THE ABSTRACT

of a thesis titled

Mechanism of Gaseous Reactions

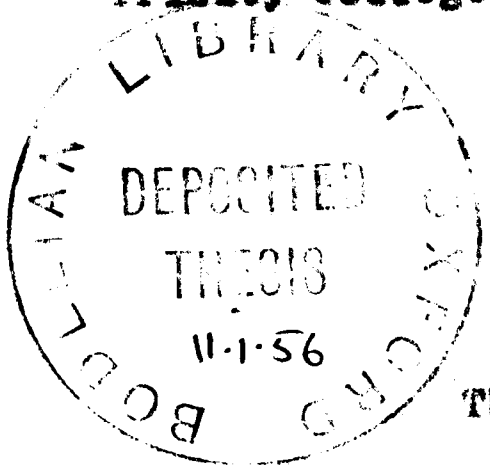
The oxidation of the Lower Aliphatic Ketones and Propane

submitted for the degree of Doctor of Philosophy
in the University of Oxford

by

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Trinity College



Trinity Term
1955

The Physical Chemistry
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ABSTRACT

The thesis describes an investigation of the gas phase oxidation of the lower aliphatic esters and of propane. The kinetics of the oxidation of methyl, ethyl, and propyl formate, methyl acetate, methyl propionate and methyl butyrate were determined at various temperatures from 280° to 450°C. The experiments were made in a silica reaction vessel and the pressure changes accompanying oxidation were followed on a mercury manometer. The pressure-time curves usually showed an induction period after which the rate of change of pressure in the reaction vessel increased up to a maximum.

Two temperature ranges of reactivity were observed with ethyl and propyl formate, methyl butyrate and propane. The rate of oxidation increased smoothly with increasing temperature up to about 350°C. Between 350° and 400°C. the rate decreased rapidly with an increase in temperature. Above 400°C. the rate increased continuously until ignition occurred.

At all temperatures, an increase in the initial concentration of the combustible material increased the rate of oxidation and decreased the induction period.

In the high temperature region an increase in the oxygen concentration similarly increased the rate of oxidation. In the low temperature region the rate of oxidation was independent of the oxygen concentration. Except at very low partial pressures of oxygen the induction period was independent of the oxygen concentration in both the low and high temperature regions.

A mass spectrometer was used to analyse the combustion gases for the unchanged ester (or propane), for residual oxygen, and for the amount of carbon monoxide and carbon dioxide formed. At all temperatures the concentrations of the major constituents were directly proportional to the pressure changes measured in the reaction vessel. Sufficient experiments were made to establish the pressure measurements as a true measure of the oxidation process. Chemical and polarographic analyses were made for formaldehyde, acetaldehyde, total acid and peroxide substances. In each case the concentration of the intermediate species passed through a maximum as the reaction went to completion. No significant oxidation was detected during the induction period.

The outstanding feature of the general kinetics of the esters was the marked dependence of the rate of oxidation, in the low temperature region, on the

molecular structure of the combustible material. An increase in the carbon chain length increased the rate of oxidation much more than would have been expected from the normal organic chemistry of a homologous series. The effect was most pronounced between the esters of higher molecular weight. An increase in the carbon chain length on the ethereal side of the ester configuration had a much greater effect than a corresponding increase on the carbonyl side. Where only methyl groups, and no methylene groups occurred, the ease of oxidation was greatly reduced.

The kinetic results are interpreted in terms of a series of reaction steps analogous to those proposed by Cullis and Hinshelwood for paraffin oxidation. The scheme postulates the formation of peroxide substances capable, in the low temperature region, of decomposition and the propogation of a branching chain reaction. The rate expression for the oxidation reaction is of the form

$$\frac{f([O_2],[RH])}{1 - 2kP}$$

The remarkable effects of the substituent groups are attributed largely to the effect of the structural changes on the rate of decomposition, k , of the peroxide species. The theories of Walsh and Norrish are discussed in relation to the experimental evidence of the present investigation.

The analytical investigation of the cool flame mixtures of propane indicated that the products of cool flame combustion are very similar to those detected in the low temperature region of oxidation. The changes in the concentrations of the initial reagents and final products followed the same pattern as that observed at lower temperatures. The polarograms of the combustion samples collected immediately before, and after, the occurrence of a cool flame, showed a marked decrease in the concentration of peroxide material with the explosion.

The analyses support the theory of Hardwell and Hinshelwood, that cool flames result from the self-heating of the gas mixture by the thermal decomposition of the peroxide intermediates. The general scheme proposed is

$$R\text{-} + O_2 = ROO\text{-}$$

$$ROO\text{-} + RH = ROOH + R\text{-}$$

$$ROOH = RO\text{-} + \text{-}OH$$

where the temperature coefficient of the rate of decomposition of the peroxide is greater than that of the rate of formation. If the decomposition reaction is highly exothermic, under appropriate conditions of concentration and reaction temperature, self-heating would be expected, and the rate would increase rapidly until the peroxide substances are largely consumed.

MECHANISM OF GASEOUS REACTIONS

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INTRODUCTION

The present investigation is concerned with the gaseous oxidation of a series of organic esters, methyl, ethyl and propyl formate, methyl acetate, methyl propionate and methyl butyrate. Previous investigations into general combustion phenomena have shown the remarkable dependence of the rate of oxidation, on the one hand, on the reaction temperature, and on the other hand, on the molecular structure. The study of the oxidation of the esters is proposed as an extension of these investigations. In the following few pages brief summaries of the experimental facts and theoretical considerations of oxidation chemistry are presented as an introduction to the field.

Summary of the Experimental Facts

Many of the experimental effects of combustion are common to a great variety of normal and substituted hydrocarbons. Recently both normal and branched-chain paraffins have been studied in England (1-3), and in the United States (4). Some attention has also been focused on the oxidation of ketones (5-8) and olefines (9-10).

Several of the features of these and other investigations are:

1. The combustion of hydrocarbons may proceed either explosively or at a measurable rate. The main conditions determining the rate of reaction are the temperature and the concentrations of the reagents.

2. Under non-explosive conditions, the progress of the oxidation may be followed by the measurement of the change of pressure in the reaction vessel (11-13). There is usually an induction period after which the rate increases to a maximum. The maximum rate of pressure change is usually regarded as the most significant measure of the rate of oxidation.

3. An increase in the temperature does not always result in an orderly increase in the rate of oxidation. With many substances the rate increases normally up to 350°C., then decreases very quickly over perhaps a fifty degree range and thereafter increases up to the point where ignition occurs. The two regions of positive temperature effect are usually called the low and high temperature regions.

4. At all temperatures the maximum rate increases and

the induction period decreases with an increase in the concentration of the combustible material. In the low temperature region the rate of oxidation and the induction period are frequently independent of the oxygen concentration. In the high temperature region the maximum rate is usually directly proportional to the pressure of oxygen in the reaction vessel.

5. An increase in the surface to volume ratio of the reaction vessel may retard the rate of reaction.

6. The induction period can be reduced considerably by the addition of an inert gas, of peroxides or of acetaldehyde. An increase in the temperature generally shortens the induction period, but over certain ranges of temperature, the opposite effect has been observed.

7. Carbon monoxide, carbon dioxide, acids and water are the principal end products of the oxidation reaction. Peroxides and aldehydes have been shown to be present during the reaction, but do not appear as end products.

8. At temperatures well below the critical ignition temperature, "cool flames" have been observed to pass through the reaction mixture. Cool flames occur with all the paraffins from propane upwards and with all the aldehydes from acetaldehyde upwards, (14). Cool flames are usually pale blue in colour and travel

very slowly through the mixture. They give only a small overall pressure rise and analysis reveals many substances intermediate to complete combustion, such as peroxides and aldehydes. Cool flames rarely deposit carbon in the reaction vessel.

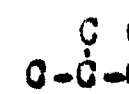
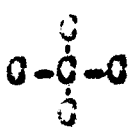
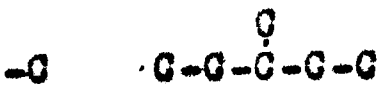
Hot flames or explosions, on the other hand, usually give rise to a white or yellow emission and develop much greater pressure changes. Intermediate compounds occur only in small amounts after a hot flame. Carbon is frequently deposited throughout the reaction system.

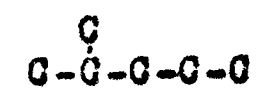
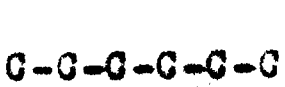
Emeléus (15), succeeded in recording the spectra of the cool flames of diethyl ether, acetaldehyde, propanaldehyde and hexane, and found they were all identical. For some time the emitter of the bands was unknown, but now it has been firmly established as formaldehyde (16).

9. The oxidation process appears to be more sensitive to the structure of the hydrocarbon than the simple decomposition reaction (17). The experimental results of Cullis, Mulcahy and Hinshelwood (23,18) show that the rate of oxidation increases with extraordinary rapidity with an increase in the chain length of the paraffin:

Compound	Rate of Oxidation, relative to Pentane
Propane	0.1
Butane	0.5
Pentane	1.0
Hexane	7.5
Octane	200.
Decane	1380.

and decreases considerably with the degree of branching:

			
relative oxidation rate	1	12	60

		
	560	1580

In the case of ethane, acetone and di-methyl ether, where there are only methyl groups the maximum rate is very much lower than the rate of the corresponding compound containing a methylene group.

The substitution of chlorine into the molecule increases the oxidation rate (19), and carbonyl and amino groups (20) likewise tend to increase oxidizability. Ethers are also much more easily oxidized than the paraffins (21), diethyl ether reacting about 2500 times as rapidly as pentane.

The overall effects of the carbonyl and amino groups is small, relative to the effect of an additional methylene group in the carbon skeleton. Acetone oxidizes

more slowly than propane, but about twenty times as fast as ethane. The slower rate relative to propane is attributed to the destruction of the CH_2 group. The effect of the amino group is greatest with ethane, where the symmetry of a methyl group is destroyed and a CH_2 group appears in the molecule.

Theories of the Oxidation Process

The present investigation is primarily concerned with the mechanism of the oxidation process as it occurs in the low temperature region. Semenov (22) introduced the broad principles of chain branching to the theory of low temperature oxidation in 1935. Some years later Cullis and Hinshelwood (2) attempted to bring the foundations of this theory into closer relationship with the remarkable temperature and structural effects described in the previous section. Before the various experimental features of gaseous oxidation were thoroughly investigated, several theories were proposed involving rather complex rearrangement and substitution reactions. These theories have been reviewed by Cullis (23) and Walsh (24), but mention of one or two of them seems to be in order, if only to show the background leading to the development of the chain branching theory.

1. <u>The Pope, Dykstra and Edgar Theory</u>(25)

The theory supposed that paraffins are oxidized through the medium of higher aldehydes which are in turn degraded step by step to lower aldehydes.

$RCH_2CHO + O_2 = RCHO + CO + H_2O = \ldots\ldots\ldots\ldots$

$\ldots\ldots\ldots = HCHO + CO + H_2O$

These beliefs were founded on the remarkable similarity between the oxidation of paraffin hydrocarbons and aldehydes and the frequent occurrence of aldehyde species as intermediate products.

The theory has been criticised(24) on the basis that several reactions are known where higher aldehydes than formaldehyde have not been observed. To explain the formation of formaldehyde it is necessary to postulate a "non-stop-run" through the higher aldehyde stages. The theory also supposes the initial attack to occur at the end methyl group. Both Grun(26) and Burwell(27) in the very early stages of the research concluded from the nature of the products that oxygen tended to enter a carbon chain at a point removed as far as possible from a methyl group.

Walsh(14) has examined the energetics of the degradation in some detail. He concludes that where cool flames occur the theory does not allow for the formation of formaldehyde in a sufficiently excited state for the emission of light.

Lewis and von Elbe in 1938 (28) modified the scheme to a degradation of radicals instead of molecules.

$$RCH_2\dot{C}O + O_2 = R\dot{C}O + CO + H_2O = \ldots\ldots\ldots\ldots\ldots\ldots\ldots = CH_3\dot{C}O + CO + H_2O$$

To explain the formation of excited formaldehyde, they postulate a different reaction for CH_3CO,

$$CH_3\dot{C}O + O_2 = HCHO + CO + \text{-}OH$$

which they consider to be exothermic to the extent of 110 Kcals.

This modification has also been criticised (24) as it implies the same point of attack as the molecular scheme, and that CH_3CO radicals decompose into methyl radicals and carbon monoxide almost instantaneously at all temperatures above 60°C.

Both degradation schemes also predict the formation of a ketone when the reaction reaches a branch in the chain.

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!\dot{C}HCHO + O_2 = \begin{matrix} R \\ R' \end{matrix}\!\!>\!CO + CO + H_2O$$

Beatty (29) was unable to find any ketones during the slow oxidation of 2,5 dimethyl hexane, and Walsh reports the occurrence of ketones during the oxidation of straight chain fuels.

The same sort of difficulties arise with almost every "simple" free radical or molecular mechanism. The structural sensitivity and temperature effects appear to be only compatible with a branching chain theory.

2. The Theory of Cullis and Hinshelwood (2)

The essential intermediate of the oxidation of hydrocarbons at low temperatures is assumed to be a dialkyl peroxide. Peroxide substances have been detected by many workers as early products of partial combustion (30), and others have related the presence of peroxides to phenomena such as "knock". Several of the earlier researches (Bone and co-workers) report no such species, but it was not realized at that time that the titanium reagent, which affords such a sensitive test for hydrogen peroxide is not equally sensitive to organic peroxides (14,30).

The formation of the dialkyl peroxide is ascribed to the following series of reaction steps:

$$RH + O_2 = R\text{-} + HO_2 \qquad (1)$$

the rate being ϕ

$$R\text{-} + O_2 = ROO\text{-} \qquad (2)$$

$$ROO\text{-} + RH = ROOR \qquad (3)$$

$$ROO\text{-} + RH = \text{relatively inactive products} \qquad (4)$$

The reaction between ROO- radicals and hydrocarbons may yield a number of different peroxides, depending on the point of attack, and some of these may be less effective than others in continuing the oxidation process. Step (4) is intended to include such comparatively unfruitful reactions.

The active peroxide ROOR may decompose in two different ways, either by a branching reaction:

$$ROOR = 2RO- \quad (5)$$

or by a non chain degradation:

$$ROOR = \text{inactive products} \quad (6)$$

The radical RO is assumed to decompose to yield an aldehyde and a lower alkyl radical R'-, e.g.

$$RO- = R'- + CH_2O \quad (7)$$

This radical may then react with RH regenerating R-

$$R'- + RH = R'H + R- \quad (8)$$

or it may react with oxygen

$$R'- + O_2 = R'OO- \quad (9)$$

This scheme is somewhat simplified by making use of the experimental fact that the rate of oxidation decreases very markedly with diminishing numbers of carbon atoms. Thus it is permissible to neglect the contribution to chain branching arising from further reaction of the radical R'OO- , and step (9) may be treated as a chain breaking reaction.

A scheme such as the above, in which a relatively stable intermediate substance may decompose in two ways, one of which can eventually regenerate the intermediate itself, has been designated a "degenerate" branching process by Semenov, who has discussed the generalized kinetics of such reactions (22). The development of the

rate under conditions of degenerate branching may lead either to a "stationary" or to a "non-stationary" reaction, depending upon whether the rate of regeneration of the intermediate is less than or greater than its rate of destruction. In applying the above reaction scheme to the oxidation of pentane and hexane, Cullis and Hinshelwood consider the reaction to be of the "stationary type" and obtain the following expressions for the rate of reaction:

$$\rho = \rho_{max}(1 - e^{-At}) \qquad (I)$$

$$\rho_{max} = \frac{2k_5 \left(\frac{k_3}{k_3 + k_4}\right) \phi}{(k_5 + k_6) - 2k_5 \left(\frac{k_3}{k_3 + k_4}\right)\left(\frac{k_8(RH)}{k_8(RH)+k_9(O_2)}\right)} \qquad (II)$$

"A" is an abbreviation for the denominator in equation II.

The remarkable structural effect observed in combustion phenomena is attributed to the relative stabilities of the labile peroxides. A slight change in the structure of the hydrocarbon will affect the terms $k_3/k_3 + k_4$ and $k_5/k_5 + k_6$ and from the form of the equation, small changes in these would have a greatly magnified effect on the rate.

The theory has also met with some success in interpreting the effect of reactant pressures on the

maximum rate. It has been shown that with suitable choice of numerical values for the rate constants involved in equation II the predicted dependence of the rate on oxygen and hydrocarbon pressures is of the same general form as that found experimentally.

The apparent decrease in reaction rate as the temperature is increased, i.e. during the transition from the low to high temperature regions, is attributed to either step (4) or step (6) of the oxidation scheme. The regenerative yield of the branching reaction would be lowered by either the formation of peroxides incapable of degenerate decomposition or the increased non-chain degradation of the active species.

The higher aldehydes frequently detected as intermediate products are attributed to the decomposition of certain type peroxides:

$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!\diagdown\!\!\diagup CH\text{-}O\text{-}O\text{-}CH_2R_3 \;=\; R_1CHO + R_2\text{-} + HCHO + R_3\text{-}$$

Thus formaldehyde and higher aldehydes could, in appropriate circumstances, be formed in more or less equivalent amounts.

Recently Bardwell and Hinshelwood (7,8) have modified the reaction scheme to the formation of a hydroperoxide rather than a dialkyl peroxide. This slight change does not affect the basic postulates or the mathematical development.

The opposite effects of chain branching and lengthening have been used by Hinshelwood (17) as a means of determining the likely point of initial attack on the carbon skeleton. He ascribes to the methyl group an antagonistic influence of 1.0 unit where it acts at an adjacent carbon atom, 1/3 when at a carbon atom one removed, and 1/9 when at an atom two removed.
Thus in the case of 2, Methyl pentane

$$CH_3\text{-}\overset{\overset{CH_3}{|}}{CH}\text{-}CH_2\text{-}CH_2\text{-}CH_3$$
$$\quad\quad\quad

differences arise on several issues, from the likely transition stages between the high and low temperature regions, to the selection of the probable location of the initial attack on the carbon skeleton.

Walsh postulates two active forms of the peroxide complex, i.e. the hydroperoxide molecule, ROOH , and the peroxide radical, ROO- . In the low temperature region the chain branching reaction is maintained by the decomposition of the hydroperoxide molecule; while at higher temperatures the peroxide radical is imagined as decomposing in a non branching fashion. At intermediate temperatures a negative temperature coefficient would be observed where the radical decomposition reduces the formation of hydroperoxide sufficiently to lower the degree of chain branching.

Rather than postulate wide differences in the stabilities of ROOH and ROO-, Walsh has suggested that at low temperatures the decomposition of the molecule is catalysed by aldehydes. Aldehydes are known to condense with hydroperoxides yielding hydroxy peroxides:

$$ROOH + HCHO = ROOCH_2OH$$

The hydroxy peroxides are probably less stable than the normal hydroperoxide as the result of the withdrawal of electrons from the O-O bond by the OH group.

Subsequent decomposition of the hydroxy peroxide regenerates the initial aldehyde molecule according to:

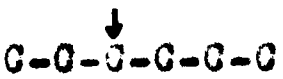
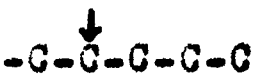
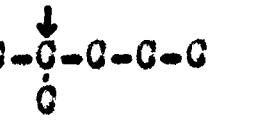
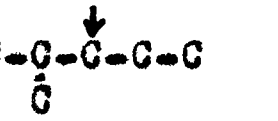
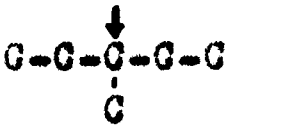
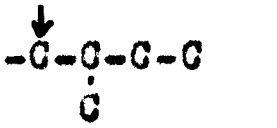
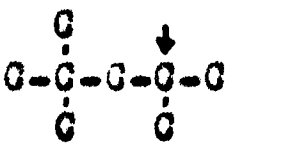
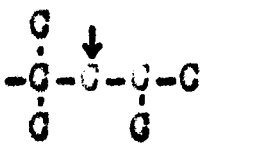
$$ROOCH_2OH = RO\text{-} + \text{-}OCH_2OH$$

$$\text{-}OCH_2OH = HCHO + \text{-}OH$$

and yields the same products of decomposition as the normal hydroperoxide.

Walsh proposes that the initial attack on the carbon skeleton occurs at a tertiary carbon atom, in preference to a secondary, and at a secondary carbon atom in slight preference to a primary. This mode of attack is based on the experiments of Rice,(31) who found at 300°C. that the relative probabilities of attack of alkyl radicals at 1°, 2°, and 3° carbon atoms to be 1:3:33 . At 600°C. the ratios were 1:2:10 .

Recently the ignition behaviour of the hexanes has been re-examined in the United States (4) with the view of comparing the likely point of attack on the carbon skeleton with the observed industrial octane numbers. According to the theories of Hinshelwood and Walsh the point of attack would be as follows:

Compound	Walsh	Hinshelwood
n-hexane		
2-methylpentane		
3-methylpentane		
2,2,4-trimethyl-pentane		

Very close agreement was observed between the minimum ignition temperatures and the methyl retardation factors and the octane numbers.

Compound	M. I.T. C.	methyl retardation factor	octane number
n-hexane	262	0.44	24.8
2-methylpentane	279	1.00	73.4
3-methylpentane	293	1.44	74.5
2,2-dimethylbutane	302	2.00	91.8
2,3-dimethylbutane	318	2.67	101.7
n-octane	249	0.15	below 0.
n-heptane	252	0.22	0.0

It seems remarkable that such a close relationship should exist between data obtained under such markedly different conditions and in entirely different types of apparatus.

4. The Theory of Norrish

Norrish has lately re-examined the combustion intermediates of propane and ethane (32,33). His results are in general agreement with the theory of branching chains, but he was unable to detect any peroxide species other than hydrogen peroxide. He concludes that the critical branching agents in the low temperature region are aldehyde substances.

During the oxidation of propane the concentration of the olefines was observed to increase considerably as the temperature was increased. Norrish supposes an olefine forming chain reaction to operate effectively above 400°C., which could formally "replace" the normal aldehyde-forming reactions and thus, Norrish states, bring about the observed negative temperature coefficient. That is, $CH_3CH_2CH_2- + O_2 = CH_3CH_2CHO + -OH$ is"replaced"by $= CH_3CH{=}CH_2 + HO_2$ and the branching due to the molecular oxidation of the aldehyde is reduced.

Cool Flames

The most significant property of cool flame phenomena appears to be the ability of the flame to repeat itself several times in the same reaction mixture.

Salnikov (34) considers the matter to depend upon a homogeneous reaction of the type

$$A = X = B$$

where the temperature coefficient of the second step is greater than the first. If the step X = B is highly exothermic, marked self-heating may occur and the rate will increase rapidly until X is largely consumed. The temperature then drops, X is built up again and the process is repeated.

Frank-Kamenetzki (35) has proposed a scheme where the periodicity is not ascribed to changes of temperature but to a reaction of one intermediate with another. The reactions supposed are of the type

$$A + X \overset{k_1}{=} B + 2X$$

$$X + Y \overset{k_2}{=} B + 2Y$$

$$A + Y \overset{k_3}{=} B$$

where A is a molecule of the original hydrocarbon

X is an intermediate formed autocatalytically from A

Y is an intermediate formed autocatalytically from X

B represents inert final products

The corresponding rate expressions for X and Y are

$$\frac{dX}{dt} = k_1AX - k_2A\widetilde{Y}X$$

$$\frac{dY}{dt} = k_2XY - k_3AY$$

Initially the formation of Y will not begin until X becomes greater than the value X_k given by

$$k_2XY - k_3AY = 0$$

$$X_k = k_3A/k_2$$

However, X and Y react with each other and an autocatalytic increase of Y eventually leads to a decrease of X . When X falls below its critical value Y begins to decrease and a repetition of the cycle becomes possible. The rate of formation of X changes from positive to negative at the critical value of Y given by

$$k_1AX - k_2XY = 0$$

$$Y_k = k_1A/k_2$$

Where the reaction conditions are not favourable for the occurrence of cool flames the concentrations of X and Y will change periodically about the values of X_k and Y_k.

Frank-Kamenetzki considers X to represent peroxide and Y aldehyde. In a recent review of the theory, Walsh (36) has proposed that Y must be formaldehyde. The experimental basis of this proposal is the fact that formaldehyde frequently lengthens the induction period of paraffin oxidation and acts as an anti-knock in engine fuels.

Bardwell and Hinshelwood (6) have tested the two theories experimentally and have concluded that the theory of Salnikov offers a better explanation. They determined the concentrations of both peroxide and aldehyde species as a function of time between the successive cool flames of butanone. The variation of peroxide concentration resembled a series of exponential curves more closely than a sine wave, and the formaldehyde concentration was scarcely affected by the passage of a cool flame. They also found that the addition of moderate amounts of formaldehyde to the reaction mixture had very little effect on the reaction and that even comparatively large amounts did not appear to inhibit the development of peroxides during the induction period.

EXPERIMENTAL

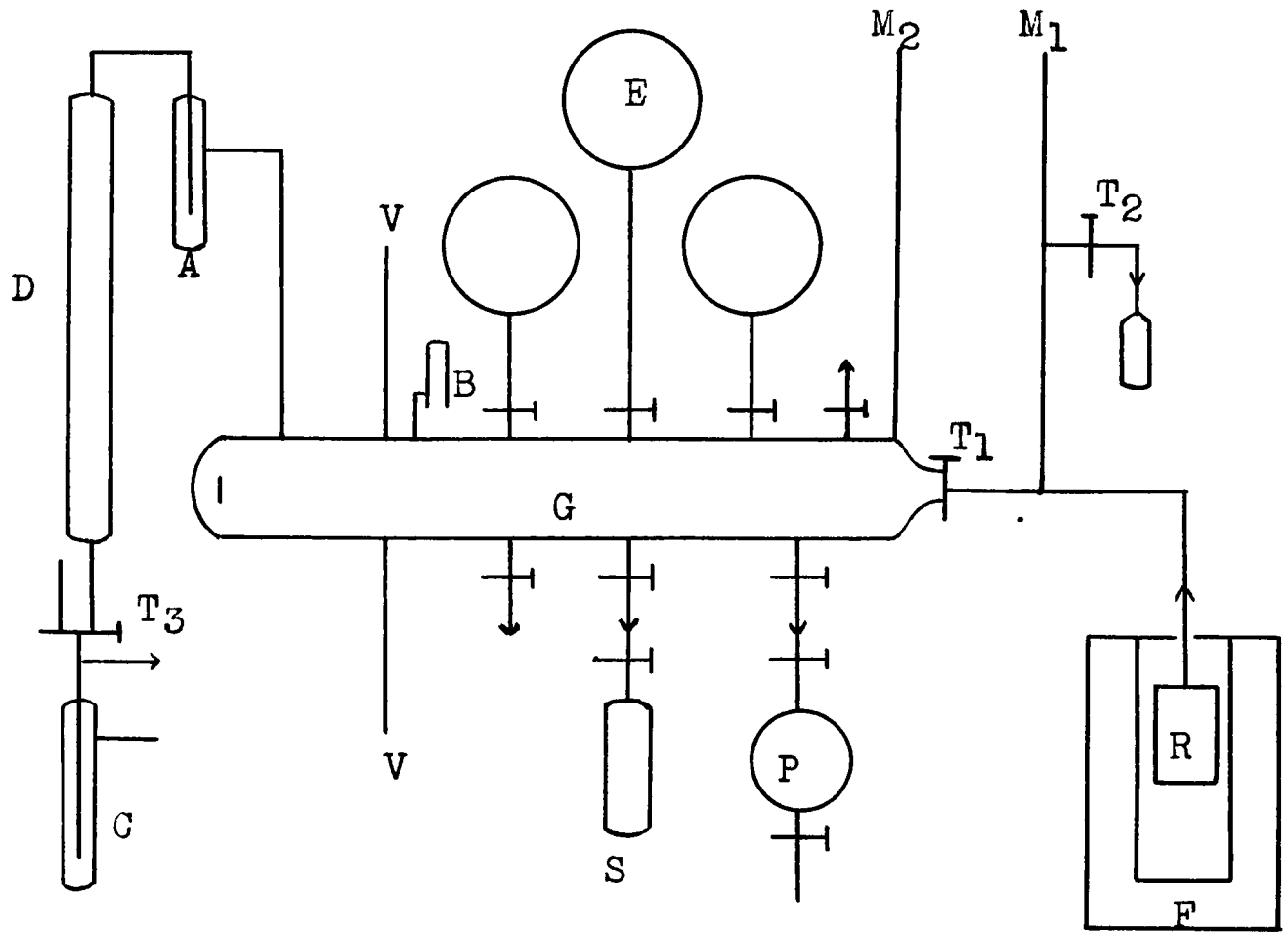
EXPERIMENTAL

Apparatus:

The apparatus used in the present investigation was very similar to those used previously for oxidation studies. The reactant gases were placed in a heated silica reaction vessel and the pressure changes accompanying oxidation were followed on a manometer. For chemical or mass spectrometric analyses the gases in the reaction vessel could be shared with a gas pipette or a sampling globe. A diagram of the apparatus is presented as Figure 1.

