ABSTRACT OF THESIS

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Title of Thesis The oxidation of ethane.

The oxidation of ethane like that of other aliphatic hydrocarbons, apart from methane, can proceed by two distinct mechanisms. One operates above and the other below ca. 400°C. Analytical work on ethane oxidation has shown that in the later stages of the high temperature oxidation ethylene is the major product whereas in the low temperature region oxygenated compounds are the major products. Through the development of gas chromatography it is now possible to analyse the products in the early stages of reaction. The aim of the present work was to apply this technique to the analysis of the products in the initial stages of ethane oxidation and to determine the relative importance of ethylene and of oxygenated compounds in the early stages. At the same time analysis of the products formed throughout the course of the whole reaction would provide valuable analytical data for the elucidation of the oxidation mechanism.

The oxidations were carried out in a static system between 318-386°C using mixtures of different composition. The relative yields of the initial products did not change appreciably when the ethane:oxygen ratio was altered by a factor of six. However the initial yields changed with temperature, and at the higher temperature ethylene was the main initial product whereas at the lower temperatures formaldehyde predominated. A value is given for the difference in activation energy between the reactions producing ethylene and formaldehyde. The kinetics of the oxidation at 362°C were investigated and the variation of the acceleration constant with oxygen, ethane, "inert" gas, and ethylene oxide pressure was determined.

Ethylene oxidations were carried out at 318 and 362°C with mixtures

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of different composition and the products from both the early and later stages of reaction were examined. The oxidation of acetaldehyde at 362°C was also investigated and a mechanism for the oxidation has been put forward.

In the latter part of this thesis the experimental results were discussed. It appears that the degradation of the ethane molecule is a stepwise process involving the intermediate formation of ethylene and formaldehyde. It was concluded that the ethylene was formed by oxygen abstracting hydrogen directly from ethyl radicals, and that the formaldehyde was formed by isomerisation and decomposition of ethyl peroxy radicals. In the later stages of reaction the ethylene and formaldehyde are themselves oxidised, ethylene mainly to formaldehyde, and formaldehyde to the final oxidation products carbon monoxide, carbon dioxide, and water. A mechanism involving the intermediate formation of a cyclic peroxide has been proposed for the oxidation of ethylene to formaldehyde. As no experiments were carried out on the oxidation of formaldehyde the scheme proposed by Lewis and von Elbe for formaldehyde oxidation has been adopted. A reaction scheme, which can explain the formation of the products of ethane oxidation and which embodies the basic schemes of ethylene and formaldehyde oxidations, has been put forward for the oxidation of ethane.

THE OXIDATION OF ETHANE

Thesis

submitted for the Degree of

Doctor of Philosophy

by

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INTRODUCTION

1. SLOW OXIDATION OF HYDROCARBONS

1. 1. Early Theories

During the combustion of hydrocarbons the fuel molecule is degraded stepwise into "end" products, such as carbon monoxide, carbon dioxide, water etc. This basic idea of stepwise degradation was originated by Armstrong[1] in 1874 with his suggestion that the successive stages in hydrocarbon oxidation involved the transient formation of hydroxylated molecules which decomposed into simple intermediates. However no attempt was made to verify this idea experimentally and it was Bone and his co-workers[2] in the years 1900-1912 who provided an experimental basis for this "hydroxylation" theory, in which it was thought that each successive C-H bond in the molecule was replaced by a C-OH bond, accompanied by the gradual degradation of the hydrocarbon molecule. Bone[3] further developed the theory in the period 1930-1936, and for ethane the final form of the oxidation was represented as :-

$$
\begin{array}{l}
CH_3.CH_3 \longrightarrow CH_3CH_2OH \longrightarrow \left[CH_3CH\ (OH)_2\right] \longrightarrow \underline{CH_3CHO} + \underline{H_2O} \\
\longrightarrow \underline{CH_3COOH} \longrightarrow CH_2OH.COOH \longrightarrow \underset{\displaystyle \underline{H_2} + \underline{CO}}{\underline{CH_2O}\big\downarrow} + \underline{H_2O} + \underline{CO} \\
\longrightarrow \underline{HCOOH} \longrightarrow \underline{H_2O} + \underline{CO}
\end{array}
$$

