph (No. 31) shows three curves (one relating to table No. 61 and two to table No. 60).

It may be emphasised here that this graph proves the parallelism between the relationships of $\frac{1}{\theta}$ and $\frac{1}{\gamma}$.

TABLE NO. 60

Initial $p_{cp}$ = 250 m.m. $p_{O_2}$ = 70 m.m. Vessel B

| Run No. | $T$ | $\frac{10^3}{T}$ | $\theta$ | $\log \frac{100}{\theta}$ | $\gamma$ | $\log \frac{100}{\gamma}$ |
|---|---|---|---|---|---|---|
| B 89 | 651 | 1•536 | 109 | 0•9626 | 90 | 1•0457 |
| B 88 | 658 | 1•520 | 75 | 1•1249 | 55 | 1•2596 |
| B 87 | 665 | 1•504 | 55 | 1•2596 | 40 | 1•3979 |
| B 86 | 671 | 1•490 | 38 | 1•4203 | 30 | 1•5228 |
| B 77 | 678 | 1•475 | 25 | 1•6021 | 18 | 1•7448 |
| B 83 | 683 | 1•464 | 17•5 | 1•7569 | 12•5 | 1•9031 |
| B 80 | 689 | 1•451 | 13•5 | 1•8696 | 9 | 2•0457 |
| B 81 | 697 | 1•435 | 8•5 | 2•0705 | 6 | 2•2219 |
| B 84 | 702 | 1•425 | 6•75 | 2•1706 | 4 | 2•3979 |

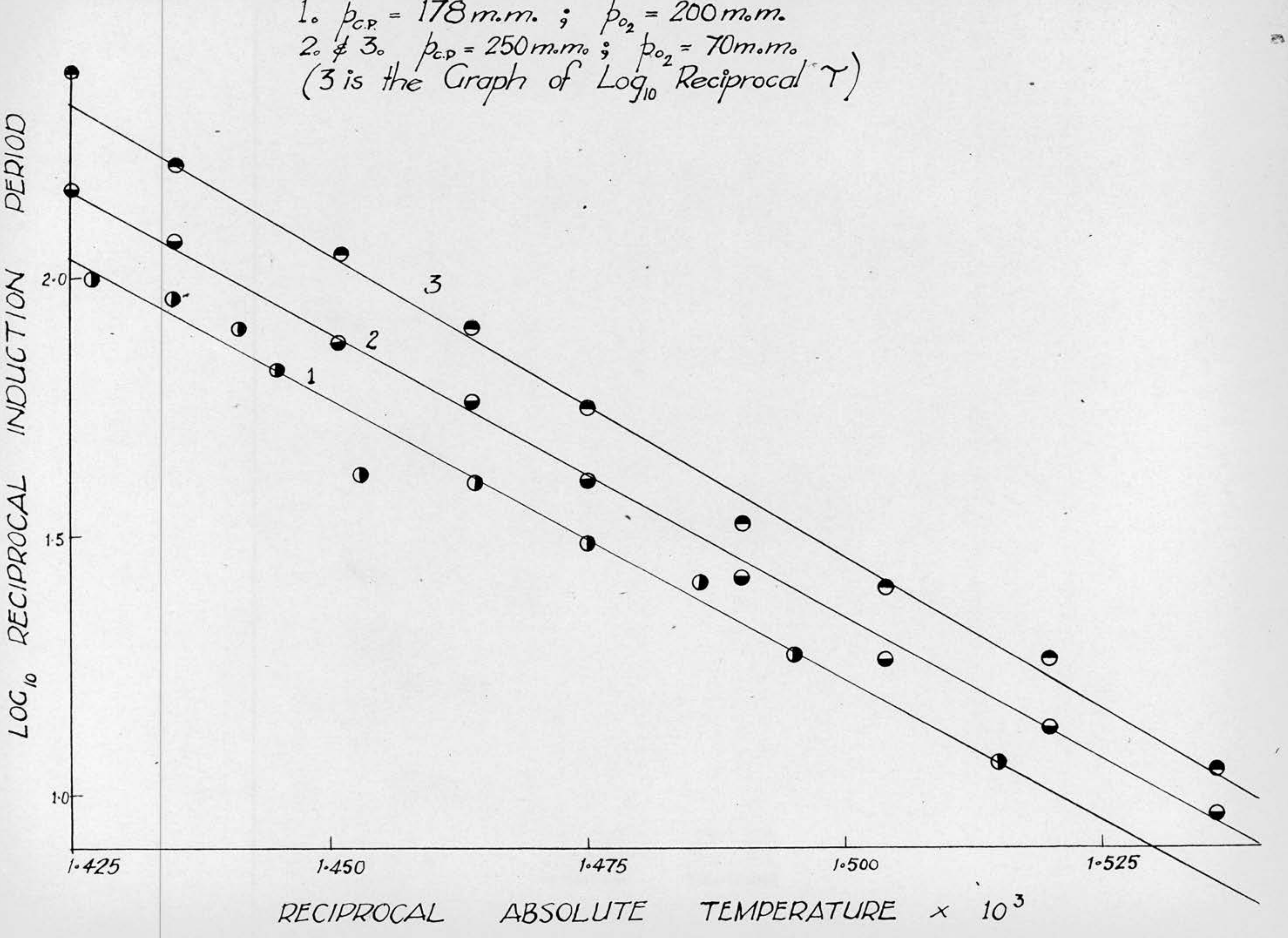
TABLE NO. 61

Initial $p_{cp}$ = 178 m.m. $p_{O_2}$ = 200 m.m. Vessel B

| Run No. | $T$ | $\frac{10^3}{T}$ | $\theta$ | $\log \frac{100}{\theta}$ |
|---|---|---|---|---|
| B 56 | 660 | 1•515 | 87 | 1•0603 |
| B 57 | 669 | 1•495 | 54 | 1•2677 |
| B 58 | 673 | 1•486 | 39 | 1•4089 |
| B 49 | 678 | 1•475 | 33 | 1•4814 |
| B 48 | 683 | 1•464 | 25 | 1•6021 |
| B 50 | 688 | 1•453 | 24 | 1•6198 |
| B 52 | 692 | 1•445 | 15 | 1•8240 |
| B 51 | 694 | 1•441 | 12•5 | 1•9031 |
| B 47 | 697 | 1•435 | 11 | 1•9586 |
| B100 | 701 | 1•427 | 10 | 2•0000 |

The activation energies were calculated from the gradients of the three lines. They were found to be 50•9, 51•7 and 54•2 kcals/mole respectively. It will be noted that these energies are considerably higher than those determined for the maximum

GRAPH No31


1. $p_{C.P.}$ = 178 m.m. ; $p_{O_2}$ = 200 m.m.
2. & 3. $p_{C.P.}$ = 250 m.m. ; $p_{O_2}$ = 70 m.m.
(3 is the Graph of $\log_{10}$ Reciprocal $\tau$)
LOG₁₀ RECIPROCAL INDUCTION PERIOD
2·0
1·5
1·0
1·425
1·450
1·475
1·500
1·525
RECIPROCAL ABSOLUTE TEMPERATURE × 10³
1
2
3

rate and the net-branching factor. Further, there is good agreement between the values found for the energy referring to $\frac{1}{\theta}$ in the two cases of partial pressure. The energies of activation of $\frac{1}{\theta}$ and $\frac{1}{\tau}$ do appear to differ, although not by very much.

## 4. The Effect of Added Nitrogen

In the experiments with added nitrogen it was found that the induction period, as well as the rate and net-branching factor, was not affected by the addition of nitrogen to the system, irrespective of whether the operative kinetics were Rate $\propto p_{cp}^{2} \cdot p_{O_2}^{0}$ or Rate $\propto p_{cp} \cdot p_{O_2}$. Table No. 62 contains the results obtained with experiments in vessel B at 678°A using 200 m.m. each of cyclopropane and oxygen while table No. 63 refers to experiments at 701°A in the same vessel but with 178 m.m. of hydrocarbon and 79 m.m. of oxygen.

TABLE NO. 62

Initial $p_{cp}$ = 200 m.m. $p_{O_2}$ = 200 m.m.
T = 678°A Vessel B

| Run No. | $p_{N_2}$ | $\theta$ |
|---|---|---|
| B 122 | - | 32 |
| B 121 | 50·0 | 35 |
| B 120 | 98·4 | 34 |

TABLE NO. 63

Initial $p_{cp}$ = 178 m.m. $p_{O_2}$ = 79 m.m.
T = 701°A Vessel B

| Run No. | $p_{N_2}$ | $\theta$ |
|---|---|---|
| B 106 | - | 9 |
| B 103 | 50·3 | 9 |
| B 104 | 99·6 | 9 |

## 5. The Effect of Added Hydrogen

The experiments illustrating the influence of added hydrogen upon the reaction have already received some attention. Unfortunately, the induction periods measured showed no trend at all and varied quite haphazardly between 26 and 66 minutes.

While this is disappointing, it can hardly be described as unexpected since it has always been observed that $\theta$ is very much more sensitive to changes, particularly of wall conditions, than is $\rho_{max}$. Thus the completely illogical variation of with the hydrogen treatment and pretreatment can be regarded as further evidence that the hydrogen effect is a wall phenomenon. The results are given in table No. 64 along with the details of the pretreatment in each case.

TABLE No. 64

| Run No. | Pretreatment | $p_{H_2}$ | $\theta$ |
|---|---|---|---|
| D 3 | One hour's evacuation | - | 27 |
| D 4 | One hour's evacuation | 50 | 54 |
| D 5 | 50 m.m. of products from run No. D4 (incl. 5 m.m. $H_2$) left in the hot vessel for 37 hours followed by one hour's evacuation | - | 65 |
| D 6 | One hour's evacuation | - | 26 |
| D 7 | One hour's evacuation | - | 27 |
| D 8 | 50 m.m. of products from run No. D7 (no $H_2$) left in the hot vessel for 67 hours; followed by one hour's evacuation | - | 66 |
| D 9 | 50 m.m. of hydrogen heated in the vessel for 40 minutes; followed by one hour's evacuation | - | 54 |
| D 10 | Seven hour's evacuation | - | 47 |

## THE DEPENDENCE OF $\Delta p_{max}$ UPON CONDITIONS

It should be pointed out that, experimentally, the pressure change occurring before the attainment of maximum rate is the characteristic of a chain reaction in the gas phase which is least accurately determined. This is so because the maximum rate is never actually determined as such but is calculated from pressure changes over comparitively long time intervals (of the order of 60 seconds). Thus, in the case of a fairly speedy reaction whose maximum rate was 14·5 m.m. per minute but which maintained a rate of over 13 m.m. per minute for a period of say, three minutes, it was very difficult to decide, with any great accuracy, the $\Delta p_{max}$ although $\rho_{max}$ and even $\theta$ might be stated with an accuracy of better than 98%. Bearing this in mind, the results which are presented here must be regarded as accurate only to a certain extent, becoming less accurate in the case of experiments in which higher maximum rates were observed.

### 1. Dependence Upon Initial Oxygen Pressure

The experiments which furnished the figures in tables Nos. 65, 66, 67, 68, 69, 70, 71 and 72 have been described elsewhere. Along with each table are given the conditions of cyclopropane pressure and temperature. Graph No. 32 illustrates the linear relationship existing between $\Delta p_{max}$ and $p_{O_2}$, demonstrates the independence of $\Delta p_{max}$ upon initial hydrocarbon pressure and indicates a temperature effect, and, to some extent the existence of a specific factor due to the reaction vessel.

### TABLE NO. 65

Initial $p_{cp}$ = 178 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_{max}$ |
|---|---|---|
| B 43 | 50·0 | 12·8 |
| B 42 | 89·7 | 29·4 |
| B 44 | 101·0 | 32·3 |
| B 39 | 108·4 | 32·2 |
| B 41 | 149·4 | 41·8 |
| B 49 | 200·9 | 56·2 |

### TABLE NO. 66

Initial $p_{cp}$ = 200 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_{max}$ |
|---|---|---|
| B 24 | 50·0 | 13·3 |
| B 26 | 70·0 | 19·8 |
| B 25 | 100·5 | 26·1 |
| B 27 | 130·0 | 36·4 |
| B 30 | 199·8 | 55·7 |
| B 28 | 248·7 | 70·0 |

### TABLE NO. 67

Initial $p_{cp}$ = 250 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_{max}$ |
|---|---|---|
| B 35 | 48·3 | 13·9 |
| B 34 | 94·5 | 28·0 |
| B 33 | 109·8 | 28·6 |
| B 38 | 124·7 | 32·5 |
| B 32 | 134·8 | 39·4 |
| B 31 | 180·0 | 49·8 |
| B 36 | 198·8 | 56·2 |
| B 37 | 250·0 | 69·7 |

### TABLE NO. 68

Initial $p_{cp}$ = 300 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_{max}$ |
|---|---|---|
| B 67 | 49·5 | 14·3 |
| B 62 | 97·4 | 29·8 |
| B 68 | 101·7 | 30·9 |
| B 70 | 147·2 | 39·8 |
| B 71 | 149·7 | 40·9 |
| B 72 | 178·3 | 48·7 |
| B 64 | 198·0 | 56·0 |
| B 66 | 252·7 | 70·7 |

### TABLE NO. 69

Initial $p_{cp}$ = 250 m.m. T = 651°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_{max}$ |
|---|---|---|
| B 95 | 40·0 | 13·0 |
| B 94 | 69·9 | 17·6 |
| B 93 | 99·0 | 24·7 |
| B 92 | 134·2 | 33·1 |
| B 91 | 180·4 | 42·0 |
| B 90 | 233·7 | 55·3 |

### TABLE NO. 70

Initial $p_{cp}$ = 178 m.m. T = 701°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_{max}$ |
|---|---|---|
| B 97 | 50·7 | 13·1 |
| B106 | 78·8 | 26·2 |
| B 98 | 98·6 | 32·3 |
| B 99 | 151·4 | 56·4 |
| B100 | 200·3 | 69·1 |

TABLE NO. 71

Initial $p_{cp}$ = 200 m.m. T = 678°A

Vessel A

| Run No. | $p_{O_2}$ | $\Delta p_{max}$ |
|---|---|---|
| A 41 | 52·1 | 14·0 |
| A 42 | 84·7 | 22·7 |
| A 37 | 106·5 | 26·0 |
| A 40 | 150·9 | 39·0 |
| A 38 | 189·8 | 50·1 |
| A 39 | 234·8 | 63·1 |

TABLE NO. 72

Initial $p_{cp}$ = 100 m.m. T = 701°A

Vessel D

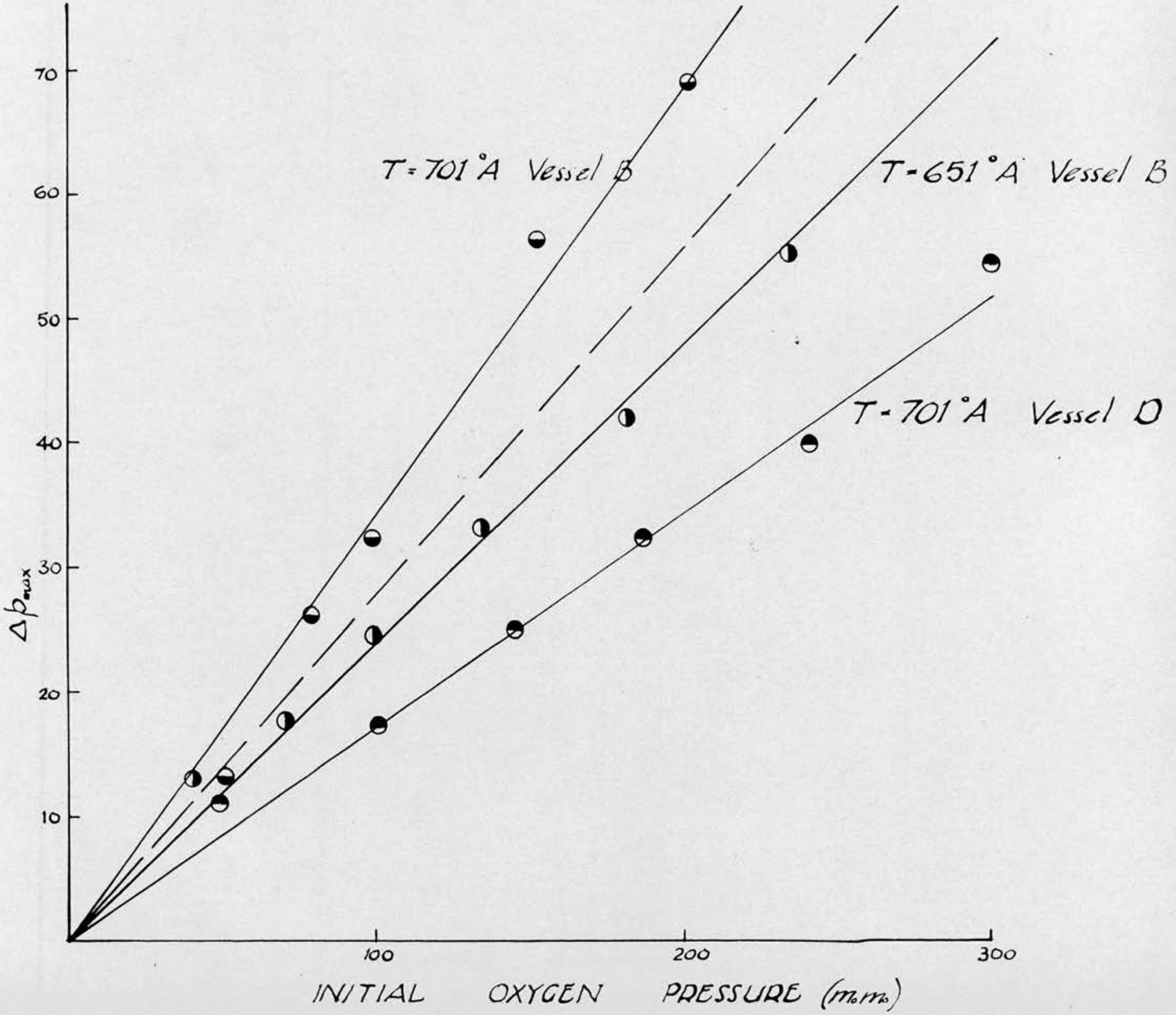
| Run No. | $p_{O_2}$ | $\Delta p_{max}$ |
|---|---|---|
| D 18 | 49·0 | 11·1 |
| D 13 | 100·5 | 17·3 |
| D 17 | 144·5 | 25·2 |
| D 15 | 186·3 | 32·4 |
| D 16 | 240·0 | 40·0 |
| D 14 | 298·8 | 54·5 |

## 2. Dependence Upon Initial Cyclopropane Pressure

It will be evident from the fact that the same line (graph No. 32) is the best line for the points given in tables Nos. 65, 66, 67 and 68, that the change of pressure occurring before the attainment of the maximum rate is not at all dependent upon the initial cyclopropane pressure.

GRAPH N°32

To avoid confusion individual points are not marked.



## THE DEPENDENCE OF $\Delta p_\infty$ UPON CONDITIONS

The total pressure change occurring during the oxidation is a very important characteristic of the reaction since it may indicate the relative predominance of various competing overall reactions. Since, in nearly every experiment performed, there was a stoichiometric excess of cyclopropane it was not surprising to find that $\Delta p_\infty$ was not at all dependent upon the initial hydrocarbon pressure.

Tables Nos. 73, 74, 75 and 76 and the graph No. 33, however, show that $\Delta p_\infty$ is directly proportional to the initial oxygen pressure, the constant of proportionality being approximately 0·5. Tables Nos. 77 and 78 contain data obtained at 651°A and 701°A respectively and these figures are also plotted on the graph (No. 33).

TABLE NO. 73

Initial $p_{cp}$ = 178 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_\infty$ |
|---|---|---|
| B 43 | 50·0 | 24·9 |
| B 42 | 89·7 | 44·9 |
| B 44 | 101·0 | 50·5 |
| B 39 | 108·4 | 54·2 |
| B 41 | 149·4 | 74·8 |
| B 49 | 200·9 | 102·1 |

TABLE NO. 74

Initial $p_{cp}$ = 200 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_\infty$ |
|---|---|---|
| B 24 | 50·0 | 24·7 |
| B 26 | 70·0 | 34·9 |
| B 25 | 100·5 | 50·1 |
| B 27 | 130·0 | 65·1 |
| B 30 | 199·8 | 100·0 |
| B 28 | 248·7 | 124·7 |

TABLE NO. 75

Initial $p_{cp}$ = 250 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_\infty$ |
|---|---|---|
| B 35 | 48·3 | 22·9 |
| B 34 | 94·5 | 46·0 |
| B 33 | 109·8 | 54·2 |
| B 38 | 124·7 | 62·4 |
| B 32 | 134·8 | 68·5 |
| B 31 | 180·0 | 91·0 |
| B 36 | 198·8 | 100·2 |
| B 37 | 250·0 | 125·3 |

TABLE NO. 76

Initial $p_{cp}$ = 300 m.m. T = 678°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_\infty$ |
|---|---|---|
| B 67 | 49·5 | 24·1 |
| B 62 | 97·4 | 48·4 |
| B 68 | 101·7 | 50·7 |
| B 70 | 147·2 | 73·5 |
| B 71 | 149·7 | 74·2 |
| B 72 | 178·3 | 89·2 |
| B 64 | 198·0 | 98·5 |
| B 66 | 252·7 | 125·4 |

TABLE NO. 77

Initial $p_{cp}$ = 250 m.m. T = 651°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_\infty$ |
|---|---|---|
| B 95 | 40·0 | 19·7 |
| B 94 | 69·9 | 34·0 |
| B 93 | 99·0 | 49·5 |
| B 92 | 134·2 | 67·1 |
| B 91 | 180·4 | 86·4 |
| B 90 | 233·7 | 116·0 |

TABLE No. 78

Initial $p_{cp}$ = 178 m.m. T = 701°A

Vessel B

| Run No. | $p_{O_2}$ | $\Delta p_\infty$ |
|---|---|---|
| B 97 | 50·7 | 25·4 |
| B106 | 78·8 | 42·2 |
| B 98 | 98·6 | 52·1 |
| B 99 | 151·4 | 79·5 |
| B100 | 200·3 | 104·0 |

The variation of $\Delta p_\infty$ with change of oxygen pressure in vessel A is recorded in the following table (No. 79) and the data have been plotted on graph No. 33.