The cylindrical reaction vessel was mounted vertically in a well lagged furnace. To reduce the dead space volume of the system the manometer and the short connecting tube to the gallery were constructed of 2mm pyrex capillary. The two-way tap, T_1, permitted the alternate entry of gases to the reaction vessel or the sharing of the reaction mixture with the gas pipette. The combustible material, for the most part ester vapour, was admitted to the reaction vessel from a vial of the liquid attached to the manometer, M_1, at tap T_2. For the experiments with propane the small vial was replaced by a three litre globe.

Figure 1 The Apparatus



A	liquid air trap	S	sampling globe
B	discharge tube	P	gas pipette
C	blow off trap	R	reaction vessel
D	P_2O_5 drying tube	V	vacuum line
E	Storage globes	M_1M_2	manometers
F	furnace	⊣⊢	tap
G	gallery	⊣→	ground joint

To prevent the condensation of the higher boiling esters and reaction products in the dead space portions of the apparatus, it was necessary to heat the affected taps and tubes to approximately 100°C. Electric heating elements were used around the taps and nichrome resistance wire was wound around the tubing. Any reasonable temperature could be obtained by varying the current passed through the coils.

The storage globes, reaction vessel and sampling vessels were evacuated by a two stage mercury diffusion pump backed by a mechanical oil pump. The vacuum was tested with a small "U" shaped discharge tube sealed into the upper gallery. When the pressure in the system was between 10 and 0.1mm. the discharge occurred through the gas in the "U" shaped arm. At pressures below 10^{-2} the discharge occurred across the 7-8mm. air gap between the two terminal electrodes.

When the apparatus was assembled particular care was taken to reduce the temperature gradient across the reaction zone in the electrically operated furnace. Asbestos lagging was packed around the top of the furnace to a depth of three inches. After a few attempts a zone of constant temperature ($\pm$1 degree) was obtained for the full length of the reaction vessel. The temperature of the reaction vessel was measured

with a Pt:RhPt thermocouple pressed against the side of the vessel at approximately the mid point. The reaction zone was maintained at a constant temperature by a "STATEX" thermostatic regulator which operated a simple electronic relay, controlling a portion of the heating current.

Reagents and Purification methods

The principal reagents used in the present investigation were oxygen, propane, helium and the simple organic esters. These were supplied by the British Oxygen Company and the British Drug Houses Ltd.

The esters were dried over anhydrous sodium carbonate, then distilled from phosphorus pentoxide to remove any traces of the corresponding alcohol, according to the procedure of Timmerman (37). The purified ester was poured into a small vial and attached to the apparatus with a cone and socket ground joint. The dissolved air was removed by repeated freezing in liquid air and prolonged pumping. No appreciable quantity of impurity was detectable with the mass spectrometer.

The propane was reported to be 99% pure in the stock reagent and no elaborate purification was attempted. After a preliminary flushing of the P_2O_5 drying tube, D, (See figure 1), the gas was condensed in the trap A, the

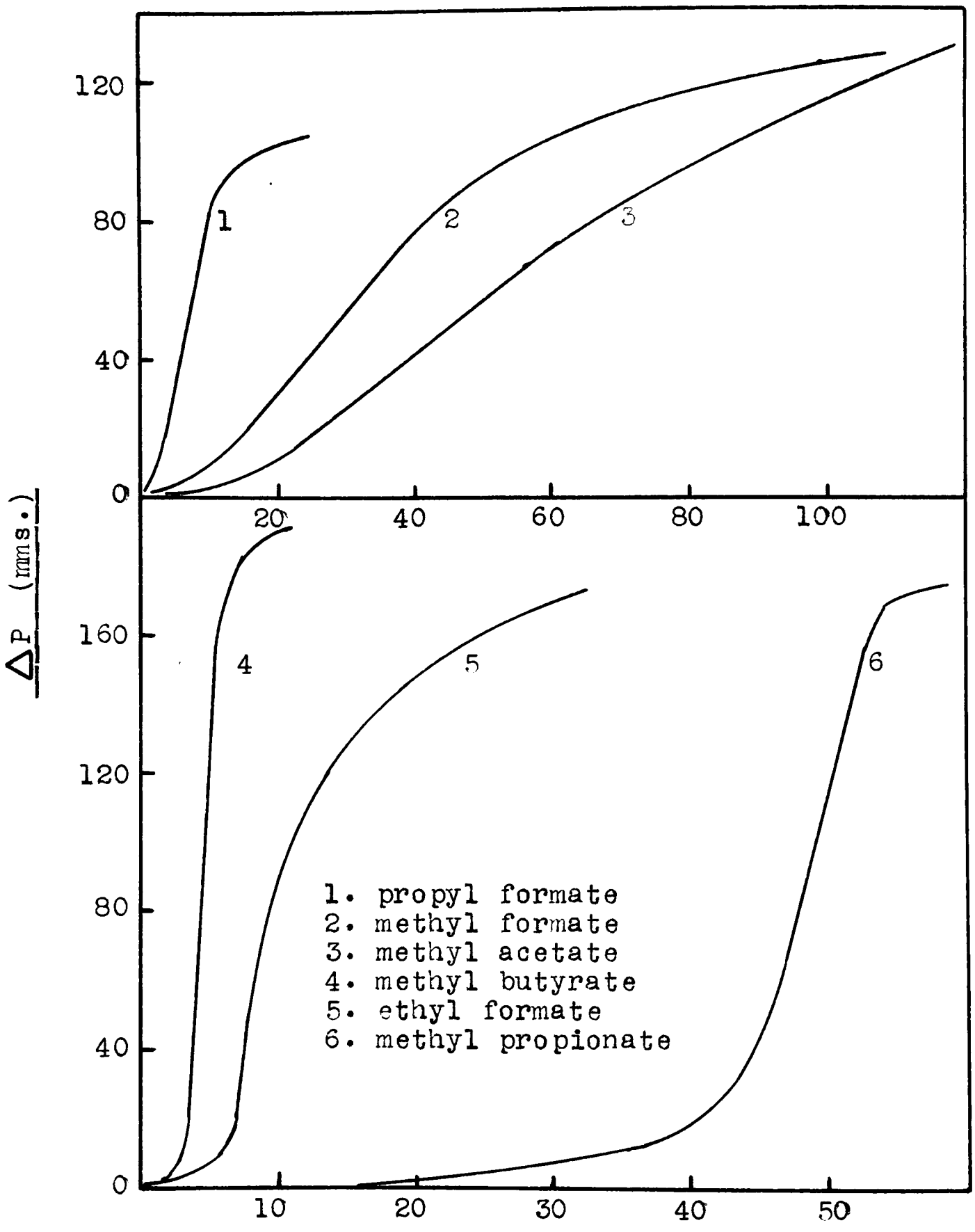
flow rate being adjusted from observation of the level in the blow-off trap, C. When a suitable amount had been collected, the tap T_3 was closed and the first fraction was pumped off through the upper gallery. The middle fraction was then allowed to distil into an evacuated globe, and the last fraction was rejected.

The oxygen was passed through the drying tube and a liquid air trap before storage. No impurities were detected in either the oxygen or the helium, and they were used as supplied.

Several other reagents were used in conjunction with the chemical analysis for formaldehyde, total aldehyde and total acid. The purity of these substances was not critical and the B.D.H. Laboratory grade was found to be quite satisfactory.

General Operating Procedure:

The combustible material was admitted to the reaction vessel through tap T_2 (See figure 1). The oxygen was then added as quickly as possible from the gallery through tap T_1. The initial pressure was recorded and the changes in pressure, (ΔP), in the reaction vessel was measured as a function of time. Typical pressure-time records for the six esters investigated are illustrated in figure 2.



initial pressure of ester = 100 mms.
initial pressure of oxygen = 200 mms.
temperature: curves 2 to 6; 380°C.
curve 1 ; 260°C.

Figure 2 Typical pressure-time records

The maximum rate of reaction and the induction period were measured from the ΔP-time curves by drawing a line through the region of maximum rate of pressure change. The slope of this tangent corresponded to the maximum rate(expressed as mms. per minute) and the "x" intercept to the induction period.

For chemical or mass spectrometric analysis the gases in the reaction vessel were expanded into a gas pipette or sampling vessel attached to the gallery. The detailed procedures varied with the nature of the analysis and as each section is described, the appropriate details will be included.

Before beginning a series of experiments with a new ester it was necessary to "condition" the reaction vessel to the new combustible material. This was most easily accomplished by raising the temperature of the furnace and exploding the new material three or four times in the presence of an excess of oxygen. If this precaution was not taken, the day to day reproducibility would fall well outside 10%, and month to month reproducibility outside 100%. With the establishment of the preliminary explosion technique, the overall reproducibility of the maximum rate of reaction was within 10%.

The reproducibility of the induction period varied

with the ester under consideration. Methyl and ethyl formate and methyl acetate gave induction values agreeing within 10%. The remaining esters gave reproducibility of this order only when the reaction vessel was evacuated for at least 10 minutes between consecutive runs. The value of the induction period for propane depended much more on the length of time the reaction vessel was under vacuum, and great care had to be taken to keep the pumping period between runs exactly constant.

Mulcahy and Ridge (10) have described in considerable detail their views on the erratic behaviour of the induction period observed during the oxidation of propylene. They finally adopted a rigid evacuation routine and ascribed the changes to variation in the condition of the surface of the reaction vessel, and to traces of products remaining from the previous reaction.

EXPERIMENTAL RESULTS

Pressure Measurements:

An investigation has been made of the effect of reagent concentration and reaction temperature on the induction period and the maximum rate of oxidation of the esters. The most striking variations occurred during the investigation of the effect of temperature. Negative

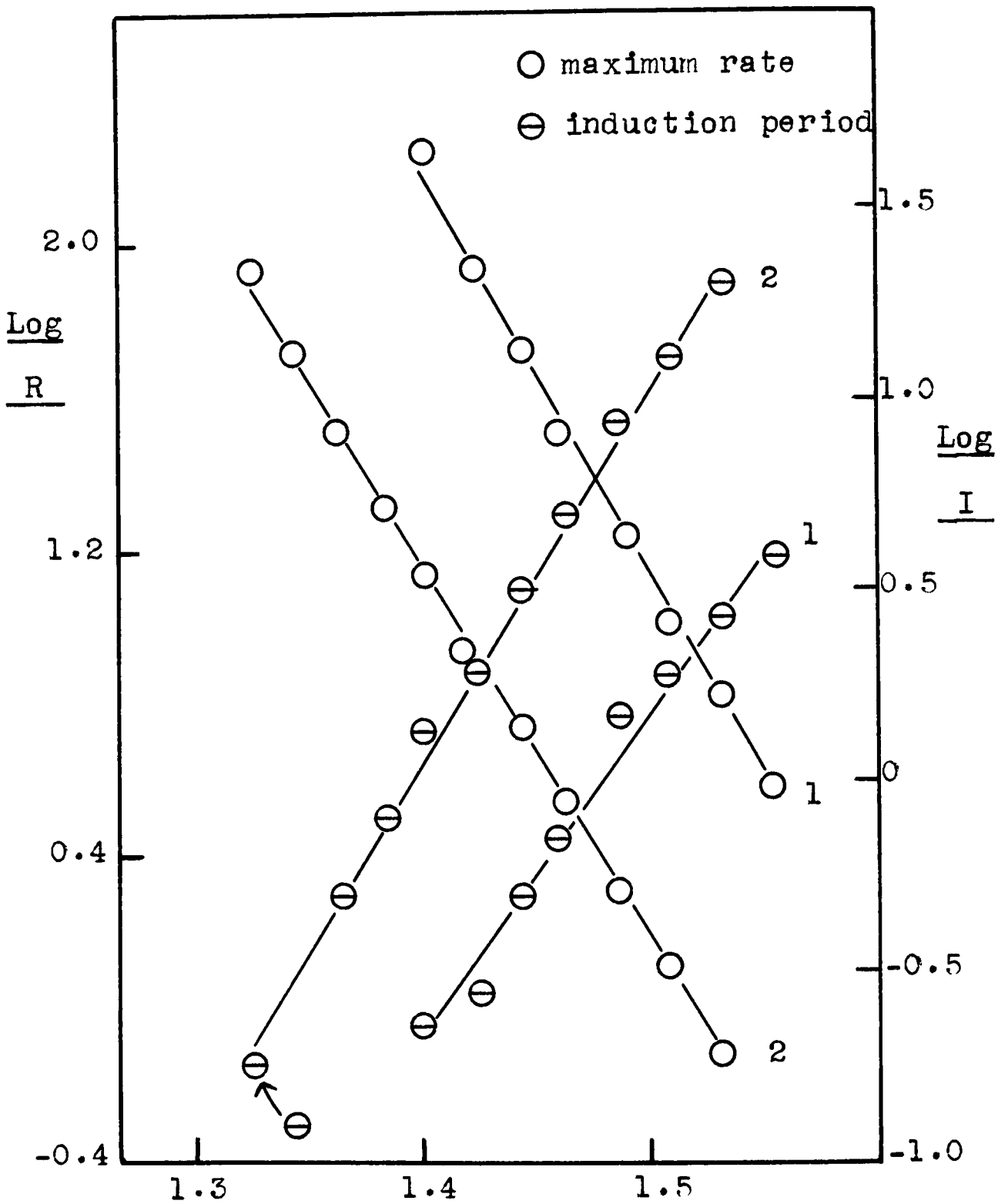
temperature coefficients were observed over certain ranges with three of the esters, and cool flames occurred during the oxidation of ethyl and propyl formate.

Wherever possible the volume of the available data has been reduced to typical curves and trends. For the most part the ΔP-time curves have been omitted, and the maximum rate and induction period data compared directly.

The Effect of Temperature:

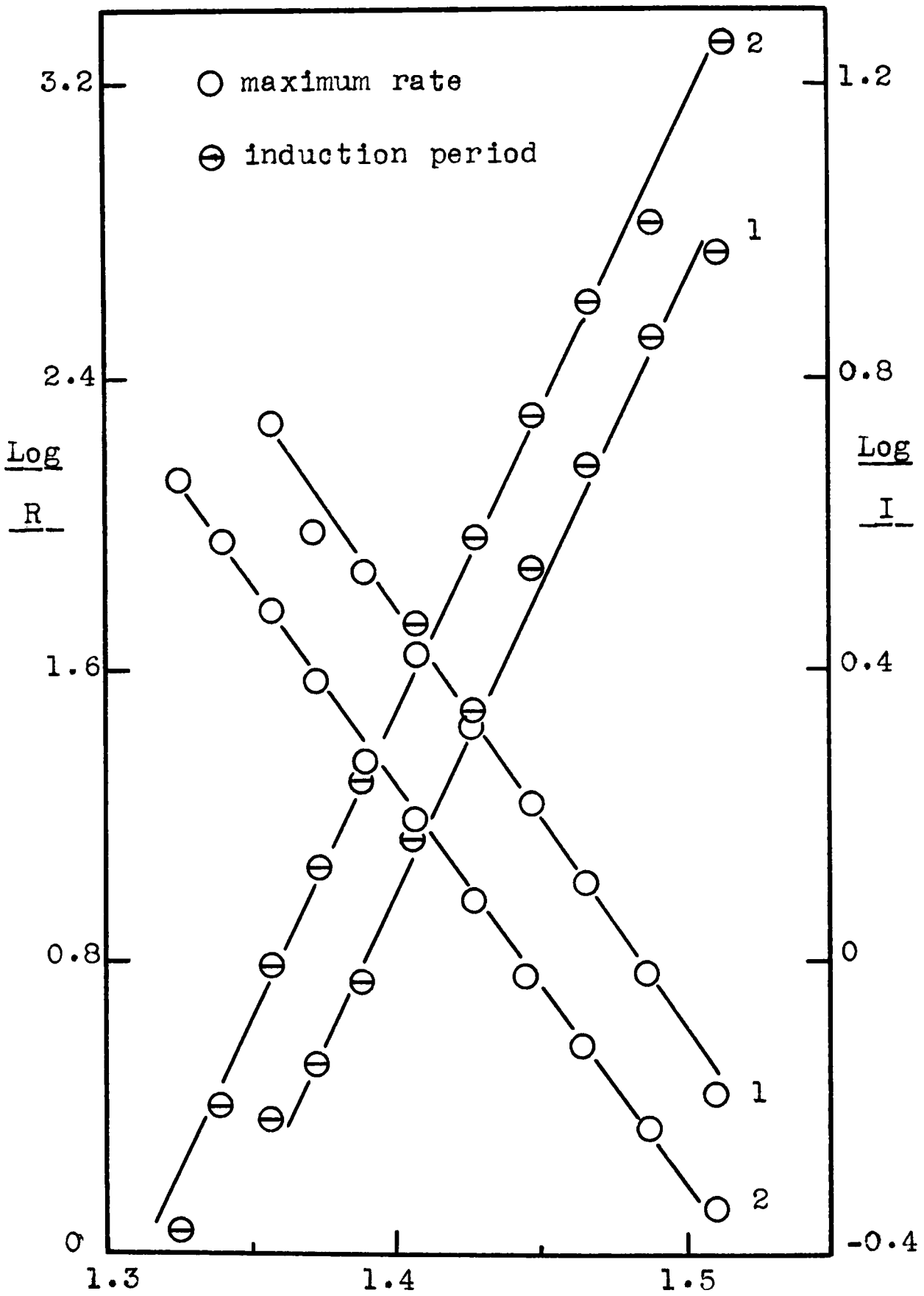
The effect of temperature on the maximum rate and on the induction period was determined in two series of experiments. In the first series the amount of oxygen supplied to the combustible compound was about equal to that required for complete combustion (as shown by the mass spectrometer). In the second series the ratio of oxygen to ester pressure was increased by a factor of three or more.

The results for each ester are summarized in figures 3 to 9 . In each case the logarithm of the maximum rate or of the induction period is plotted against the reciprocal of the absolute temperature. The symbols R and I are used throughout the thesis as representing the maximum rate and the induction period, respectively.



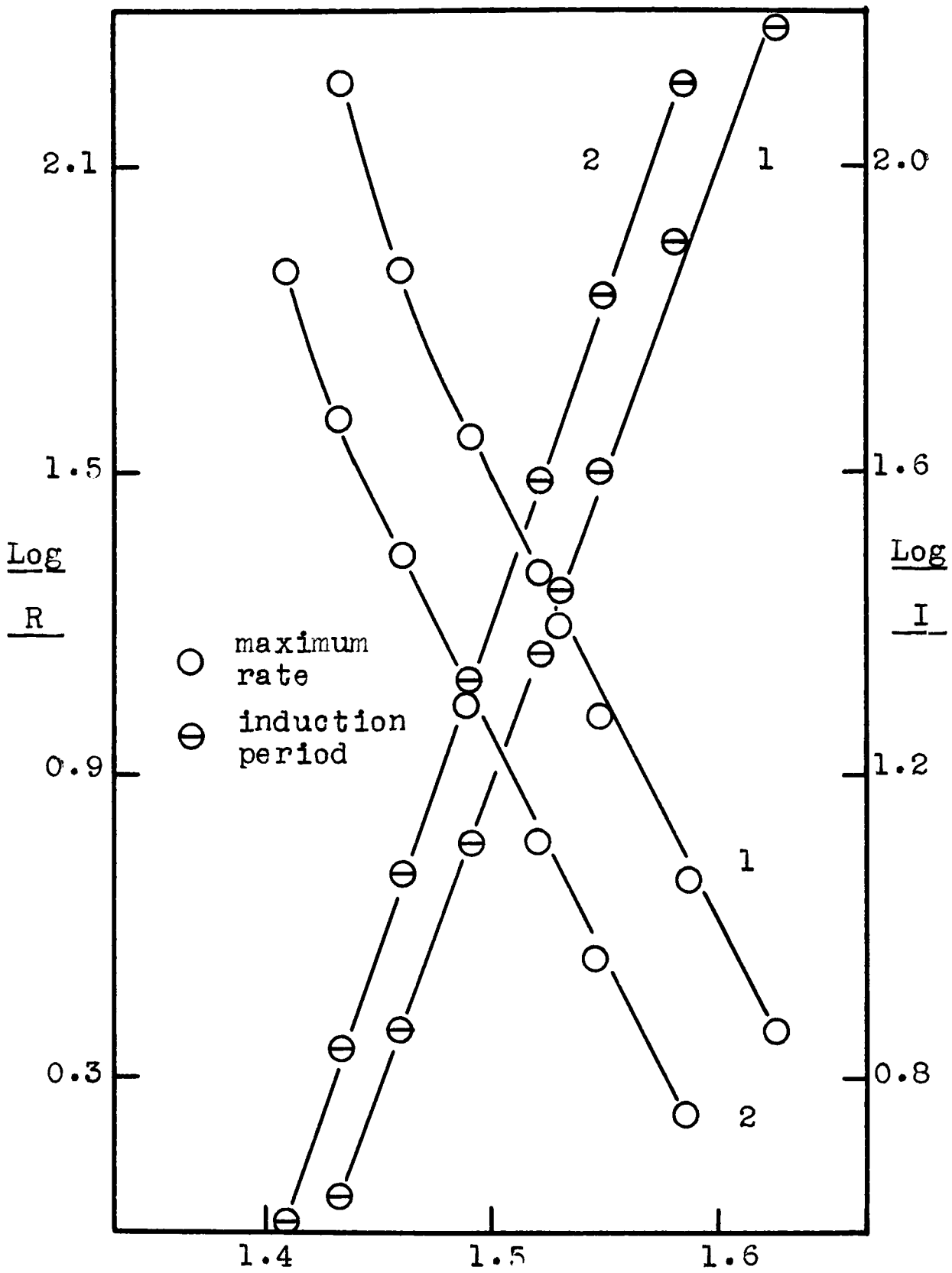
1. 200 mms. MF; 200 mms. Oxygen
2. 50 " " 300 " "

Figure 3 The effect of temperature on the oxidation of methyl formate



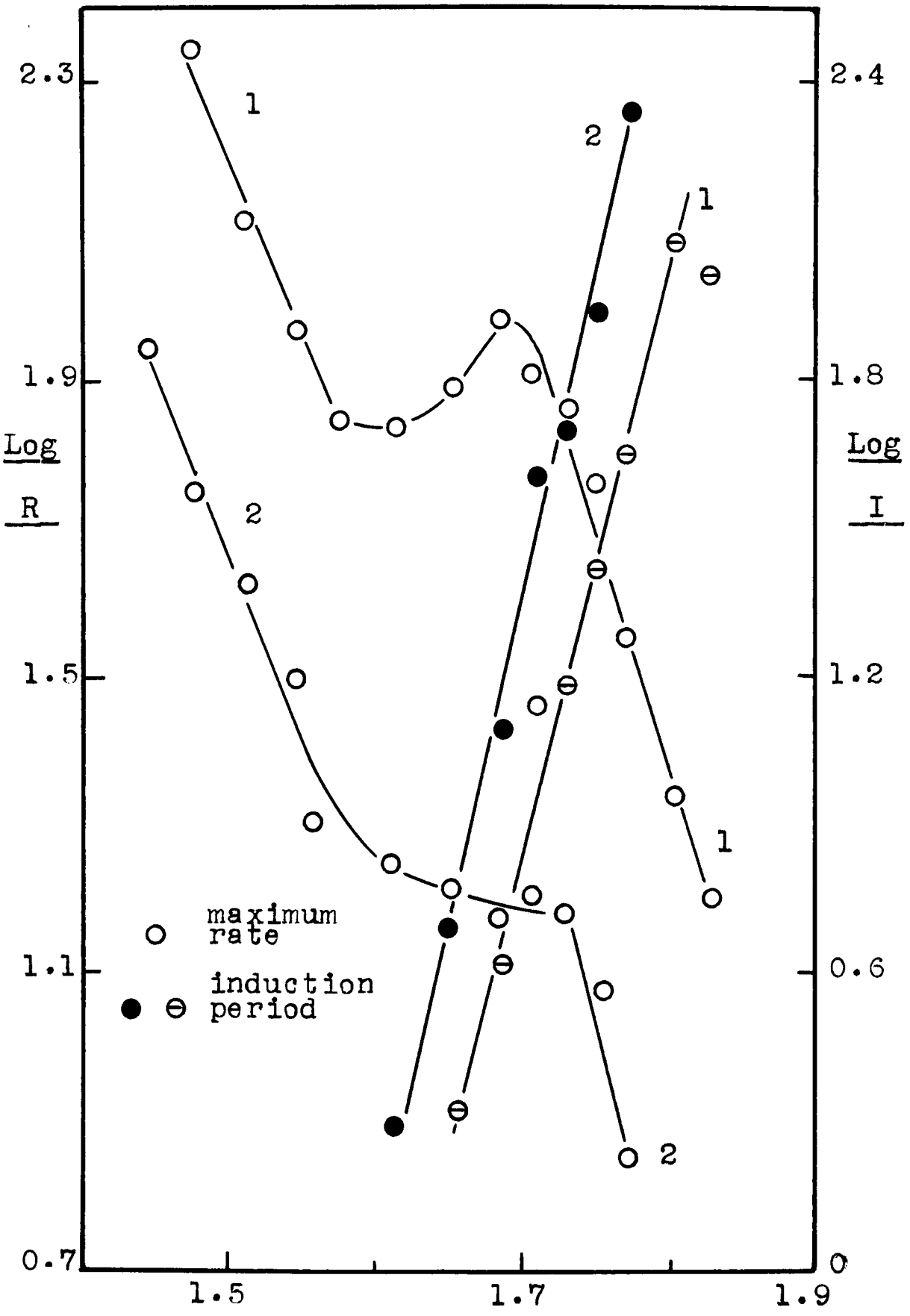
1. 100 mms. MA; 200 mms. Oxygen
2. 50 " " 300 " "

Figure 4 The effect of temperature on the oxidation of Methyl Acetate



1. 100 mms. MP; 200 mms. Oxygen
2. 50 " " 300 " "

Figure 5 The effect of temperature on the oxidation of methyl propionate



1. 100 mms. MB; 200 mms. Oxygen
2. 50 " " 300 " "