The theory was satisfactory in that it provided an explanation for certain analytical data such as aldehydes being formed prior to the formation of steam and oxides of carbon, but the weakness lay in the fact that the supposed primary intermediate, the alcohol, could not be detected. This was partially remedied by Newitt & Haffner[4] who showed that methanol was formed in the high pressure oxidation of methane. However Bone[5] himself provided evidence which invalidated the theory when he found that methanol oxidised more slowly than formaldehyde, and so ought to have a higher stationary state concentration in the oxidation of methane whereas the experimental evidence was to the contrary.

Prior to this, in 1935, Norrish[6] had examined the experimental results of the period and he had concluded that whereas Bone's theory might explain the analytical data it could not explain the kinetic data. Norrish proposed an atom chain theory to explain the phenomenon of combustion e.g. for ethane

Propagation - - - - $O + C_2H_6 = CH_3\,CH + H_2O$

$$CH_3CH + O_2 = \underline{CH_3CHO} + O$$

Branching - - - - $CH_3CHO + O_2 = CH_3COOH + O$

Termination - - - $O + \text{Wall} = \frac{1}{2}\,O_2$

$$C_2H_6 + O + X = C_2H_5OH + X$$

Thus ethane oxidation was considered to be an alternative formation of free ethylidene radicals and oxygen atoms, with the steady generation of acetaldehyde.

The chief difference between Norrish's theory and the "hydroxylation" theory was in the production of the aldehyde.

The "hydroxylation" theory visualised an alcohol as the corresponding intermediate whilst Norrish's view was that the aldehyde was formed directly as a result of the chain mechanism.

In the same year, Ubbelohde[7] raised objections to the theories of Bone and Norrish, and he put forward an alternative scheme in which the oxidation of hydrocarbon was initiated by an aldehyde. Previously, in 1934, Backstrom[8] studying aldehyde oxidations had surmised that the radical $\overset{o-o}{R-c=o}$ would play a part in the chain process, and Ubbelohde suggested that it was possibly this radical which initiated the chain in hydrocarbon oxidation.

Initiation - - - -

$$\overset{o-o}{R-c=o} + RCH_3 = \overset{o-OH}{R-c=o} + RCH_2$$

$$RCH_2 + O_2 = RCH_2OO$$

Propagation - - - -

$$RCH_2OO + RCH_3 = RCH_2OOH + RCH_2$$

Branching - - - - $RCH_2OOH = RCH_2O + OH$

This scheme was similar to Norrish's in that it involved a chain reaction in the propagating step but in this case it was considered that a hydroperoxide rather than an aldehyde was produced.

These theories of Norrish and Ubbelohde were widely accepted and although they have since been modified the general concept that the propagating step involved a chain reaction which produced either an aldehyde or peroxide and that branching occurred through further reaction of this aldehyde or peroxide, has, until recently, been taken as the basis of all hydrocarbon oxidation mechanisms.

In view of the important part played by the theory of chain reactions in the elucidation of hydrocarbon oxidation mechanisms, it is convenient at this point to give a short account of its development.

1. 2. The Development of Chain Theories

The idea of a chain reaction was first put forward by Bodenstein[9] in 1913 to account for the high quantum yield in the photochemical reaction of hydrogen with chlorine. He suggested chains involving electrons but this was later modified in 1918 by Nernst[10], who proposed an atomic chain.

In order to interpret the speeds of some first order reactions Christiansen[11] and Christiansen & Kramers[12] also postulated chain reactions, but this time energy chains instead of electron or atomic chains were invoked. They reasoned that molecules of reaction products just after reaction would contain excess energy and these "hot" molecules would have sufficient energy to activate molecules of reactant at their first encounter, and the subsequent reaction products would also have excess energy, and so on. The ready application of energy or thermal chain theory to the explanation of the phenomenon of negative catalysis [Christiansen 1924[11]] gave greater credence to the theory of energy chains. It was thought that the negative catalyst or inhibitor was able to react with one of the links of the chain, consequently breaking the chain and thus lowering the reaction velocity.