TABLE NO. 79

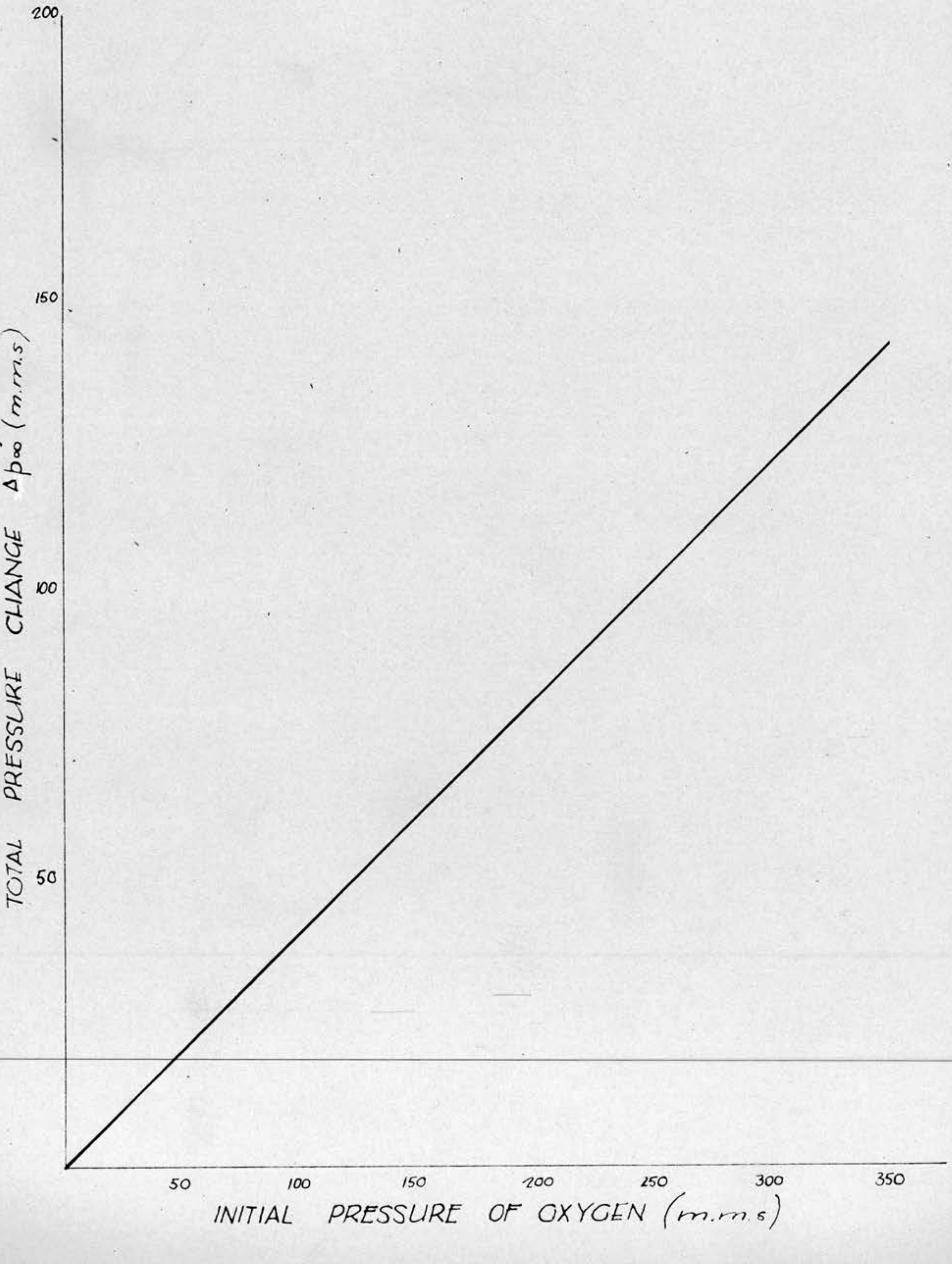
Initial $p_{cp}$ = 200 m.m. T = 678°A

Vessel A

| Run No. | $p_{O_2}$ | $\Delta p_\infty$ |
|---|---|---|
| A 41 | 52·1 | 26·1 |
| A 42 | 84·7 | 45·0 |
| A 37 | 106·5 | 57·0 |
| A 40 | 150·9 | 77·5 |
| A 38 | 189·8 | 95·4 |
| A 39 | 234·8 | 116·1 |

On graph No. 33 only one line has been drawn and no points are indicated. This is to avoid the confusion which would arise if it were attempted to mark each individual point. Suffice to say that $\Delta p_\infty$ was independent of the initial cyclopropane pressure, proportional to the initial oxygen pressure, was largely independent of the vessel but showed a very small temperature effect.

GRAPH Nº 33


200
150
100
50
TOTAL PRESSURE CHANGE Δp∞ (m.m.s)
50
100
150
200
250
300
350
INITIAL PRESSURE OF OXYGEN (m.m.s)

# ANALYSIS

## VARIATION OF THE CHEMICAL COMPOSITION OF THE REACTION MIXTURE

The variation of the chemical composition of the mixture during reaction was followed by stopping the reaction after various times and analysing for unchanged cyclopropane and oxygen and for oxides of carbon, water, formaldehyde, hydrogen and hydrocarbons. Due to the previously observed variance in induction times, the reaction was stopped when certain noted pressure changes had occurred. The stopping of the reaction was effected by opening the tap at the reaction vessel (when the pressure had increased by the desired amount) so that the gases expanded into the comparatively large space between the taps A and F, the trap J being maintained at -180°C by liquid oxygen. After a few minutes, when equilibrium had been attained, the tap K was opened and the permanent gases were collected over mercury by use of the Toepler pump. Fractionation of the gases was achieved as described previously and the condensible substances were analysed for water or formaldehyde as indicated earlier. Having repeated this operation at several points along the pressure-time curve the results were tabulated and plotted together on a graph against time (the time co-ordinates being obtained by reference to the pressure-time curve and from a knowledge of the pressure change which had occurred when the analysis was performed).

In view of the existence of two regions kinetically rather distinct this technique was applied to two typical experiments, one where the operative rate expression was Rate $\propto p_{CP}^2$ and the other where the relationship Rate $\propto p_{CP} \cdot p_{O_2}$ held. The data in table No. 80 refer to the former experiment and are plotted on the graph (No. 34).

TABLE NO. 80 COMPOSITION OF GASES IN THE REACTION VESSEL.

Initial cyclopropane pressure = initial oxygen pressure = 200 m.m. T = 678°A

| Run No. | E10 | E11 | E12 | E 9 | E54 | E13 | E 8 |
|---|---|---|---|---|---|---|---|
| Time of extraction (mins) | 16 | 25•05 | 31•8 | 34•1 | 36•14 | 40•16 | 46 |
| Pressure change (m.m.) | 0 | 4•3 | 24•9 | 38•0 | 53•2 | 75•0 | 100•2 |
| Cyclopropane (m.m.) | 197•6 | 194•6 | 182•3 | 178•5 | 172•1 | 155•9 | 140•7 |
| Oxygen (m.m.) (including nitrogen) | 197•4 | 188•9 | 158•1 | 128•1 | 103•0 | 64•5 | 20•9 |
| Carbon monoxide (m.m.) | 0•9 | 6•4 | 32•5 | 55•5 | 75•1 | 106•5 | 142•8 |
| Carbon dioxide (m.m.) | 0•0 | 0•0 | 1•6 | 3•5 | 7•2 | 12•6 | 17•8 |
| Water (m.m.) | 0•9 | 6•4 | 34•1 | 59•0 | 82•3 | 119•1 | 160•6 |
| Hydrogen (m.m.) | 0•0 | 0•6 | 1•1 | 2•5 | 1•5 | 2•0 | 2•3 |
| Methane (m.m.) | 0•0 | 0•0 | 1•6 | 1•9 | 0•7 | 1•4 | 2•9 |
| Formaldehyde (m.m.) | 0•1 | 0•3 | 4•6 | 5•1 | 5•6 | 4•3 | 1•5 |

The next table (No. 81) is a record of the variation of the composition of the reaction mixture at 701°A with an initial hydrocarbon pressure of 200 m.m. and 100 m.m. of oxygen. The results are plotted on graph No. 35.

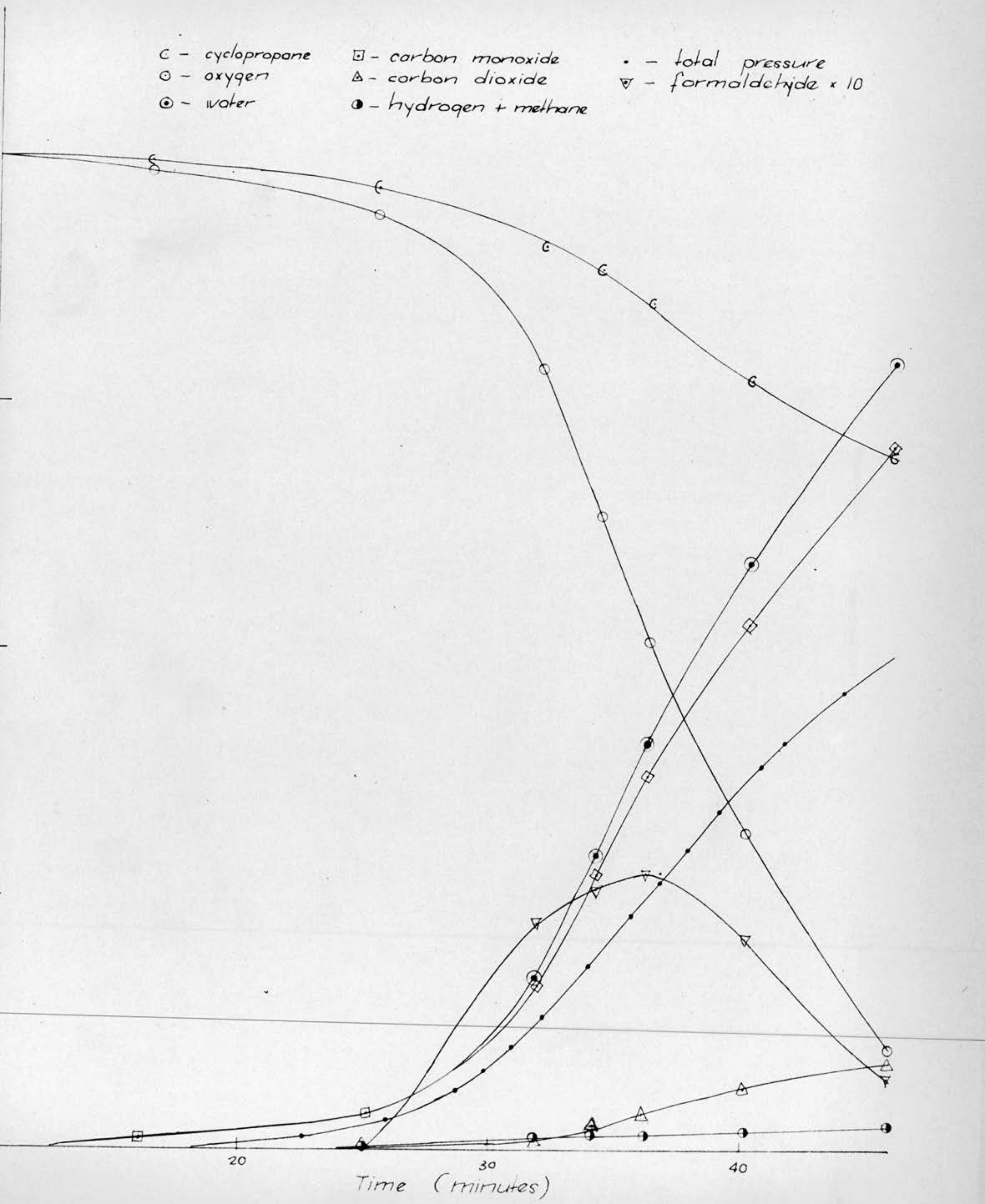
TABLE NO. 81. COMPOSITION OF GASES IN THE REACTION VESSEL

Initial cyclopropane pressure = 200 m.m. Initial oxygen pressure = 100 m.m. T = 701°A

| Run No. | E24 | E23 | E21 | E19 | E18 | E17 | E16 | E15 |
|---|---|---|---|---|---|---|---|---|
| Time of extraction (min.) | 7•0 | 10•42 | 14•05 | 14•95 | 15•48 | 15•77 | 16•58 | 17•72 |
| Pressure change (m.m.) | 0 | 1•0 | 9•4 | 18•0 | 25•0 | 28•7 | 39•7 | 49•9 |
| Cyclopropane (m.m.) | 198•2 | 193•9 | 189•4 | 184•1 | 179•9 | 180•7 | 173•0 | 164•0 |
| Oxygen (m.m.) | 99•5 | 96•9 | 82•6 | 67•2 | 53•5 | 46•5 | 25•5 | 11•2 |
| Carbon Monoxide (m.m.) | 0•7 | 3•1 | 14•1 | 24•1 | 35•8 | 39•5 | 55•5 | 67•9 |
| Carbon Dioxide (m.m.) | 0•0 | 0•0 | 0•0 | 0•9 | 2•6 | 4•2 | 6•3 | 9•9 |
| Water (m.m.) | 0•7 | 3•1 | 14•1 | 25•0 | 38•4 | 43•7 | 61•8 | 77•8 |
| Hydrogen (m.m.) | 0•0 | 0•0 | 1•1 | 1•3 | 0•2 | 2•1 | 4•0 | 3•5 |
| Methane (m.m.) | 0•0 | 0•0 | 0•6 | 0•0 | 0•7 | 0•0 | 2•1 | 2•5 |
| Formaldehyde (m.m.) | 0•0 | 1•0 | 4•75 | 6•0 | 7•5 | 5•8 | 3•9 | 1•8 |

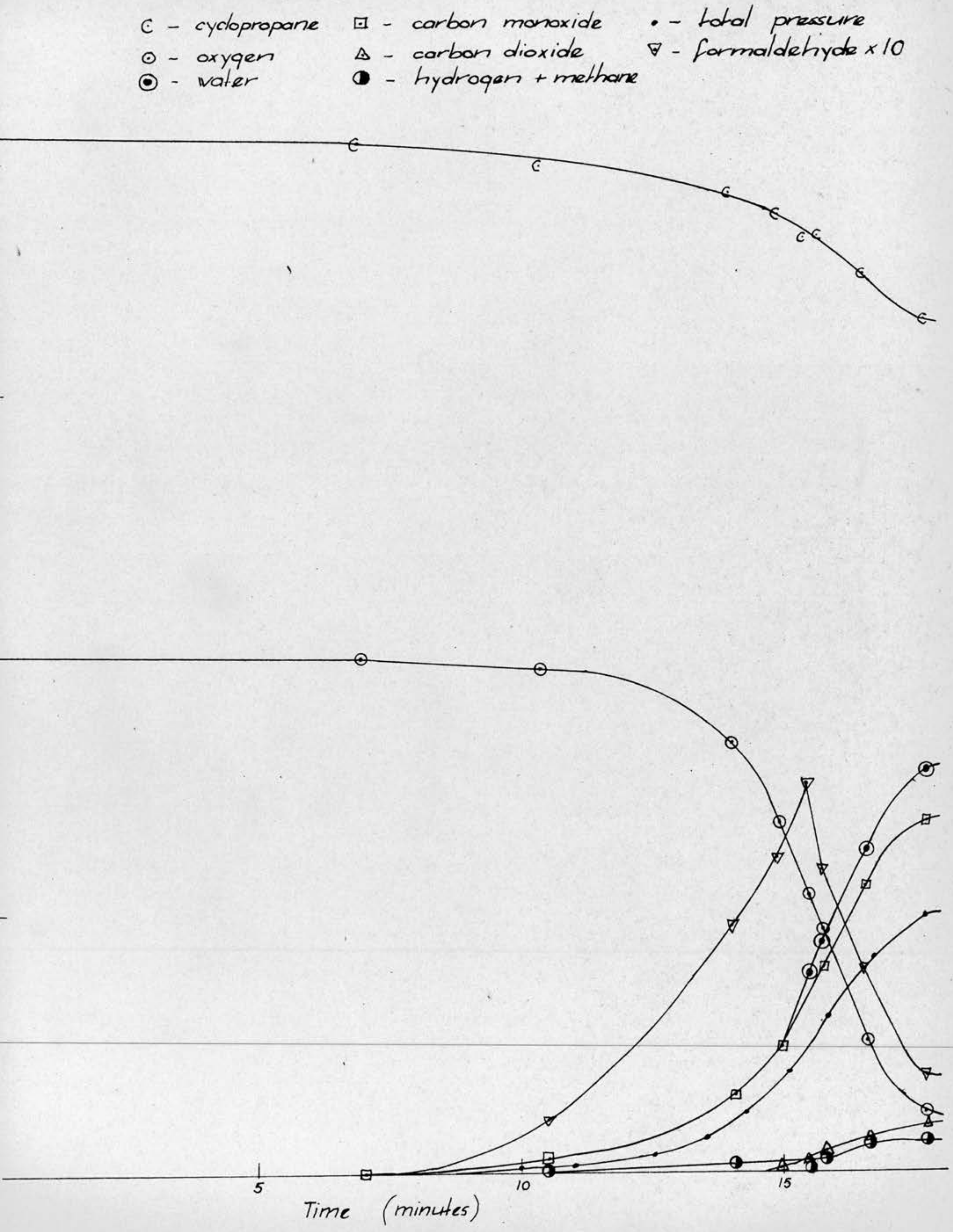
Graph № 3

VARIATION OF COMPOSITION OF GASES DURING REACTION (T = 678° A)



Graph N° 33

# ARIATION OF COMPOSITION OF GASES DURING REACTION (T-701°A)



In work such as this it is necessary to attempt to show that the products of reaction are quantitatively equivalent to the reactants consumed. In each analysis quoted the criteria of equivalence have been (1) that the output volume agreed to within 5% with the volume anticipated from a knowledge of the pressure in the vessel at the moment of extraction, and (2) that the carbon, hydrogen and oxygen found in the output gases each agreed to within 5% with the amounts of these elements in the original mixture. A typical input-output balance is given below for run No. E13 (table No. 80).

Pressure at time of extraction = 475·0 m.m.

Pressure by sum of constituent determined pressures = 466·3 m.m.

i.e. loss = 8·7 m.m. = 1·83 %

Carbon input (in m.m. atoms of carbon) = 3 x 200 m.m. = 600 m.m. atoms.

Carbon output = 3 x 155·9 + 106·5 + 12·6 + 1·4 + 4·3 = 592·5 m.m. atoms.

Loss of carbon = 7·5 m.m. atoms = 1·25 %

Hydrogen input = 6 x 200 m.m. = 1,200 m.m. atoms

Hydrogen output = 6 x 155·9 + 2 x 119·1 + 2 x 2·0 + 4 x 1·4 + 2 x 4·3 = 1,191·8 m.m. atoms.

Loss of hydrogen = 8·2 m.m. atoms = 0·68 %

Oxygen input = 2 x 200 m.m. = 400 m.m. atoms

Oxygen output = 2 x 64·5 + 106·5 + 2 x 12·6 + 119·1 + 4·3 = 384·1 m.m. atoms.

Loss of oxygen = 15·9 m.m. atoms = 3·98%

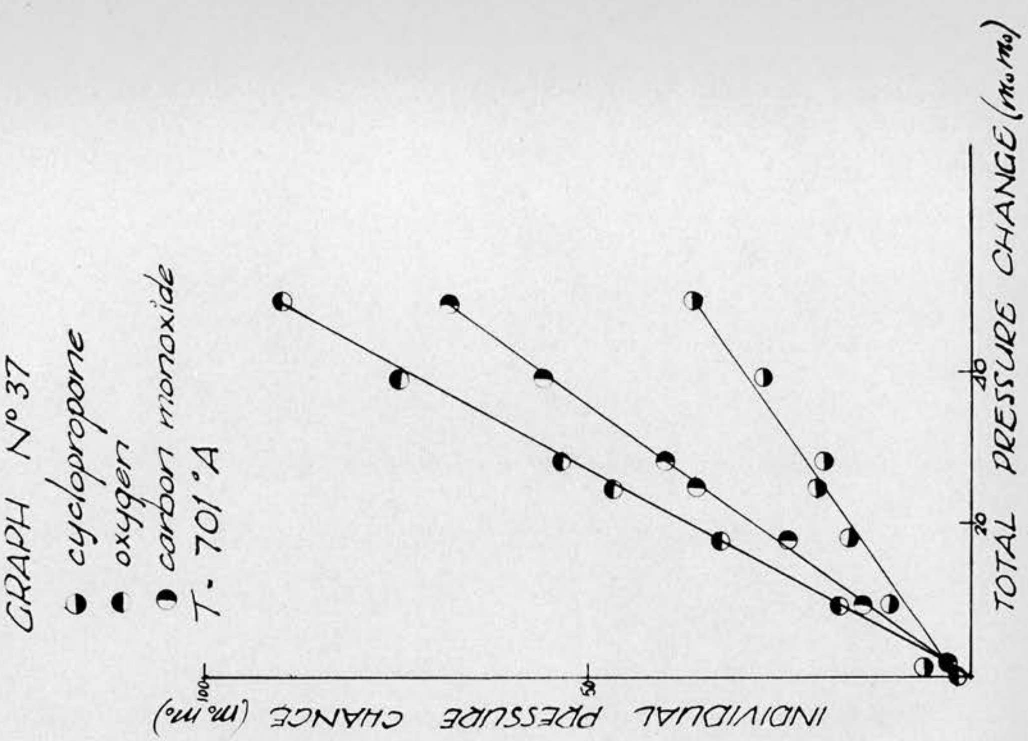
Balances were not always so accurate as this but analyses were disregarded if one of the losses exceeded 5%. When one considers this fact in conjunction with the report of the negative results in the qualitative analysis of accumulated samples of the condensible products ( q.v.) it becomes evident that if any products, apart from those shown in tables Nos. 80 and 81, are formed in the reaction they must be formed in minute quantities indeed.