Figure 6 The effect of temperature on the oxidation of methyl butyrate

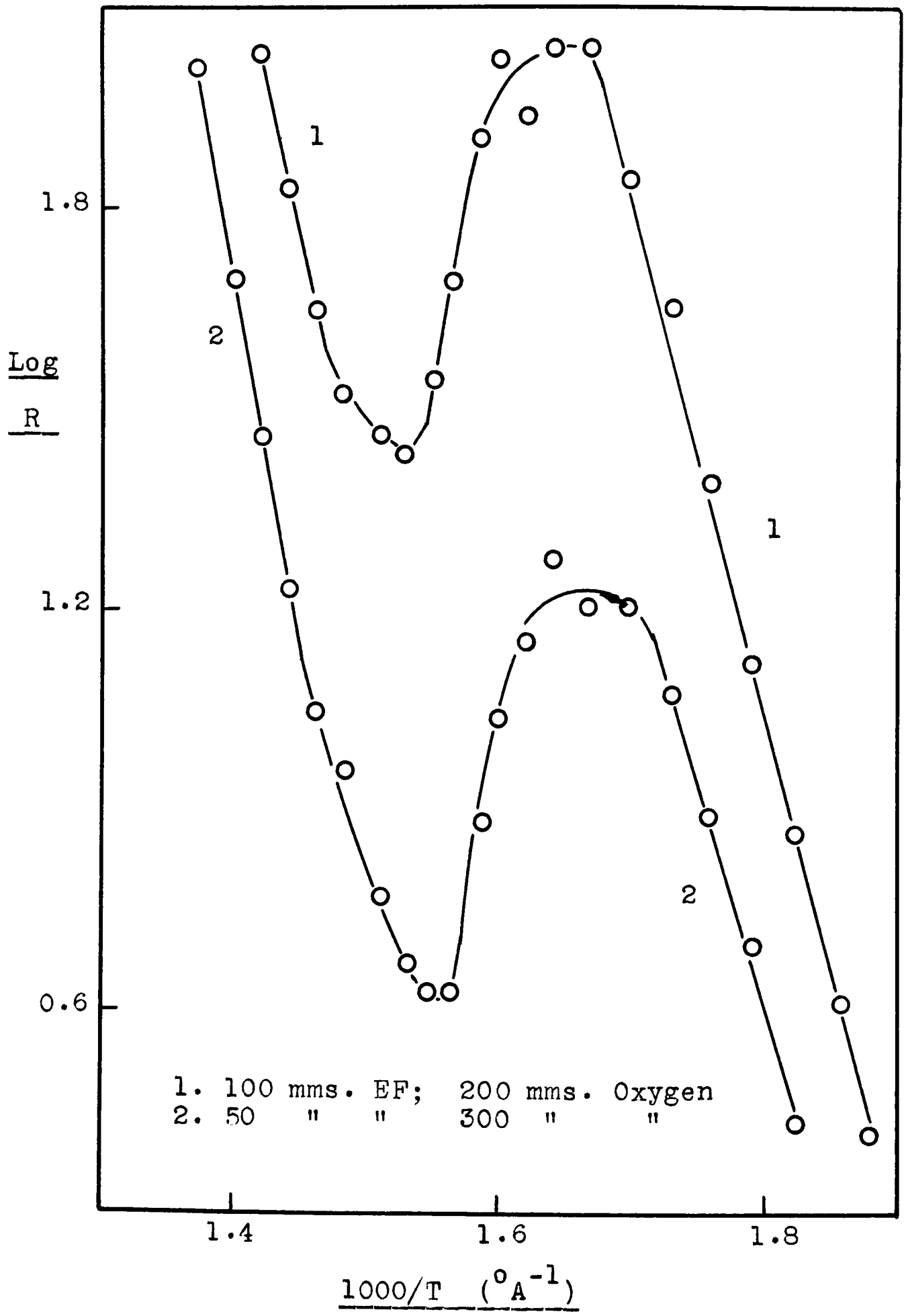


Figure 7 The effect of temperature on the maximum rate of oxidation of Ethyl Formate

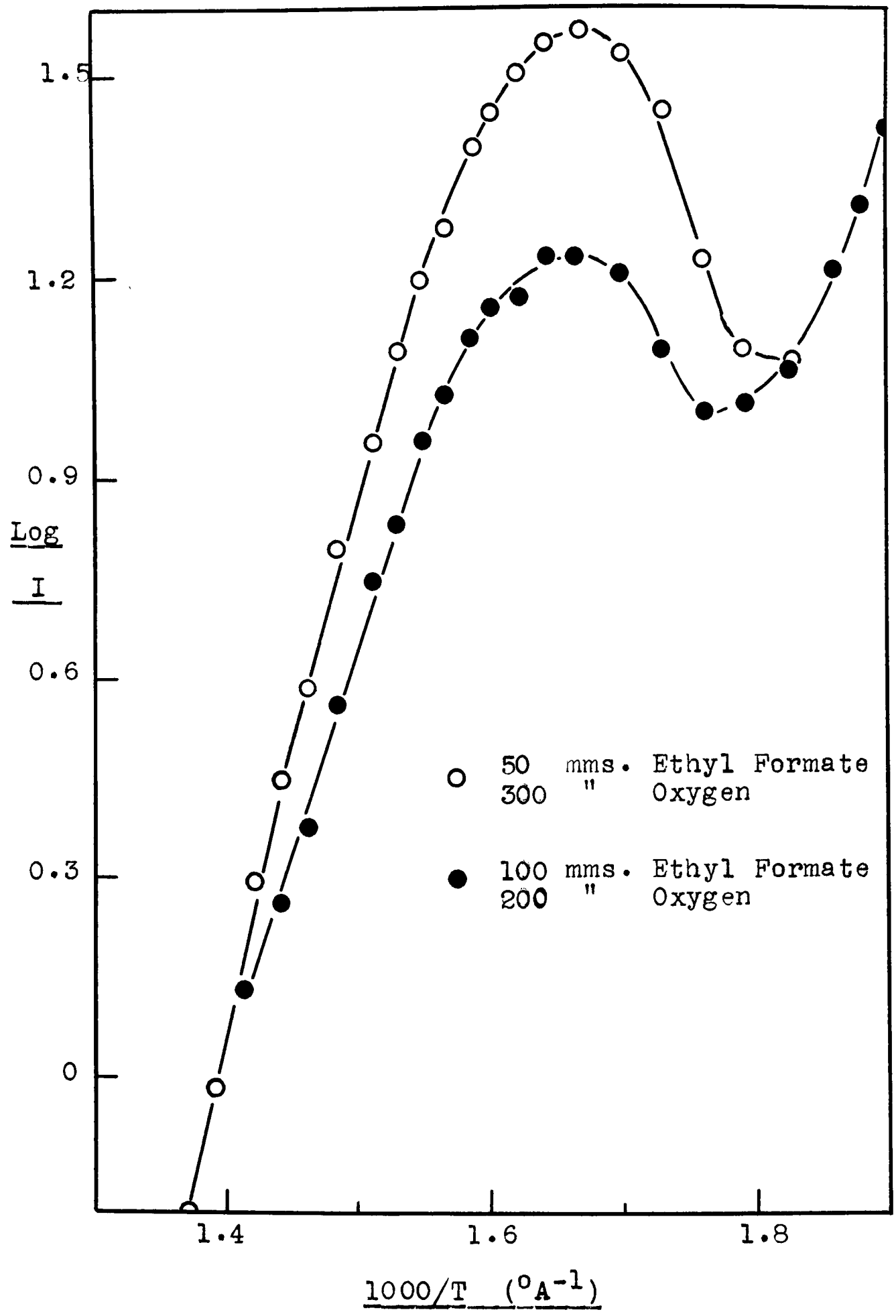
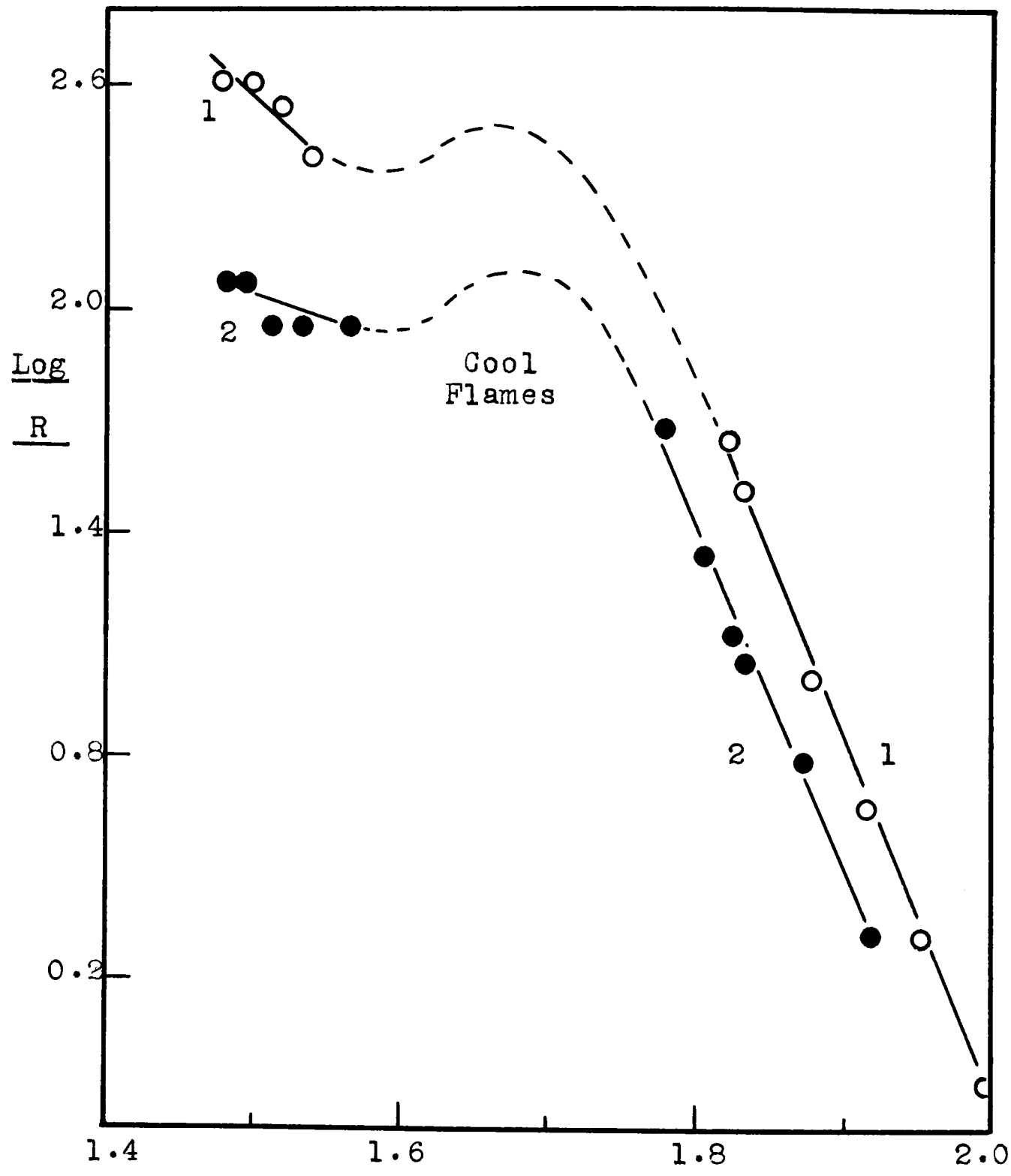


Figure 8 The effect of temperature on the induction period observed during the oxidation of ethyl formate



1. 100 mms. PF; 200 mms. Oxygen
2. 50 " " 300 " "

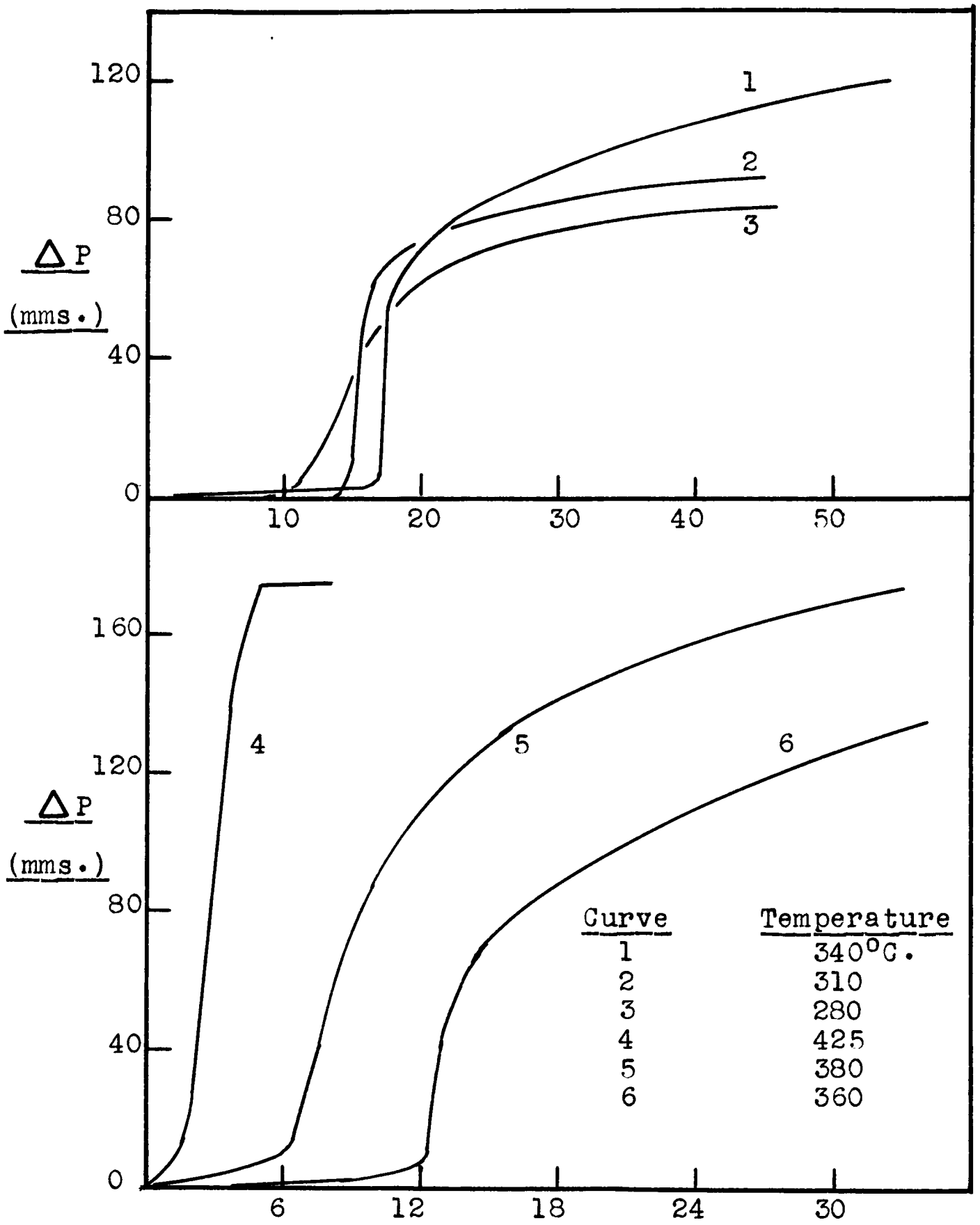
Figure 9 The effect of temperature on the maximum rate of oxidation of Propyl Formate

The "activation energy" plots of methyl formate, methyl acetate and methyl propionate were straight lines. The remaining esters showed sigmoid temperature curves. The presence of an excess of oxygen did not effect the general trend of the experimental results.

During the oxidation of ethyl formate and methyl butyrate, the maximum rate of oxidation increased regularly up to about 320°C. The rate then decreased rapidly until about 380°C. and thereafter increased regularly up to the ignition temperature. The exact temperature values varied with the ester under consideration, but, in general, the transition occurred around 350°C.

For these esters showing a region of negative temperature coefficient, the shape of the pressure-time curve changed considerably across the transition part of the curve. As the temperature was increased the smooth "S" shaped ΔP-time curve became more sharply segmented and the maximum rate more difficult to measure. Examples of this change, as observed during the oxidation of ethyl formate, are illustrated in figure 10.

In the low temperature region,(curve 3), the maximum rate of oxidation was slow to develop and considerable pressure change was observed before the



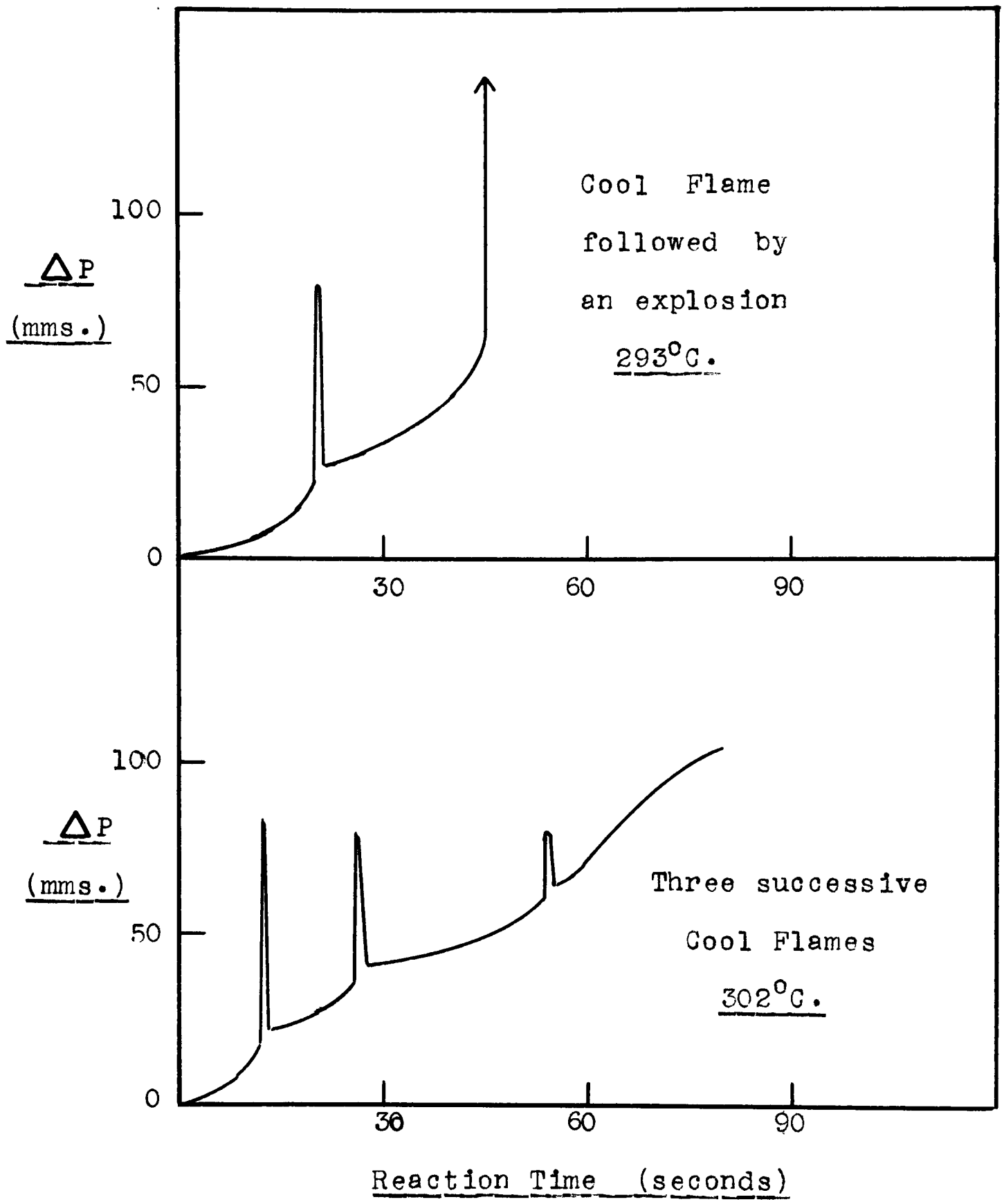
initial pressure of ethyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 10 The effect of temperature on the ΔP-time curves of the oxidation of Ethyl Formate

reaction got under way. At the point where transition to the high temperature region was about to begin, the shape of the pressure-time curve was such, as to show at one stage, a reaction almost explosive in character (curve 1). A very small pressure change preceded a rate of oxidation of 100mms. per minute. As the high temperature region was approached, the ΔP-time curve was restored to its smooth sigmoid shape and changes of 20mms. would precede the development of the maximum rate of reaction.

Cool flames were first observed during the investigation of the effect of temperature on the oxidation of propyl formate. The high and low temperature regions were sharply defined, as shown in figure 9 , but in the transition range, cool flames and explosions were observed. The general shape of the pressure-time curve of cool flame combustion is shown in figure 11.

The cool flames were easily distinguished from the hot explosive flames by the relatively slow rate of development, and comparatively small surge in pressure. Several such flames frequently followed each other in succession through the same reaction mixture. The overall change in pressure after the passage of one or more cool flames was scarcely more than that observed after complete combustion in the low temperature region.



initial pressure of propyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 11 Pressure-time curves of the cool flame oxidation of Propyl Formate

The gas pressure after a hot flame was always two to three times this final value.

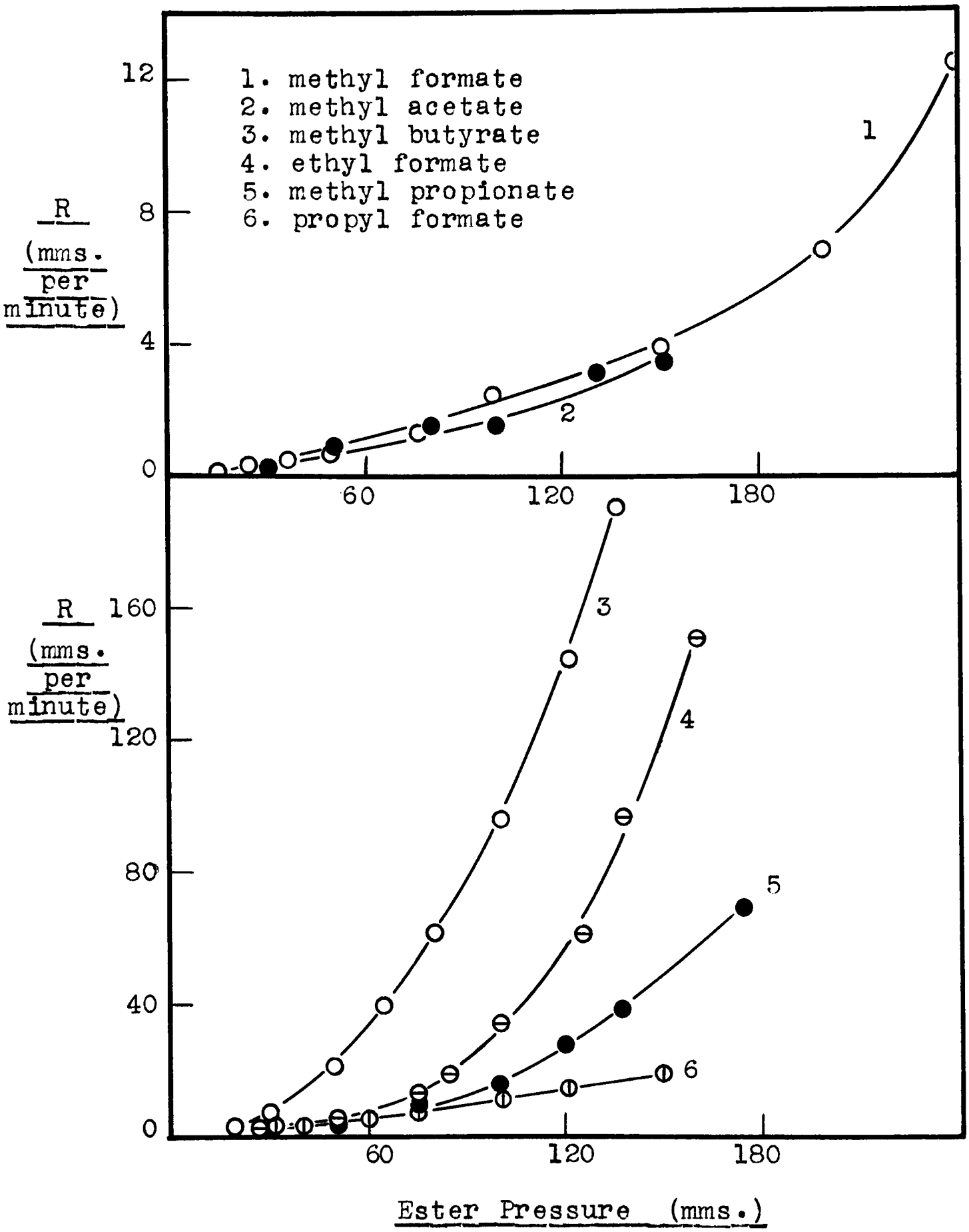
During some of the experiments part of the lagging was removed at the top of the furnace and direct observations were made on the reaction vessel. No detectable visible light was emitted during the passage of a cool flame, but a bright yellow flash was observed to accompany a hot flame. The apparatus was not designed for close visual examination, and the apparent absence of any light during a cool flame cannot be regarded as final.

After the experiments with propyl formate, further tests were made for cool flame activity during the oxidation of ethyl formate. At 340°C. cool flames were observed when the initial pressure of ethyl formate was about 150mms. The general trend of the experiments confirmed what had been observed with propyl formate, although the flames were not as well defined. High concentrations of ethyl formate were not easy to work with as the vacuum grease absorbed appreciable quantities of the vapour. Sufficient experiments were made to establish the presence of cool flame activity, but a detailed examination was not attempted.

The Effect of Reagent concentration:

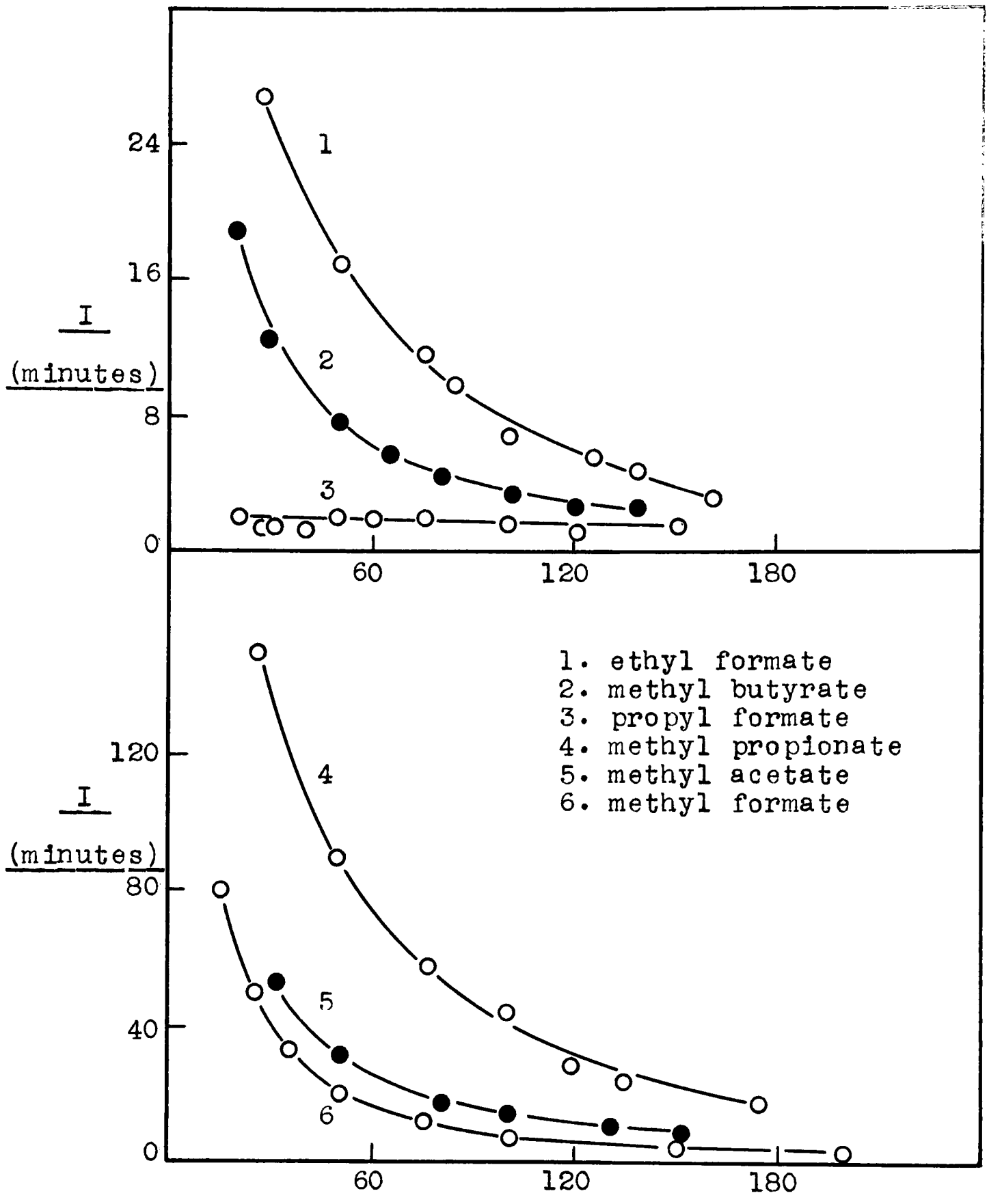
Several series of experiments were made with each ester to determine the effect of increasing pressures of the ester itself or of oxygen on the maximum rate and on the induction period. At a constant temperature and with a fixed pressure of oxygen, the concentration of ester was increased until either the limiting vapour pressure of the liquid was reached or ignition occurred. The corresponding effect of oxygen pressure at constant temperature was determined at fixed concentrations of ester vapour. A few typical results for each ester are summarized in figures 12, 13, and 14.