In the following five years several workers applied the concept of energy chains to other reaction schemes. For instance, Backstrom[13] explained the observation that the photochemical oxidation of benzaldehyde had a quantum yield of about 10,000 and that it exhibited the same characteristics with regard to negative catalysts as the thermal oxidation, on the basis of thermal chains. Egerton[14] discovered that inhibitors, such as phenol or aniline, had the same effect on hydrocarbon oxidation as on the photochemical oxidations of aldehydes carried out by Backstrom, and he suggested that both reactions were similar in nature and that hydrocarbon oxidations also included thermal chains.

At the same time as these investigations, Hinshelwood[15] was investigating the reaction between hydrogen and oxygen in a static system, and he accounted for the inhibitory effect of the walls of the reaction vessel at certain temperatures as being due to the breaking of the thermal chains when a "hot" molecule collides with the wall and comes into thermal equilibrium with it.

Whereas Hinshelwood considered the H_2-O_2 reaction to be a thermal chain process, Bonhoeffer & Haber[16] believed that it proceeded by means of a free radical chain. However, this idea of free radical chains was not widely accepted at the time, and Semenov[17], who developed the theoretical aspects of chain reactions between the years 1928-1929 still thought that the chain was carried by energy rich molecules. However in 1934 Backstrom[8] applied a free radical chain mechanism to the photo-chemical oxidation of aldehydes, and in the present day most chain reaction schemes, apart from therma explosions, involve free radicals.

1. 3. Branching & Degenerate Branching Chains

One important development of chain theory which Semenov introduced was that of branching chain reactions. In a branching chain it is envisaged that one of the active centres is capable of producing two new active centres which are each capable of initiating new chains. Consequently the velocity of the reaction will increase and may run off to explosion. In the hydrogen-oxygen reaction two of the possible steps are:-

$$OH + H_2 = H_2O + H \qquad (a)$$

$$H + O_2 = OH + O \qquad (b)$$

In case (a) one free radical is produced from one other free radical, and we have a normal chain, but in case (b) two free radicals are produced which can each propagate the chain and therefore we have a branching reaction.

For branching reactions Semenov(17) deduced that the velocity of the reaction was given by

$$w = \frac{n}{\Delta\tau} = \frac{n_0}{\delta-\beta}\left(e^{(\delta-\beta)t/\Delta\tau} - 1\right) \quad \text{if } g-f<0,\ \beta-\delta<0$$

$$w = \frac{n}{\Delta\tau} = \frac{n_0}{\substack{\cancel{\delta-\beta}\\ \beta-\delta}}\left(1 - e^{-(\beta-\delta)t/\Delta\tau}\right) \quad \text{if } g-f>0,\ \beta-\delta>0$$

δ = probability of chain branching at any link.

β = " " " breaking " " "

$\Delta\tau$ = time required for formation of a link.

= lifetime of branching intermediate

n_0 = number of active centres initially formed per unit time and volume.

n = concentration of active centres at time t.

g = coefficient depending on the composition and pressure of the mixture and on the temperature.

f = coefficient to account for secondary generation of chains due to branching.

In the first case the velocity of the reaction increases with t to infinity and at high values of t the expression reduces to the form

$$w = Ae^{\phi t} \quad \text{where } \phi = \frac{\delta-\beta}{\Delta\tau}, \; A = \frac{n_0}{\delta-\beta} = \frac{n_0}{\phi\Delta\tau}$$

Assuming values of δ, β, and $\Delta\tau$ which were reasonable for free radical or energy-rich molecule reactions, Semenov showed that the velocity of the reaction might be expected to increase by a factor of e every second. In the case of hydrogen oxidation the increase in velocity is much smaller than this predicted value and Semenov concluded that in order to comply with experimental facts $\Delta\tau$ would have to have a value of the order of minutes or hours. To incorporate this in the theory of branching chain reactions he put forward the idea of "degenerately" branching chains, where in the normal course of the chain reaction a stable intermediate is produced which can survive long after the initial chains have terminated and which can then react to produce active centres capable of propagating new chains.