Several remarks may be made at this stage, with regard to these products. Firstly, there is the striking fact that there is no significant difference in the products or their rate of formation in the two cases; that is, although the two rates of reaction are governed by different kinetic relationships the products are essentially the same. Secondly it will be observed that the nature and relative amounts of the major products are very similar to those noted in the slow combustion of many other hydrocarbons. The data in the tables can be used to justify the belief that the rate of pressure increase is a true measure of the rate of reaction. The latter may certainly be measured by the rate of removal of the reactants and by the rate of formation of the main products. The graphs Nos. 36 and 37 illustrate the linear dependence of changes of cyclopropane, oxygen and carbon monoxide concentration upon changes of total pressure. The first of these graphs was constructed from the data in table No. 82 while the second refers to the experiments reported in table No. 83 with initial oxygen pressure = 100 m.m. at 701°A.

TABLE NO. 82

| Run No. | E10 | E11 | E12 | E9 | E54 | E13 | E18 |
|---|---|---|---|---|---|---|---|
| Time of extraction | 16 | 25·05 | 31·8 | 34·1 | 36·14 | 40·16 | 46 |
| Increase in total pressure | 0 | 4·3 | 24·9 | 38·0 | 53·2 | 75·0 | 100·2 |
| Decrease in cyclopropane pressure | 2·4 | 5·4 | 17·7 | 21·5 | 27·9 | 44·1 | 59·3 |
| Decrease in oxygen pressure | 6·2 | 11·1 | 41·9 | 71·9 | 97·0 | 135·5 | 179·1 |
| Increase in carbon monoxide pressure | 0·9 | 6·4 | 32·5 | 55·5 | 75·1 | 106·5 | 142·8 |

GRAPH N°'s 36 & 37.



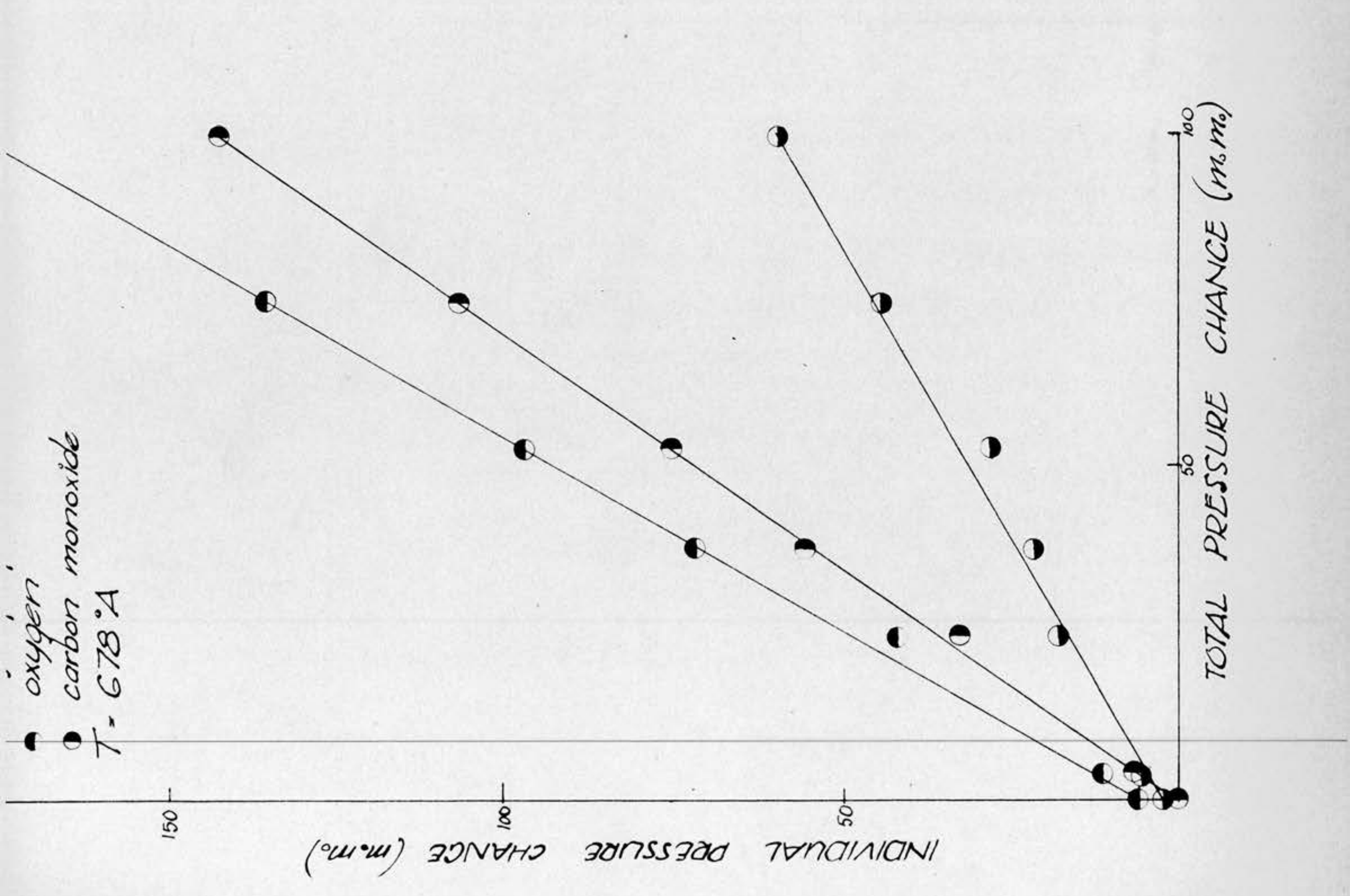


TABLE NO. 83

| Run No. | E24 | E23 | E21 | E19 | E18 | E17 | E16 | E15 |
|---|---|---|---|---|---|---|---|---|
| Time of extraction | 7 | 10•42 | 14•05 | 14•95 | 15•48 | 15•77 | 16•58 | 17•72 |
| Increase in total pressure | 0 | 1 | 9•4 | 18•0 | 25•0 | 28•7 | 39•7 | 49•9 |
| Decrease in cyclopropane pressure | 1•8 | 6•1 | 10•6 | 15•9 | 20•1 | 19•3 | 27•0 | 36•0 |
| Decrease in oxygen pressure | 0•5 | 3•1 | 17•4 | 32•8 | 46•5 | 53•5 | 74•5 | 89•8 |
| Increase in carbon monoxide pressure | 0•7 | 3•1 | 14•1 | 24•1 | 35•8 | 39•5 | 55•5 | 67•9 |

In consequence of these straight line graphs we may conclude that $\Delta p_t \propto -(\Delta p_{cp})_t \propto -(\Delta p_{O_2})_t \propto (\Delta p_{co})_t$

$$\therefore \frac{d(\Delta p)}{dt} \propto \frac{-d(\Delta p_{cp})}{dt} \propto \frac{-d(\Delta p_{O_2})}{dt} \propto \frac{d(\Delta p_{co})}{dt}$$

Perhaps the most important feature of the analytical results is the way in which the formaldehyde concentration varies during an experiment. It is seen to increase to a maximum at about the time of the attainment of maximum rate and then decreases rapidly leaving, however, some fairly low pressure of formaldehyde at the end of the pressure increase. The graph (No. 38) compares the variation of formaldehyde pressure during the reaction of 200 m.m. of cyclopropane and 200 m.m. of oxygen at 678°A with the variation of the rate of reaction with time. The line shows the variation of rate with time and the points refer to the pressures of formaldehyde determined at the times indicated. These pressures of formaldehyde have been adjusted by multiplying them all by a factor of 1•16. The pressures of formaldehyde plotted are those given in table No. 80. This procedure was repeated with the results of the experiments which are in table No. 81 (i.e. with 200 m.m. of hydrocarbon and 100 m.m. of oxygen at 701°A), the appropriate multiplication factor, in this case, being 1·77. The correspondence between formaldehyde pressure and rate under these conditions is shown on graph No. 39.

It will be noted that, particularly in the former case (graph No. 38), a definite relationship seems to exist between instantaneous rate and formaldehyde pressure. The parallelism is not so marked after the time of attainment of maximum rate (since there was always some residual formaldehyde after the reaction had ceased) or in the very early stages, but is very striking over a considerable portion of the reaction, up to and including the time of maximum rate and formaldehyde pressure.

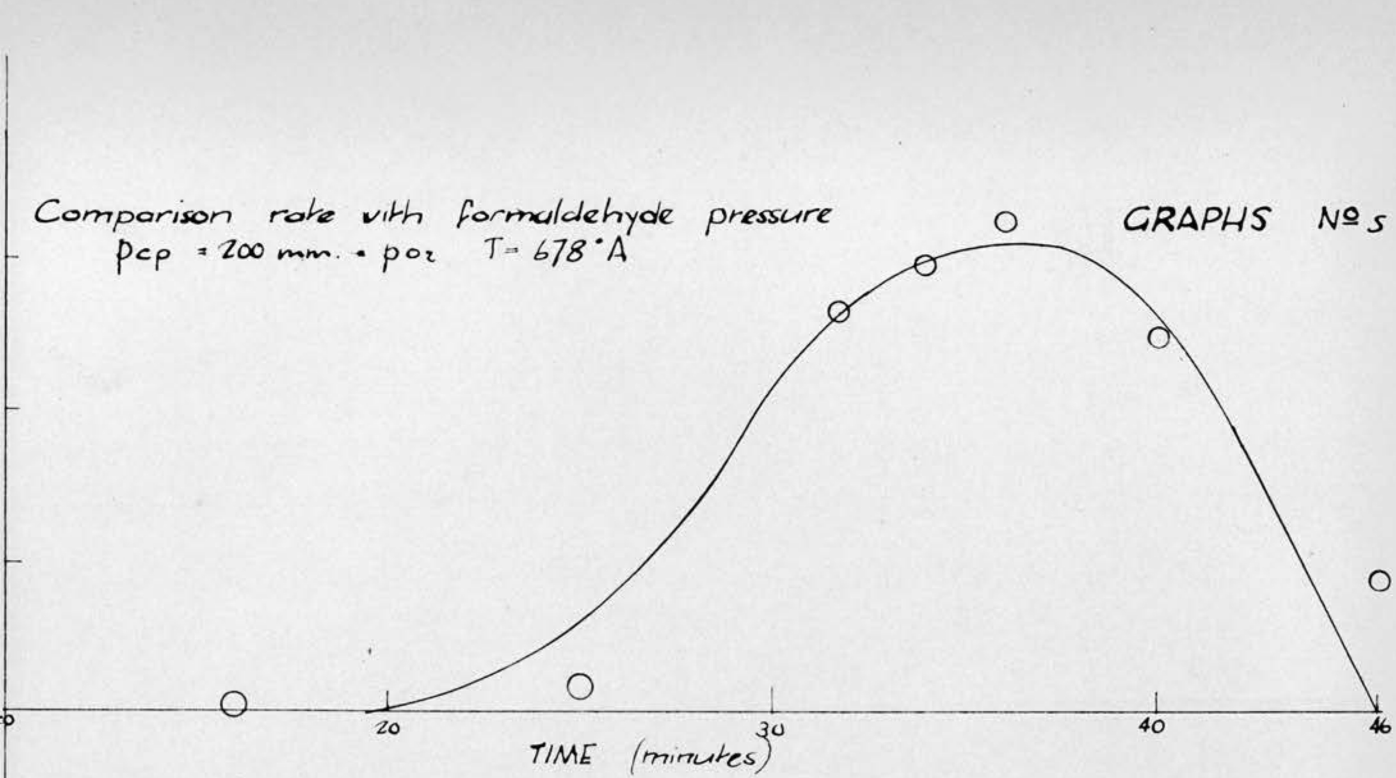
Since formaldehyde appeared to be a highly important intermediate in the reaction the variation of its pressure during the slow combustion was considered in more detail. It seemed of interest to investigate the manner in which the maximum formaldehyde pressure observed in an experiment depended upon conditions of pressure and temperature.

### 1. Variation of the initial oxygen pressure

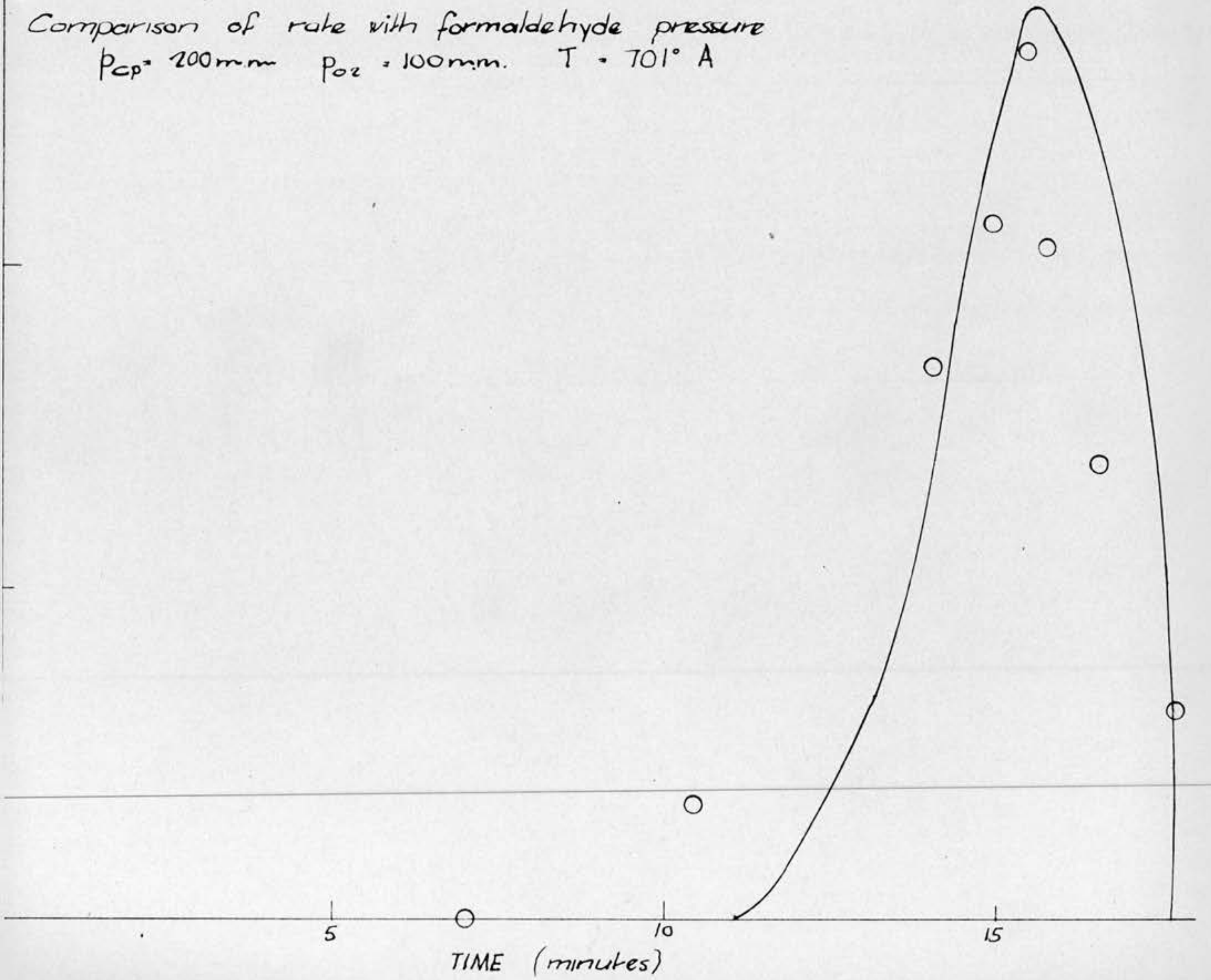
A series of experiments was conducted in which an initial cyclopropane pressure of 200 m.m. was always taken and in which the temperature was kept at 701°A. From a knowledge of the pressure change occurring before the attainment of the maximum rate, it was possible to extract the gases, in the usual way, at that point in each experiment. The permanent gases were pumped away by the Toepler pump and a definite volume of water was pipetted into the cold trap. The Dewar flask was then removed and the contents allowed to warm up. One ml. of the

GRAPHS Nºs 38 & 39.

Comparison rate vith formaldehyde pressure
$p_{cp}$ = 200 mm. = $p_{o_2}$ T = 678°A



Comparison of rate vith formaldehyde pressure
$p_{cp}$ = 200 mm $p_{o_2}$ = 100 mm. T = 701° A



resultant solution was analysed for formaldehyde as described earlier. The results are embodied in table No. 84 while table No. 85 gives the variation of maximum rate with oxygen pressure under the same conditions of temperature and hydrocarbon pressure. The data in the two tables are plotted together on the same paper (graph No. 40)

TABLE NO. 84

| Run No. | Initial pressure of oxygen | Max. pressure of formaldehyde |
|---|---|---|
| E 28 | 28 | 3·29 |
| E 27 | 50 | 4·48 |
| E 31 | 70 | 6·28 |
| E 20 | 102 | 7·49 |
| E 26 | 150 | 7·12 |
| E 29 | 200 | 7·12 |
| E 30 | 250 | 6·94 |

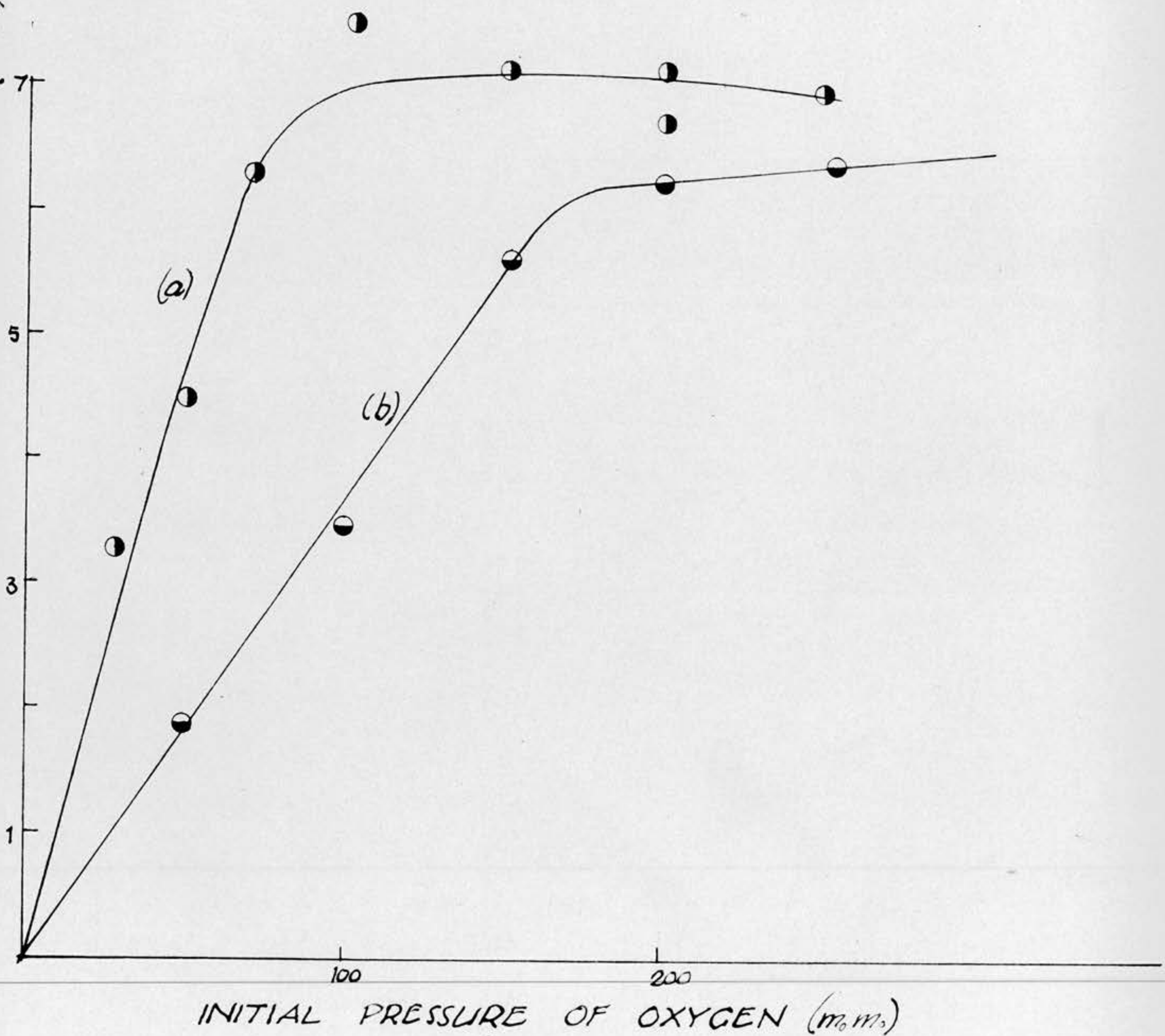
TABLE NO. 85

| Run No. | Initial pressure of oxygen | Maximum Rate. |
|---|---|---|
| E 35 | 50 | 7·5 |
| E 33 | 100 | 13·9 |
| E 32 | 152 | 22·4 |
| E 31 | 200 | 24·8 |
| E 34 | 254 | 25·5 |

The graph shows that both rate and formaldehyde pressure become independent of oxygen pressure as the latter is increased but that the two curves could not be made to be coincident by the introduction of a suitable factor. The critical oxygen pressure at which the rate loses its dependence upon oxygen pressure is about 180 m.m. whereas the critical oxygen pressure for formaldehyde dependence is much lower, namely about 80 m.m.

Variation of the maximum formaldehyde pressure with the initial oxygen pressure

Initial cyclopropane pressure - 200 m.m.
Temperature = 701 °A
(a) Maximum formaldehyde pressure
(b) Maximum rate



## 2. Variation of the initial cyclopropane pressure.

Two sets of experiments were performed under this heading:- (a) with 200 m.m. of oxygen and (b) with 50 m.m. of oxygen (temperature = 701°A in each case). The results are given in the following two tables and are plotted together on graph No. 41.