Most of the data in the figures were collected at 380°C. At this temperature, with ethyl formate and methyl butyrate, the measurements occurred in the high temperature or fast reaction zone. The experiments with methyl formate, methyl acetate and methyl propionate at the same temperature occurred in the slow reaction region of the oxidation range. In the case of propyl formate, cool flames were observed at 380°C., and measurements were made in the low temperature region at 260°C.



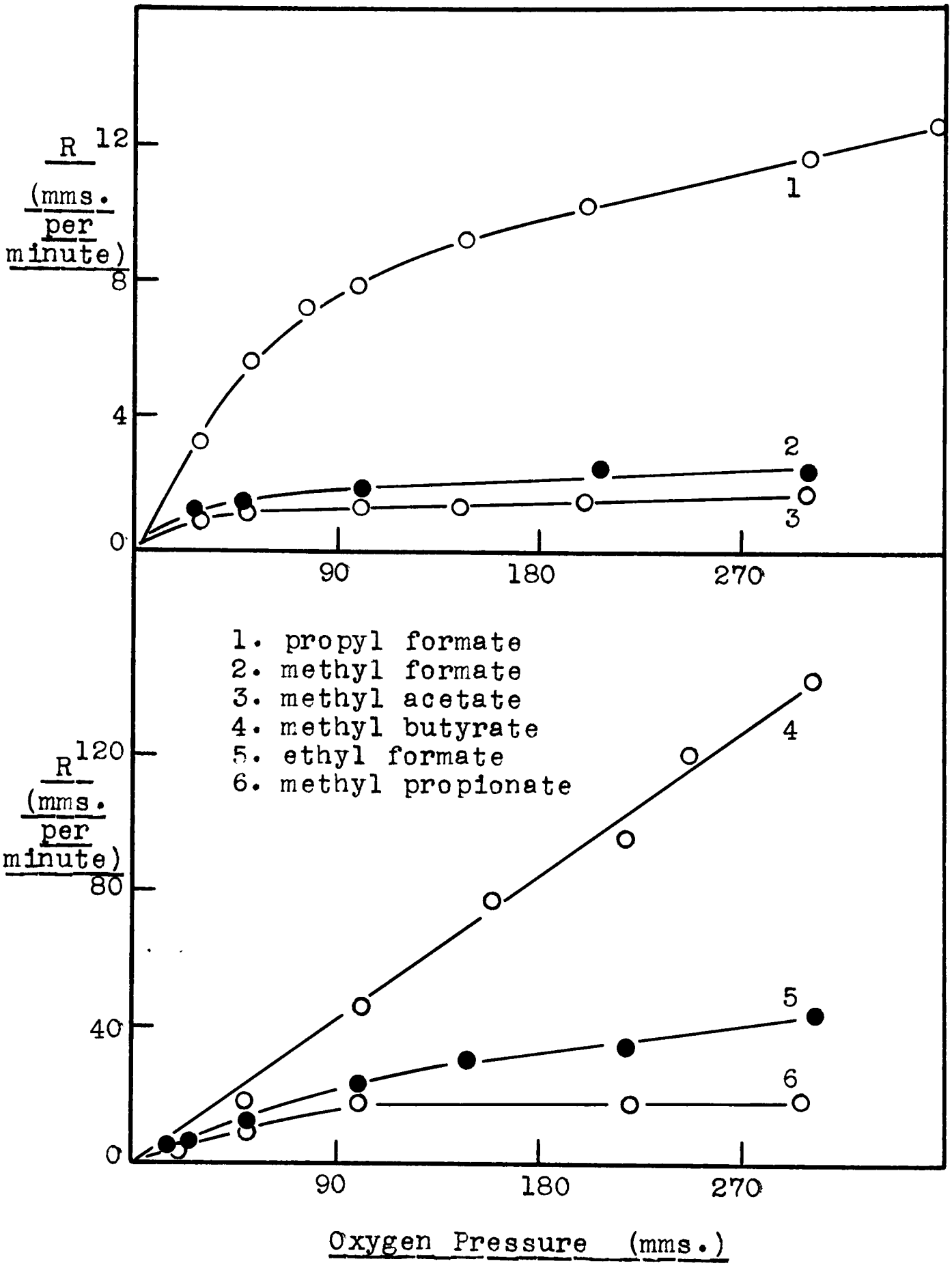
initial pressure of oxygen = 200 mms.
temperature: curves 1 to 5; 380°C.
curve 6 ; 260°C.

Figure 12 The effect of ester concentration on the maximum rate of oxidation



initial pressure of oxygen = 200 mms.
temperature: curves 1,2,4,5,6; 380°C.
curve 3 ; 260°C.

Figure 13 The effect of ester concentration on the induction period



INITIAL pressure of ester = 100 mms.
temperature: curves 2 to 6; 380°C.
curve 1 ; 260°C.

Figure 14 The effect of oxygen concentration on the maximum rate of oxidation

The maximum rate of oxidation increased and the induction period decreased with an increase in the ester concentration. The general effect of the concentration of combustible material was independent of both temperature and oxygen pressure.

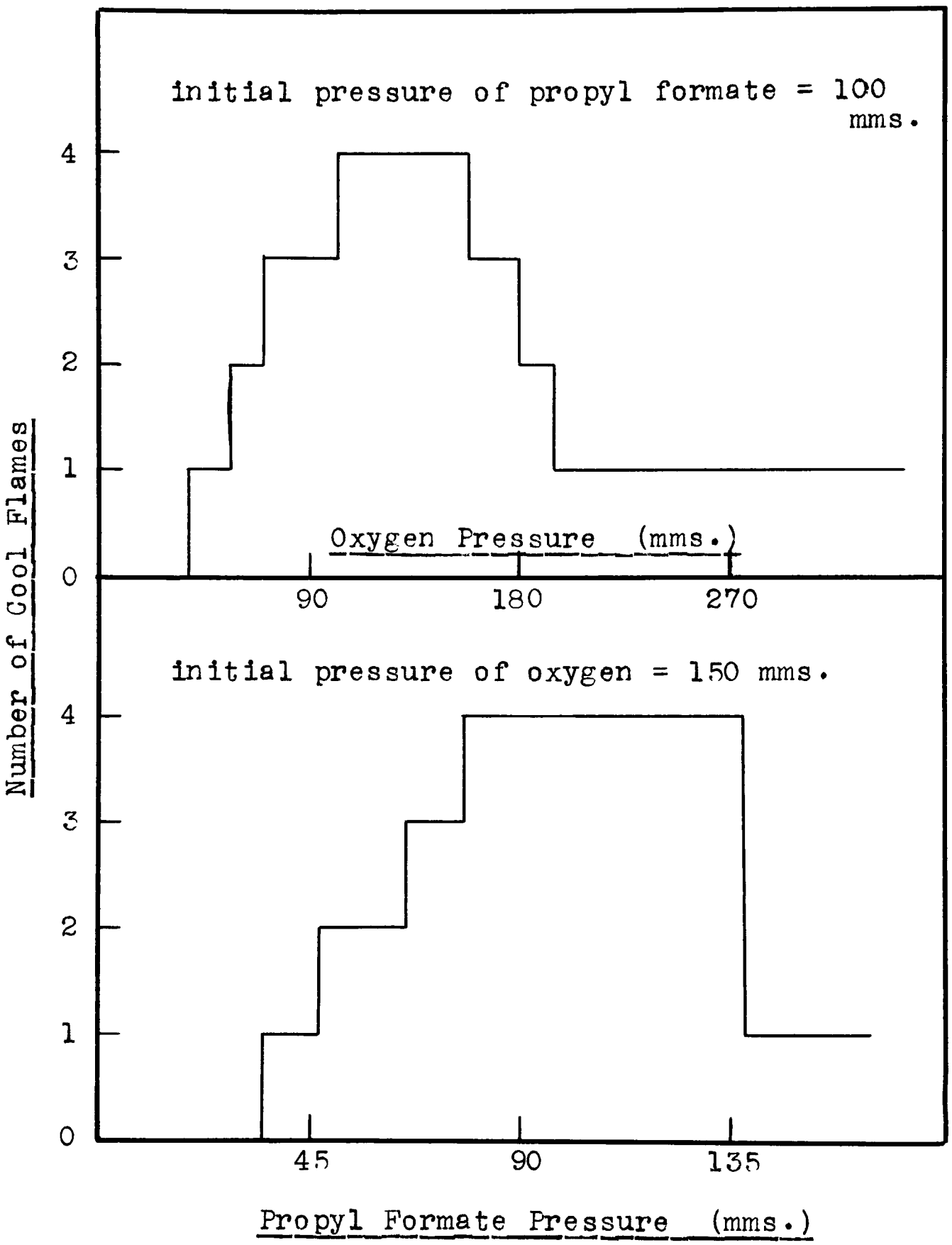
In the low temperature region the maximum rate of oxidation tended to become independent of the oxygen concentration. Curves similar to those shown for the formate esters (curves 1, 2, and 5, of figure 14) were obtained for all the esters. As the temperature was increased and the fast reaction region was approached, the maximum rate became more and more dependent on the oxygen pressure. For each ester the limiting case was similar to that shown for methyl butyrate (curve 4, figure 14).

The induction period was independent of the oxygen pressure in both the high and low temperature regions. Some variation was observed in the fast reaction region when the amount of oxygen supplied to the ester was much less than that required for complete combustion. However, under reasonable oxidation conditions significant changes did not occur.

An exception to the general trend of the effect of reagent concentration on the induction period occurred in the oxidation of propyl formate. With this ester, the induction period was independent of almost every experimental variable. It existed only in the low temperature region and rarely exceeded five minutes under any set of conditions. However, this exceptional behaviour was restricted to the induction period measurements only. The results for the maximum rate measurements paralleled the general trend of the sister esters.

The effect of reagent concentration on the occurrence of cool flames was determined with propyl formate at 340°C. The general trends are indicated in figure 15.

Cool flame activity was greatest when the concentration of oxygen was considerably less than that required for complete combustion. Optimum conditions appeared to exist at about equal pressures of propyl formate and oxygen.



temperature: 330°C.

Figure 15 The effect of reagent concentration on the number of cool flames observed during the oxidation of propyl formate

The Analytical Investigation of the Combustion Gases:

The broad principles of the chain branching theory of the oxidation process have not been seriously challenged for some years. The more recent investigations have been concerned with the establishment of the details of the mechanism as they apply to particular hydrocarbons. The intermediate products of combustion have been searched for likely chain branching agents (5,7), and comparative studies have been made with structural isomers for the point of initial attack (2,17). Some progress has been made but no conclusive evidence has been advanced.

The greatest problem has been the development of suitable analytical techniques. Various peroxide and aldehyde species have been identified as combustion intermediates but it has not been possible to prove which is critical to the oxidation reaction. The pressure-time curve itself has never been indisputably established as a true measure of the oxidation process. There is every indication that the maximum rate of change of pressure in the reaction vessel is essentially a direct function of the rate of consumption of the reagents, but clear-cut analytical proof has not been possible.

When the rate-pressure experiments with the esters were finished, it was decided to attempt some contribution

to the analytical investigation of the combustion mixture. A mass spectrometer was available for the analysis of the major constituents and three new micro-analysis procedures were known for aldehyde and peroxide species. It was hoped that with the esters, sufficient similarities and differences would arise to permit some conclusion to be drawn.

In the following paragraphs the various analytical techniques will be described in some detail. Instead of summarizing the results at the end of each section, they have been collected for presentation at the end of the text.

The Mass Spectrometer and the Principles of Analysis:

The instrument was a Metropolitan-Vickers type M.S.2 very similar to that described by Nier in 1940 (38).

The gas sample to be analysed is allowed to flow from a reservoir through a very fine leak into an ionization chamber. In the chamber the gas molecules are bombarded by a collimated beam of electrons of accurately controlled energy and constant beam current. The positive ions formed in the collisions are driven out of the ionization chamber by the application of a positive potential to an ion repelling electrode.

The charged particles are then passed through a fixed potential gradient of 2000 volts. The fixed energy gained by each particle is represented by:

$$\tfrac{1}{2}Mv^2 = eV$$

where e is the charge on the ion
V is the accelerating potential
M is the molecular weight of the ion
v is the final velocity of the ion

Various electronic devises are used to keep the ion beam condensed and well defined.

From the electrostatic field the ion beam is conducted into a magnetic field. The action of the magnet causes the charged particles to describe a circular path. The radius of trajectory of the individual ions depends on the ratio of charge to mass, according to

$$e/M = v/Hr$$

where H is the intensity of the magnetic field
r is the radius of curvature

or $$r = Mv/eH$$

In the first instance the velocity of the accelerated particles is proportional to $1/\sqrt{M}$. The resultant radius of curvature is therefore proportional to $\sqrt{M}/e$.

During an analysis the magnetic flux of the instrument is increased until the radius of curvature of each ion species is such that it passes through a

narrow slit into an amplifier-recorder unit. The relative abundances of the ion species form the mass spectrum of the mixture.

The complexity of the spectrum is increased considerably when one or more of the components is an organic compound. In an ionization chamber an organic substance frequently undergoes decomposition as well as primary and possibly secondary ionization. The relative abundances of the different ions formed sometimes differ by several powers of ten.

The use of the mass spectrometer for the analysis of mixtures of organic compounds depends on the fact that under carefully controlled conditions the relative abundances of the different ions produced by a given molecule remain constant. This pattern is used to identify the molecule. At the same time the absolute abundance of the ions is proportional to the partial pressure of the substance in the ionisation chamber of the instrument. Both the mass spectrum and the relation between ion abundance and partial pressure, the"sensitivity", have to be determined empirically for each possible component of a mixture, by seperate experiments with pure samples.

The mass spectrum of a mixture is the sum of the spectra of the constituents, each multiplied by the sensitivity for that constituent, and by its partial pressure. The compounds of the present investigation were of the same order of molecular weight and ions of the same mass frequently appeared in the spectra of the different compounds.

Fortunately with the mixtures under study it was possible to find a mass number in the mixture spectrum which appeared in the mass spectrum of only one of the constituents. This greatly simplified the calculations as the abundance of this ion could be related immediately to the partial pressure of the substance producing it by means of the calibration experiments.

The mass spectrum of a molecule and the sensitivity were, in principle, constant under controlled conditions. However, the presence of a large excess of oxygen often caused significant changes in the sensitivities of the organic substances. Errors of this kind were reduced by repeated calibration both before and after a given set of analyses. Deviations greater than 5% were rejected.

During the preliminary experiments it was apparent that the large concentrations of water vapour formed in the oxidation reaction were interfering with the efficient operation of the mass spectrometer. Tests showed that it was possible to remove the water by drying the gas sample over anhydrous phosphorus pentoxide. To correct the resulting high analysis values, an inert reference gas, helium, was added to the initial reaction mixture. The analyzed concentrations were scaled to the known partial pressure of helium in the reaction vessel.

General Procedure:

The pressure-time curve of the particular reaction was determined in the usual way, the helium, ester vapour, and oxygen being admitted to the reaction vessel in that order. A 200cc. globe containing 5-7gms. of phosphorus pentoxide was attached to the upper gallery (figure 1) and evacuated to 10^{-3}mms. At the required point on the pressure-time curve the contents of the reaction vessel were shared with this sampling globe. The reaction conditions were duplicated several times until a series of samples had been collected, representing the whole range of pressure change.

In each case it was possible to analyse the mixture

for the unchanged ester and oxygen, and the final products, carbon monoxide and carbon dioxide. Ethylene was also detected in appreciable quantities in the combustion gases of ethyl formate.

Before and after each set of samples the appropriate calibration substances were put through the mass spectrometer. Typical mass spectra for the esters are summarized in Table 1 . The exact method of analysis varied slightly with the particular ester, but in general, the contribution of the ester was subtracted from the mixture spectrum followed by the carbon dioxide, oxygen, and carbon monoxide.

Analyses for Aldehyde and Acid:

The concentrations of the aldehyde and acid species were too low for accurate analysis with the mass spectrometer. The spectra of these substances overlapped almost completely the patterns for the corresponding esters. When the contribution of the ester was subtracted from the mixture spectrum the residue peaks were of the same order of magnitude as the possible error of the instrument. A series of chemical tests were therefore undertaken to support the main analyses.

Table 1 MASS SPECTRA OF THE ESTERS

m/e	Relative Peak Height			
	Methyl Formate	Ethyl Formate	Methyl Acetate	Methyl Propionate
26	0.02	10.7	0.5	8.8
27	0.09	42.8	0.6	32.3
28	6.3	88.8	2.4	15.9
29	80.3	61.4	8.3	100.
30	6.3	5.1	0.9	3.7
31	100.	100.	4.8	7.2
32	42.3	1.3	1.3	0.3
42	0.1	1.9	9.6	2.9
43	0.1	8.8	100.	2.6
44	1.3	1.9	2.9	0.5
45	0.9	30.5	1.2	5.8
46	-	1.3	-	-
47	-	8.2	-	-
57	0.0	0.3	-	99.2
58	0.0	0.1	-	3.5
59	0.7	1.1	6.3	33.4
60	37.2	0.1	-	1.3
74	-	9.7	16.8	-
88	-	-	-	28.4

General Sampling Procedure:

The gases in the reaction vessel were shared with a 404cc. gas pipette. Twenty mls. of distilled water were added and the pipette was vigorously agitated for five minutes. The contents of the pipette were then drained into a small flask. This solution acted as the stock for all the analysis procedures.

Between experiments the pipette was rinsed twice with acetone and air dried with a suction pump.

Procedure for Formaldehyde: Chromotropic Acid Method(39)

In strong mineral acid solution chromotropic acid forms a deep red complex with formaldehyde. Concentrations as low as 5 micrograms/ml. can be accurately estimated on a spectrophotometer.

The originators of the method tested the effect of the presence of alcohols, higher aldehydes and acids. They found no interference with methyl and ethyl alcohol, or formic and acetic acid. They report some interference from acetaldehyde, if present in large amounts, and considerable interference from alcohols higher than ethanol.

The mass spectrometric analyses indicated no appreciable concentration of alcohol of any kind and only trace quantities of aldehyde. Subsequent chemical

analysis for total aldehyde showed the concentration of acetaldehyde to be below the range of interference.

One ml. of the stock solution was placed in a 50 ml. volumetric flask. One ml. of chromotropic acid solution (2.50gms. in 25 mls.) and 10 mls. concentrated sulphuric acid were added. The flask was then heated in hot water at 90-100°C. for 30 minutes. When cold, the contents were diluted with water to 50 mls.

Samples of the test solution and a blank were compared colorimetrically on a "Unicam" Spectrophotometer at 5700 Å. The method was calibrated with a water soluble trimer of formaldehyde, S-Trioxane, and checked with a sample of commercial 40% formaldehyde in water. The calibration curve was not linear.

The Procedure for Total Aldehyde:

Benzenesulphohydroxamic Acid Method (40)

The benzenesulphohydroxamic (B.S.H.A.) acid method for total aldehyde was not as sensitive as the tests for formaldehyde. Additional precautions had to be taken as the result of the action of light on the critical reagent.

10 mls. of the test solution were placed in a 100 ml. conical flask. Two mls. of freshly prepared M/10 B.S.H.A. (in methanol) and 10 mls. of N/10 KOH were added. The flasks were then allowed to stand in the dark

for thirty minutes. After standing, two mls. of N sulphuric acid and two mls. of M/10 ferric chloride were added to the solution. Colorimetric comparisons against blank determinations were made on the spectrophotometer at 4600 $\mathring{A}$.

The original procedure called for the neutralization of the test solution instead of the addition of 2mls. of N sulphuric acid. However, some unknown species from the combustion gases precipitated in neutral solution and prevented any chance of analysis. Repeated standardization experiments indicated that the sensitivity was scarcely affected by the presence of excess acid.

The method was standardized with pure samples of formaldehyde and acetaldehyde. Linear calibration curves were obtained with both aldehydes but the procedure was slightly less sensitive to formaldehyde than to acetaldehyde.

The concentration of formaldehyde in the combustion samples was determined independently by the Chromotropic Acid method. The contribution of this aldehyde was then subtracted from the value for the total aldehyde, and the remainder calculated as acetaldehyde.

The Procedure for Total Acid:

The total acid concentration of the samples was determined by direct titration with 0.014 N sodium hydroxide at 0°C. The indicator used was phenolphthalein.

The titrating solutions were cooled in ice to prevent the rapid hydrolysis of the excess ester from obscuring the end point.

The Polarographic Analyses:

Industry has made special use of the polarograph as a means of analysing for peroxide substances. The fundamentals for these analyses were first established by Shtern and Pollyak in 1939 (41). The waves formed by the organic peroxides are flat and drawn out but with suitable standardization, comparative analyses can be made quite easily.

Very recently, Norrish,(32) used the polarograph to examine the combustion gases of propane. He used a flow system to collect large samples of the intermediate products. The results he reports indicate the presence of peroxides,but he was not able to investigate the region of slow oxidation sufficiently to be able to show the variation in concentration during the reaction.

The present apparatus was particularly suited to a comparative investigation and it was decided to test the combustion gases of one or two of the esters for peroxide species.

The General Principles of Polarography:

Polarography is an electrochemical method of analysis and incorporates features of both potentiometry and electrolysis. The sample to be examined is dissolved in an aqueous solution containing an excess of a "base" or "supporting" electrolyte. The solution is placed in a special electrolytic cell, where the anode is a relatively large pool of mercury, and the cathode is formed by mercury dropping from a glass capillary at a steady rate of one drop every 2-4 seconds. A gradually increasing voltage is applied to the cell and the corresponding current measured on a galvanometer. If the current is plotted against the applied voltage, a characteristic "S" shaped curve, a polarogram, is obtained. From this curve it is possible to determine both the nature and the concentration of the reducible substances in the sample. Polarograms may be plotted manually or recorded automatically, either on photographic paper or with ink on a paper chart.

The limiting current measured on the polarograph is essentially the sum of two contributions.

1. The residual current: When a supporting electrolyte is polarographed in the absence of any reducible material, a small condenser or residual current is observed. For quantitative measurements the residual current must always be subtracted from the total observed current.

2. The diffusion current: When the potential across the dropping mercury electrode is sufficiently large, the reducible material is discharged at the cathode. Throughout the bulk of the sample the current is carried principally by the ions of the supporting electrolyte. The concentration of the base electrolyte is kept deliberately high to prevent any appreciable migration of the reducible substance due to the potential gradient. At the surface of the drop of mercury then, the current across the interface is dependent on the diffusion coefficient of the material in question. The factors controlling the diffusion current have been established by Ilkovic (42).

$$i_d = 607 D^{1/2} n c m^{2/3} t^{1/6}$$

where i_d is the diffusion current in microamperes
D is the diffusion coefficient in sq. cms. per sec.
n is the number of electrons involved in the reduction
c is the concentration of reducible material in millimoles per liter
m is the weight of mercury in milligrams, flowing out of the capillary in one second
t is the drop time in seconds

The relationship between the limiting current and the concentration of the dissolved material follows directly from the Ilkovic equation. Under standard conditions:

$$i_d = Kc$$

where K is a constant

Considerable experimentation has shown that the half-wave potential of the polarogram is characteristic of the reducible material. The half-wave potential is the potential of the dropping mercury electrode, measured against a standard reference electrode, at the point on the current-voltage curve where the current is one half its limiting value. It is independent of the concentration of the substance and the characteristics of the dropping mercury electrode. The standard calomel electrode is generally accepted as the standard of reference.

General Procedure:

The operating procedure of Shtern and Pollyak (41) was used for the polaropraphic analysis of the oxidation products. The combustion samples were prepared in the usual way except that the gas was extracted from the pipette with 20mls. of the supporting electrolyte, M/10 LiCl, instead of pure water. The polarograph used for the present study was the standard laboratory model supplied by the Cambridge Instrument Co. The polarograms were recorded photographically. The characteristics of the capillary according to the Ilkovic equation were as follows:

m = 1.99mgms. per second

t = 2.36 seconds

Two mls. of the stock sample solution were pipetted into the electrolytic cell. The dissolved oxygen was removed by flowing hydrogen gas through the sample at a rate of 2 to 3 bubbles per second for eight minutes. The polarogram of the combustion mixture was then determined.

Satisfactory reproducibility was only achieved when the timing of the operations was rigidly standardized. The volatile nature of the species made the procedure particularly critical to the length of time hydrogen was passed through the solution.

The voltage range investigated with the polarograph was zero to 2.3 volts. At 2.3 volts the supporting electrolyte broke down and hydrogen was evolved at the cathode. For each combustion series the height of the waves in the polarogram were plotted as a function of the pressure change, ΔP, in the reaction vessel.

Analytical Results:

The combustion samples were analysed for the remaining ester and oxygen, and the carbon monoxide and carbon dioxide, formaldehyde, acetaldehyde, total acid and peroxide formed. The major constituents were determined from the mass spectra of the mixtures and the minor constituents by chemical analysis.

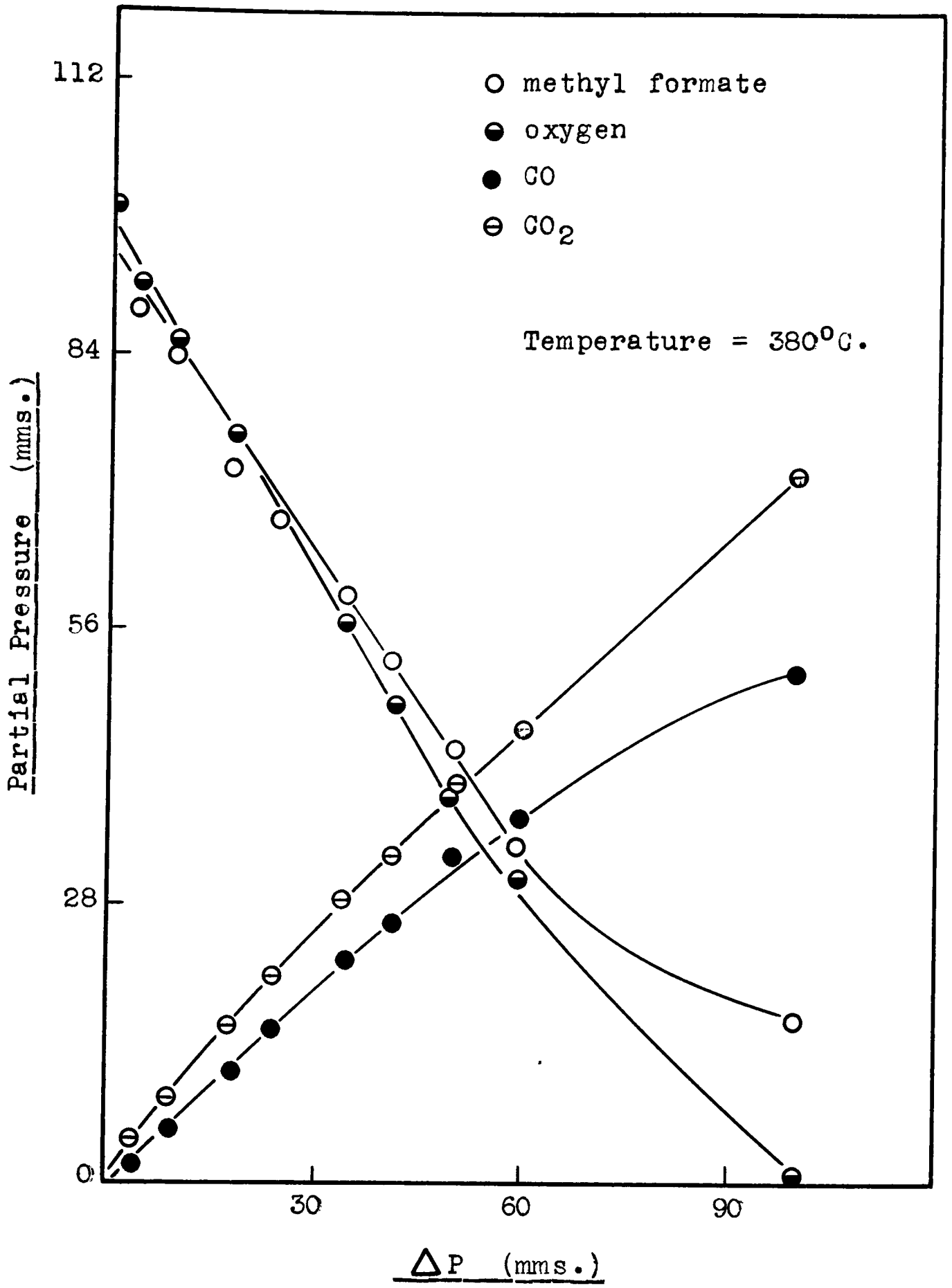
The major constituents of the oxidation of methyl formate, methyl acetate and methyl propionate were determined at 330°C. The major and minor constituents of the oxidation of ethyl formate were estimated at six temperatures across the high and low temperature regions, 280, 310, 340, 360, 380, and 425°C. The initial concentrations of the reagents were as follows:

methyl formate and methyl acetate	100mms. ester; 100mms. oxygen; (100mms. helium)
ethyl formate and methyl propionate	100mms. ester; 200mms. oxygen ; (100mms. helium)

Helium was added to the reaction mixture for the mass spectrometer analyses only. The presence of 100mms. of helium sometimes increased the maximum rate by about 5%, but the effect was not consistent. The induction periods were generally lowered by 10%.

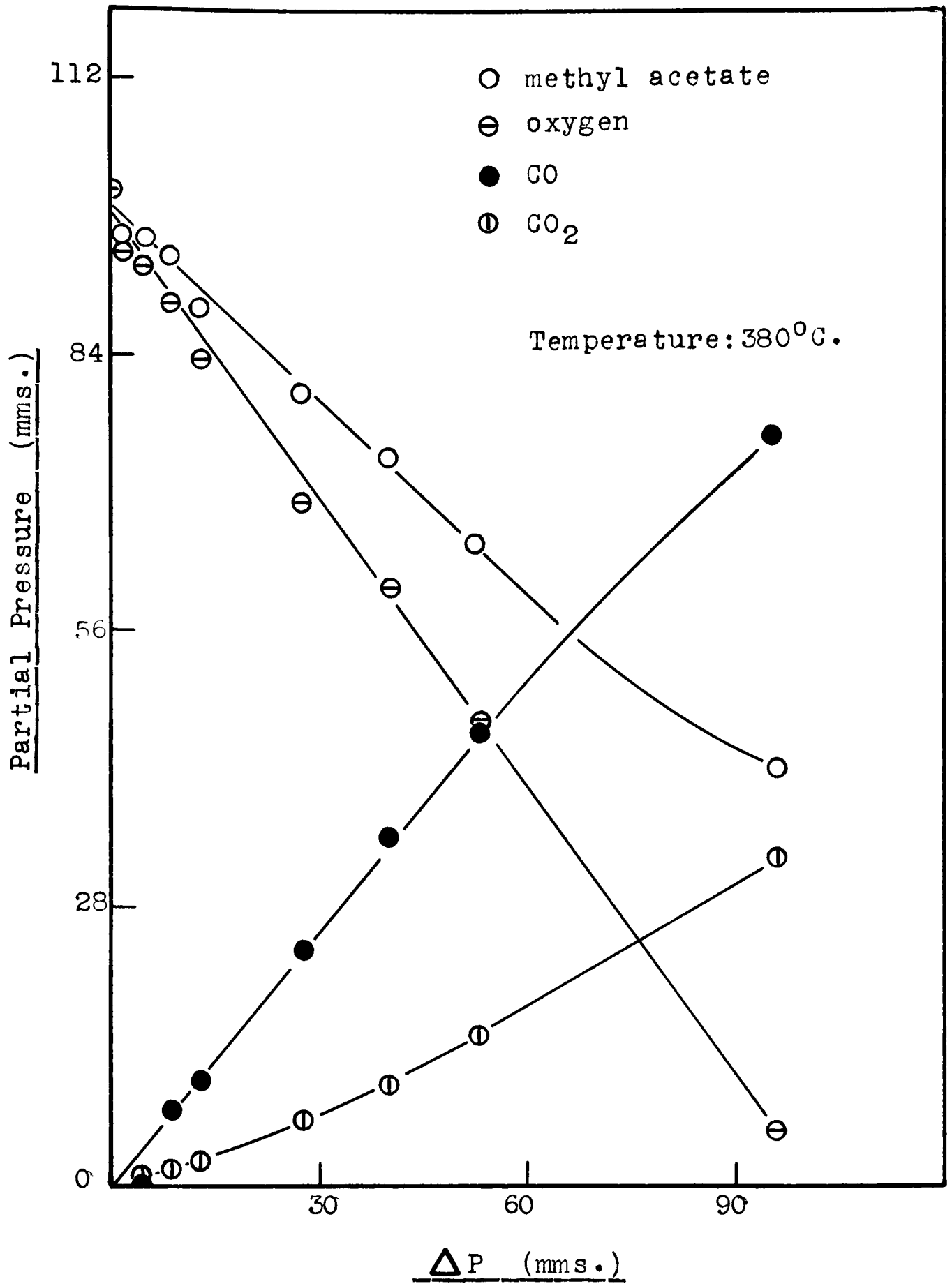
The results calculated from the mass spectra are summarized in figures 16 to 24 . In the case of the oxidation of methyl propionate (figure 18) the analyses for the ester are open to serious question. Methyl propionate is an excellent solvent for most commercial tap greases and it is very unlikely that the true concentration of ester vapour survived the operations of the mass spectrometer. Some difficulty in this respect was also observed with ethyl formate, but the losses were relatively small.

Over most of the reaction course the changes in the concentrations of the major constituents, ester, oxygen, CO and CO_2 were each directly proportional to the observed total pressure change in the reaction vessel. The concentration of CO relative to that of CO_2 was greater for the esters of methyl alcohol than for the esters of formic acid. The amount of carbon monoxide formed during the oxidation of ethyl formate increased considerably as the temperature was increased. In table 2 the ratios of $CO:CO_2$ are



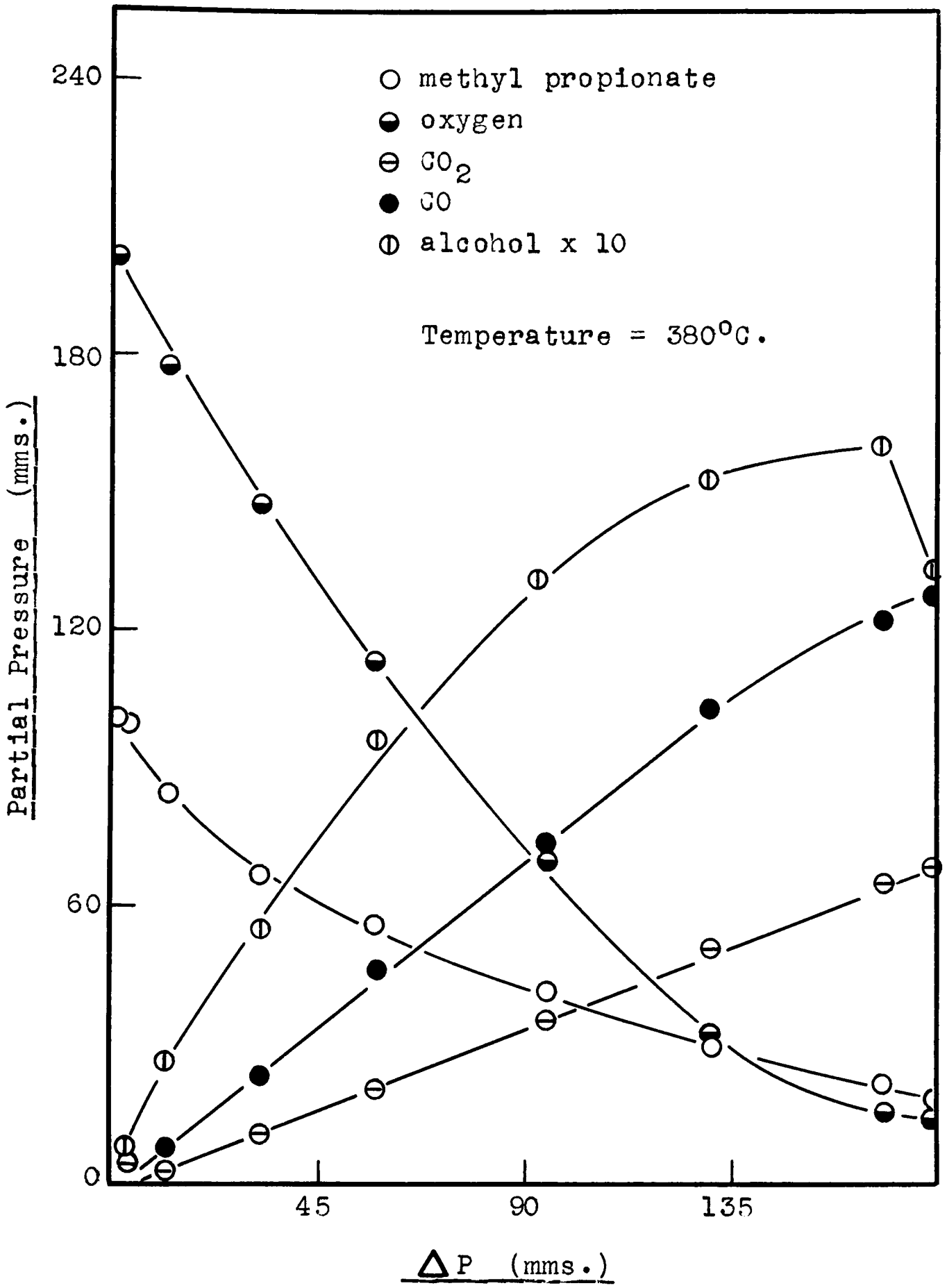
initial pressure of methyl formate = 100 mms.
initial pressure of oxygen = 100 mms.

Figure 16 The concentration of methyl formate and the oxidation products as a function of the pressure measurements



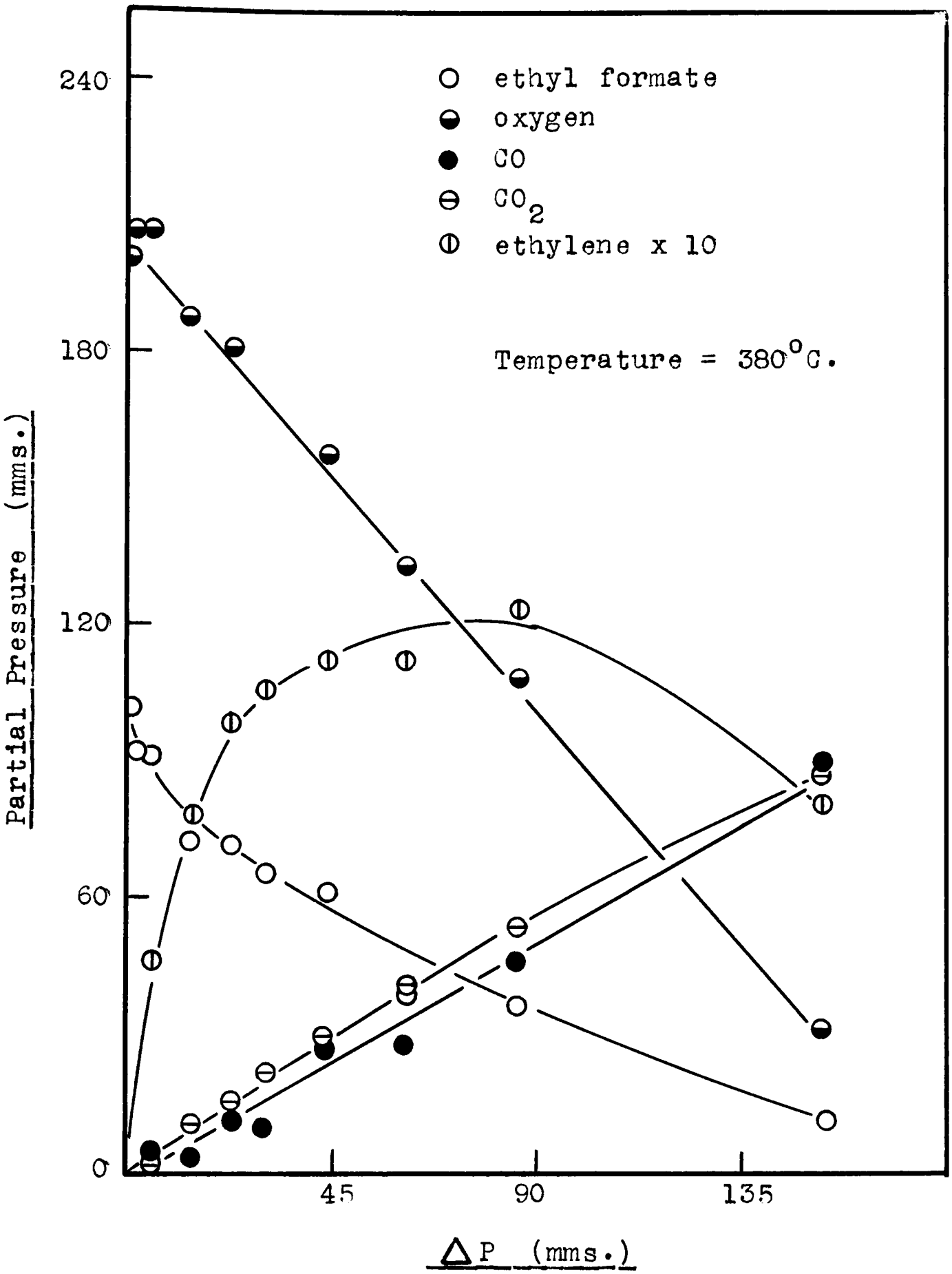
initial pressure of methyl acetate = 100 mms.
initial pressure of oxygen = 100 mms.

Figure 17 The concentration of methyl acetate and the oxidation products as a function of the pressure measurements



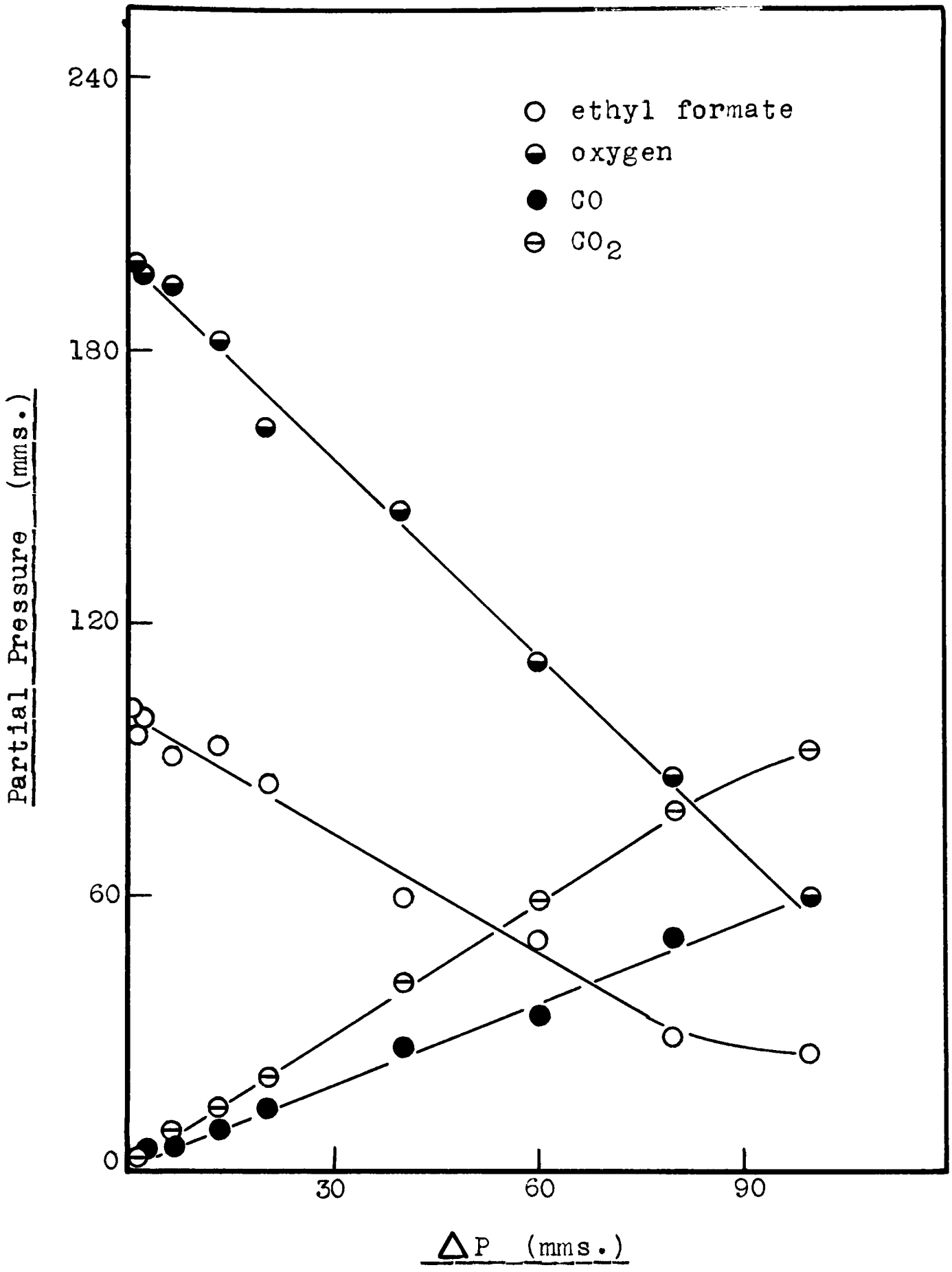
initial pressure of methyl propionate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 18 The concentration of methyl propionate and the oxidation products as a function of the pressure measurements



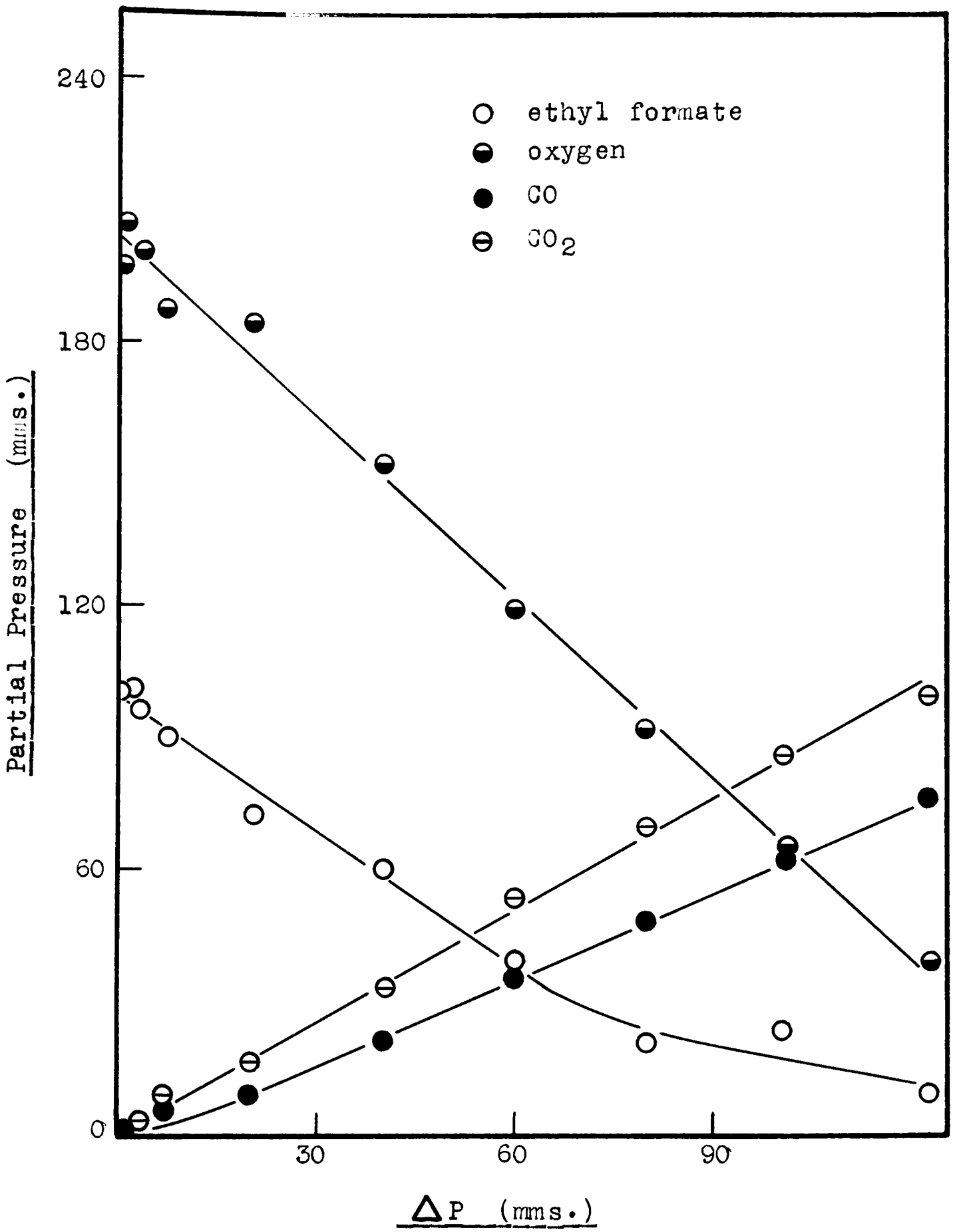
initial pressure of ethyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 19 The concentration of ethyl formate and the oxidation products as a function of the pressure measurements



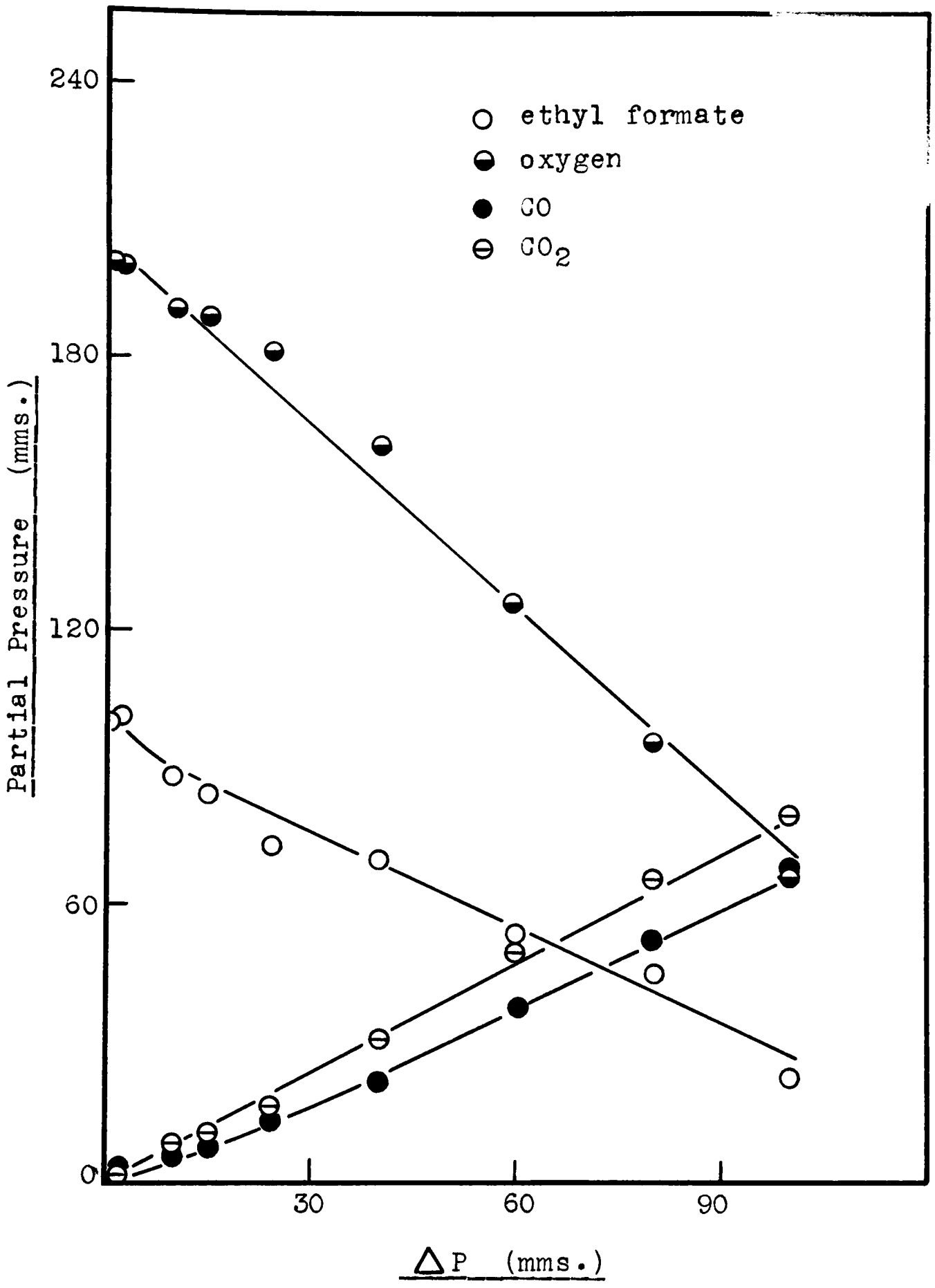
initial pressure of ethyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 20 The oxidation of ethyl formate at 280°C.