TABLE NO. 86

Initial oxygen pressure = 200 m.m. Temperature = 701°A

| Run No. | Initial pressure of cyclopropane | Max. pressure of formaldehyde |
|---|---|---|
| E 29 | 200 | 7•12 |
| E 37 | 150 | 4•93 |
| E 40 | 50 | 1•74 |
| E 41 | 100 | 3•47 |

TABLE NO. 87

| Run No. | Initial pressure of cyclopropane | Max. pressure of formaldehyde |
|---|---|---|
| E 49 | 100 | 2•24 |
| E 46 | 150 | 4•02 |
| E 27 | 200 | 4•48 |
| E 44 | 300 | 4•66 |
| E 43 | 350 | 5•02 |
| E 48 | 500 | 5•66 |

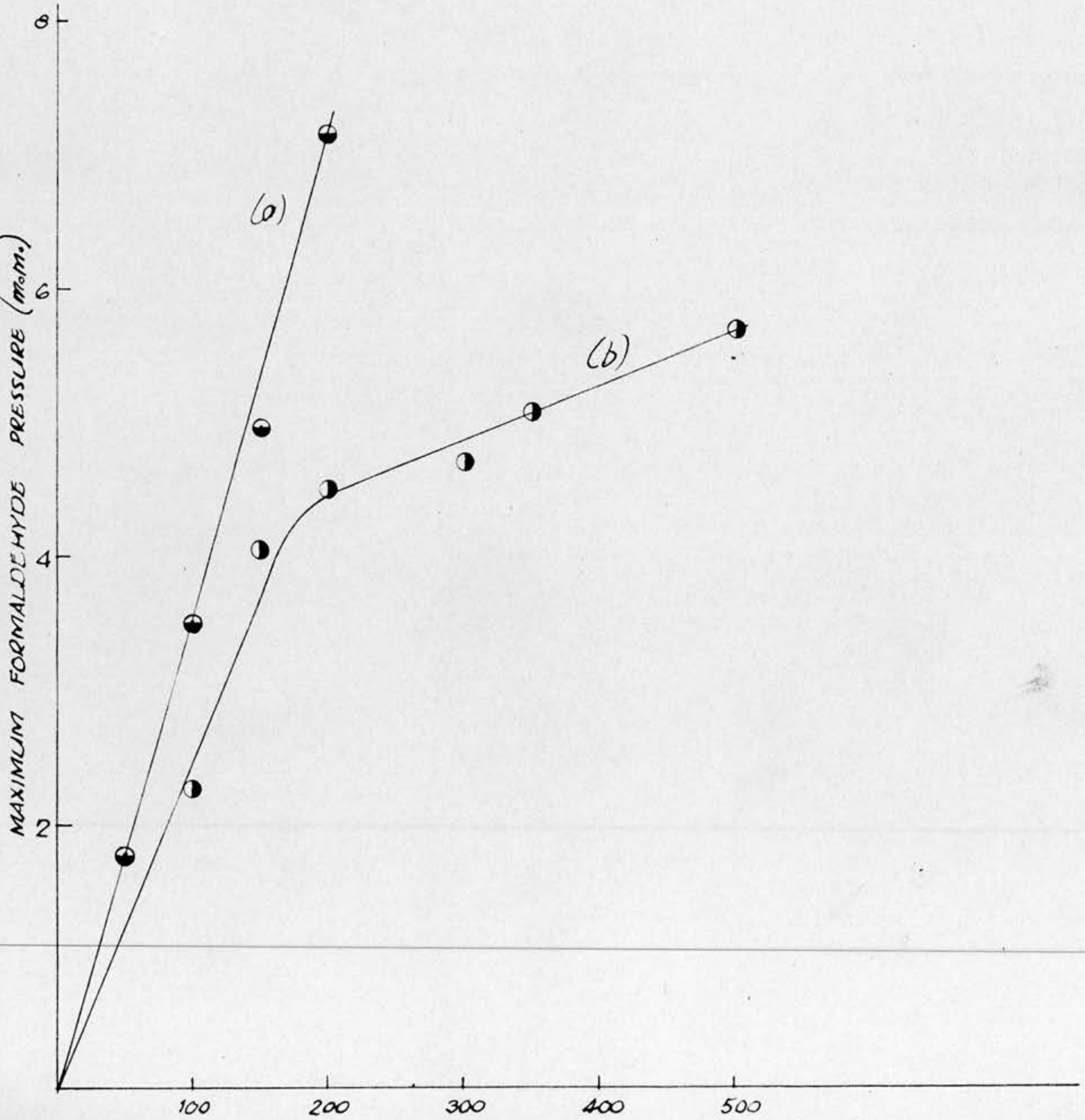
The graph indicates quite clearly that the formaldehyde pressure depends linearly upon the initial hydrocarbon pressure but that the dependence falls away at higher cyclopropane pressures, i.e. when the initial oxygen pressure is low. In neither case is there any similarity to the corresponding rate relationships.

GRAPH N°41.

VARIATION OF THE MAXIMUM FORMALDEHYDE PRESSURE WITH THE INITIAL CYCLOPROPANE PRESSURE (TEMP. = 701°A)

(a) INITIAL OXYGEN PRESSURE = 200 m.m.

(b) INITIAL OXYGEN PRESSURE = 50 m.m.



## 3. Variation of the temperature.

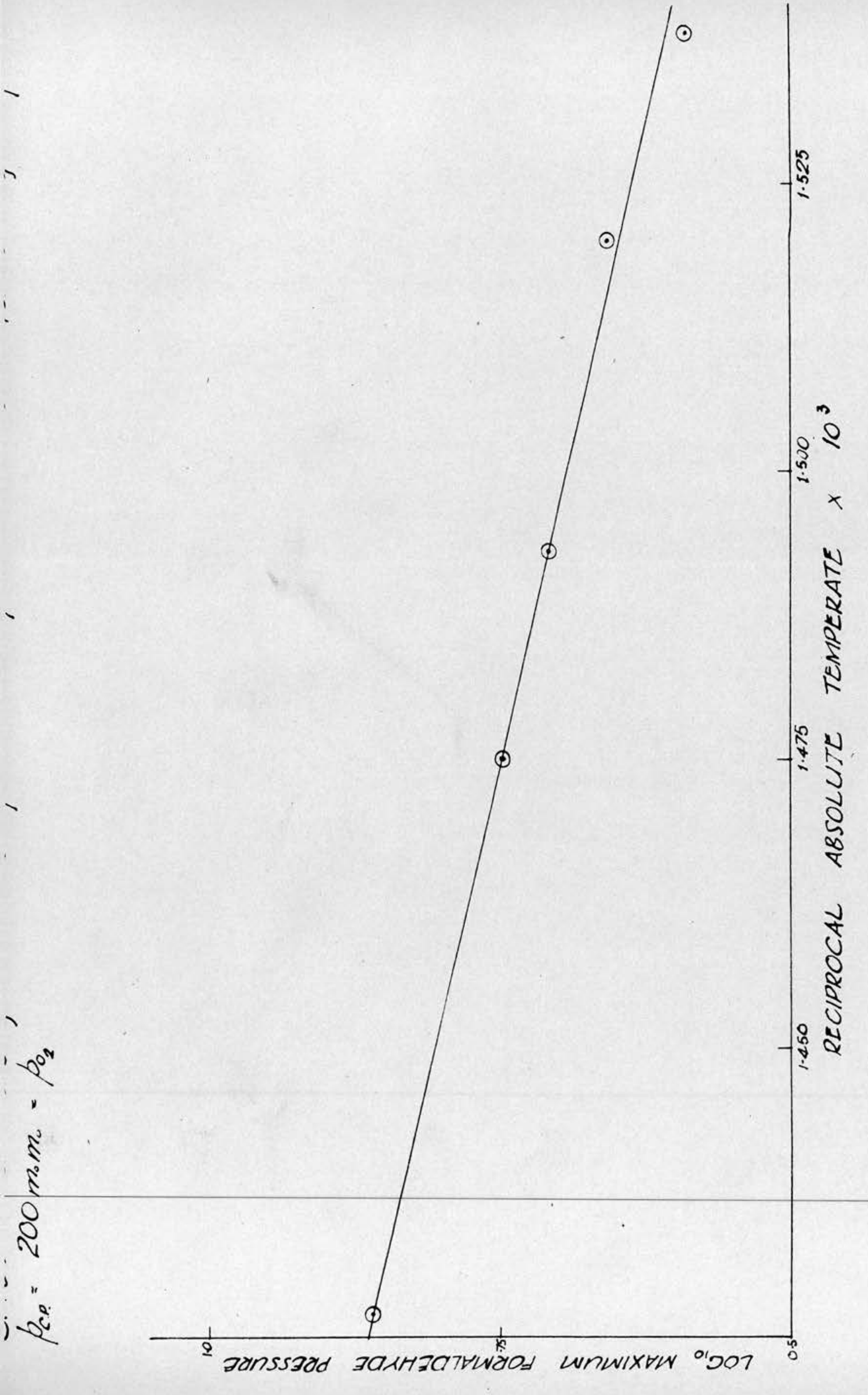
A series of experiments was carried out using a mixture of 200 m.m. each of cyclopropane and oxygen at various temperatures over the range 650°A to 701°A i.e. the range over which the kinetics of the reaction had been studied. The results are embodied in the table No. 88 and the Arrhenius plot of log maximum formaldehyde pressure against reciprocal absolute temperature is given (graph No. 42).

TABLE NO. 88

| Run No. | Temp. °A. | $\frac{10^3}{T}$ | $p_{CH_2O\,max}$ | $\log_{10} p_{CH_2O}$ |
|---|---|---|---|---|
| E 56 | 650 | 1·538 | 3·89 | 0·5899 |
| E 55 | 658 | 1·520 | 4·54 | 0·6571 |
| E 53 | 670 | 1·493 | 5·10 | 0·7076 |
| E 54 | 678 | 1·475 | 5·61 | 0·7490 |
| E 29 | 701 | 1·427 | 7·12 | 0·8525 |

The graph provides a straight line of little gradient and yields an "energy of activation" of some 10·5 kcals./mole. The interpretation of this figure is not a simple matter and consideration of its significance will be deferred until the discussion of results.

GRAPH N°42.


$p_{C.P.}$ = 200 mm. = $p_{O_2}$
LOG$_{10}$ MAXIMUM FORMALDEHYDE PRESSURE
1.0
.75
0.5
RECIPROCAL ABSOLUTE TEMPERATE × 10$^3$
1.450
1.475
1.500
1.525

## THE EFFECT OF ADDING WATER VAPOUR TO THE REACTION MIXTURE

Several workers have reported that the addition of water vapour to hydrocarbon-oxygen mixtures exerted a considerable influence upon the reaction rates and induction periods. A recent study of the methane oxidation indicated that the kinetics of the water-catalysed reaction might be expressed:-(58)
Rate $\propto p_{CH_4}^{2.3} \cdot p_{O_2}^{0.4} \cdot p_{H_2O}$ .

In view of the possibility that water might affect the reaction between cyclopropane and oxygen, a series of experiments was carried out using 200 m.m. of hydrocarbon and 100 m.m. of oxygen and various amounts of water vapour at 701°A. The results are embodied in table No. 89 and are illustrated on the graphs (No. 43 and No. 44).

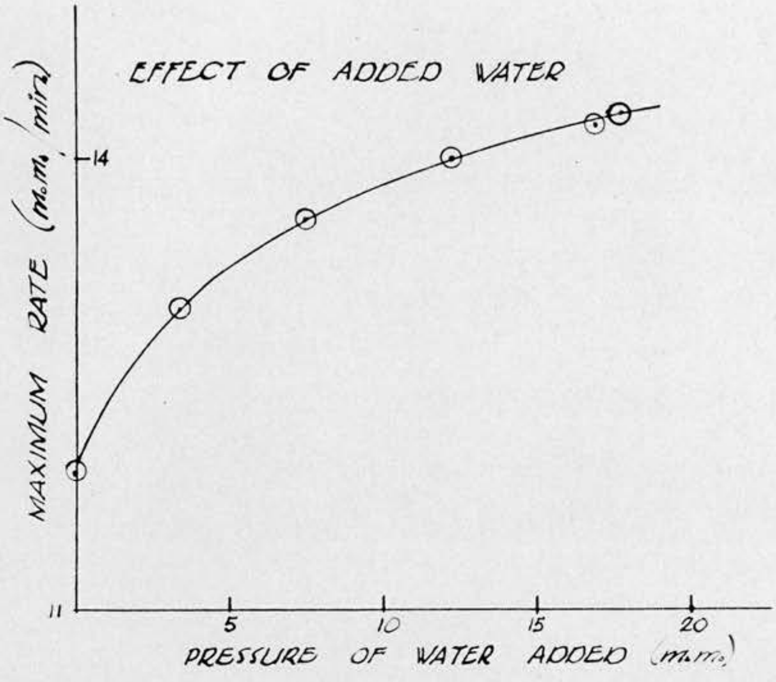
TABLE NO. 89

EFFECT OF ADDED WATER VAPOUR.

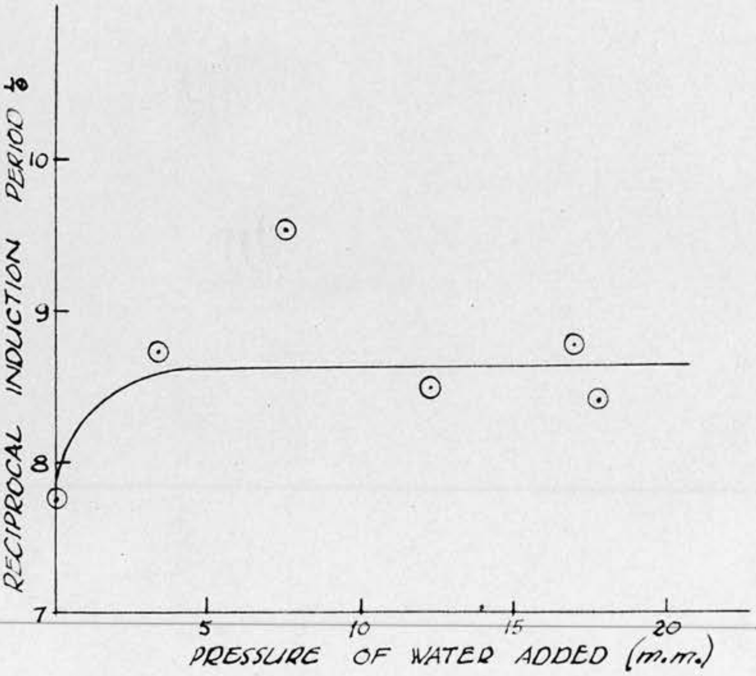
| Run No. | Pressure of water vapour (m.m.) | Maximum rate | Induction period | $\frac{100}{\theta}$ |
|---|---|---|---|---|
| E 109 | - | 11·9 | 12·88 | 7·76 |
| E 111 | 3·3 | 13·0 | 11·47 | 8·72 |
| E 110 | 7·4 | 13·6 | 10·50 | 9·52 |
| E 112 | 12·2 | 14·0 | 11·80 | 8·48 |
| E 108 | 16·9 | 14·2 | 11·43 | 8·75 |
| E 113 | 17·7 | 14·3 | 11·93 | 8·38 |

In addition it was observed that the net-branching factor increased in a similar way but results were less consistent. In this connection it may be noted that the experiments involving the addition of water vapour yielded results very difficult to reproduce. The experiments reported in table No. 89 were all carried out in the same day and were all preceded by rigidly controlled conditions of evacuation.

GRAPH N°s 43 & 44.



GRAPH N° 43



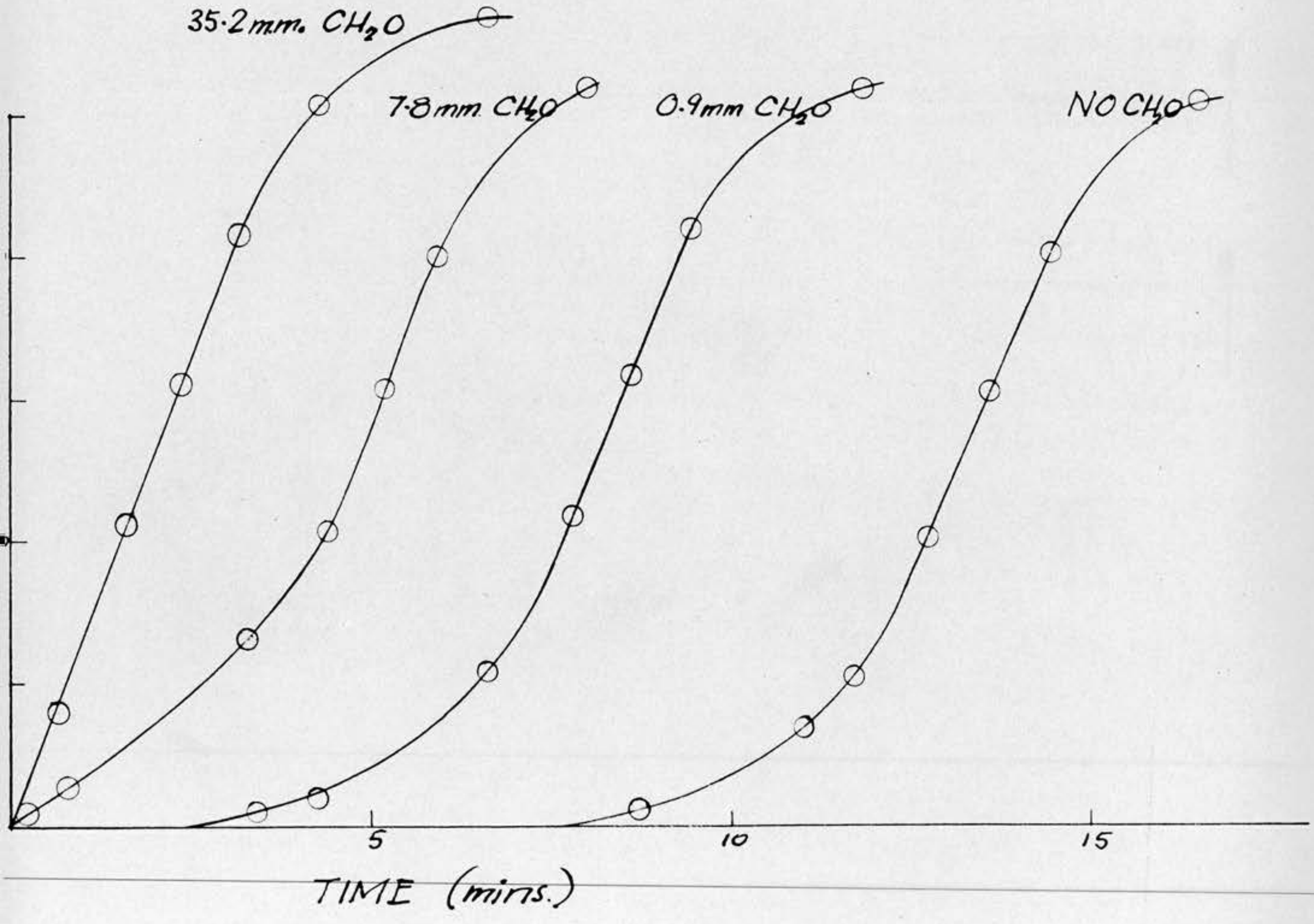
GRAPH N°44

## THE EFFECT OF ADDING FORMALDEHYDE TO THE REACTION MIXTURE

Since formaldehyde was the only intermediate product detected and since it was known to react with oxygen at 400°C, a series of experiments was carried out with varying quantities of formaldehyde, added to 200 m.m. of cyclopropane and 100 m.m. of oxygen at 701°A in vessel E before the beginning of the reaction. It was found that progressive addition of formaldehyde to the mixture reduced the induction period without considerably affecting the maximum rate or the pressure change preceding the attainment of maximum rate. The total pressure change showed a gradual increase but not a considerable one as the pressure of added formaldehyde was increased. These facts are obvious from the pressure-time records shown in the graph No. 45. It should be pointed out that the addition of quantities of formaldehyde less than about 10 m.m. produced no change in the maximum rate (11·9 m.m./minute). The addition of greater quantities of formaldehyde did lead to some increase of maximum rate (e.g. the experiment with 35·2 m.m. of added formaldehyde showed a maximum rate of about 14 m.m./minute) but it should be emphasised that in such cases the rate increased to the maximum at about the usual $\Delta p_{max}$ and fell away again in the usual way. Even when the pressure change appeared to begin at a rate of 12·0 m.m./minute, its rate of change accelerated slowly to 14 m.m./minute.

It will be seen that the effect of added formaldehyde upon the induction period was very great at first but that the effect decreased in importance as the amount of additive was increased.

Effect of addition of formaldehyde to 200 m.m. cyclopropane + 100 oxygen at 701°A



This fact is clearly demonstrated by the data in table No. 90 and by the graph (No. 46). The values of $\theta$ were computed in the usual way but some of the shorter values of $\tau$ could not be determined directly and were taken from the pressure-time records of the experiments concerned.