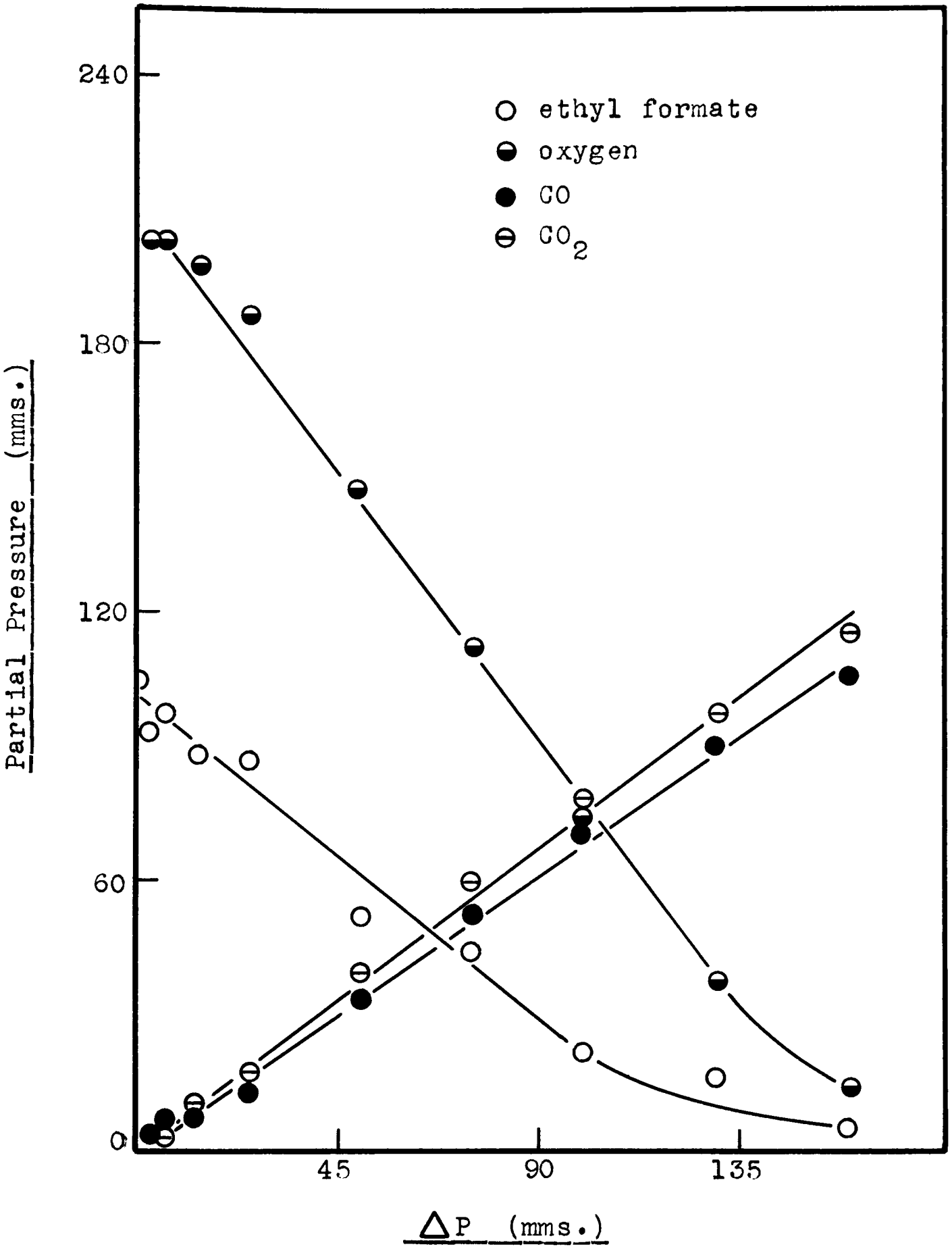
initial pressure of ethyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 21 The oxidation of ethyl formate at 310°C.



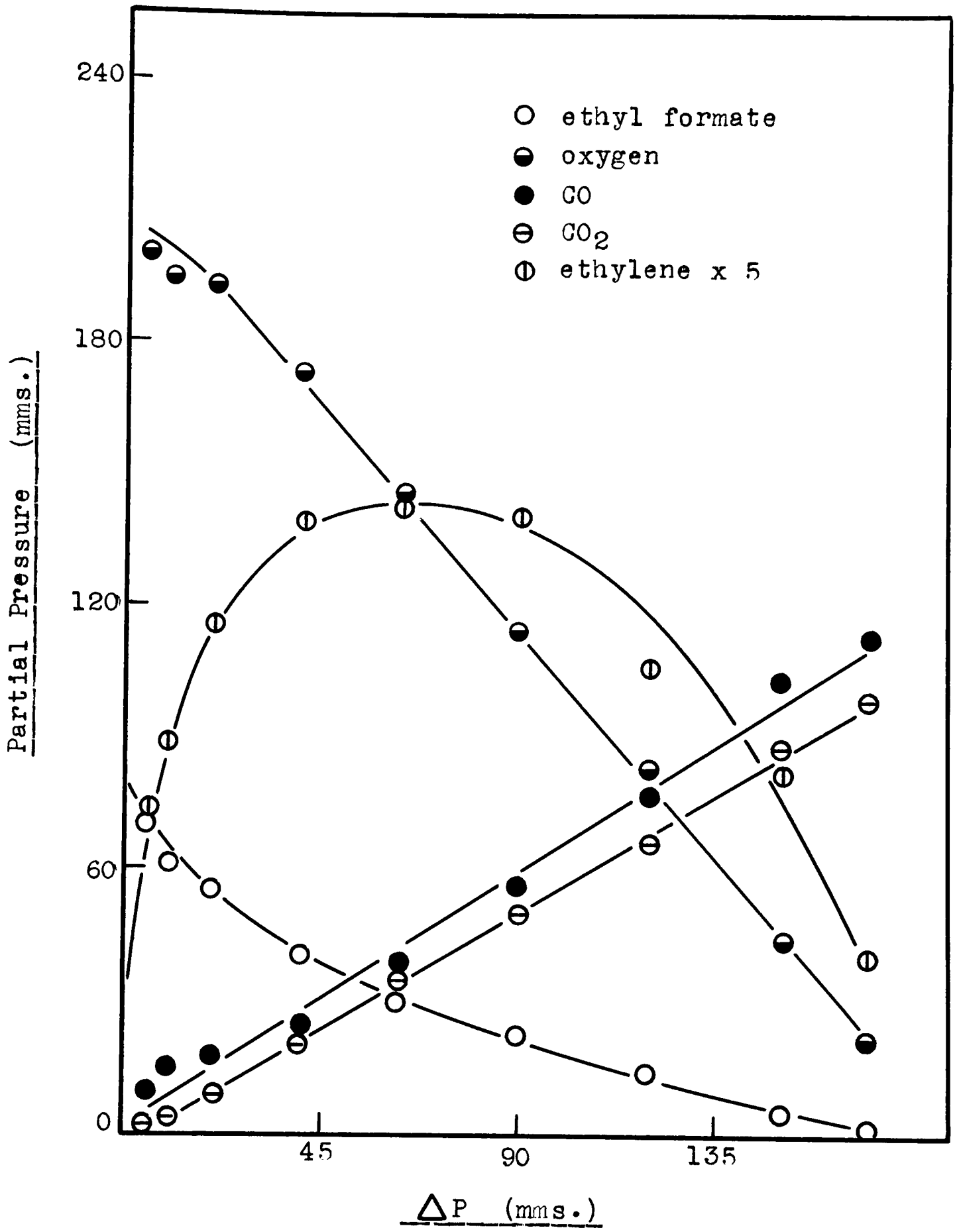
initial pressure of ethyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 22 The oxidation of ethyl formate at 340°C.



initial pressure of ethyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 23 The oxidation of ethyl formate at 360°C.



initial pressure of ethyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 24 The oxidation of ethyl formate at 425°C.

compared as a function of the ester and the temperature.

Appreciable quantities of ethylene were also detected in the mass spectra of the combustion samples of ethyl formate. The concentration of ethylene passed through a maximum as the reaction was allowed to go to completion. At 425 and 380°C. the maximum partial pressures were 28 and 12mms. respectively.

Samples of the ethyl formate mixtures for the aldehyde and acid analyses were collected at three temperatures, 280 and 340°C. in the low temperature region, and 425°C. in the high temperature region. The results of the analyses are shown in figures 25 and 26 . The partial pressure of each species in the reaction vessel was calculated from the known volumes and temperatures of the gas pipette and the reaction vessel according to :

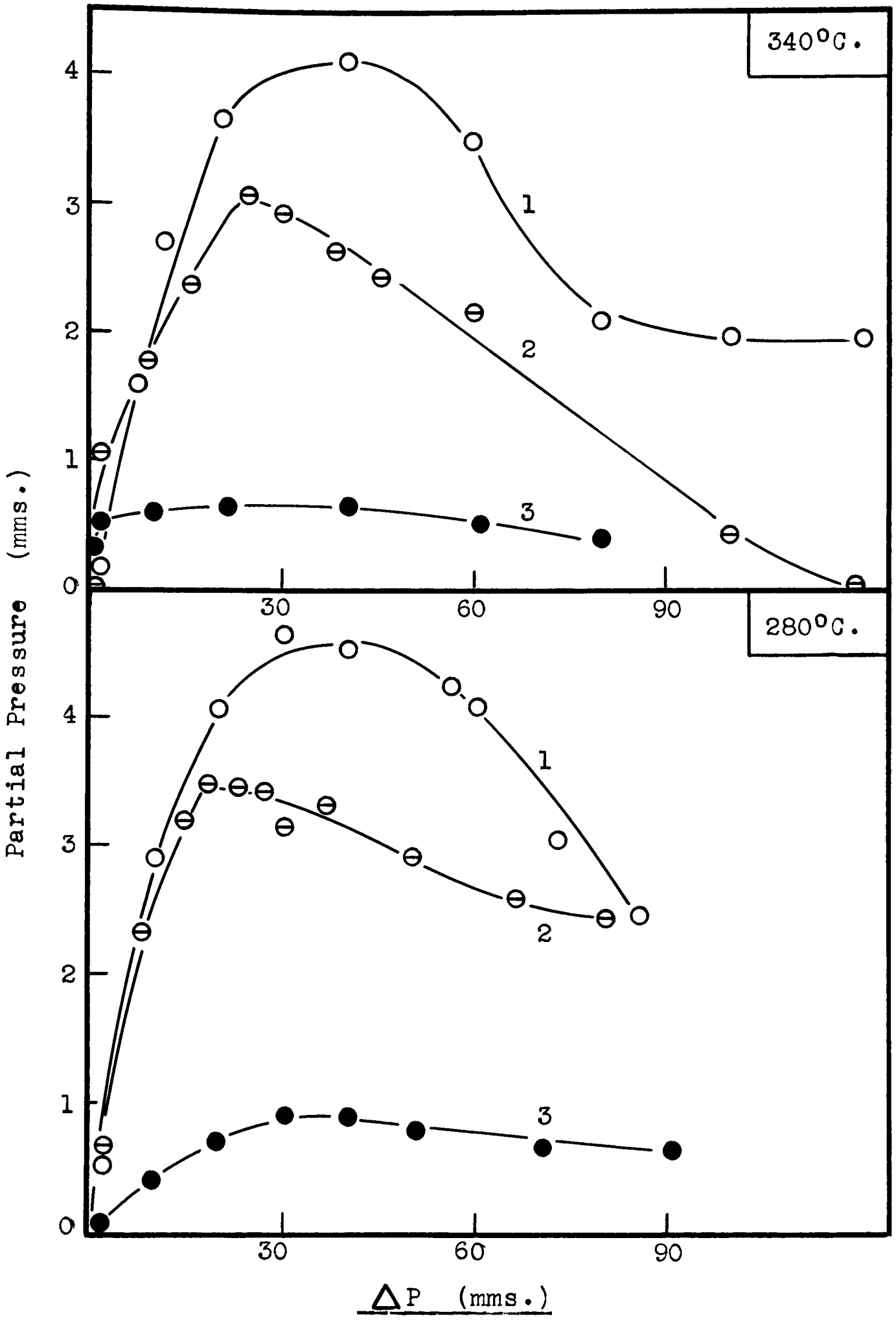
$$P = \frac{RT_2}{V_2}\left[n_1 + \frac{n_1 V_2 T_1}{V_1 T_2}\right]$$

where P is the partial pressure in the reaction vessel
R is the gas constant
T_1 is the temperature of the gas pipette
T_2 is the temperature of the reaction vessel
V_2 is the volume of the gas pipette (404mls.)
V_1 is the volume of the reaction vessel (202mls.)
n_1 is the number of moles in the gas pipette

Table 2 THE $CO:CO_2$ RATIOS

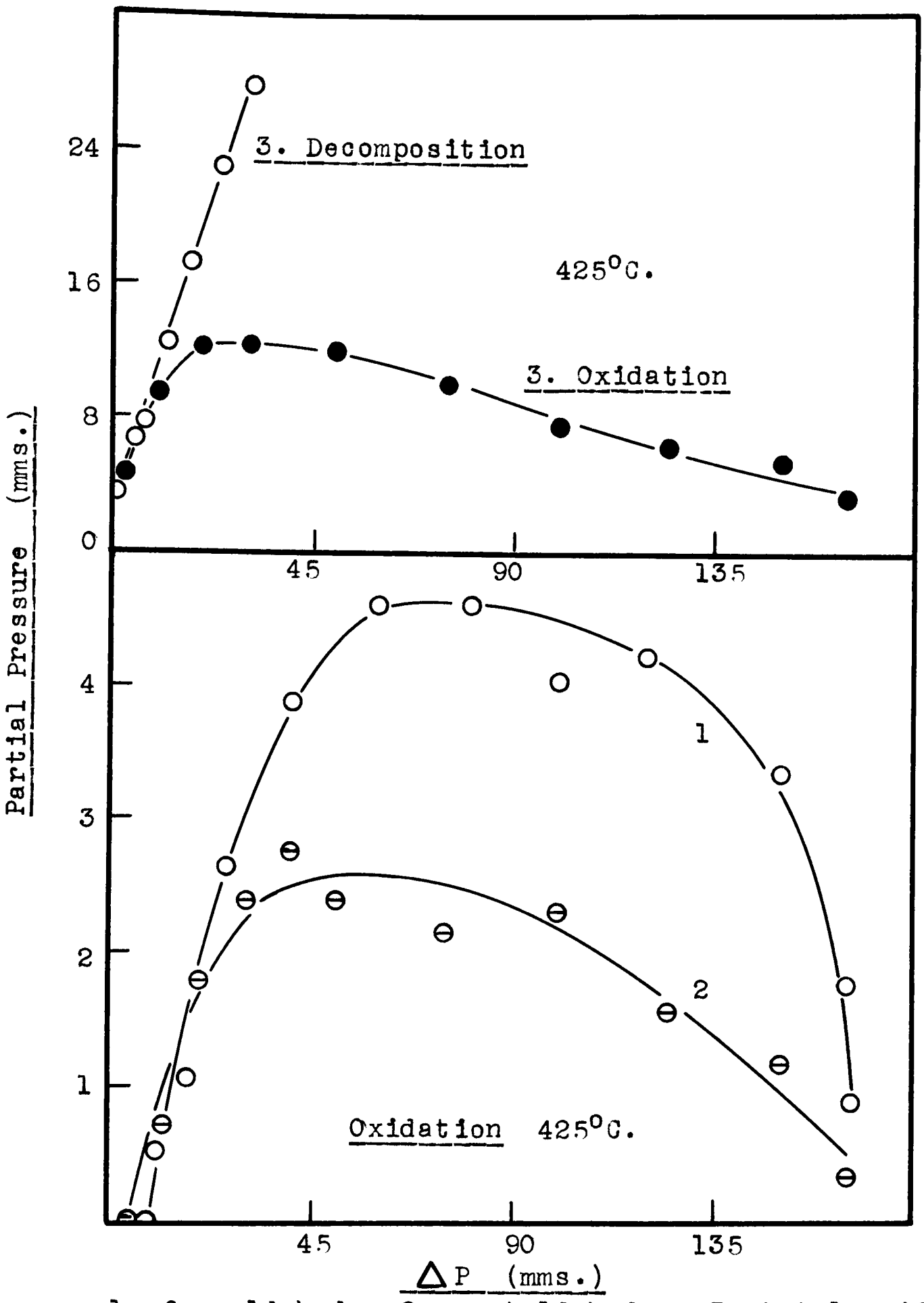
Ester	$CO:CO_2$
Methyl Formate	0.77
Methyl Acetate	3.5
Methyl Propionate	2.0
Ethyl Formate	1.0

Temperature of oxidation of Ethyl Formate	
280° C.	0.58
310	0.67
340	0.73
360	0.90
380	1.0
390	1.0
425	1.1



1. formaldehyde 2. acetaldehyde 3. total acid
initial pressure of ethyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 25 The occurrence of aldehyde and acid during the oxidation of ethyl formate



1. formaldehyde 2. acetaldehyde 3. total acid
initial pressure of ethyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 26 The occurrence of aldehyde and acid during the oxidation and decomposition of ethyl formate

The partial pressures of formaldehyde and acetaldehyde passed through a maximum as the reaction was allowed to go to completion. An increase in the temperature had no effect on the general trend of the experiments. The approximate maximum pressures of formaldehyde and acetaldehyde in the reaction vessel were 4.5 and 3.5mms. respectively.

In the low temperature region very little acid was detected in the combustion samples. However, when the temperature was increased into the high temperature region, appreciable quantities of acid were formed. The maximum partial pressure of acid at 425°C. was 12mms.

A few experiments were made to examine the possibility that the excessive amount of acid occurring in the high temperature region resulted from the simple decomposition of the ester. While the pyrolysis rate was small compared to the rate of oxidation, it was still significant at all temperatures above 400°C.

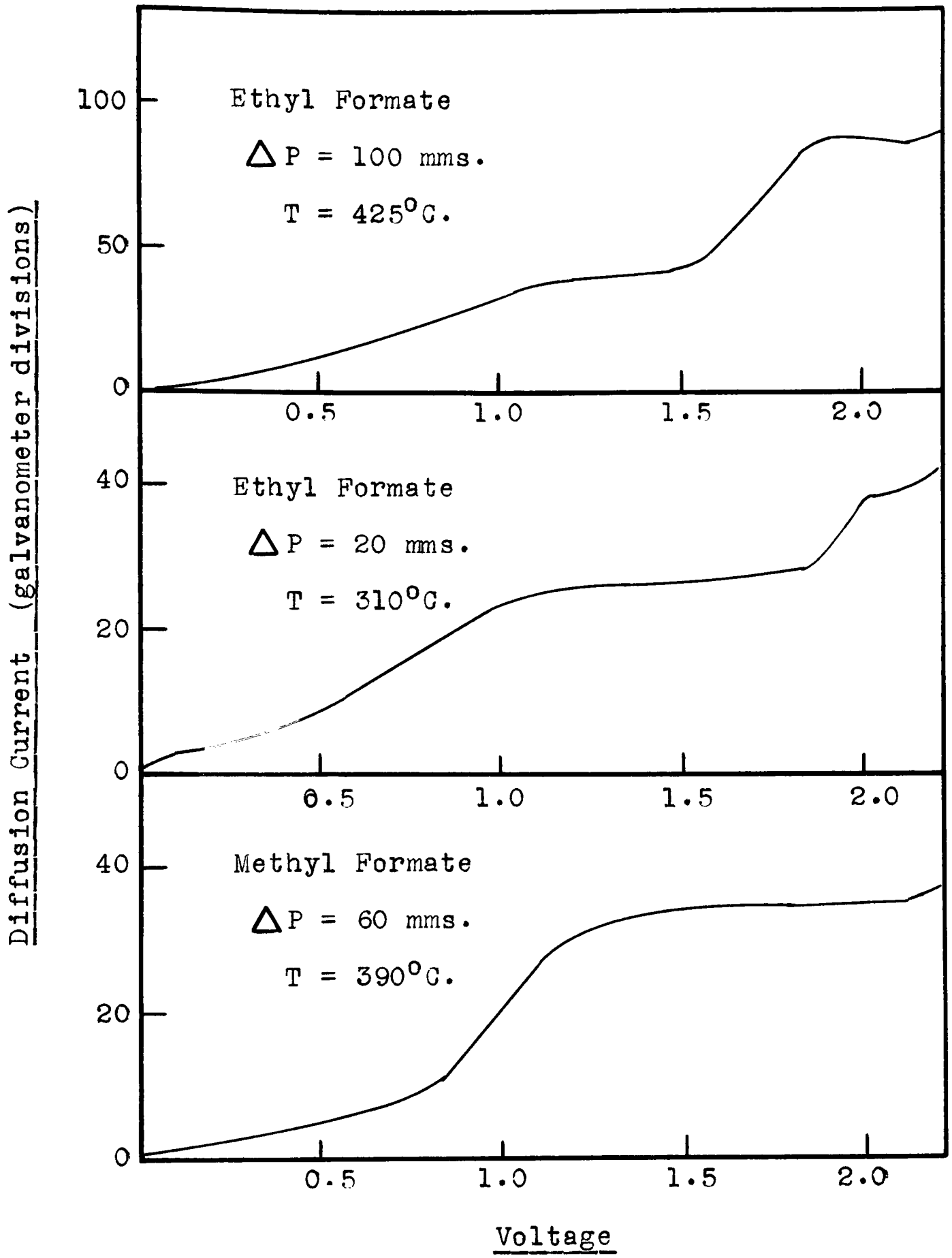
At 425°C. several 100mms. portions of ethyl formate were placed in the reaction vessel for various lengths of time. The gases were expanded into the gas pipette in the usual way and the acid titrated with sodium hydroxide. The results are summarized in figure 26 .

The acid concentration increased almost linearly with the increase in pressure accompanying decomposition. The results compare favourably with the acid concentrations observed towards the end of the induction period of the oxidation reaction.

Polarographic analyses were carried out on the combustion mixtures of methyl and ethyl formate. Samples were collected at several temperatures throughout the high and low temperature regions:
methyl formate: 390°,415°,and 450°C.
ethyl formate: 280°,310°,340°,360°,380°,and 425°C.
At each temperature the initial pressures of the reagents were 100mms. of ester and 200mms. of oxygen.

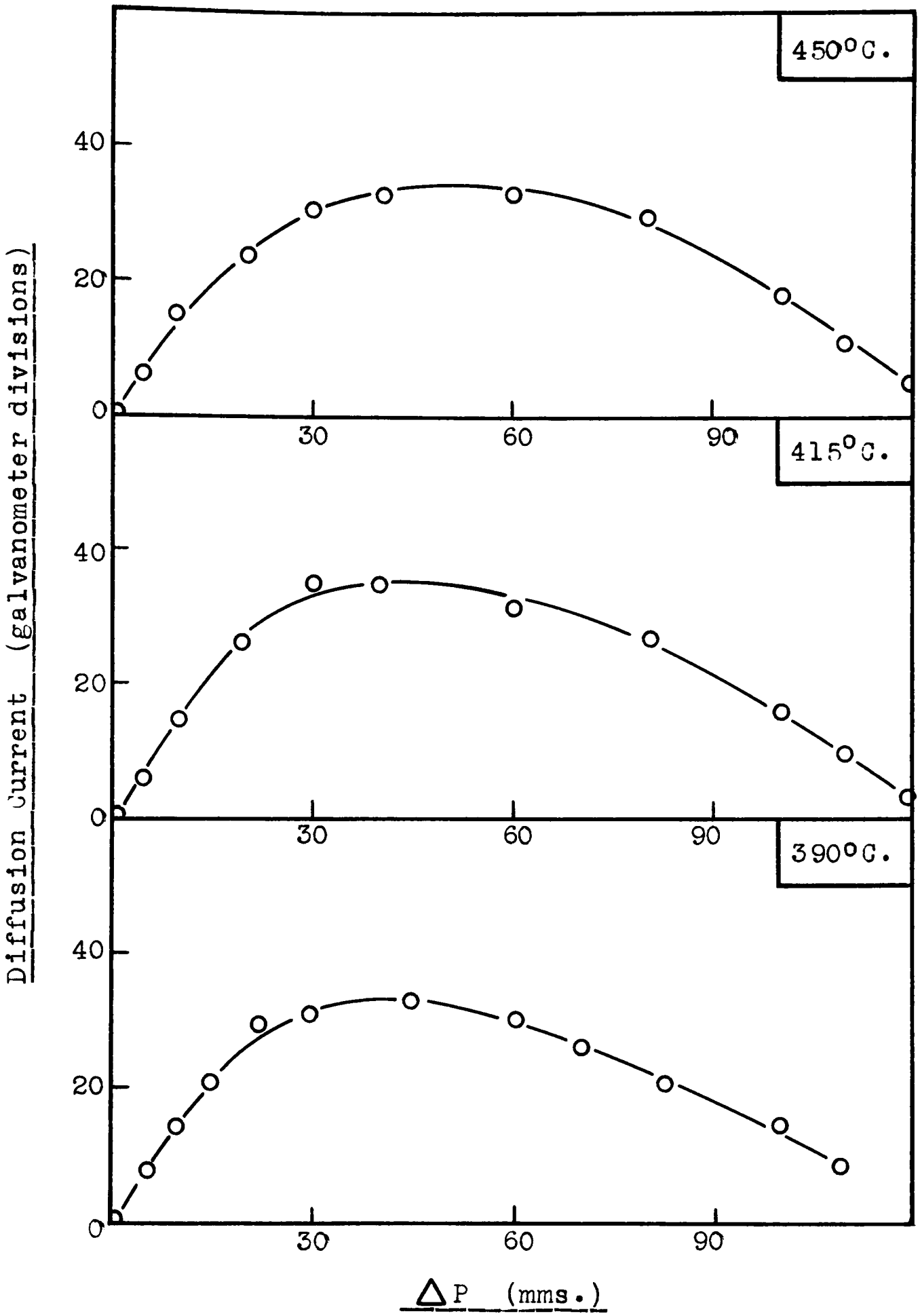
Typical polarograms of the combustion samples are illustrated in figure 27 . The oxidation mixtures of ethyl formate usually showed two waves or steps. The first was a broad,drawn out wave at about 0.9 volts, characteristic of peroxidic substances (41). The second occurred at 1.9 volts in the low temperature region, and at 1.7 volts in the high temperature region. The polarograms of the methyl formate mixtures showed only the broad peroxide wave at 0.9 volts.