### TABLE NO. 90

### THE EFFECT OF ADDED FORMALDEHYDE.

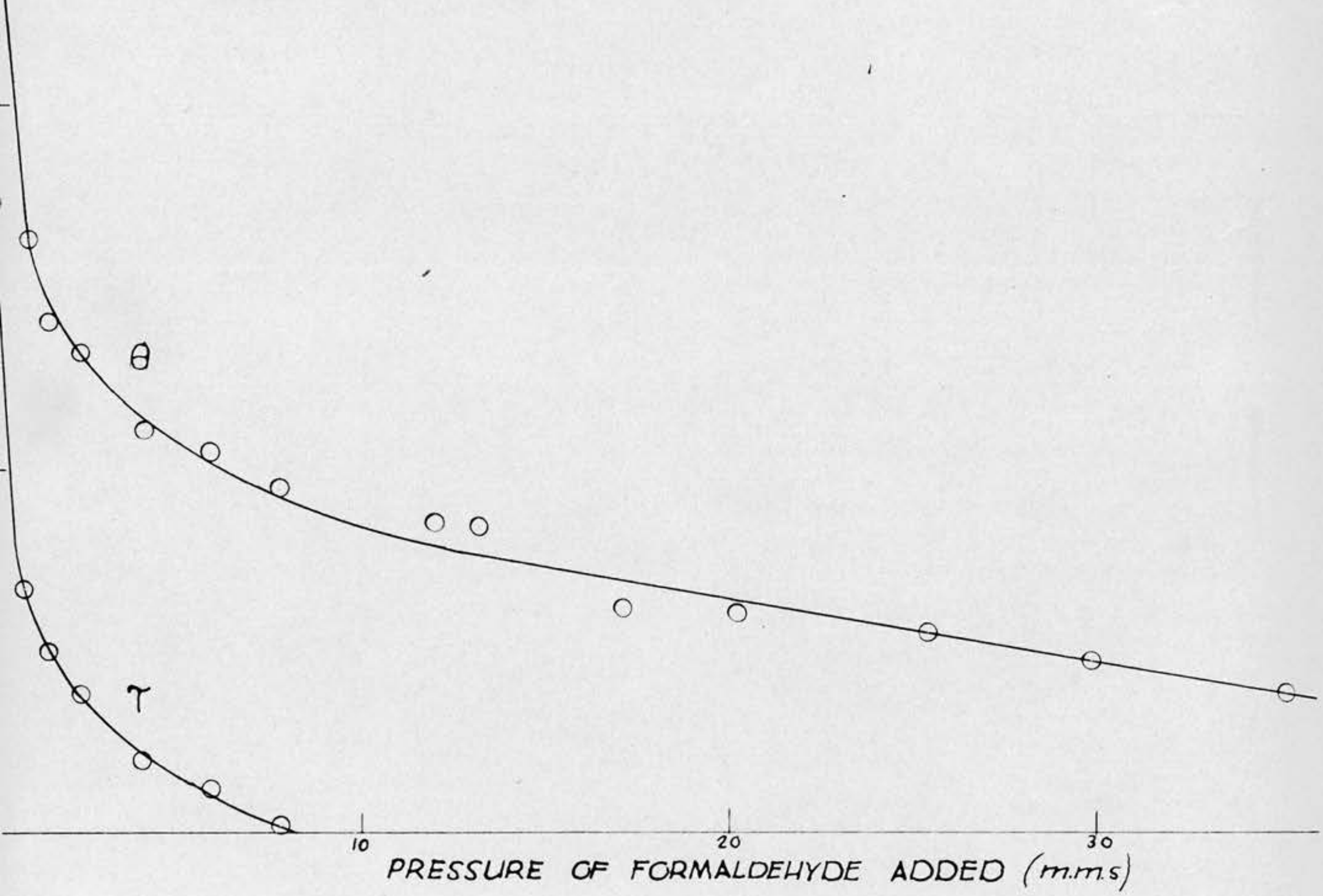
| Run No. | Pressure of added formaldehyde | $\theta$ | $\tau$ |
|---|---|---|---|
| E 128 | - | 13·05 mins. | 8·7 mins. |
| E 136 | 0·9 m.m. | 8·17 | 3·4 |
| E 125 | 1·5 | 7·03 | 2·5 |
| E 117 | 2·4 | 6·63 | 1·9 |
| E 119 | 4·1 | 5·58 | 1·0 |
| E 118 | 5·9 | 5·25 | 0·6 |
| E 121 | 7·8 | 4·75 | 0·1 |
| E 122 | 12·0 | 4·28 | - |
| E 127 | 13·2 | 4·23 | - |
| E 123 | 17·1 | 3·07 | - |
| E 126 | 20·2 | 3·02 | - |
| E 131 | 25·4 | 2·78 | - |
| E 132 | 29·9 | 2·37 | - |
| E 135 | 35·2 | 1·98 | - |

GRAPH Nº 46

Effect of added formaldehyde upon the induction period (θ & τ)

Initial cyclopropane pressure = 200 m.m.s

Initial oxygen pressure = 100 m.m.s
Temperature = 701 ° A
Vessel E



## THE EXTENT OF THERMALLY-INDUCED ISOMERISATION OF CYCLOPROPANE.

The thermal isomerisation of cyclopropane (to propylene) has been studied by several workers (59),(60) over the temperature range 440°C to 520°C (Corner and Pease (60)). It seemed important to determine the degree of isomerisation at the lower temperatures at which the oxidation had been studied. In consequence, samples of 200 m.m. of cyclopropane were enclosed in the reaction vessel for various periods as indicated in the table (No. 91). Analysis then showed the extent of isomerisation.

TABLE NO. 91

| Run No. | Temp. °A. | $p_{cp}$ | Time | Propylene |
|---|---|---|---|---|
| A 78 | 678 | 200 m.m. | 24 hours. | 18% |
| A 79 | 701 | 200 m.m. | 24 hours | 47% |
| A 80 | 701 | 200 m.m. | 1 hour | 2·5% |

It was concluded from these experiments that the isomerisation of cyclopropane was unlikely to be of any great importance in the study of its oxidation, since at 701°A (the highest temperature employed in the slow combustion studies) the induction periods were very much shorter than an hour (of the order of 5 - 10 minutes) and since at 678°A induction times were only of some 30 - 40 minutes duration. It was possible that the isomerisation was facilitated by the presence of oxygen but this was not tested. In any event it was probable that an oxygen-catalysed isomerisation would follow a reaction mechanism similar to that of oxidation.

It was of great interest to note, however, that in one experiment 255 m.m. of cyclopropane was heated at 693°A for about 24 hours. On the addition of 110 m.m. of oxygen, a small explosion occurred almost immediately. The pressure change which had occurred after the explosion was only 38·6 m.m. as compared with the usual change of 55 m.m. This seemed to suggest that the propylene formed by isomerisation at 693°A oxidised very rapidly when the oxygen was admitted to the vessel but failed to stimulate the oxidation of the remaining cyclopropane. If this were so then the isomerisation of cyclopropane could be disregarded as a factor of importance in the slow combustion of that compound. The matter was not studied further and the suggestion is a very tentative one.

# DISCUSSION OF THE RESULTS

In the first instance it will be instructive to collect and compare certain of the results and to emphasise their significance. The experimental results constitute a considerable body of evidence for the legitimate application of the Semenov theory (10) of a reaction with degenerate branching chains to the thermal oxidation of cyclopropane. Firstly many similar reactions proceed by such a mechanism. Furthermore the shape of the pressure change - time curves is typical and the linear relationship shown to exist between the logarithm of the pressure change and the time demonstrates that, in the early stages at least, the law of pressure change is an exponential one. The long induction periods observed (of the order of minutes and hours) are also characteristic of chains with degenerate branching while the extreme sensitivity of the rate and net-branching factor and more particularly of the induction period to the state of the surface of the reaction vessel and its extent provides strong evidence for the occurrence of such chains. In this connection there has been adequate demonstration of the importance of the immediate past-history of the vessel (cooling, admission of air, and variation of the duration and efficiency of the evacuation all producing characteristic effects).

One of the features predicted by the Semenov analysis is a pronounced inert gas effect. This might manifest itself as a third-body effect or might operate by deactivation of "hot" radicals or simply by preventing diffusion to the walls and since the effect might be applied to an initiation, propagation, branching or termination reaction the overall effect might lead to an increase or a decrease in the reaction rate. In the present investigation the addition of nitrogen to the system did not change any of the reaction characteristics at all. This was rather surprising since the observed differences of rate etc. in vessels of similar dimensions and the drastic changes in kinetic characteristics of the reaction following a twelve-fold increase of the surface: volume ratio seemed interpretable as indicative of the heterogeneous nature of the branching and/or non-branching reactions and possibly of the initiation and termination reactions too. Consequently one might have anticipated that the addition of inert gas might influence the rate and induction period. It was possible of course that the absence of an overall effect was due to balancing of several effects some enhancing and some retarding the progress of the reaction. This seemed less likely, however, when it was found that, under an entirely different set of conditions of temperature and pressure, there was still no inert gas effect. A second possible explanation of the results was that the amount of nitrogen added was too small to exert any great influence. In the most favourable case the nitrogen constituted about 28% of the mixture and yet showed no effect. Experimental difficulties would attend any very great increase in this percentage but it would be of interest to find whether 30% of nitrogen did increase the rate of reaction in a vessel whose walls had been treated so as to increase their chain-terminating activity (e.g. by coating with potassium chloride).

In striking contrast to the ineffectiveness of adding nitrogen to the reaction mixture, addition of hydrogen had a most pronounced result. Induction periods became quite irreproducible (their inconstancy persisted for some time) but the investigation of the effect of hydrogen upon the rate showed that the rate was reduced either by the fact that hydrogen was present during reaction or by the pretreatment of the vessel with hydrogen (the normal evacuation technique being adopted before the commencement of the next experiment). Furthermore the rate gradually returned to normal after a few combustions or more rapidly if the products from an oxidation were left in the vessel for some time. These facts, combined with the observation that even prolonged evacuation of the vessel in its "low rate" state had very little effect upon the maximum rate of the next experiment, made it clear that hydrogen removed from the walls some substance which normally facilitated reaction and that this wall-catalyst was gradually replaced in the next experiments or by leaving a few centimetres pressure of the products of reaction in the hot vessel. There was no evidence that the hydrogen did not exert a homogeneous gas-phase effect (such as has been studied by Ubbelohde (56)) as well as the wall effect. Two possible explanations of the results seemed feasible. The first was that hydrogen changed the nature and hence the catalytic activity of the adsorbed substance and that this altered form was gradually rechanged by the ensuing reactions and reaction products. This did not seem very probable since the hydrogen was likely to reduce the adsorbed material which could be re-oxidised by the oxygen involved in the next experiment but which could probably not be re-oxidised by the products of reaction which contained little or not oxygen (this being far less than the stoichiometric requirements of the cyclopropane in these particular experiments). The second possible explanation was that hydrogen removed the substance from the adsorbed phase altogether, leaving a clean glass surface. This seemed a more reasonable suggestion since, it had been noted that rate results in a new clean vessel were, at first, low and gradually increased as the number of experiments increased. The precise nature of the reaction product which was normally resident on the walls can not be stated with certainty but of the products detected in reaction the one most likely to exert a catalytic effect upon the rate was water. Just why hydrogen should be so effective in desorbing water from the walls is a very difficult question to answer and further speculation as to the nature of the catalyst and its mode of action can be of no great value.

Semenov has shown that $\Delta p = \frac{B}{\phi^2} \cdot e^{\phi t}$ where $\Delta p$ = pressure change, $\phi$ = the net-branching factor, t = time and $B = \frac{n_o v}{\theta}$ where $n_o$ = the number of active centres formed per second by the primary initiation process, $v$ = the chain length and $\theta$ = the time elapsing between the commencement of the primary chains and that of the secondary chains. Taking logarithms, $\log_{10} \Delta p = \log_{10} \frac{B}{A'^2} + A't$ and plotting $\log_{10} \Delta p$ against t, a straight line of gradient A' should result. The intercept of this line on the $\log_{10} \Delta p$ axis should be $\log_{10} \frac{B}{A'^2}$ which we shall call $\log_{10} N$. N was obviously determinable from the graphs normally employed for net-branching factor evaluation and from a knowledge of the net-branching factor it was possible to calculate B. Now B(and N) are dependent upon the rate of initiation of primary chains by other means than by radicals formed by the intermediate responsible for the degenerate branching. It seemed of great interest to consider the variation of B and N with the experimental conditions but little success was had so far as reactant pressure variation was concerned. On the other hand B and N were found to vary in a remarkable way with the temperature. The results which are given in tables No. 92 and 93 were calculated from the data previously determined. In graphs No. 47 and 48 $\log_{10} N$ and $\log_{10} B$ have been plotted against reciprocal absolute temperatmre. Calculation showed the activation energies for N to be 160 and 280 kcals/mole and those for B to be 280 and 340 kcals/mole. Now of the various factors of B, $\upsilon$ and $\theta$ are unlikely to have very high activation energies so that the very high activation energy of B must be largely attributed to the rate initiation of primary chains. This primary initiation could hardly have been a homogeneuos one and probably took place on the walls of the vessel, since the apparent activation energies of heterogeneous reactions may include heats of adsorption which may be considerable.

It was therefore concluded that the slow combustion of cyclopropane proceeded by a chain reaction with degenerate branching of the chains and that the primary initiation reaction was heterogeneous in nature having a very high energy of activation.

## TABLE NO. 92

Initial $p_{cp}$ = 250m.m. Initial $p_{O_2}$ = 70m.m. Vessel B

| Run No. | Temp.T | $\frac{10^3}{T}$ | $\log_{10}N$ | $\log_{10}B$ (= $\log_{10}N + 2\log_{10}A'$) |
|---|---|---|---|---|
| B 89 | 651° A | 1.536 | -9.45 | -11·41 |
| B 88 | 658 | 1·520 | -6.60 | - 8·44 |
| B 87 | 665 | 1.504 | -4·92 | - 6·74 |
| B 86 | 671 | 1·490 | -5.43 | - 6.91 |
| B 77 | 678 | 1.475 | -3.89 | - 5.22 |
| B 83 | 683 | 1.464 | -3.26 | - 4.42 |
| B 80 | 689 | 1.451 | -2.88 | - 3.87 |
| B 81 | 697 | 1.435 | -2.86 | - 3.50 |
| B 84 | 702 | 1.425 | -2.30 | - 2.78 |

## TABLE NO. 93

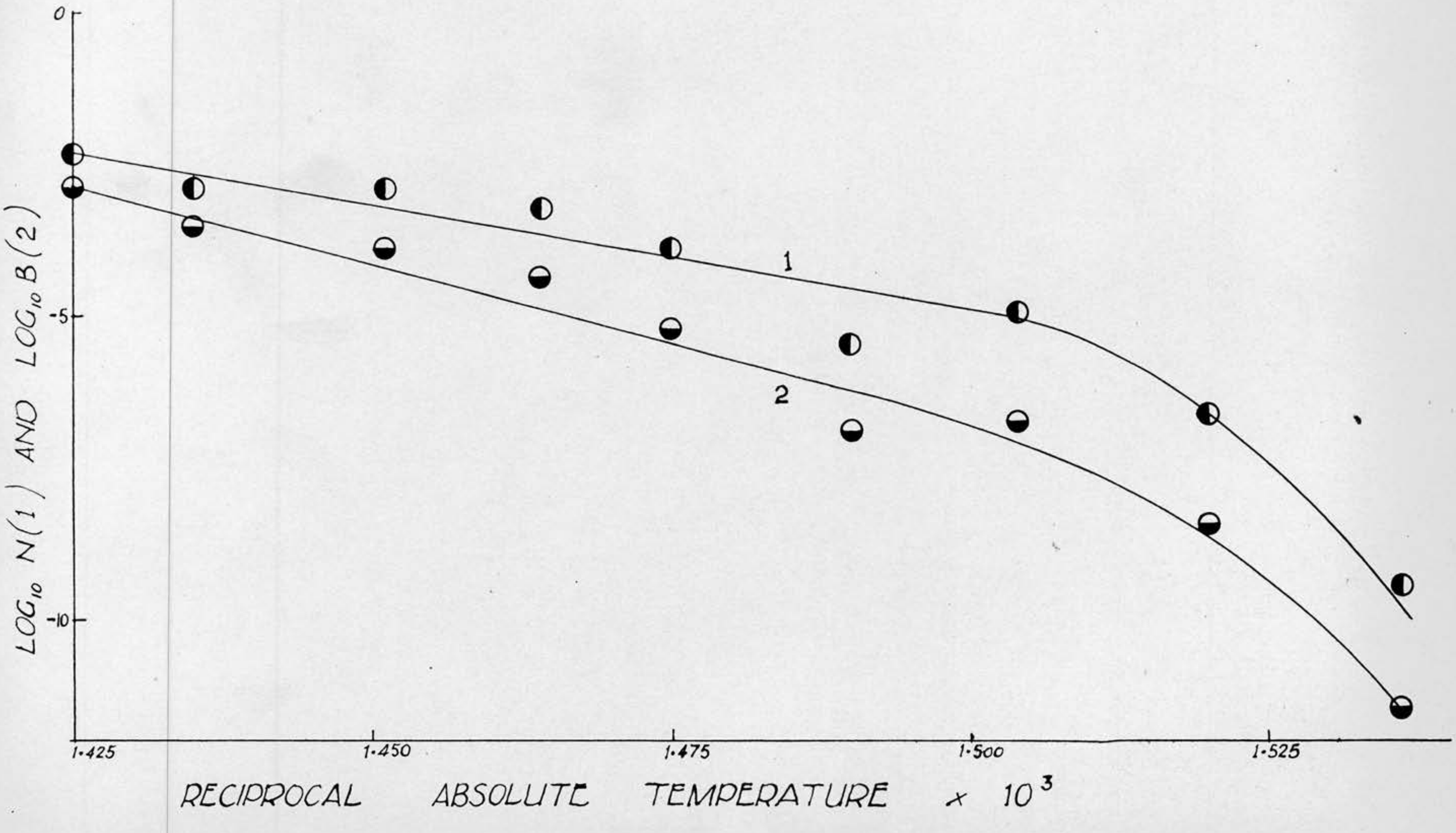
Initial $p_{cp}$ = 178m.m. Initial $p_{O_2}$ = 200m.m. Vessel B

| Run No. | Temp.T. | $\frac{10^3}{T}$ | $\log_{10}N$ | $\log_{10}B$ (= $\log_{10}N + 2\log_{10}A'$) |
|---|---|---|---|---|
| B 56 | 660° A | 1.515 | -7.84 | -9.74 |
| B 57 | 669 | 1.495 | -5.40 | -7.14 |
| B 58 | 673 | 1.486 | -5.15 | -6.82 |
| B 49 | 678 | 1.475 | -3.57 | -5.11 |
| B 48 | 683 | 1.464 | -3.80 | -5.20 |
| B 50 | 688 | 1.453 | -3.52 | -4.84 |
| B 52 | 692 | 1.445 | -2.95 | -3.97 |
| B 51 | 694 | 1.441 | -2.85 | -3.69 |
| B 47 | 697 | 1.435 | -2.83 | -3.62 |
| B 100 | 701 | 1.427 | -1.55 | -2.38 |

GRAPH N°47

Effect of Temperature Change upon N and B

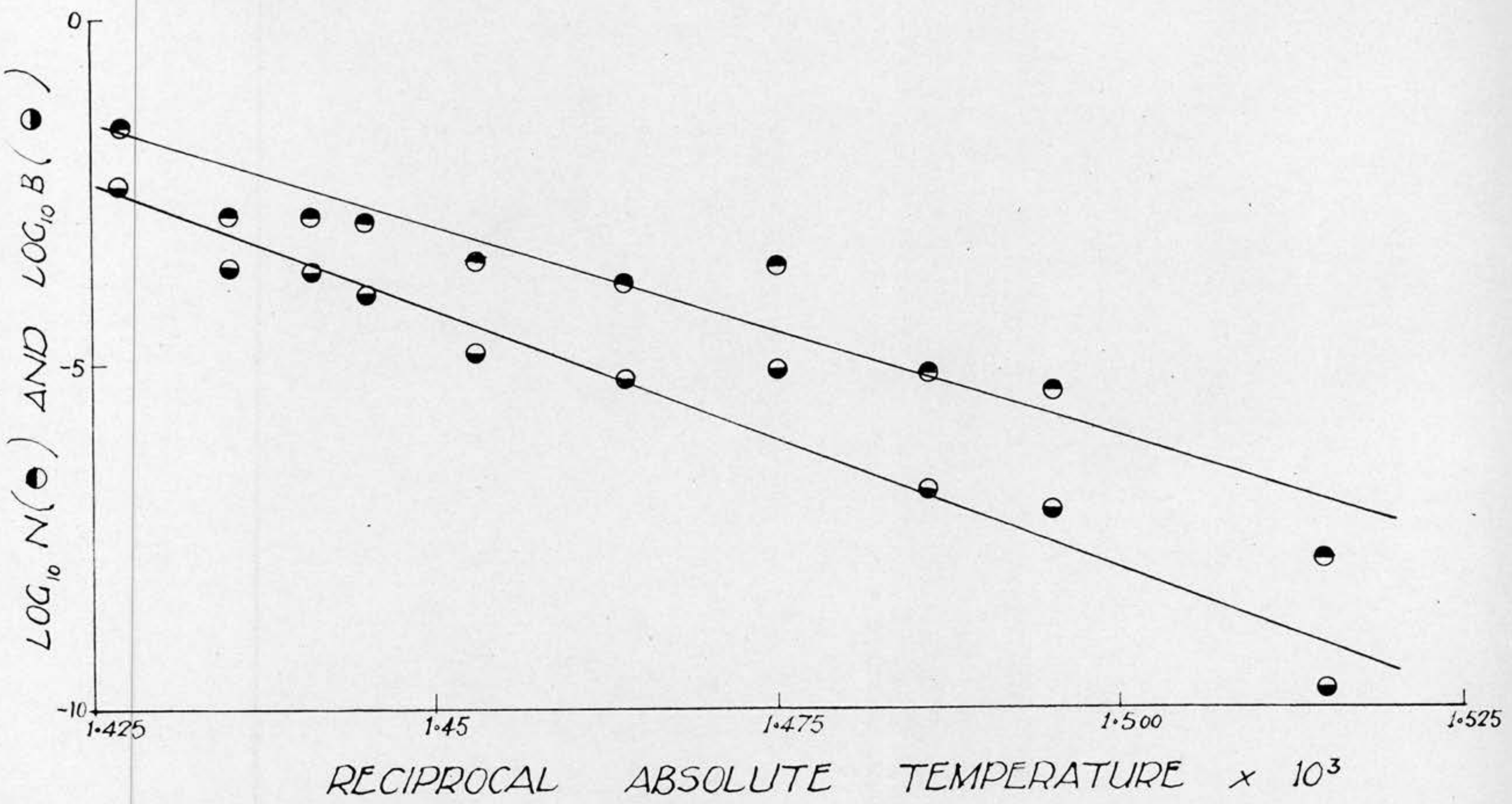
$p_{C.P.} = 250$ m.m. ; $p_{O_2} = 70$ m.m. ; Vessel B



GRAPH N°48

# Effect of Temperature Change upon N and B

$p_{C.P.} = 178$ m.m. ; $p_{O_2} = 200$ m.m. ; Vessel B



Several workers have attempted to derive theoretical expressions relating the various characteristics. Bardwell (61), discussing the oxidation of butanone, integrated the general rate expression $\rho = \frac{B}{A'}(e^{A't} - 1)$ to obtain $\Delta p = \frac{B}{A'^2}(e^{A't} - A't - 1)$ Substitution of the rate $\rho$ for $\frac{B}{A'}(e^{A't} - 1)$ in the integrated expression and disregard for A't in comparison with $e^{A't} - 1$ yielded the simple relationship $\Delta p = \frac{\rho}{A'}$ or $\rho = A'\Delta p$. At the time of the maximum rate this became $\rho_{max} \propto A'\Delta p_{max}$. Walsh derived the same expression in a similar way in a paper on the slow combustion of di-isopropyl ether and methane (62). These authers then showed that $\Delta p_{max}$ was virtually constant and thus were able to explain their observations that the dependences of maximum rate upon the conditions ran parallel with the net-branching factor dependences upon pressure and temperatures.

In the present work it was shown that the pressure change occurring up to the attainment of maximum rate $\Delta p_{max}$ was independent of the initial cyclopropane pressure but was directly proportional to the initial pressure of oxygen and showed a small temperature effect. The combination of this knowledge with the derived relationship between maximum rate, net-branching factor and $\Delta p_{max}$ predicted that at constant oxygen pressure, variation of the initial cyclopropane pressure would produce parallel effects upon maximum rate and the net-branching factor. That this is in fact true is shown on the graph No. 49 where the lines refer to the variation of the maximum rate and the points to net-branching factors. To obtain this graph each line was drawn to a special scale so as to coincide with the net-branching factor points. This was achieved by multiplying all the rates obtained under one set of conditions of oxygen pressures and temperatures by a factor. These factors and the conditions of the experiments to which they were applied are listed in table No. 94 along with two other sets of data.

TABLE NO. 94

| $p_{O_2}$ | Temp°A | Vessel | Factor |
|---|---|---|---|
| 200 | 678 | B | 0.0154 |
| 70 | 678 | B | 0.0244 |
| 79 | 701 | B | 0.0248 |
| 150 | 678 | A | 0.0192 |
| 300 | 701 | D | 0.0232 |

The theories of Walsh and Bardwell predict that, in experiments with constant hydrocarbon pressure and at a constant temperature, the net-branching factor would be independent of the pressure of oxygen when this was low, and inversely proportional to it at higher pressures (since $f_{max} \propto p_{O_2}^{1}$ or $f_{max} \propto p_{O_2}^{0}$ and $\Delta p_{max} \propto p_{O_2}^{1}$ ). This, of course, was not the case and the graph (No. 49) shows the parallelism between rate and branching factor when the initial oxygen pressure was varied. The graph was constructed in the same manner as the previous one from some of the data in table No. 95 which contains details of initial cyclopropane pressures, temperatures, vessels and the necessary rate-adjustment factors.

GRAPH Nº49

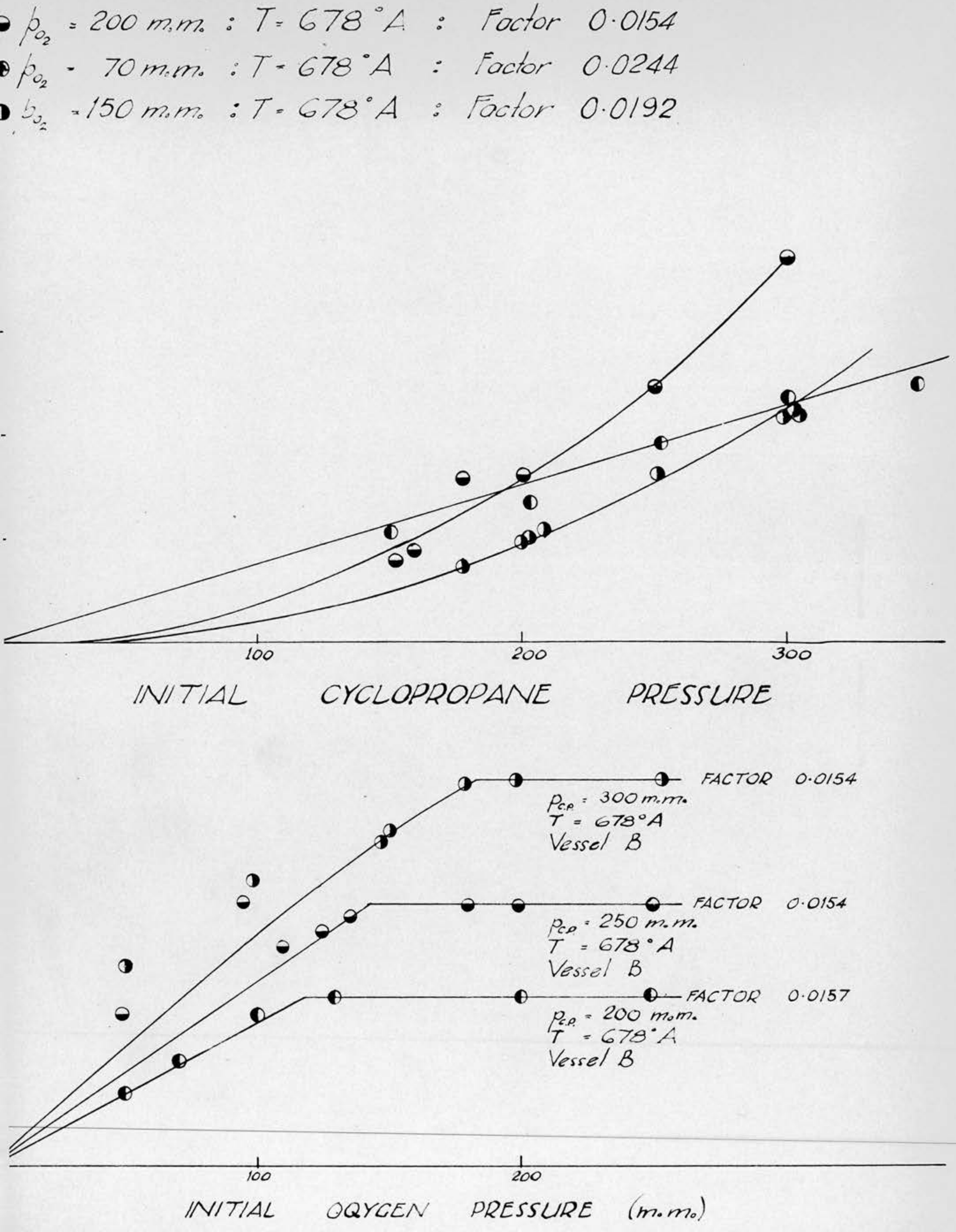

◒ $p_{O_2}$ = 200 m.m. : T = 678 °A : Factor 0·0154
◐ $p_{O_2}$ - 70 m.m. : T - 678 °A : Factor 0·0244
◑ $p_{O_2}$ = 150 m.m. : T = 678 °A : Factor 0·0192
100
200
300
INITIAL CYCLOPROPANE PRESSURE
FACTOR 0·0154
$P_{C.P.}$ = 300 m.m.
T = 678°A
Vessel B
FACTOR 0·0154
$P_{C.P.}$ = 250 m.m.
T = 678 °A
Vessel B
FACTOR 0·0157
$P_{C.P.}$ = 200 m.m.
T = 678 °A
Vessel B
100
200
INITIAL OQYGEN PRESSURE (m.m.)

TABLE NO. 95

| $p_{CP}$ | Temp° A | Vessel | Factor |
|---|---|---|---|
| 178 | 678 | B | 0.0200 |
| 200 | 678 | B | 0.0157 |
| 250 | 678 | B | 0.0154 |
| 300 | 678 | B | 0.0154 |
| 250 | 651 | B | 0.0221 |
| 178 | 701 | B | 0.0105 |
| 200 | 678 | A | 0.0526 |
| 100 | 701 | D | 0.0333 |

It was noted, then, that a distinct parallelism obtained between the variation of rate and net-branching factor with external conditions but that the theoretical relation $\rho_{max} \propto A' \Delta p_{max}$ was not verified unless the "constant of proportionality" itself depended upon conditions. It seemed probable that $\rho_{max} \propto A'$ but that the proportionality constant was not $\Delta p_{max}$.

Various attempts have been made to deduce a theoretical expression relating the induction period with maximum rate and net-branching factor. Thus Bardwell (61) showed that the reciprocal of the time $\theta$ elapsing before the attainment of a definite rate $\rho$ was given by $\frac{1}{\theta} = \frac{A'}{\log\ (1 + \frac{PA'}{B})}$ so that $\frac{1}{\theta}$ should be more strongly dependent upon the net-branching factor A' than upon the initiation factor B. Similarly Walsh (62) indicated that $\frac{1}{\tau}$ was proportional to the maximum rate. These authors found experimental verification of these expressions in certain cases. In the cyclopropane oxidation, there was a striking contrast between the dependence of rate (or net-branching factor) upon conditions and the behaviour of reciprocal induction period, the latter being apparently proportional to the product of the pressures of cyclopropane and oxygen. The only theoretically derived induction period-constituent pressures relationship differing from the rate expression was that of Mulcahy (63) which was deduced on the basis of the hydroperoxide theory of low-temperature slow combustion. This was of the form $\frac{1}{\theta} = k_1(RH)(O_2) \pm F_s$ where $F_s$ was a function of the surface conditions while the corresponding rate expression was, as usual, $\rho_{max} = k_2(RH)^2$

It does seem strange that Mulcahy verified his expression in the cases of n-butane and propylene while Bardwell verified his in the case of butanone oxidation; and yet both authors seek to explain their general results in terms of the hydroperoxide intermediate theory.

Before proceeding to compare the kinetic relationships in the cyclopropane oxidation with those reported for the slow combustion of other hydrocarbons it will be wise to summarise the kinetic results. It was shown that the dependence of the maximum rate upon the initial pressure was extremely complicated. The maximum rate could be either strictly proportional to the initial pressure of oxygen or quite independent of it, Which of these two laws operated was found to depend upon (a.) the initial oxygen pressure itself, since at lower oxygen pressures the former dependence was observed while at higher oxygen pressures the independence was hoted, (b.) the initial hydrocarbon pressure, since as this was increased (all other things being equal) the region of oxygen independence was diminished, the critical oxygen pressure being increased, and (c.) the temperature, because as this was increased the critical oxygen pressure again rose so that at higher temperatures the maximum rate was dependent upon the initial oxygen pressure over a wider range of oxygen pressures.

It was also shown that the maximum rate varied sometimes with the square of the cyclopropane pressure and sometimes was directly proportional to the hydrocarbon pressure. Which of these two dependences held good in any particular case was found to depend upon the initial pressures of both cyclopropane and oxygen and the temperature of reaction. The total order of reaction was found to be always two so that the two regions of kinetic dependence were described by the equations $\rho_{max} \propto p_{cp}^2 \, p_{O_2}^0$ and $\rho_{max} \propto p_{cp} \cdot p_{O_2}$. It was possible to combine these in an empirical but single expression

$$\rho_{max} = \frac{k_1 p_{cp}^2 \cdot p_{O_2}}{k_2 p_{cp} + k_3 p_{O_2}}$$

Thus under the appropriate conditions when $k_2 p_{cp} \gg k_3 p_{O_2}$ then the maximum rate was given by $\frac{k_1}{k_2} \cdot p_{cp} \cdot p_{O_2}$. Suitable conditions for such a simplification were considered to be increase of cyclopropane pressure, reduction of the oxygen pressure or increase of temperature if $k_2$ were more temperature dependent than $k_3$ by a large amount. This simple relationship was verified when such conditions prevailed. On the other hand, at lower cyclopropane pressures, higher oxygen pressures or lower temperatures $k_3 p_{O_2}$ would become the more significant term in the denominator whence $\rho_{max} = \frac{k_1}{k_3} \cdot p_{cp}^2$

A term must be included in the rate expression to account for the powerful influence of surface extent and character upon the maximum rate. Inserting a term and the exponential factor to account for the overall temperature affect the general equation for the maximum rate of the reaction became

$$\rho_{max} = \frac{k_1 \, p_{cp}^2 \cdot p_{O_2}}{k_2 p_{cp} + k_3 p_{O_2}} \cdot \frac{1}{f_s} \; e^{\frac{-35,000}{RT}}$$

With reference to the overall activation energy of the reaction, Arrhenius diagrams were constructed for experiments where the kinetics could be represented $\rho_{max} \propto p_{cp}^2$ and $\rho_{max} \propto p_{cp} \cdot p_{O_2}$. Some curvature was noted at the ends of the lines but the graphs were straight and parallel over a considerable temperature range. This indicated that the major factor contributing to the activation energy was $k_1$ in the above equation.

Expressions of a similar type have been reported for other hydrocarbons although the cyclopropane oxidation kinetics were not quite the same as any others. The variation of the maximum rate with the conditions of the reaction has been investigated in a systematic way for the slow combustion of only a very few substances. Apparent orders of up to six with respect to the pressure of the organic substances have been reported for the butanone combustion (61), though for the majority of compounds studied the order is about two. For example methane (16), ethylene (64), propane (65), n - pentane (28), n - hexane (28), di-isopropyl ether (30), chloroparaffins (66) and certain aliphatic amines (67) oxidise at a rate determined by the pressure of fuel raised to about the second power. It is possible that very high or fractional orders with respect to the fuel, which have been reported, may find an explanation in the observation that the dependence of maximum rate of oxidation of cyclopropane upon the initial cyclopropane pressure could change from second to first order as the hydrocarbon was increased. For example two rate-hydrocarbon pressure curves reported for n - butane by Mulcahy (63) might be interpreted as showing the transition from second to first order. In this connection it is interesting to note that if the kinetics changed from $\rho_{max} \propto p_{RH}^2$ to $\rho_{max} \propto k_2 p_{RH}$ and if the constant $k_2$ were high, then the apparent order of the overall rate - hydrocarbon pressure curve would be high. The maximum rate of the slow combustion of methylamine at 330°C was approximately proportional to both the methylamine and oxygen pressure but this reaction was perhaps somewhat anomalous in that it showed no period of inappreciable pressure change and started off at a finite rate (68). In all other oxidations in the "low-temperature" range the change from dependence to independence of the maximum rate on the oxygen pressure has been noted. Sometimes the curve exhibited a maximum (e.g. with the lower ethers (69) and butanone (70)) but in general the curves illustrating the effect of varying the oxygen pressure were of the same type as those reported for the cyclopropane oxidation. The observation that the critical oxygen pressure depended upon conditions had not been previously reported but, with the exception of Bardwell's experiments with butanone, no workers appear to have studied the oxygen dependence of the maximum rate in any detail.

In the case of butanone there was no shift of the critical oxygen pressure (in this case the position of the maximum of the curve) with changing conditions. The butanone combustion must, however, be regarded as exceptional in many ways since there is a maximum in the oxygen-rate curve and also since the oxidative degradation is not complete, there being a high concentration of acetone (which is comparatively stable to oxidation) in the final products.

In the slow combustion of carbon compounds at higher temperatures (27) and in the oxidation of methane (16) at all feasible temperatures, it has been generally agreed that the maximum rate was strongly dependent upon the oxygen concentration. In view of the discovery that the maximum rate of oxidation of cyclopropane could be made dependent upon or independent of the oxygen pressure by suitable choice of conditions of pressure and temperature, it seemed reasonable to consider the possibility that there was really no sharp distinction between "high" and "low" temperature kinetics of hydrocarbon oxidation. If this were so, one might expect to find that the rate might become independent of the oxygen pressure in the high temperature zone of the combustion of a hydrocarbon, if the ratio of oxygen to hydrocarbon pressure became high enough. The results of a recent investigation of the ethylene exidation at 400°C were interpreted by Harding and Norrish (64) as indicating rate-oxygen pressure proportionality but certainly appeared to show a tendency to oxygen independence at higher oxygen pressures.

One of the other characteristic features of slow combustions in the "high-temperature" region is the dependence of maximum rate upon the total pressure of the system. In the "low-temperature" range, the absence of an inert gas effect is equally characteristic. This property of "low-temperature" combustions is hardly unexpected since, in such cases, the maximum rate is largely independent of the oxygen pressure and because there seems to be no very great reason why nitrogen or other inert gas should be much more efficient in the prevention of diffusion of radicals to the walls than oxygen. In the cyclopropane oxidation, added nitrogen had no effect under any circumstances. It may be significant that the data published on the effect of total pressure on the rate of oxidation of methane (16) and ethylene (64) indicated that the dependence of rate upon total pressure tended to become less at the highest pressure used. It is interesting to speculate whether the rate of a slow combustion in the "low-temperature" zone would become total-pressure-dependent at very low pressures.

The kinetic dependences of the net-branching factor closely paralleled those of the maximum rate of oxidation of cyclopropane and a very similar rate-equation could be set up to describe its variation with changes of pressure and temperature. As has been indicated Walsh (62) studied the oxidation of methane and di-isopropyl ether and found that A' was proportional to $\rho_{max}$ . Bardwell's studies of the butanone oxidation have also been discussed with reference to $\rho_{max}$ - A' relationship. Apart from these investigations very little mention is to be found of the kinetic dependences of A' in the literature of hydrocarbon slow combustion.

On the other hand, the reciprocal induction period depended upon the conditions in a manner quite different from the maximum rate and the net-branching factor. It was shown that there was no significant difference between the behaviour of $\frac{1}{\theta}$ and $\frac{1}{\tau}$ , although there was some evidence that in experiments where high maximum rates were subsequently attained the value of $\frac{1}{\theta}$ tended to become fairly constant at some high level when the time $\theta$ was so small that $(\theta - \tau)$ became larger in comparison with $\tau$ . The general equation for the reciprocal induction period might be written:-

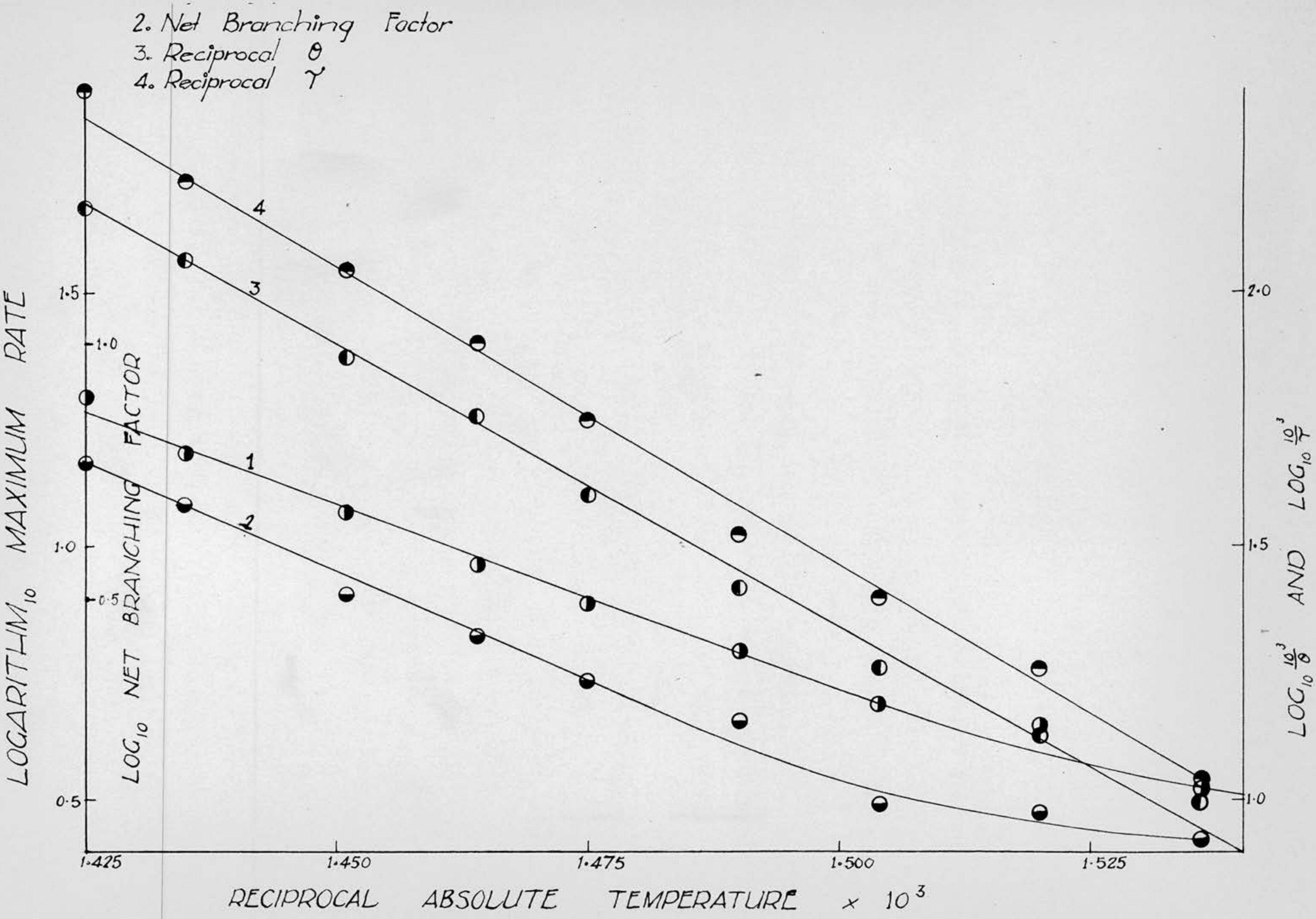
$$\frac{1}{\theta} = k p_{cp} \cdot p_{O_2} \cdot f'_s \cdot e^{-\frac{53{,}000}{RT}}$$

The linear dependence of the reciprocal induction period upon the initial hydrocarbon pressure was compared with a similar finding in the cases of propylene (63), n-butane (63), n-hexane (28) and 2-methyl pentane (71) and its proportionality to the initial oxygen pressure has been previously reported in almost every oxidation studied. Notable exceptions to this latter type of behaviour are butanone and propane (61). Some slow combustions are characterised by a greater than linear dependence of reciprocal induction period upon the pressure of combustible substance e.g. methane (16), ethane (72), isobutane (63), n-pentane (28), butanone and di-isopropyl ether(30). It is very difficult to generalise with reference to these observations but it should be pointed out that in some cases $\frac{1}{\theta}$ behaves similarly to $\rho_{max}$ and in some cases $\frac{1}{\theta} \propto p_{RH} \cdot p_{O_2}$ .