The heights of the three waves are summarized as the function of the pressure measurement,ΔP, in figures 28, 29, and 30 . At all temperatures the



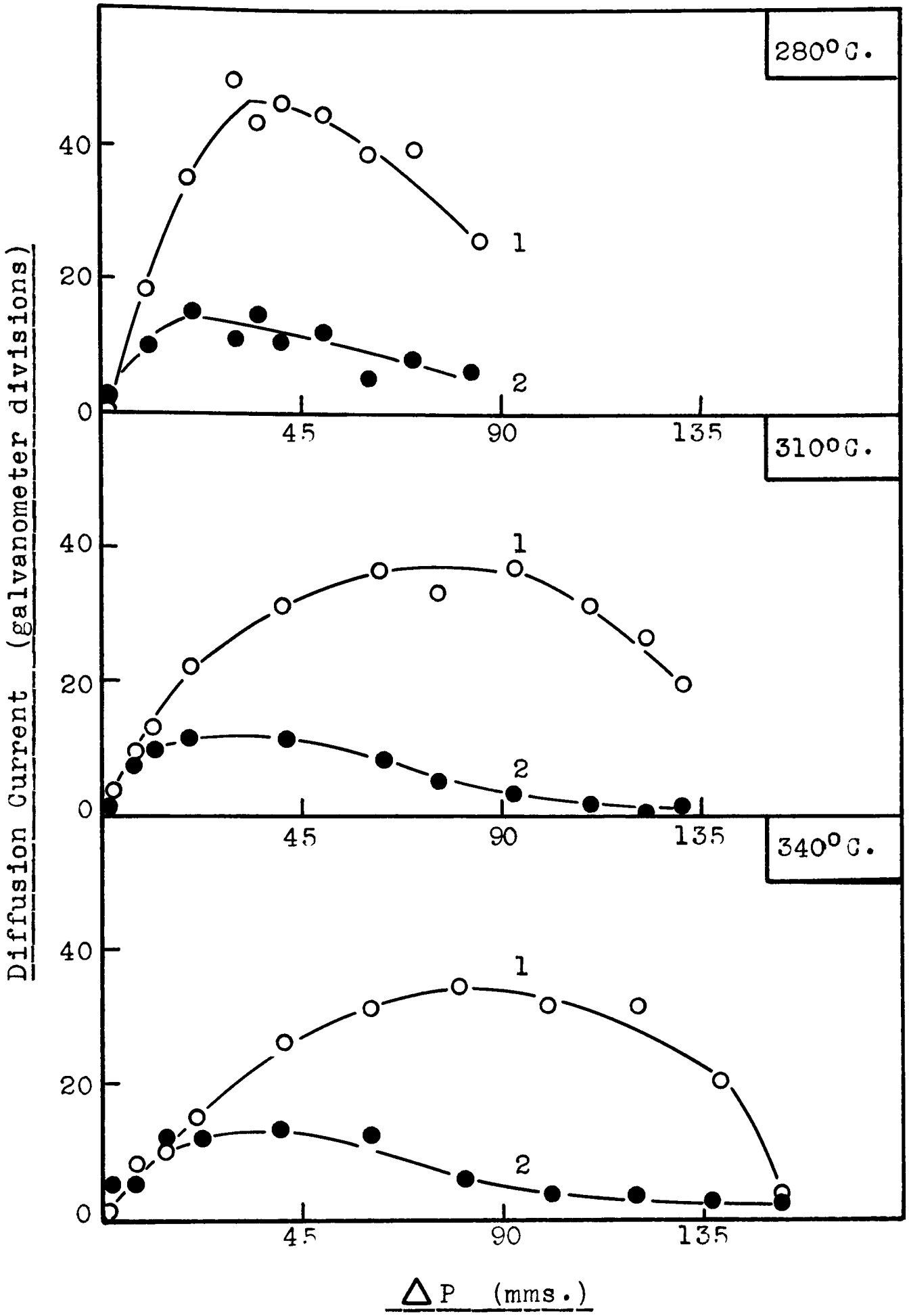
initial pressure of ester = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 27 Typical polarograms of the combustion mixtures of methyl and ethyl formate



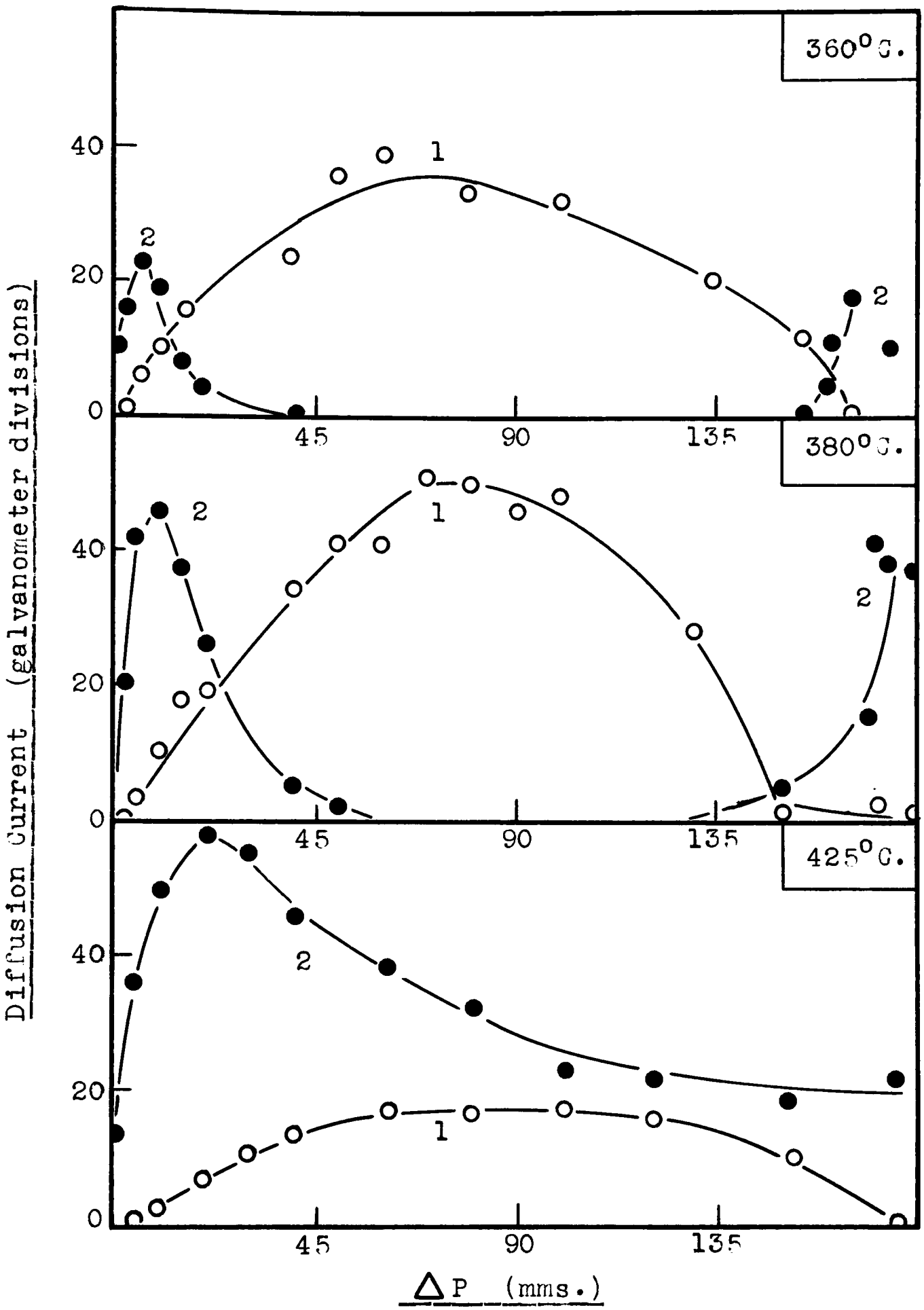
initial pressure of methyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 28 The variation in the height of the polarographic wave at 0.9 volts during the oxidation of methyl formate



1. step at 0.9 volts 2. step at 1.9 volts
initial pressure of ethyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 29 The variation in the height of the polarographic waves during the oxidation of ethyl formate



1. step at 0.9 volts 2. step at 1.7 volts
initial pressure of ethyl formate = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 30 The variation in the height of the polarographic waves during the oxidation of ethyl formate

wave at 0.9 volts increased to a maximum as the reaction went to completion. The maximum diffusion current was between 30 and 40 galvanometer divisions for both methyl and ethyl formate.

In the low temperature region the variation of the second wave in the polarograms of ethyl formate was very similar to that of the peroxide step. At 280°C. the maximum diffusion current was 15 divisions. As the temperature was increased the height of the step at 1.9 volts gradually decreased. At 350°C. it was no longer measurable.

In the high temperature region the second wave, at 1.7 volts, also passed through a maximum with ΔP. However, the maximum was more sharply defined and showed no similarity to the behaviour of the peroxide wave. At 360°,380°, and 425°C. the maximum diffusion currents were 23, 46, and 115 divisions respectively.

Several experiments were made with pure samples of formaldehyde, acetaldehyde and formic acid, in an attempt to identify either the 1.7 or the 1.9 volt steps. The polarogram of formic acid showed a well defined step at 1.7 volts, very similar to the polarograms of the combustion mixtures. The sharp increase in the height of the wave in the high temperature region is in agreement with the results of the chemical analyses for total acid.

The Oxidation of Propane:

The results of the mass spectrometric and polarographic analyses of the combustion samples of the esters indicated significant differences between the high and low temperature regions. It was not possible, however, to examine the reactions under conditions of cool flame oxidation. The rapidity with which the cool flames passed through the reaction mixture, and the tendency for the high molecular weight esters to dissolve in the tap grease, made normal analysis very difficult.

A previous investigation of the effect of temperature on the oxidation of propane (3) indicated more favourable conditions for the examination of cool flame combustion. It was decided, therefore, to apply the mass spectrometric and polarographic techniques to the cool flames of propane, rather than to continue the investigation with the esters.

No significant changes were required in the apparatus and the only change made in the experimental method was the omission of the P_2O_5 drying agent from the mass spectrometer sampling pots. There always existed the possibility of solution or reaction of the combustion intermediates in the watery surface of the drying agent, and as the demands on the mass spectrometer were not as great during this period of investigation the P_2O_5 was omitted.

The Experimental Results:

The effect of temperature on the maximum rate of oxidation and the induction period is shown in figures 31 and 32 . The initial pressures of propane and oxygen were:

100mms. propane and 200mms. oxygen
50mms. propane and 300mms. oxygen

The results paralleled those reported by Mulcahy (3), and were very similar to those observed during the oxidation of propyl formate.

No induction periods were observed in the region of transition between the zones of cool flame combustion and high temperature oxidation. In the high temperature region the induction periods were short (1-2 minutes) and independent of the reaction temperature.

The polarographic investigation was made on combustion samples collected at four temperatures, 280°, 300°,370°, and 400°C. The initial pressures of the reagents at each temperature were 100mms. propane and 200mms. oxygen. The results are summarized in figures 33 to 36 .

The general shape of the polarograms of the oxidation mixtures of propane were very similar to those

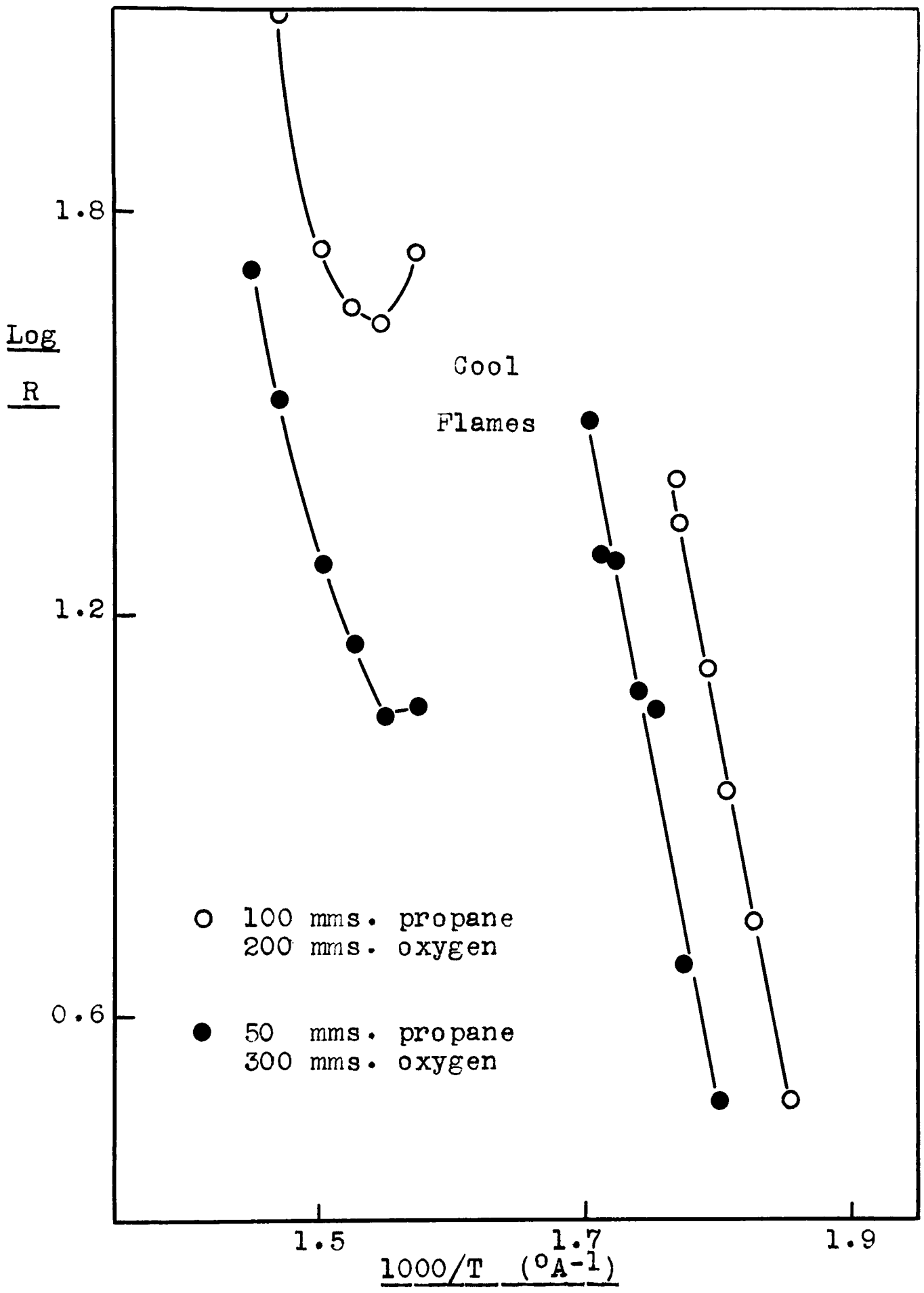
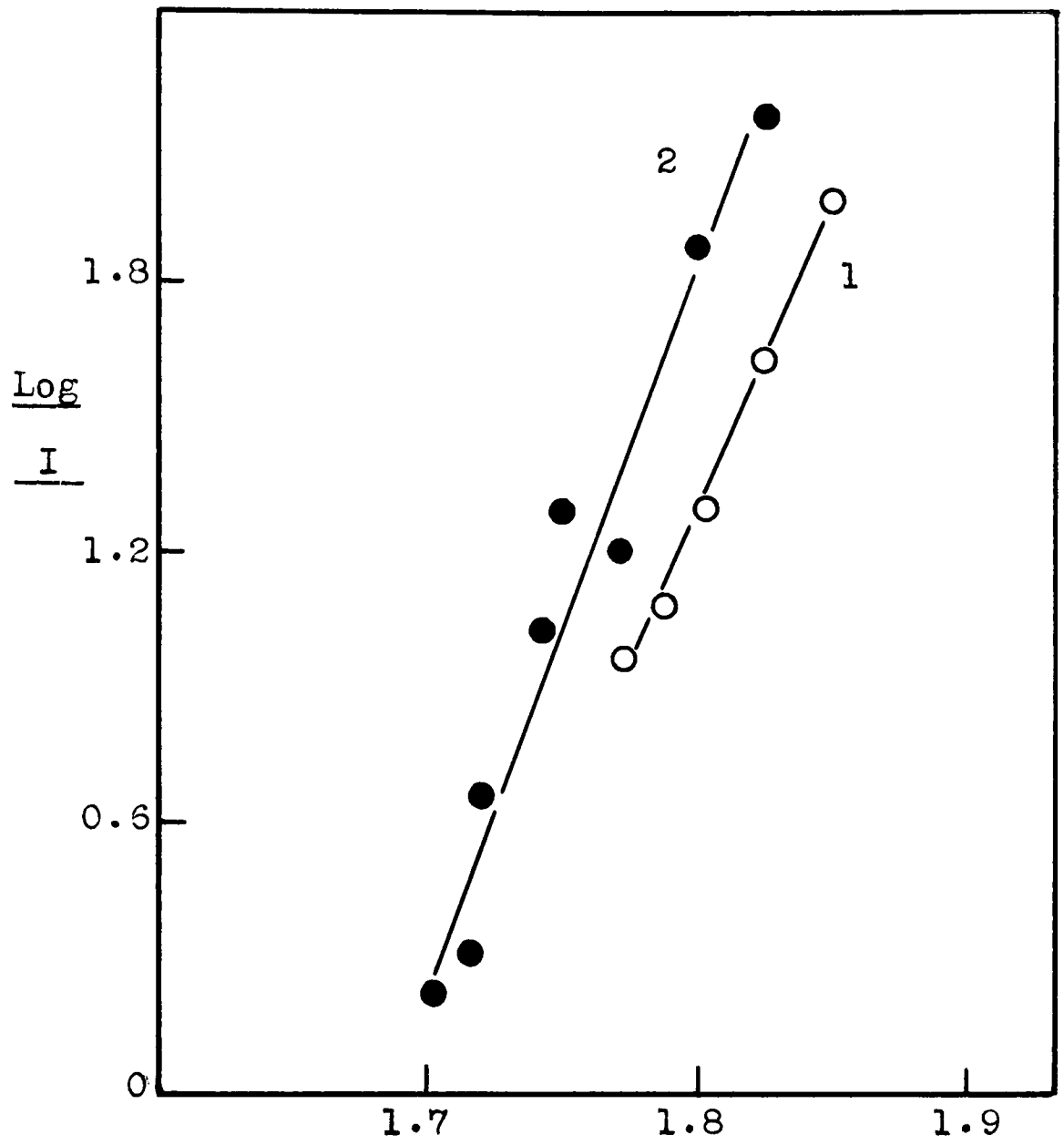
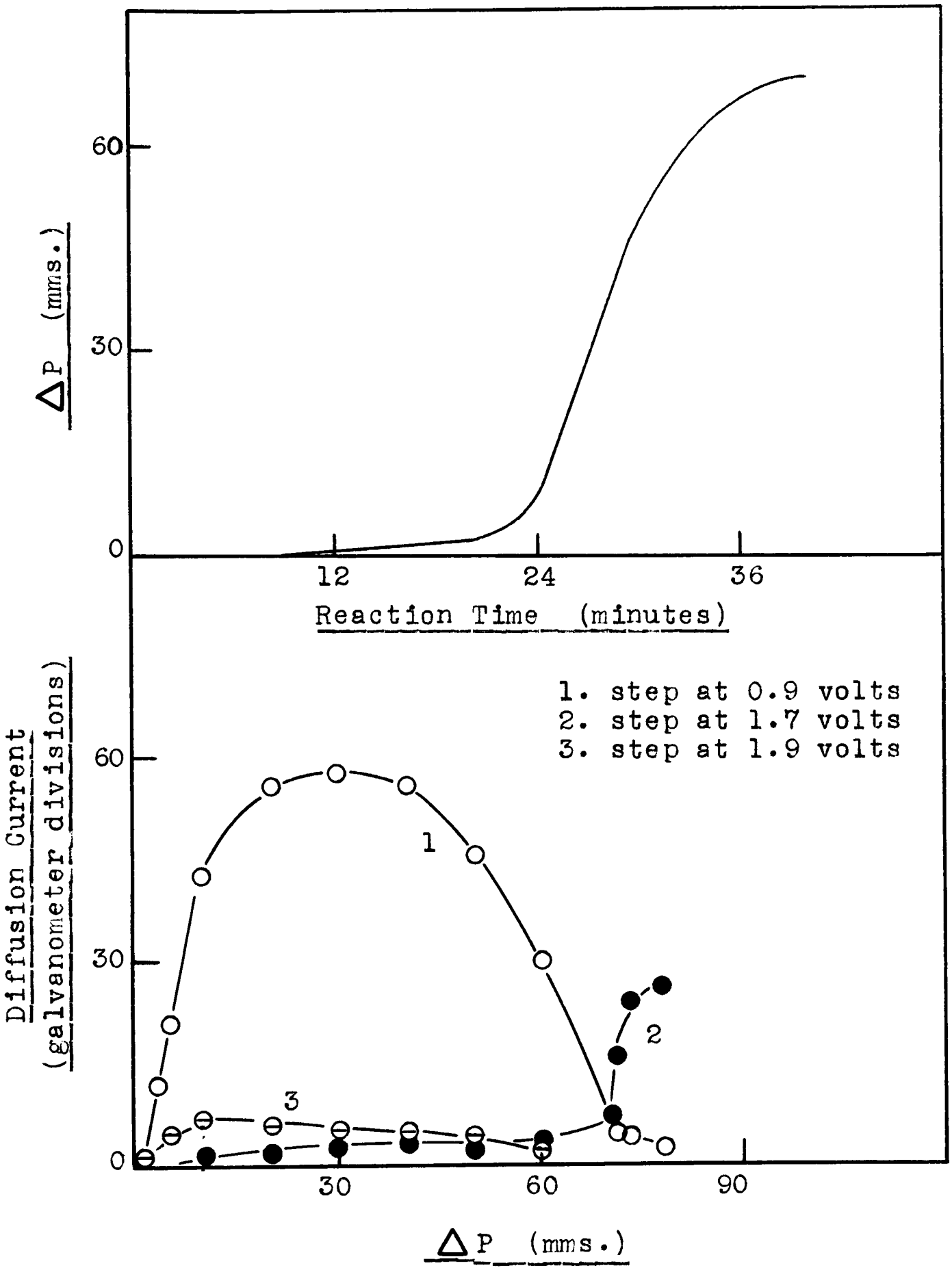


Figure 31 The effect of temperature on the maximum rate of oxidation of propane



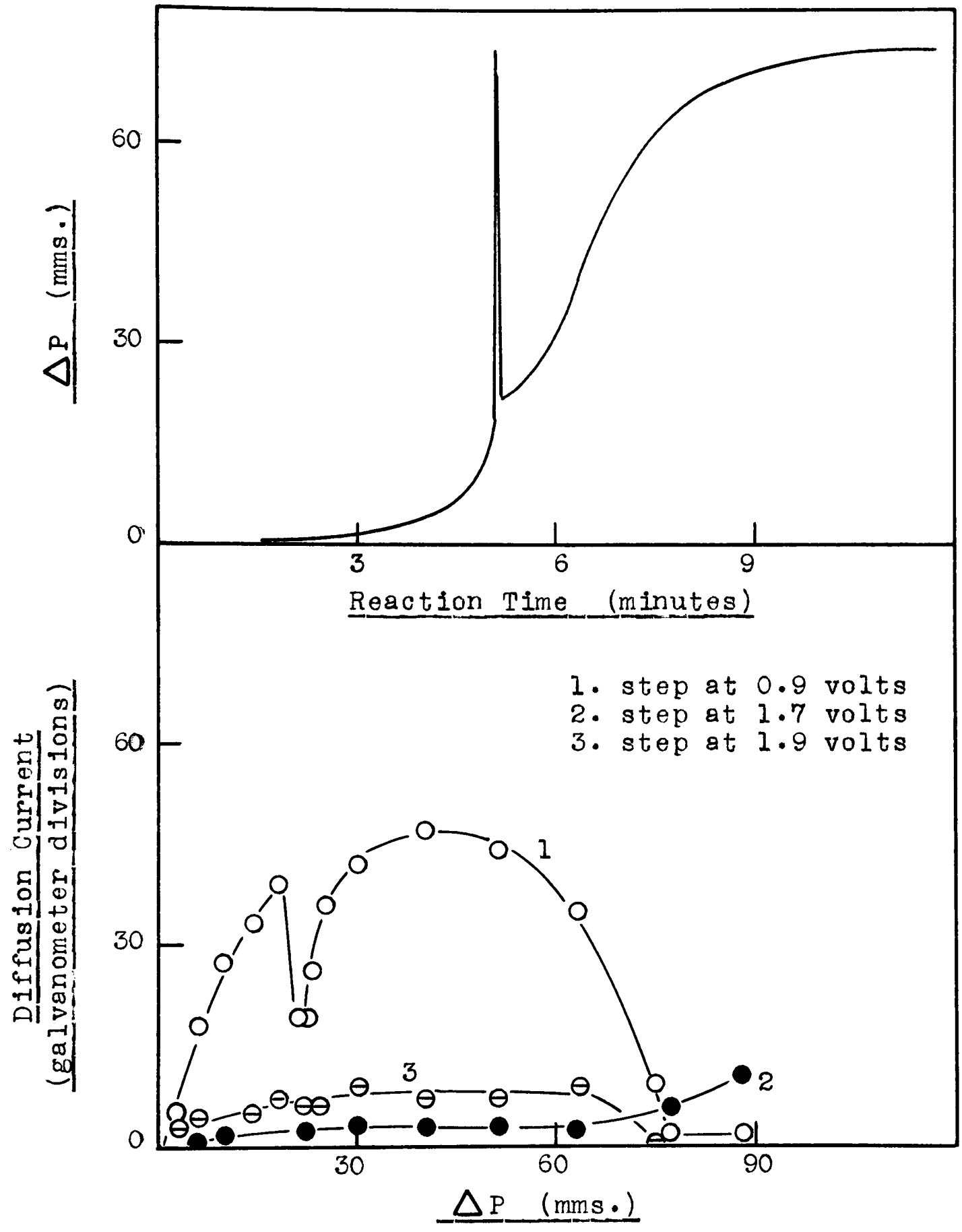
1. 100 mms. C_3H_8; 200 mms. O_2
2. 50 " " 300 " "

Figure 32 The effect of temperature on the induction period of the oxidation of propane



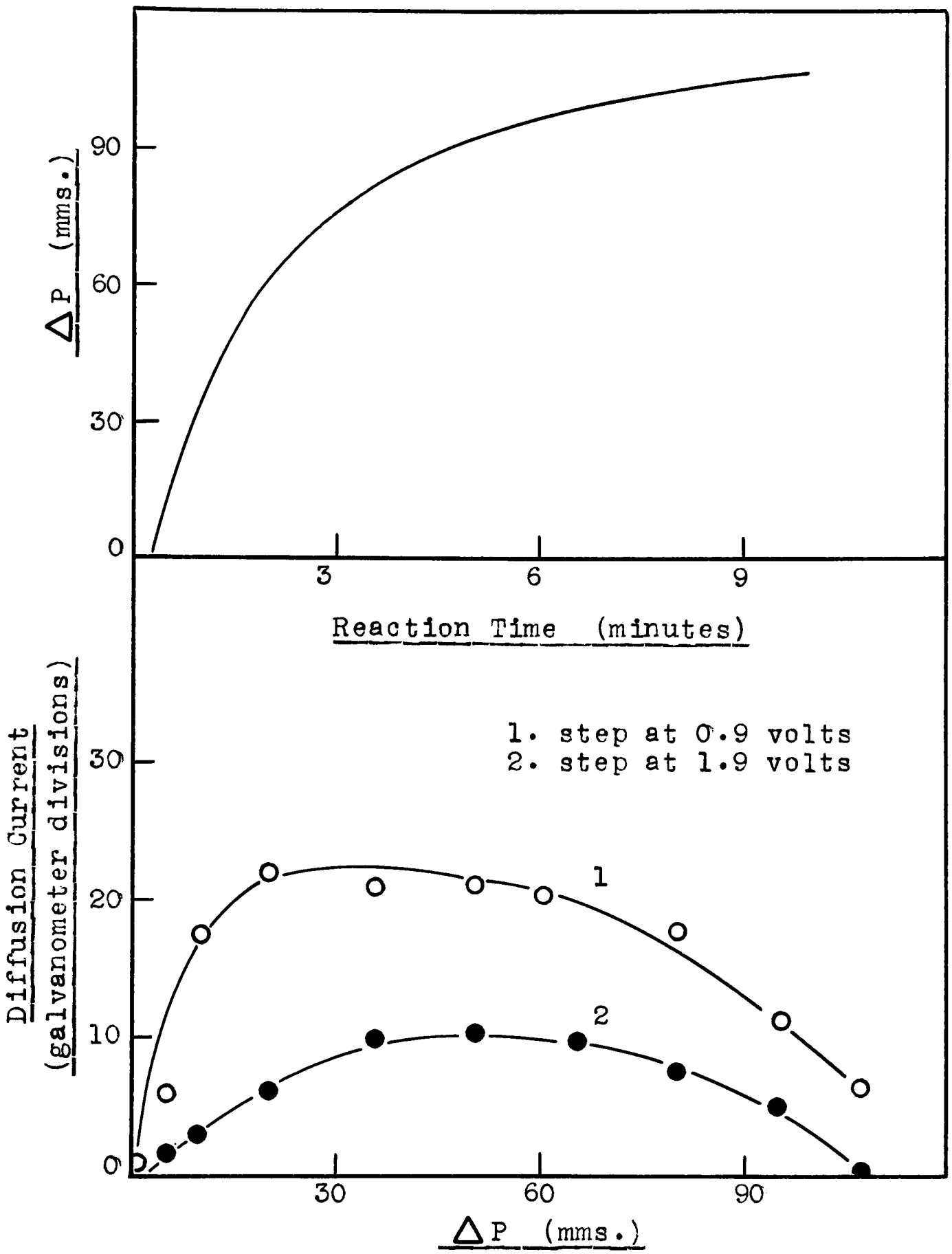
initial pressure of propane = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 33 The variation in the height of the polarographic waves during the oxidation of propane at 280°C.