The presence of inert gas had no effect upon the induction period in the cyclopropane oxidation but it has been reported that in the slow combustion of methane, n-pentane and di-isopropyl ether the induction period was reduced by increasing the total pressure.

The effect of change of temperature on the oxidation of cyclopropane was, in general terms, to increase the maximum rate and the net-branching factor and to reduce the induction period. On graph No. 50 are plotted the Arrhenius graphs for maximum rate, net-branching factor and the reciprocal induction periods ( $\frac{1}{\theta}$ and $\frac{1}{\tau}$ ). The experiments were carried out with 250 m.m. of cyclopropane and 70 m.m. of oxygen in vessel B and the temperature range was about 50°. It will be noted that the two lines referring to reciprocal induction period are parallel and show no tendency to curve at the ends, their gradients correspond to activation energies of 51·7 and 54·2 kcals./mole. The two other curves are parallel to each other, the activation energies referring to the maximum rate and the net-branching factor being 35 kcals./mole. These observations were seen to be very different from some made by Chamberlain and Walsh (62) who found that the activation energy of the maximum rate, net-branching factor and the reciprocal induction period were all close to a value of 51 kcals./mole. for the oxidation of methane between 470°C and 510°C. Mulcahy, however, has reported that the activation energy of the reciprocal induction period in the propylene oxidation was twice

GRAPH IV 30


2. Net Branching Factor
3. Reciprocal θ
4. Reciprocal γ
4
3
1
2
LOGARITHM₁₀ MAXIMUM RATE
LOG₁₀ NET BRANCHING FACTOR
1·5
1·0
1·0
0·5
0·5
2·0
1·5
1·0
LOG₁₀ 10³/θ AND LOG₁₀ 10³/γ
1·425
1·450
1·475
1·500
1·525
RECIPROCAL ABSOLUTE TEMPERATURE × 10³

that of the maximum rate (63). In the same communication Mulcahy reported that the effect of change of temperature was very much greater upon $\frac{1}{\theta}$ than $\rho_{max}$ in the slow combustion of propane.

As to the particular values determined for the activation energies, little can be said. In most cases, Arrhenius plots have been found to be curved so that in the case of any particular hydrocarbon the activation energy could be said to vary. For instance the overall activation energy of the reaction of ethylene with oxygen (64) was found to vary from 26 kcal. at 400°C to 53 kcal. at 500°C. This represents a gradual change in comparison with the activation energy of the propane oxidation which was found to become actually negative over part of the range (26). A very important observation was made by Mulcahy (27) who compared the effect of change of temperature of propylene, propane and several substituted propanes. He found that the very great differences in rate observed at low temperatures tended to disappear at higher temperatures. Now since the effect of structure upon reaction rate at low temperatures had been attributed to the effect of structure upon the ease of breakdown of the intermediate hydroperoxide ROOH (by fission of the -O-O- bond), Mulcahy concluded that the results showed that peroxide breakdown was of less consequence (or none at all) at the higher temperatures and that at these temperatures oxidation proceeded by a more general mechanism involving the same or similar radicals irrespective of the fuel. These radicals would be expected to be less complex than alkylperoxyl radicals - hydroxyls, alkyls etc. being more likely.

The total pressure change occurring during an oxidation was considered to be a measure of the extent of reaction and it was hardly surprising to find that it was proportional to the oxygen pressure when this was in excess and independent of the cyclopropane pressure. Increase of temperature produced a small increase of the total pressure change. Since analysis showed the main products of oxidation to be oxides of carbon and water it was possible to write down two stoichiometric chemical equations to describe the complete oxidation. These were:-

1. $C_3H_6 + 3O_2 \rightarrow 3CO + 3H_2O$

2. $2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O$

Comparing the pressure changes involved in these reactions it was seen that, relative to nine volumes of oxygen in each case, the pressure changes were six volumes in equation 1. and one volume in equation 2. This suggested that the small temperature effect on the pressure change was due to the gradual withdrawal from prominence of reaction 2. as the temperature was increased. This was a reasonable idea since it was likely that carbon dioxide was produced from carboxylic acids which would be less likely to be formed at higher temperatures and analysis showed that increase of temperature did, in fact, bring about an increase of the ratio carbon monoxide: carbon dioxide. The relatively small amounts of carbon dioxide found seemed to be nearly all formed after the attainment of maximum rate.

Other important facts revealed by analysis were that the process of isomerisation of cyclopropane was probably negligible under the conditions of experiment, that the rate of pressure change was a measure of the rate of reaction of both cyclopropane and oxygen and was a measure of the rate of production of the end products. Only a few compounds were found in the products and only one intermediate was detected. The possibility of the presence of other intermediate products in small quantity was a real one but the relative accuracy of the carbon, hydrogen and oxygen balances made it less likely. In fairness it should be pointed out, however, that the outputs of these elements were almost without exception lower than their imputs. The analytical results were discussed rather fully in the experimental section.

Semenov's simple scheme for a chain reaction involving degenerate branching is:-

Stage (a) Production of active centres, i.e. radicals, which initiate Stage (b).

Stage (b) Primary chains involving oxygen and the combustible substance and of average length $\nu$. These chains lead to the production of a substance M which has a reasonable life-time and stability.

Stage (c) Reaction of the intermediate M in two ways (one producing active radicals, the other not)

Thus

$$M \begin{cases} \xrightarrow{k_1} \text{inactive products, causing a pressure rise} \\ \xrightarrow{k_2} \text{radicals which can initiate the primary chains, leading to the formation of more M.} \end{cases}$$

The conditions to be obeyed are that $k_1 \gg k_2$ and that M should have a lifetime of the order of seconds or minutes. Norrish (23) has demonstrated that if the molecule M can survive for one minute between its formation and its entering into a branching reaction then it would be expected to attain a pressure of several m.ms. during the reaction. For this scheme the net branching factor is given by $k_2 (\nu - 1) - k_1$. Presumably the acceleration of the rate falls off to zero because $\nu$ or $k_2$ decreases after the initial autocatalytic period due to depletion of reactants or accumulation of products. Harding (73) suggested the existence of a second type of degenerate branching in which the radicals from M, as well as initiating primary chains, can decompose molecules of M to give inactive products. According to this scheme a limiting rate could occur early in the reaction before there was any serious depletion of reactants. This latter type of chain branching seemed to be out of the question in the oxidation of cyclopropane since analysis had shown that at the time of attainment of maximum rate, the reaction was well on its way to completion and that about half of the reactant not present in excess had been consumed. This suggested that the reason for the failure of the rate to continue to increase exponentially was, in fact, the serious depletion of reactants.

The identity of the intermediate M in the cyclopropane oxidation was decided to be formaldehyde. Only two types of slow combustion intermediate have been described previously - peroxides and formaldehyde. In the present investigation all the evidence was against peroxides. Despite repeated and very careful attempts to detect peroxides in the products of the reaction (the condensible products removed at the time of attainment of maximum rate of several experiments were collected and the aggregate was tested for peroxide by the ferrous thiocyanate and starch-iodide methods) it was quite certain that even at the lowest temperature studied (378 C) no peroxide could be detected in the products. On the other hand, formaldehyde was found to be present in reasonable amount under all conditions of temperature and pressure. It was considered to be very significant that its concentration varied with time in a manner analagous to the rate and, in particular, that its pressure reached a maximum value at just about the same time as the rate reached its maximum. Thus in any single experiment the rate at any given time appeared to depend upon the amount of formaldehyde present at that time. In contrast with this was the fact that the maximum rate depended rather upon the initial pressures of reactants.

The study of the effect of adding formaldehyde to the oxidation system yielded some extremely interesting results. The first was that the addition of a small quantity of formaldehyde (about 0·3% of the total) reduced the induction period $\theta$ by 37% and, still more striking, reduced $\gamma$ by 61% without altering the maximum rate at all. Increase of the amount of formaldehyde added progressively reduced $\gamma$ which was very close to zero (0·1 minutes) when the quantity of additive was 7·8 m.m. This increased addition of the aldehyde had a less profound effect upon $\theta$ since the pressure change preceding the attainment of maximum rate was constant and independent of the added formaldehyde within the limits of experimental error and since a certain, finite time was always necessary for the occurrence of that pressure change. Thus the effect of formaldehyde addition upon $\theta$ was great at first but decreased in magnitude later. When the amount of additive exceeded about 10 m.m. a slight effect upon the maximum rate was observed and this rate gradually increased from 11·9 to 14 m.m./minute when the pressure of added formaldehyde was increased from 7·8 m.m. to 35·2 m.m.

These results were rather different from those of Harding and Norrish (64) who added formaldehyde to ethylene-oxygen mixtures and found that the decrease in induction period (measured by the intercept on the time axis of the tangent to the pressure-time curve at $\Delta p_{max}$ ) was proportional to the pressure of added formaldehyde and that addition of the intermediate in amounts greater than that required to eliminate the induction period led to increases in the initial rate of oxidation over the normal maximum rate. The rate subsequently fell to its normal value. In the ethylene-oxygen reaction, however, the rate reached a maximum after a comparatively small pressure change whereas the maximum rate of slow combustion of cyclopropane occurred after about 50% of the reactant not in excess had been consumed. Thus the failure of the rate to continue to increase with time was due to consumption of the reactants in the latter reaction. The two combustions, therefore, must be regarded as essentially different.

In view of these facts it was concluded that the essential intermediate responsible for the degenerate chain branching in the slow combustion of cyclopropane was formaldehyde. Experiments showed that the maximum pressure of formaldehyge was independent of the initial oxygen pressure except when this was very low and was proportional to the initial cyclopropane pressure, although this proportionality was less marked at higher cyclopropane pressures (possibly due to difficulties of extraction or analysis). The maximum pressure of formaldehyde varied with the temperature in a manner corresponding to an activation energy of 10.5 kcals. per mole. There was, thus, despite the proportionality between rate and pressure of intermediate during one experiment, a great differnece between the pressure and temperature relations of the maximum rate and those of the maximum formaldehyde pressure.

Before attempting to deduce a mechanism for the reaction it would be well to summarise the various types of elementary reaction which are regarded as sufficiently plausible to be postulated in a gas phase chain reaction scheme. Walsh emphasised the necessity of writing reaction steps energetically feasible and having a favourable steric factor (74). Such elementary reactions he divided into four classes:-

(a) reactions involving the breaking of one bond, e.g.

$$CH_3 - CH_3 \longrightarrow CH_3 + CH_3$$

(b) reactions involving the formation of one bond, e.g.

$$CH_3 + CH_3 \longrightarrow CH_3 - CH_3^{*}$$

(c) abstractions of an atom (particularly of hydrogen) from a molecule by a radical (involving the breaking of one bond and the formation of another), e.g.

$$CH_4 + OH \longrightarrow CH_3 + H_2O$$

(d) reactions involving the transfer of energy from a radical or molecule e.g.

$$CH_3 - CH_3^{*} + M \longrightarrow CH_3 - CH_3 + M^{*}$$

Some of the reactions which have been suggested by Norrish do not fall into one of these four classes and might therefore appear suspect. Ubbelohde too has criticised some of Norrish's proposed reaction steps, mainly on the grounds that their geometry indicates that their activation energies may be almost as high as the energies required for fission of the bonds concerned and that there is no obvious source of these activation energies (75).

Walsh did make one very important exception to his rules, stating that it was not unplausible to suppose the occurrence of a reaction more complicated than those given above for an energy-rich radical $A^{*}$ particularly if this were a large enough body to allow distribution of the excess energy over various vibrational degrees of freedom. If such were the case the radical would be undergoing far greater geometrical distortions than usual thus facilitating the occurrence of what would normally be described as less likely reactions. Furthermore an energy-rich radical, if not deactivated by collisions, would be expected to take part in reactions normally requiring an activation enrgy high enough to make such reactions improbable. So long as the radical preserves its energy of formation, however, the energy of activation of a subsequent reaction will be considerably less than the endothermicity of that reaction. These considerations were borne in mind in the deduction of reaction mechanism.

The elucidation of the mechanism of the reaction was divided into two parts - a consideration of the possible modes of formation of formaldehyde and an examination of its function as the degenerate branching-chain intermediate.

One might write down various possible reactions involving cyclopropane and leading to the formation of formaldehyde e.g.

$$C_3H_6 + O \longrightarrow C_2H_4 + CH_2O$$

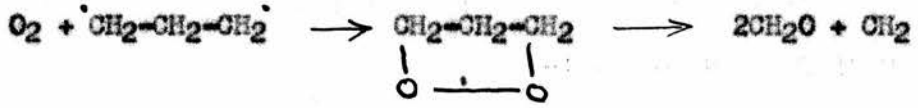
This reaction was disregarded immediately since tests for the presence of ethylene in the reaction products were quite negative. In any event much critism could be directed at such a reaction from the point of view that the participation of oxygen atoms was unlikely at the temperatures involved. A second possible reaction was:-

$$C_3H_6 + O_2 \longrightarrow C_2H_4O + CH_2O$$

It was immediately noted that this involved the fission of two C-C bonds and one O-O bond, and the formation of two C-O and one C=O bonds. Thus it would be expected that the reaction would have a very low steric factor since such a large rearrangement would be necessary in the activated complex and for that reason this reaction also was disregarded.

A third suggestion involved the initial breaking of a C-C bond in cyclopropane and the subsequent reaction of the diradical formed. Thus:-

$$C_3H_6 \longrightarrow \dot{C}H_2-CH_2-\dot{C}H_2$$



$$O_2 + \dot{C}H_2-CH_2-\dot{C}H_2 \longrightarrow \underset{O\,-\!-\!-\!-\,O}{CH_2-CH_2-CH_2} \longrightarrow 2CH_2O + CH_2$$

Now the production of methylene radicals in that way would lead to the formation of oxygen atoms which might degrade the $C_3H_6$ diradical by successive destruction of $CH_2$ groups. Thus:-

$$CH_2 + O_2 \longrightarrow CH_2O + O$$

$$O + \dot{C}H_2-CH_2-\dot{C}H_2 \longrightarrow CH_2O + \dot{C}H_2-\dot{C}H_2 \qquad \text{etc.}$$

This idea was discarded largely because of the fact that the $C_3H_6$ diradical had been suggested as the intermediate in the isomerisation of cyclopropane and because the activation energy of its formation from cyclopropane had been found to be 65,200 cals/mole (60). If the mechanism above were adopted the splitting of the ring would be the rate controlling step and the activation energy of the combustion would have had to be 65,200 cals/mole (which it was not) since it was difficult to imagine how the diradical formation could proceed in any way other than unimolecularly. This also raised the point that this mechanism did not suggest any explanation of the autocatalysis.

A very frequently postulated reaction is hydrogen abstraction from hydrocarbons by radicals (including oxygen molecules). Thus:-

$$RH + X \longrightarrow R + HX$$

$$\text{or} \qquad C_3H_6 + X \longrightarrow C_3H_5 + HX$$

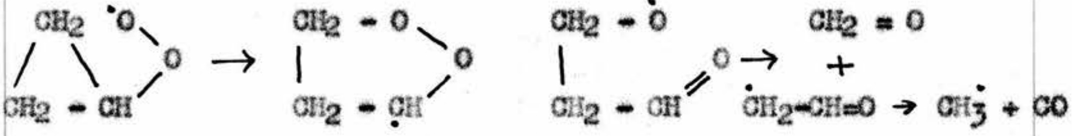
Consideration of the value of such a reaction step was made with a view to determining whether it facilitated explanation of the formation of formaldehyde and whether this could proceed by a simple chain reaction involving the cyclopropyl radical. It is well known that alkyl radicals react with oxygen to form alkylperoxyl radicals which, if stable, can react with another fuel molecule to form peroxides (this is the basis of the peroxide theory of the "low-temperature" mechanism of hydrocarbon oxidation). In the event of instability of the peroxyl radical (which is endowed with a great excess of energy just after its formation) due to its chemical constitution or to the temperature, it may decompose to yield active products. Since no peroxides had been detected at any time, even at lower temperatures, the cyclopropylperoxyl radical would have been unstable, if formed.

$$C_3H_5^{\bullet} + O_2^{\cdot} \longrightarrow C_3H_5O_2^{\bullet}$$

The possible decomposition of this radical according to the equation

$$C_3H_5O_2^{\bullet} \longrightarrow CO + CH_2O + CH_3^{\bullet}$$

was stoichiometrically possible but at first sight such a reaction would appear to violate all the rules regarding simplicity of elementary changes, since it requires the fission of one C-H, three C-C bonds, one O-O bond and the formation of one C=O bond and one C-H bond. However, in view of the fact that the formation of methyl radicals provided the basis for a primary chain reaction involving cyclopropane (and, of course, methane had been detected, in small amounts, in the products) the reaction was considered in more detail. It was re-written as a series of simpler steps.



The first step involves the movement of one electron, presumably excited by the accumulation of sufficient of the energy (earned by the radical) in the C-C bond concerned. It leads to the production of a five-membered ring system whose weakest link is the O-O bond, particularly when the α carbon atom bears a free electron which will tend to disappear by the formation of a carbonyl group (again by the movement of only one electron). The molecule now has the structure of an aldo-alkoxyl radical and loses formaldehyde readily by the process postulated in the peroxide mechanism of hydrocarbon oxidation. It will be noted that this third step again involves the movement of only one electron. Now the remaining radical $CH_2$-CH=O may be regarded as a simple type of aldehyde, extremely unstable due to its being a radical and also on account of the large amount of energy it carries away from its exothermic formation. It would, therefore, be expected to pyrolyse to carbon monoxide and methyl very rapidly.

Thus an apparently over-complex reaction when studied, step by step, was seen to involve three separate one-electron shifts and a prototropic change all of which could be regarded as simple and quite likely, particularly in view of the fact that the original radical was energy-rich. It should, perhaps, be emphasised that, even under such favourable starting conditions, only a unimolecular decomposition could be so complex and yet so likely.

Accepting then the formation of formaldehyde from the cyclopropyl radical

$$C_3H_5^{\cdot} + O_2 \longrightarrow C_3H_5O_2^{\cdot} \longrightarrow CO + CH_2O + CH_3^{\cdot}$$

one next considered the use of the methyl radicals in propagation of a primary chain reaction. The only likely mechanism was

$$CH_3^{\cdot} + O_2 \longrightarrow CH_2O + OH^{\cdot}$$

$$OH^{\cdot} + C_3H_6 \longrightarrow C_3H_5^{\cdot} + H_2O$$

These reactions require no discussion as they have been suggested by several authors (25, 30, 31) and appear to be well established reaction steps in the methane oxidation reaction.

It would be well to summarise the reactions suggested for the primary chain leading to the production of formaldehyde.

$$C_3H_6 + OH^{\cdot} \longrightarrow C_3H_5^{\cdot} + H_2O$$

$$C_3H_5^{\cdot} + O_2 \longrightarrow C_3H_5O_2^{\cdot}$$

$$C_3H_5O_2^{\cdot} \longrightarrow CO + CH_2O + CH_3^{\cdot}$$

$$CH_3^{\cdot} + O_2 \longrightarrow CH_2O + OH^{\cdot}$$

The thermochemistry of these reactions will now be considered. The heat of the first reaction is calculable from a knowledge of the bond dissociation energy of the H-OH bond in water which is 118 kcals.(76) and the bond dissociation energy of the $H-C_3H_5$ bond in cyclopropane. Trotman-Dickenson (77) taking the energy of activation of the metathetical reaction

$$CH_3^{\cdot} + CH_4 \longrightarrow CH_4 + CH_3^{\cdot}$$

as about 12·8 kcals/mole and the bond dissociation energy D $(CH_3-H)$ = 102, showed that the relation $\Delta E = \alpha \Delta H$ held for the reaction of methyl radicals with a series of alkanes where E = the activation energy of the methyl + alkane reactions and H = the heat of these reactions, i.e. the bond dissociation energies of the C-H bonds broken in the alkanes. Trotman-Dickenson and Steacie (78) found that the energy of activation of the hydrogen abstraction reaction of methyl with cyclopropane was 10·2 kcals/mole.

Then $\Delta E = 12{\cdot}8 - 10{\cdot}2 = 2{\cdot}6$

if $\alpha = 0{\cdot}5$, then $\Delta H = 5{\cdot}2$

Hence $D(C_3H_5-H) = 102 - 5{\cdot}2 = 97$ kcals.

Trotman-Dickenson (77) suggested that due to the similarity between the bonds broken and formed, $\alpha$ should be closely equal to 0·5. Even if $\alpha$ were rather less than 0·5 the bond dissociation energy derived would not differ very greatly from 97 kcals. Thus the first reaction was written

$$C_3H_6 + \dot{OH} \rightarrow C_3\dot{H_5} + H_2O + 21 \text{ kcals. } (118-97).$$

The change of heat content involved in the second and third reactions could not be calculated since no information was available on the heat of formation of the cyclopropylperoxyl radical. It was possible to calculate the exothermicity of the overall reaction

$$C_3\dot{H_5} + O_2 \rightarrow CO + CH_2O + \dot{CH_3}$$

since the heats of formation of methyl (79), formaldehyde (80) and carbon monoxide (81) were known, and the heat of formation of the cyclopropyl radical was calculable from a knowledge of the bond dissociation energy of the $C_3H_5$-H bond in cyclopropane, the heat of formation of a hydrogen atom (79) and the heat of formation of cyclopropane (82). The latter value was obtained from the heat of combustion of cyclopropane and was preferred to other values reported in the literature (83). The values of these heats of formation and the calculation of the exothermicity of the oxidation of the cyclopropyl radical are given below.

| Compound | $\Delta H_f^\circ$ kcals. |
|---|---|
| Methyl | + 31 |
| Formaldehyde | - 28·7 |
| Carbon monoxide | - 26·8 |
| Hydrogen atom | + 52 |
| Cyclopropane | - 12·7 |

Now $D(C_3H_5\text{-}H) = \Delta H_f^\circ(C_3H_5) + \Delta H_f^\circ(H) - \Delta H_f^\circ(C_3H_6)$

$$\therefore \Delta H_f^\circ(C_3H_5) = 97-52-13 = 32 \text{ kcals.}$$

And for $C_3H_5^\cdot + O_2 \rightarrow CO + CH_2O + CH_3^\cdot$

$$\Delta H = -27-29+31-32 = -57 \text{ kcals.}$$

The exothermicity of the last reaction step (the oxidation of methyl) follows by subtraction of the heat of formation of methyl from the sum of those of formaldehyde and hydroxyl (79).

Thus $\Delta H = -29+10-31 = -50$ kcals.

The reaction steps written for the formation of formaldehyde from cyclopropane by a straight chain were, therefore, thermochemically acceptable and, at the same time, geometrically simple.

The next problem was the mechanism of oxidation of formaldehyde so that it functioned as a degenerate branching intermediate in the reaction. The reaction of the aldehyde with molecular oxygen was considered.

$$CH_2O + O_2 \longrightarrow CH\dot{O} + H\dot{O}_2$$

This is a branching reaction and would appear to be sufficiently endothermic to merit serious consideration. The bond dissociation energy of the C-H bond in formaldehyde has been the subject of some discussion but many authors believe it to be about 75-80 kcals (e.g. Gorin (84), McDowell and Thomas (85), Roberts and Skinner (86) Hoare and Walsh (87) ) and about 78 kcals seemed a reasonable value for D(HCO-H). Much more difficult to assign a value to is the energy liberated in the formation of the $H-O_2$ bond. Walsh (22) discussed previous evidence and estimates and concluded that the value of this energy lay in the range 60-70 kcals. In a later communication (87), however, Walsh took the energy evolution to be 55 ± 10 kcals. If this value is accepted, the endothermicity of the reaction between formaldehyde and oxygen is $78-55 \pm 10 = 23 \pm 10$ kcals, so that its energy of activation would be probably rather more than 25 kcals/mole. Energetically, therefore, the reaction is suitable. It is also necessary to attempt to justify the inclusion of formyl and hydroperoxyl radicals in the reaction scheme. The formation of the formyl radicals seems the only feasible result of any probably gas-phase reaction of formaldehyde and they will be destroyed either by direct reaction with oxygen to yield carbon monoxide and hydroperoxyl radicals or by decomposition to carbon monoxide and hydrogen atoms which will form $HO_2^{\cdot}$ radicals by reaction with oxygen. The overall effect will be the same and it can be shown that the choice of reaction offered will not affect the general kinetics. Little can be said about the thermochemistry of the reaction

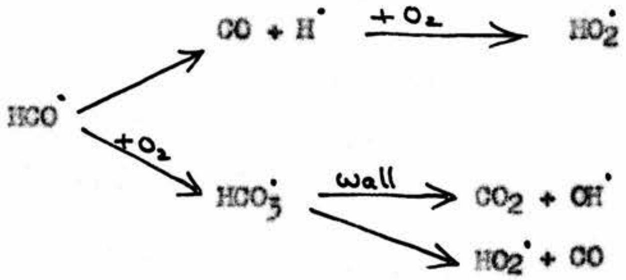
$$H\dot{C}O + O_2 \longrightarrow H\dot{O}_2 + CO$$

since there is so much doubt about the dissociation energy of the C-H bond in the formyl radical. Gorin (84) has given 26 kcals as an upper limit so that it is very probable that the reaction is quite exothermic. A possible explanation of the formation of small quantities of hydrogen towards the end of the reaction is that, at that time, the chance of a successful $\dot{H} + O_2$ collision will be smaller and hydrogen may be formed by reaction with cyclopropane molecules of hydrogen atoms formed by decomposition of formyl radicals. In addition, due to depletion of the oxygen present, the probability of unimolecular decomposition of formyl will be greater under these circumstances. A similar explanation of the production of small amounts of methane is possible due to hydrogen abstraction reactions of methyl radicals.

Another possible reaction of the formyl radical would be to add oxygen.

$$H\dot{C}O + O_2 \longrightarrow HCO_3^{\cdot}$$

The formylperoxyl radical thus formed might diffuse to the walls to decompose to carbon dioxide and a hydroxyl radical. This would explain the appearance of carbon dioxide in the end-products of the oxidation. It is, indeed, possible that the formation of hydroperoxyl radicals from formyl radicals occurs by a similar process. The destruction of the latter would then be represented:-



Disregarding the unimolecular decomposition which will not affect the kinetics of the maximum rate, the removal of formyl radicals will then depend upon the pressures of formyl and oxygen.

As to the likelihood of the participation of hydroperoxyl radicals in the reaction, it is important to consider the similarity between the methane and cyclopropane oxidations. In both, formaldehyde is the essential intermediate and there is very strong evidence that, in the former reaction, the radical responsible for the initiation of the secondary chain is the hydroperoxyl (87, 89). Walsh et al. arrived at this conclusion as a result of their study of the lead oxide inhibition of the combustion. The coating of a reaction vessel with lead oxide has been found to inhibit the slow combustion of cyclopropane (90). The $\dot{HO_2}$ radicals produced by the branching reaction will initiate the secondary chains by producing cyclopropyl radicals from the hydrocarbon by the reaction:

$$C_3H_6 + \dot{HO_2} \longrightarrow \dot{C_3H_5} + H_2O_2 \quad - 1 \text{ kcal.}$$

The endothermicity of this reaction was calculated from Walsh's estimate of the bond dissociation energy $D(HO_2-H) = 96$ (22).

Little can be said about the fate of the hydrogen peroxide thus formed although it probably decomposes heterogeneously to water and oxygen (88).

The non-branching reactions of formaldehyde probably involve its reaction with hydroperoxyl and hydroxyl radicals (thus explaining the facility of the non-branching reactions compared with the branching reaction). Thus

$$CH_2O + HO_2^{\cdot} \longrightarrow CHO^{\cdot} + H_2O_2 + 17 \text{ kcals. followed by}$$

$$CHO^{\cdot} + O_2 \longrightarrow CO + HO_2^{\cdot}$$

The nett effect is $CH_2O + O_2 \longrightarrow CO + H_2O_2$.

Thus there is no increase in the number of radicals consequent upon that non-branching reaction. The same is true for the reaction of hydroxyl with formaldehyde, although the nature of the radical changes.

$$CH_2O + OH^{\cdot} \longrightarrow CHO^{\cdot} + H_2O + 39 \text{ kcals.}$$

$$CHO^{\cdot} + O_2 \longrightarrow CO + HO_2^{\cdot}$$

These reactions are not complex changes and are suitably exothermic and since the overall effect in each case is the oxidation of formaldehyde by oxygen to inert products (catalysed by a radical), together they constitute a non-branching mechanism of intermediate-removal as required by the Semenov scheme of degenerate chain branching.

The reaction steps, so far discussed, form the basis of a reaction scheme for the slow combustion of cyclopropane. They are all chemically probable and involve simple molecules and radicals whose participation in similar reactions has often been suggested. Furthermore, the scheme explains the function of formaldehyde as degenerate chain branching intermediate. It remains to discuss possible chain initiation and chain termination reactions. Very little can be said about the former since it is almost certainly a heterogeneous reaction but it might well involve the reaction of cyclopropane with oxygen on the walls (possibly to form cyclopropyl and hydroperoxyl radicals). No initiation reaction has been included in the complete scheme. It is very doubtful if chain termination reactions could be justified experimentally but they are necessary if the scheme of reactions is to yield a rate expression. The experimentally-determined rate expression indicated that the termination of the chains involves destruction of chain carriers by reaction with either cyclopropane or oxygen and that one or both of these reactions occurs on the surface. Since the secondary chain initiation depends upon the presence of hydroperoxyl radicals and in view of Walsh's conclusions about the importance of termination by $HO_2^{\cdot}$ destruction in the methane oxidation, the following termination reactions are suggested:-

$C_3H_6 + HO_2 \longrightarrow$ Inactive products.

$O_2 + HO_2 \longrightarrow$ Inactive products.

The difficulty is, of course, to name these inactive products. The first, particularly if it occurred at the walls of the vessel, might lead to very great structural changes. Reactions similar to this one and equally vague have been postulated in reaction schemes referring to hydrocarbon combustions in the "low-temperature" region (e.g. 61). The second termination step above may possibly be explained in the following way. A hydroperoxyl radical diffusing to the wall may alight close to an adsorbed oxygen molecule. The resulting complex can be represented thus:-

$$O_2 - - -H- - -O_2$$

i.e. there is resonance between the two canonical forms

$$\dot{O}_2\text{-}H \quad O_2 \qquad \text{and} \qquad O_2 \quad H\text{-}\dot{O}_2$$

On the approach of a second hydroperoxyl radical the following reaction ensues:-

$$O_2- - -H- - -O_2 + H\dot{O}_2 \longrightarrow 2O_2 + H_2O_2$$

The rate-determining step of this termination reaction will be the first whose efficiency will depend upon the oxygen gas pressure if the extent of oxygen adsorption is small.

With the exception of the questionable primary initiation reaction the reactions are collected into a single scheme below.

1. $C_3H_6 + H\dot{O}_2 \longrightarrow C_3\dot{H}_5 + H_2O_2 - 1$ kcal.
2. $C_3H_6 + O\dot{H} \longrightarrow C_3\dot{H}_5 + H_2O + 21$ kcals.
3. $C_3\dot{H}_5 + O_2 \longrightarrow C_3H_5\dot{O}_2 \rightarrow CO + CH_2O + C\dot{H}_3 + 57$ kcals.
4. $C\dot{H}_3 + O_2 \longrightarrow CH_3\dot{O}_2 \rightarrow CH_2O + O\dot{H} + 50$ kcals.
5. $CH_2O + O_2 \longrightarrow CH\dot{O} + HO_2 - 23$ kcals.
6. $CH_2O + H\dot{O}_2 \longrightarrow CH\dot{O} + H_2O_2 + 17$ kcals.
7. $CH_2O + O\dot{H} \longrightarrow CH\dot{O} + H_2O + 39$ kcals.
8. $CH\dot{O} + O_2 \longrightarrow CO + H\dot{O}_2 + 30$ kcals.
9. $C_3H_6 + H\dot{O}_2 \longrightarrow$ inactive products
10. $O_2 + H\dot{O}_2 \longrightarrow$ inactive products

Before any theoretical relationships can be derived from this scheme it is necessary to make two assumptions. The first is, that at the time of attainment of the maximum rate, a stationary state can be supposed for all radicals and for formaldehyde (experiment showed that the rate of formation of the aldehyde was equal to its rate of removal at the time of the maximum rate). The second is that the pressures of reactants remaining at that time are proportional to their initial pressures. This can be shown for the oxygen pressures.

Analysis showed $(\Delta p_{O_2})_t \propto (\Delta p)_t$

$\therefore$ At time $\theta$ $(\Delta p_{O_2})_\theta \propto \Delta p_{max.}$

But by experiment $\Delta p_{max} \propto p_{O_2}$ (initial)

Hence $(\Delta p_{O_2})_\theta \propto p_{O_2}$ (initial)

i.e. $(\Delta p_{O_2})_\theta = K p_{O_2}$ (initial)

But $(\Delta p_{O_2})_\theta = p_{O_2}$(initial) $- p_{O_2}$ (at time $\theta$ ).

$\therefore p_{O_2}$(at time $\theta$ ) $= (1-K)\ p_{O_2}$ (initial).

It is not possible to demonstrate the existence of a similar expression for the cyclopropane pressure at the time of the maximum rate but inspection of the results of analyses carried out under quite different conditions shows that $\dfrac{p_{cp}\text{ (at time }\theta\text{ )}}{p_{cp}\text{ (initial)}}$ is constant within the limits of experimental error.

The partial justification of the two assumptions makes it possible to attempt some deduction of the kinetics of the reaction. Calling the formaldehyde pressure (F) and the cyclopropane pressure (C), we have (disregarding the less important formaldehyde removal by reaction 5)

$$\frac{d(F)}{dt} = k_4(CH_3)(O_2) + k_3(C_3H_5)(O_2) - k_6(F)(HO_2) - k_7(F)(OH)$$

At the time of the attainment of the maximum rate, $\frac{d(F)}{dt} = 0$

and $k_4(CH_3)(O_2) = k_3(C_3H_5)(O_2)$

Then $2k_3(C_3H_5)(O_2) - k_6(F)(HO_2) - k_7(F)(OH) = 0$ (1)

Applying the method of the stationary state to the cyclopropyl radicals, we obtain $(C_3H_5) = \frac{k_1(HO_2) + k_2(OH)}{k_3(O_2)}(C)$ (2)

Substitution of (2) in (1) yields the expression

$$\left\{2\,k_1(HO_2) + 2k_2(OH)\right\}(C) = k_6(F)(HO_2) + k_7(F)(OH)$$

i.e. at the time of attainment of maximum rate

$$(F) = (F)\ \text{max.} = 2\ \frac{k_1(HO_2) + k_2(OH)}{k_6(HO_2) + k_7(OH)}(C)_{\text{max.}} \qquad (3)$$

Now $\frac{d(OH)}{dt} = k_4(CH_3)(O_2) - k_2(C)(OH) - k_7(F)(OH)$

$$= k_1(C)(HO_2) + k_2(C)(OH) - k_2(C)(OH) - k_7(F)(OH)$$

$$= k_1(C)(HO_2) - k_7(F)(OH)$$

At time $\theta$, $(OH) = \frac{k_1(C)_{\text{max.}}(HO_2)}{k_7(F)\ \text{max.}}$ (4)

Substitution of (4) in (3) gives

$$(F)\ \text{max.} = 2\ \frac{k_1(HO_2) + \frac{k_1k_2(C)(HO_2)}{k_7(F)\ \text{max.}}}{k_6(HO_2) + \frac{k_1(C)(HO_2)}{(F)\ \text{max.}}}(C)\text{max.}$$

$$= 2\ \frac{k_1k_7(F)\ \text{max} + k_1k_2(C)\ \text{max}}{k_6k_7(F)\ \text{max} + k_1k_7(C)\ \text{max}}\ (C)\text{max.}$$

$$\therefore k_6k_7(F)^2_{\text{max}} + k_1k_7(C)_{\text{max}}(F)_{\text{max}} = 2k_1k_7(C)_{\text{max}}(F)_{\text{max}} + 2k_1k_2(C)^2_{\text{max}}$$

i.e. $k_6k_7(F)^2_{\text{max}} - k_1k_7(C)_{\text{max}}\ (F)_{\text{max}} - 2k_1k_2(C)^2_{\text{max}} = 0.$

This equation has two solutions for (F)max, one of which is not admissible. The other is:-

$$(F)\text{max} = \frac{k_1k_7 + \left(k_1^2k_7^2 + 8k_1k_2k_6k_7\right)^{\frac{1}{2}}}{2k_6k_7}\,(C)\text{max}.$$

i.e. (F)max = B(C) initial, where B includes a factor to account for the proportionality between (C) initial and (C) max. This result is in accord with the experimental finding that the maximum formaldehyde pressure attained during the reaction was proportional to the initial cyclopropane pressure and, except at very low oxygen pressures, independent of the initial oxygen pressure. Due to the extremely complex nature of the proportionality constant B, nothing can be said about the significance of the observed temperature coefficient with respect to the activation energies of the elementary reactions in the scheme.

The next deduction is of the theoretical relationship between the rate of the reaction and the reactant pressures. From the suggested scheme, one may write:-

$$\frac{-d(C)}{dt} = k_1(C)(HO_2) + k_2(C)(OH)$$

$$\left(-\frac{d(C)}{dt}\right)_{\text{max}} = k_1(C)\text{max}(HO_2) + \frac{k_1k_2(C)^2_{\text{max}}(HO_2)}{k_7(F)\text{max.}}$$

$$= k_1\left(1 + \frac{k_2}{k_7B}\right)(C)\text{max}(HO_2) \qquad (5)$$

Now $$\frac{d(HO_2)}{dt} = k_5(F)(O_2) + k_8(CHO)(O_2) - k_1(C)(HO_2) - k_6(F)(HO_2) - k_9(C)(HO_2) - k_{10}(O_2)(HO_2)$$

And $k_8(CHO)(O_2) = k_5(F)(O_2) + k_6(F)(HO_2) + k_7(F)(OH)$ at the maximum rate, And $k_7(F)(OH) = k_1(C)(HO_2)$ at the maximum rate,

and $(F) = B\,(C)\,\mathrm{max.}$ at the maximum rate.

$$(HO_2) = \frac{2k_5B(C)\mathrm{max}\,(O_2)\mathrm{max}}{k_9(C)\mathrm{max} + k_{10}(O_2)\mathrm{max}}$$

Substituting for $(HO_2)$ in equation 5 and making use of the relations between the initial reactant pressures and those at the time of the maximum rate, we obtain the equation:-

$$\left(-\frac{d(C)}{dt}\right)_{\mathrm{max}} = \frac{K_1(C)^2(O_2)}{K_2(C) + K_3(O_2)}$$ referring to initial pressures.

But it was proved by analysis that the rate of removal of cyclopropane at any time was proportional to the rate of pressure increase at that time. $\therefore \left(-\frac{d(C)}{dt}\right)_{\mathrm{max}} \propto \mathcal{J}_{max}$

$$\therefore \mathcal{J}_{max} \propto \frac{K_1(C)^2(O_2)}{K_2(C) + K_3(O_2)}$$

Comparison of this with the experimentally-determined rate expression is very favourable. In a general way the kinetic behaviour is explained, although nothing can be said regarding the overall activation energy of the reaction. The above proportionality does not include a term dependent upon the surface but since both the termination reactions are probably surface dependent such a term is unnecessary.

The importance of the surface in the slow combustion of cyclopropane suggests that valuable conclusions might be drawn from the results of experiments in vessels with different surfaces i.e. coated with different materials. If such experiments were performed, it might prove possible to state the initiation and termination reactions with more certainty.

Another aspect of the work, worthy of further investigation, is the effect of adding water vapour to the reaction mixture. The results obtained, so far, show a distinct positive catalytic effect. It may be that the water, in some way, facilitates the branching reaction but since the effect of adding more water became less and less, it is possible that it is due to deactivation of the surface as a chain terminator. The termination reactions suggested in the reaction scheme require the presence of oxygen (and probably also cyclopropane) on the walls so that, if water were preferentially adsorbed, the effect would be explained.

It is not possible to deduce from the scheme a theoretical expression for the induction period in terms of reactant concentrations. It was hoped to use the relationship:-

$$= k_5(\nu - 1)(F)(O_2) - k_6(F)(HO_2) - k_7(F)(OH)$$

to deduce the net branching factor in those terms but this is, unfortunately, impossible since the net branching factor refers to the early stages of the reaction where there is certainly no stationary concentration of the radicals.

## SUMMARY

The reaction between cyclopropane and oxygen has been investigated by the static method in the temperature range 380° to 430°C, and with partial pressures of the reactants between 40 and 400 m.m. There is an initial period of negligible pressure change, the rate then accelerating exponentially to a maximum. The kinetics of the reaction have been studied by measurement of rate of pressure change and analysis has shown that this is equivalent to the rates of removal of the reactants and of formation of the products which are mainly carbon monoxide and water.

The three rate characteristics - the maximum rate ($\rho$ max), the net branching factor (A') and the induction period ($\theta$ or $\Upsilon$ ) — obtained from the pressure-time curves, have been found to be surface-sensitive. Hydrogen has an inhibiting effect which is probably due to the removal of some reaction product from the vessel walls. The addition of nitrogen has no effect but the addition of water vapour leads to some increase in $\rho$ max and A' and to a reduction in $\theta$, again probably due to a surface effect.

With lower oxygen pressures the maximum rate is proportional to both the oxygen and cyclopropane pressures, while with higher oxygen pressures it varies as the square of the hydrocarbon pressure and is independent of the oxygen pressure. Which rate expression obtains, is shown to depend

upon the temperature and relative reactant pressures. The variation of the net branching factor is similar to that of the maximum rate but the reciprocal induction period always varies as the product of the cyclopropane and oxygen pressures. The overall activation energies for maximum rate and net branching factor are about 35 kcal., and for reciprocal induction period about 53 kcal. When cyclopropane is in excess the total pressure change is approximately half the initial oxygen pressure, and the pressure change preceding the attainment of the maximum rate is proportional to the oxygen pressure, independent of the pressure of cyclopropane, varies somewhat from vessel to vessel and exhibits a small temperature effect.

The products of the oxidation responsible for the increase of pressure are extremely simple, the only unstable intermediate detectable being formaldehyde whose pressure reaches a maximum at about the time of the maximum rate, the variation of its concentration parallelling the variation of rate of pressure change. The maximum pressure of formaldehyde is proportional to the initial cyclopropane pressure and, except at very low oxygen pressures, is independent of the oxygen pressure. Its variation with reaction temperature corresponds to an energy of activation of 10·5 kcal. The addition of small quantities of formaldehyde to the system leads to a drastic curtailment of the induction period and the pressure increase may commence only a few seconds after admission of the last reactant.

The results are discussed from the general point of view that the reaction involves a chain mechanism with degenerate

branching, and it is shown that the initiation step is probably heterogeneous. The kinetic characteristics of the reaction are compared with those of the slow combustion of other hydrocarbons and a mechanism is advanced. This involves the propagation of the primary reaction chain by cyclopropyl and hydroxyl radicals and the slow-branching intermediate is identified as formaldehyde which can react with oxygen to form hydroperoxyl radicals which, in turn, initiate the primary chain. The non-branching reactions of formaldehyde are believed to involve hydroxyl and hydroperoxyl radicals. Possible termination reactions are suggested and all the reaction steps have been shown to be sterically and energetically feasible. Application of the method of the stationary state to the formaldehyde and radicals at the time of the maximum rate leads to the deduction of the experimentally-determined relationships between the maximum formaldehyde pressure and the maximum rate and the initial reactant pressures. The proposed reaction scheme also explains the formation of the products, including the small amounts of carbon dioxide, methane and hydrogen also found.

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