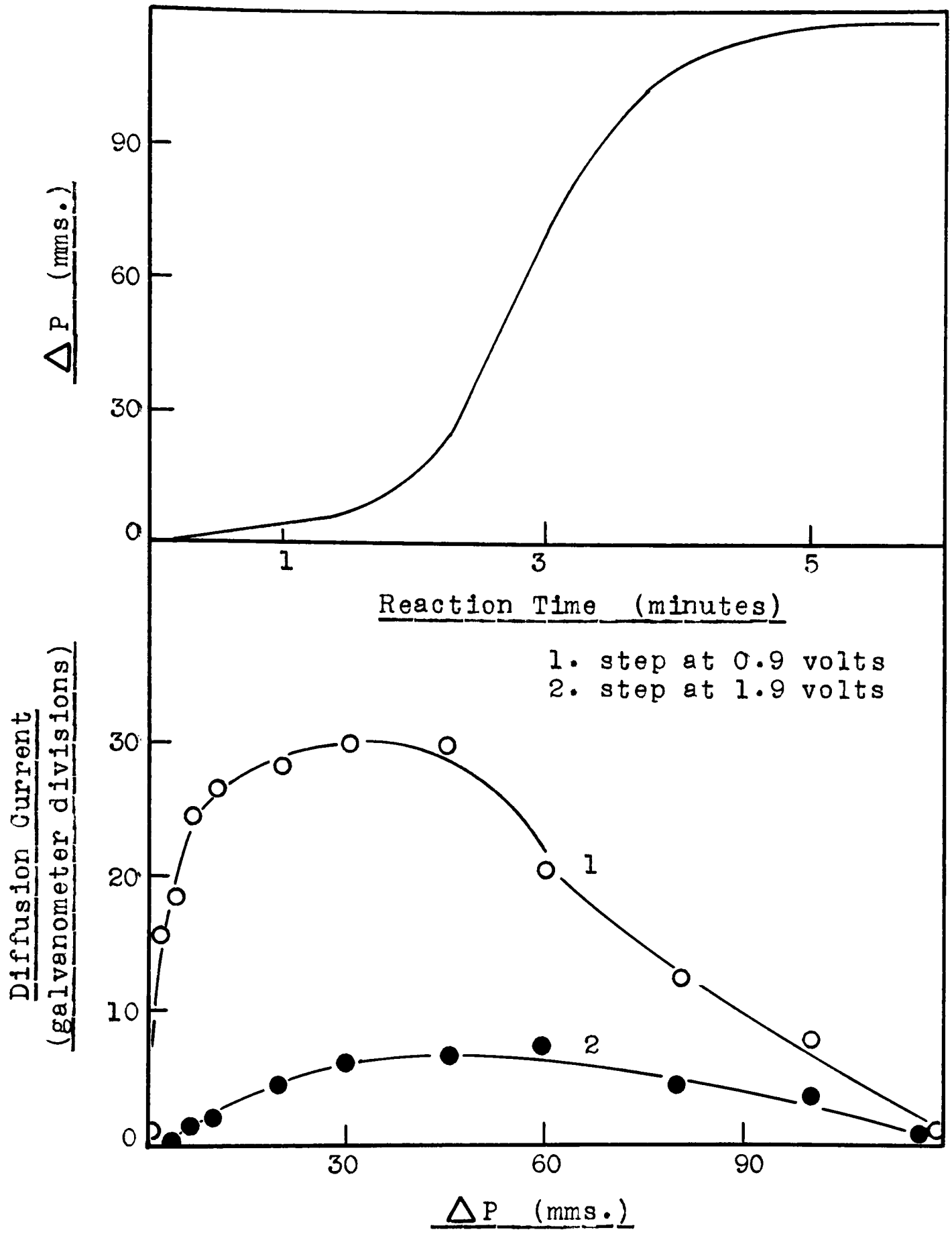
initial pressure of propane = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 34 The variation in the height of the polarographic waves during the oxidation of propane at 300°C.



initial pressure of propane = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 35 The variation in the height of the polarographic waves during the oxidation of propane at 370°C.



initial pressure of propane = 100 mms.
initial pressure of oxygen = 200 mms.

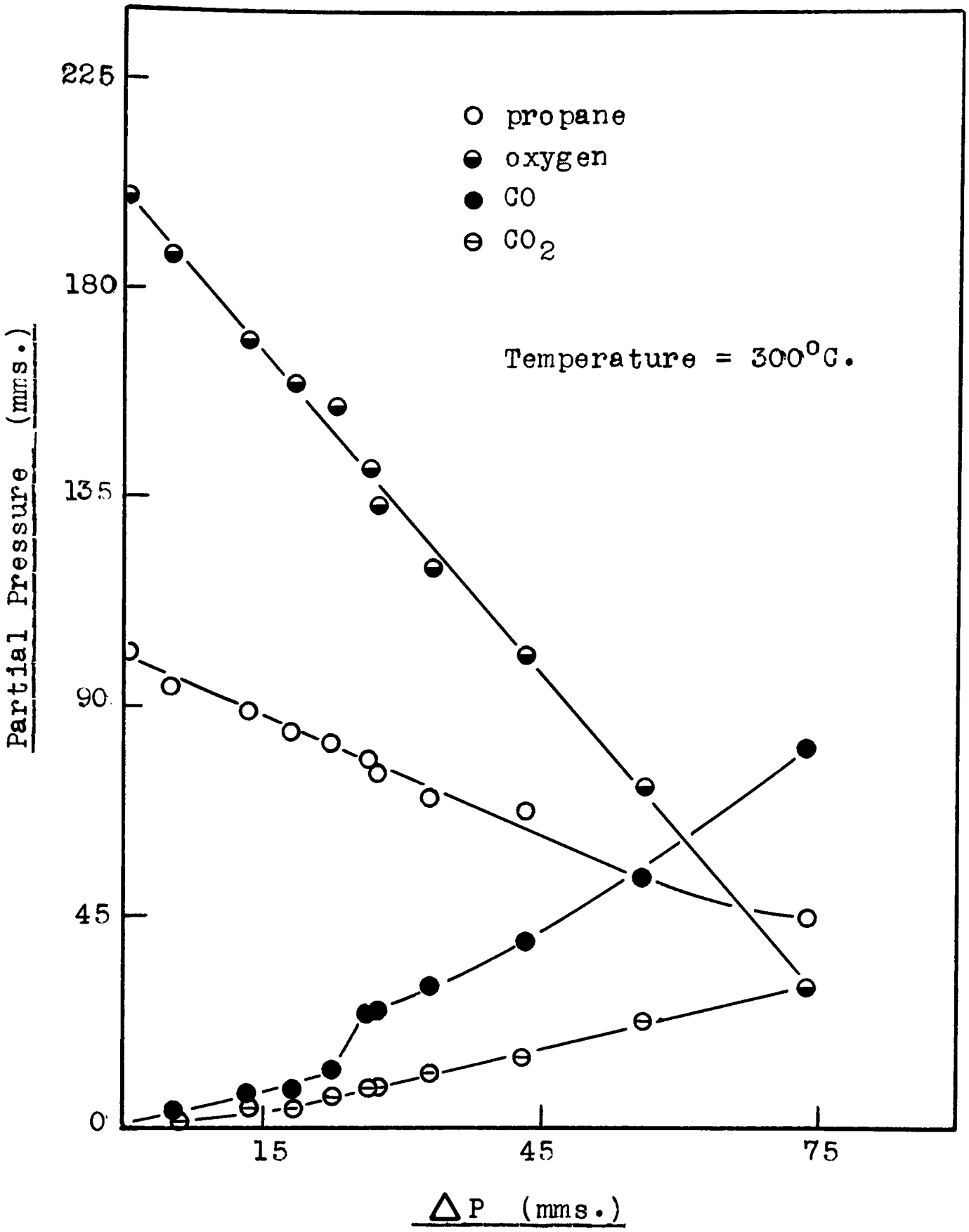
Figure 36 The variation in the height of the polarographic waves during the oxidation of propane at 400°C.

observed with methyl and ethyl formate. The predominating feature was the broad peroxide wave between 0.3 and 1.2 volts. As in the case of the esters the height of this wave passed through a maximum as the reaction went to completion. In the high temperature region this maximum value was about half that observed in the low temperature region.

In addition to the broad peroxide wave, two smaller steps were recorded at 1.7 and 1.9 volts. The wave at 1.9 volts increased to a maximum with an increase in the ΔP. The wave at 1.7 volts was only observed towards the end of the reaction in the low temperature region.

The polarograms of the mixtures collected under conditions of cool flame oxidation were similar to those recorded with samples prepared at lower temperatures. At 300°C. (figure 34) the height of the peroxide wave decreased sharply as a cool flame passed through the reaction mixture. The smaller steps of the polarogram were not affected by cool flame combustion.

The results of the mass spectrometric analyses of the combustion gases of cool flame oxidation are summarized in figure 37 . The only major constituent affected by the passage of a cool flame was carbon monoxide. An increase of 12mms. in the partial pressure of CO was observed after the cool flame. The concentration



initial pressure of propane = 100 mms.
initial pressure of oxygen = 200 mms.

Figure 37 The concentration of propane and the oxidation products as a function of the pressure measurements

of propane, oxygen and carbon dioxide were directly proportional to the pressure changes measured in the reaction vessel.

DISCUSSION

DISCUSSION

The experimental results of the oxidation of the esters can be best discussed under several headings in relation to the historical development of the general problem of combustion, and the more outstanding chemical effects. The divisions selected deal with the significance of the analytical investigation, the structural effect and the probable mechanism of attack, a discussion of previous theories and some considerations of the matter of cool flame combustion.

The inter-relationship of the various features of oxidation chemistry make it very difficult to separate each section entirely from the others. It is hoped, however, that the present discussion will correlate the kinetics of the esters to the general kinetics of combustion phenomena, and will indicate, at least to some extent, the logical steps to be taken or attempted in the immediate future.

The Analytical Investigation:

The pressure-time curves for the oxidation of the esters contain an induction period followed by a gradual acceleration of the rate of change of pressure up to a maximum. Similar observations have been made with almost every variety of normal and substituted

hydrocarbon. The pressure-time curve has been quite widely accepted as a measure of the oxidation process, although there is no particular reason why hydrocarbons and oxygen could not react in a manner producing no change in pressure. Qualitative experiments made with the olefins (Hinshelwood and Thompson (43), Lenher (44), and Bone(45)), where the problems of hydrocarbon analysis are not quite so formidable, indicate no appreciable reaction during the induction period. In the present investigation an attempt has been made to confirm these experiments in a quantitative way, for both normal and oxygen substituted hydrocarbons.

The mass spectrometer analyses of the oxidation of the esters and propane show the concentration of the reagents and final products to be a direct function of the pressure change in the reaction vessel. The chemical analyses for the intermediate products, formaldehyde, acetaldehyde and acid, support the analyses for the major constituents in the view that very little oxidation occurs during the induction period. The maximum concentrations of intermediate substances coincide with the maximum rate of change of pressure and do not exceed 2-3% of the total gas pressure. The same relationships were observed in both the low and high temperature regions and in the transition region where the temperature coefficient

of the pressure measurements is negative.

The analytical investigation thus establishes beyond all reasonable doubt the validity of the pressure measurements as a measure of the oxidation process. The pressure change measures essentially the accumulation of the final combustion products, and the various active intermediates, however important they may be for the theory of the mechanism, are never present in amounts sufficient to distort significantly the pressure changes.

The Structural Effect:

Care must be taken in the comparison of the effect of substituent groups on the maximum rate of oxidation to select data relating to the same region of reactivity. Almost all normal and substituted hydrocarbons with a carbon chain length of more than three units show two regions of reactivity, the "low" and "high" temperature regions, separated by a short range of temperatures where the temperature coefficient of the reaction is negative.

In Table 3 the maximum rates of oxidation for the six esters in both the low and high temperature regions are compared with one another, and with the corresponding data, in the low temperature region, for the normal hydrocarbons, ketones (5,6,7,) and ethers (21).

Table 3

Compound	Maximum Rate relative to Methyl Formate (low temperature region)	Maximum Rate relative to Methyl Formate (high temperature region)
Methyl Formate	1	1
Methyl Acetate	1	1
Methyl Propionate	6	6
Methyl Butyrate	350	24
Ethyl Formate	350	3.6
Propyl Formate	2000	47
n-Pentane	2000	
n-Butane	900	
Butanone	700	
2-Pentanone	2000	
3-Pentanone	9000	
Dimethyl ether	50×10^3	
Ethyl Methyl Ether	350×10^3	
Methyl n-Propyl Ether	350×10^3	
Diethyl Ether	5000×10^3	

The effect of molecular structure in the low temperature region is seen to be abnormally great. The differences in the relative rates of oxidation between the esters of high molecular weight are much greater

than those between the very simplest esters. In the normal chemistry of a homologous series of organic compounds, the effect of a unit increase in chain length rarely exceeds a factor of 2 or 3, and is frequently much less, particularly between the heavier members of a given series. The relative rates of thermal decomposition of the normal hydrocarbons have been found by Partington (46) to be as follows:

Hydrocarbon	Rate of thermal decomposition relative to ethane
ethane	1
propane	4.5
n-butane	11.2
n-pentane	25
n-hexane	25

The extraordinary dependence of the rate of oxidation on the molecular structure seems to be intimately associated with the fact, now generally accepted, that the mechanism in the low temperature region is essentially a chain-branching process. No simple free radical mechanism, similar to those encountered in pyrolysis reactions, can approximate to the kinetics of the low temperature region.

During recent years the aspect of the theory of oxidation under most discussion has been the various means whereby chain branching might come about. Both Hinshelwood and Walsh have adopted the early idea of the formation of peroxide species as the initial

step in the mechanism of oxidation. This step is followed by degenerate decomposition resulting in the acceleration of the rate of reaction. Norrish has proposed the formation of aldehyde species as the more likely chain branching agent in most oxidation processes.

The peroxide theory of chain branching is well supported experimentally and it has been generally regarded (4) as the more likely of the two theories. The aldehyde theory suffers from the fact that several reactions are known where the corresponding high molecular weight aldehydes have not been isolated as reaction intermediates (24). Peroxide species, on the other hand, have been detected in quantity in almost every combustion process. Hawkins (47), in a review of peroxide chemistry in 1950, lists the controlled gaseous oxidation of hydrocarbons as a primary method of preparing organic peroxides.

Cullis and Hinshelwood (2) have shown the maximum rate of chain branching oxidation to be of the form

$$\frac{f([O_2],[RH])}{1 - 2kF}$$

where k is the velocity constant of the key reaction involving the decomposition of the peroxide molecule, and F is a function of reactant concentrations and of various velocity constants. One of the conditions

that the chain reaction should attain a high rate is that the denominator of this expression should become small, i.e. 2kF almost equal to one. Under these conditions then, even a small structural influence on k would have a greatly magnified influence on the overall rate of oxidation.

The decrease in the reaction rate as the temperature is increased, i.e. during the transition from the low to high temperature regions, is attributed to a decrease in the regenerative yield of the chain branching reaction as the result of an increased non-chain degradation of the active peroxide species.

The various factors influencing the strength of bonds has been recently reviewed by Walsh (48,49). His conclusions, drawn on the experimental evidence of both inorganic and organic chemistry, are of particular interest in a discussion of combustion phenomena, as they form the basis of an explanation of the adverse influence of methyl groups on the ease of oxidation.

Walsh proposes that an increase of electronegativity of bonded atoms increases the bond strength up to a point where the atoms must be so close together that repulsion of the nuclei is likely to result. In general, the greater the overlap of atomic wave functions the greater the strength of molecular orbitals. The principle of "maximum overlapping" is fundamental to both the

electron pair bond and molecular orbital theory of valency.

The oxygen bonds of organic peroxides are considered to be a case of reduced strength due to reduced overlap in bonds of highly electronegative atoms. The electronegativity of the oxygen atoms is thought to be too great to allow the overlap that would correspond to the maximum O-O bond strength. Any means whereby the effective electronegativity could be reduced would increase the overlap and strengthen the bond.

If this interpretation is correct, then the stabilizing influence of methyl groups on the ease of oxidation is readily understood. The presence of methyl groups near a peroxide configuration would reduce the electronegativity of the O-O bond and increase the general stability of the molecule. An increase in the stability would decrease the regenerative yield of the chain branching reaction and decrease the overall rate of oxidation.

Walsh's theory predicts a positive influence of the more electronegative substituents, carbonyl, and ethereal linkages, relative to the action of methyl groups. Recent investigations on the ease of oxidation of the lower aliphatic ethers and ketones, and the present study of the oxidation of the esters, are in agreement with the theory.

The Point of Initial Attack:

The effect of molecular structure on the maximum rate of oxidation can be considered from a different point of view to give an indication of the likely point of initial attack. Walsh (24) has proposed that the ease of oxidation of the normal hydrocarbons should be in the order of reactivity of tertiary, secondary, and primary carbon atoms. Recent investigations, summarized in the introduction of the thesis, show the matter to be more complex than the organic chemistry of the homologous series would indicate.

Previous studies (2,5,6,7,21) have established the adverse influence of methyl and carbonyl groups relative to a methylene structure, and the positive influence of the ethereal linkage on the ease of oxidation. Considering the general structure

$$R\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}R'$$

the order of reactivity of the esters in the low temperature region is in direct agreement with previous conclusions.

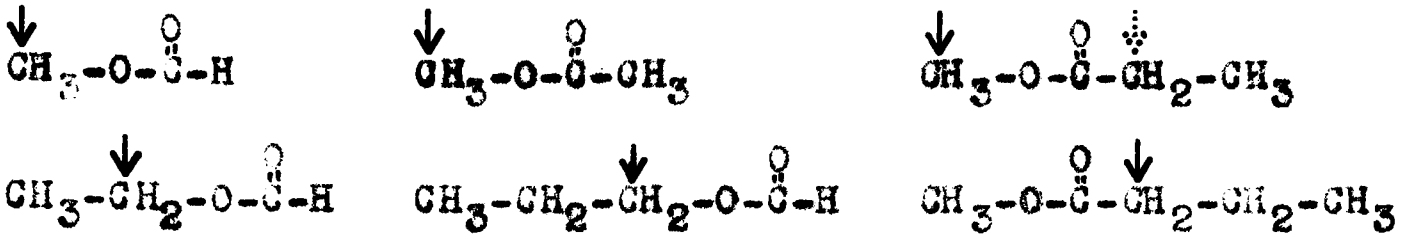
1. The rate of oxidation of the esters of formic acid is considerably greater than the rate of oxidation of the esters of methyl alcohol.

2. An increase in the chain length on the side of the ethereal linkage has much greater influence on the rate than an increase in the chain length on the carbonyl

side of the ester configuration.

3. The first ester of methyl alcohol to show two regions of reactivity is methylbutyrate.

On this basis then, the likely point of attack on the carbon skeleton of each ester would be as follows:



The initiating process is almost certainly of the form

$$RH + O_2 = R- + HO_2$$

The attacking oxygen, under the influence of RH , presumably assumes the form of a biradical. The attack would be facilitated by the presence of groups increasing the positive character of the hydrocarbon chain, i.e. groups withdrawing electrons from the carbon skeleton. The presence of substituents capable of increasing the flow of electrons to the seat of reaction, that is to say, methyl groups, would reduce the ease of attack.

The major influences of molecular structure appear to be two fold. First, the influence of substituent groups on the rate of chain branching of the reaction intermediates, and second, the effect on the initiating process. In each case, methyl groups may be expected to decrease the rate of reaction and more electropositive groups to increase the rate of reaction. How far the two factors can be separated

from one another cannot be estimated at the present stage of the investigation. Experimentally, the problem is very difficult to resolve. A decisive experiment would require a means of initiating the reaction without permitting subsequent chain branching, and a means of chain branching without the initiation process.

The Theories of Walsh and Norrish:

The theory of Walsh (14,24,36) is very similar, in principle, to the theory of Hinshelwood. Walsh proposes the formation of both peroxide molecules and peroxide radicals as the initial steps in the mechanism of oxidation.

$$RH + O_2 = R\text{-} + HO_2$$

$$R\text{-} + O_2 = ROO\text{-}$$

$$ROO\text{-} + RH = ROOH + R\text{-}$$

The peroxide molecules, formed primarily in the low temperature region, are pictured as capable of decomposition with the propogation of a chain branching mechanism. The peroxide radicals, on the other hand, are supposed to be incapable of such a decomposition. Walsh proposes that at higher temperatures, the rate of decomposition of the ROO- is such as to reduce the rate of formation of ROOH and thereby reduces the regenerative yield of the chain branching process. Thus, according to Walsh,

the negative temperature coefficient results from the decomposition of a precursor to the chain-branching peroxide.

At the present time, the analytical investigation of the decomposition and oxidation products of the likely chain branching intermediates is not sufficiently advanced to permit an accurate estimate of the precise chemical equations.

Norrish's theory(32,33) of low temperature oxidation is based on the chain branching properties of aldehyde species. The transition to the high temperature region is explained in terms of an olefine-forming chain reaction involving alkyl radicals. To quote from his paper on the oxidation of propane: "When the olefine-forming chain reaction begins to operate the normal aldehyde-forming reactions are to some extent replaced by an olefine-forming reaction. That is,

$$CH_3CH_2CH_2^- + O_2 = CH_3CH_2CHO + -OH$$

is replaced by

$$CH_3CH_2CH_2^- + O_2 = CH_3CH{=}CH_2 + HO_2$$

and branching due to the molecular oxidation of the aldehyde is thereby reduced."

Chemically, it is very difficult to see how such

a state of affairs is possible. The rate of decomposition of aldehyde substances may increase relative to the rate of formation, or a secondary reaction may intervene in the formation of the active species, but the actual reactions involving the formation of aldehyde cannot be "replaced" by another. It is more likely that the relatively high concentrations of ethylene detected by Norrish in the high temperature region result from the induced decomposition of propane. Induced decomposition would be expected, at least to some extent, if the oxidation reaction at elevated temperatures proceeds by a primarily free radical process.

Cool Flame Phenomena:

The products of the cool flame combustion of propane were very similar to those detected in the low temperature region of oxidation. The mass spectrometric analyses showed no drastic changes in the concentrations of either the reagents or the final products. Except for very minor changes, the cool flame passed through the reaction mixture without causing the ignition of the combustible material itself. These experiments leave little doubt that the substances involved in cool flame phenomena are intermediate compounds formed during the induction period.

The polarographic analyses of the propane mixtures showed a marked decrease in the concentration of the peroxide substances with the occurrence of a cool flame. The general trend of the analyses indicate that the processes culminating in the explosive oxidation of the cool flame, are the same as those resulting in branching chain oxidation at lower temperatures. Free radical reactions, not dependent on chain branching, would not be expected to be as sensitive to either the small changes in temperature, or to the structural changes between the esters of formic acid.

The theory of low temperature oxidation by branching chains has been extended to the region of cool flame combustion by Bardwell and Hinshelwood (5-8). The scheme proposes that cool flames result from the self-heating of the reaction mixture by the thermal decomposition of the peroxide intermediates. The polarographic analyses for peroxide support these ideas very strongly. In quite a general way the processes can be represented

$$R\text{-} + O_2 = ROO\text{-}$$

$$ROO\text{-} + RH = ROOH + R\text{-}$$

$$ROOH = RO\text{-} + \text{-}OH$$

where the temperature coefficient of the third step is greater than those of the first two. If the pyrolysis step

$$ROOH = RO\text{-} + \text{-}OH$$

is highly exothermic, under appropriate conditions of reagent concentration and reaction temperature, self-heating would be expected and the rate would increase until the peroxide is largely consumed.

The periodicity of cool flame phenomena, i.e. the occurrence of as many as five cool flames in the same reaction mixture, is explained as the result of the consumption of the peroxide substances. A decrease in the concentration of peroxide would decrease the rate of decomposition and allow the temperature of the reaction gases to fall. At lower temperatures the concentration of ROOH could increase again and the process repeat itself.

The "hot" explosions encountered at elevated temperatures differ considerably from the cool flames observed between the low and high temperature regions. High temperature ignition results, usually, in the total consumption of the reagents and a large increase in the concentration of the final products. The remarkable feature of the cool flame explosion is that it does not bring about the ignition of the combustible material. The true ignition reaction is almost certainly much closer to that observed in systems where none of the present complications occur.

An entirely different scheme of cool flame

combustion has been proposed by Frank-Kamenetzki (35) and Walsh (36). The phenomena are ascribed not to changes of temperature but to a reaction of one intermediate with another. (The detailed mechanisms have been described in the introductory pages of the thesis.) The schemes predict a sine wave variation in the concentration of peroxide and aldehyde during both cool flame oxidation, and under reaction conditions immediately preceding the occurrence of cool flames.

It suffices to say that the analytical investigation of the present study does not, in any way, support such a reaction mechanism. The concentration of both peroxide and aldehyde increased in an exponential manner as the reaction was allowed to go to completion. Such an exponential increase would be expected if the mechanism was of the principle proposed by Hinshelwood.

In this investigation, as in almost every study of kinetics, there are one or two aspects of the experimental evidence which do not fit nicely into the proposed scheme. The polarographic and aldehyde analyses of the combustion samples of ethyl formate are the features of the present study which might be so classified.

In both the high and low temperature regions of the oxidation of ethyl formate, the concentrations of peroxide, formaldehyde and acetaldehyde each increased to a maximum as the reaction went to completion. The maximum concentrations of each species were, to a first approximation, independent of the effect of reaction temperature. In the view of the extraordinary effect of temperature on every other measured quantity, this apparent independence is doubly outstanding.

The best explanation that can be managed at the present time, is one of complication rather than simplification. If, at higher temperatures there are factors leading to a balance between the rates of formation and the rates of decomposition of various peroxide species, then a steady state might be maintained. In the proposed mechanism of low temperature oxidation, the aldehydes result from the decomposition of peroxide substances, and a corresponding independence of reaction temperature would be expected.

At the present stage in the study of oxidation phenomena it is possible to indicate, with reasonable accuracy, the general scheme of reactions leading to

the final products. However, some difficulty is encountered if one selects various combustible species and attempts to describe in detail the likely steps in the oxidation. Both the precise structure and the modes of decomposition of the chain branching agents are still something of a mystery.

The next logical step in the investigation appears to be a thorough study of the kinetics of thermal decomposition and oxidation of the more probable chain branching species. This latter possibility, that of oxidation of the peroxides themselves, must not be overlooked as a source of information on the combustion process.

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