This proposal was fundamental to the understanding of hydrocarbon combustion and it is worthwhile examining the differences which lie between normal branching reactions and "degenerately" branching reactions.

The length of a branched chain $\nu' = \frac{1}{\beta - \delta} = \frac{\nu}{1 - \nu\delta}$

where ν = chain length of non-branching chains

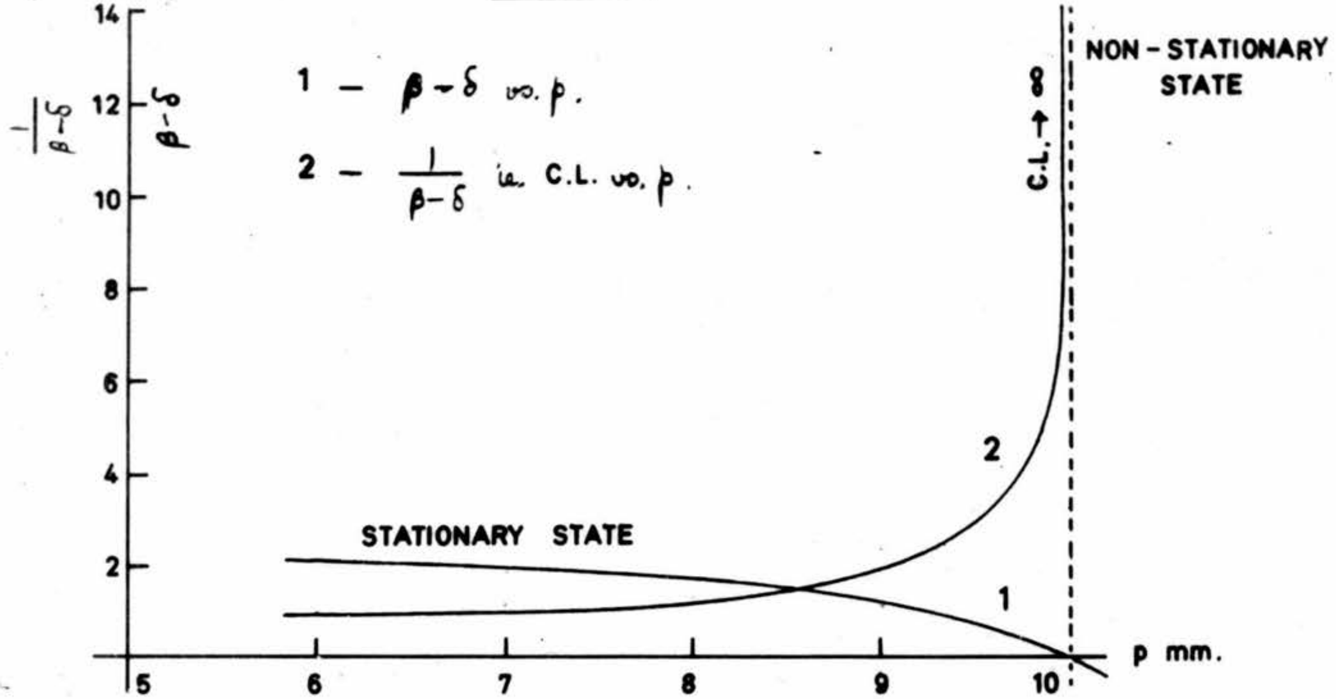
$\therefore$ Velocity of branching reaction $w = n_o v' = \frac{n_o v}{1 - \nu\delta}$

where n_o = rate of formation of active centres per unit time and volume.

Since the quantities β, δ and consequently ν, δ are functions of temperature and pressure only, there must exist certain conditions at which $\beta - \delta = 0$, corresponding to the chain length becoming infinity. This condition is realised when there is an average of one branching along the whole length of an ordinary chain i.e. $\nu\delta = 1$.

If $\beta - \delta < 0$ then the number of chain branchings exceeds the number of chain ruptures and the number of chains will steadily increase. This continuous increase in chains corresponds to a self acceleration process leading to explosion i.e. a non-stationary chain reaction. When $\beta - \delta > 0$ we have a stationary chain reaction.

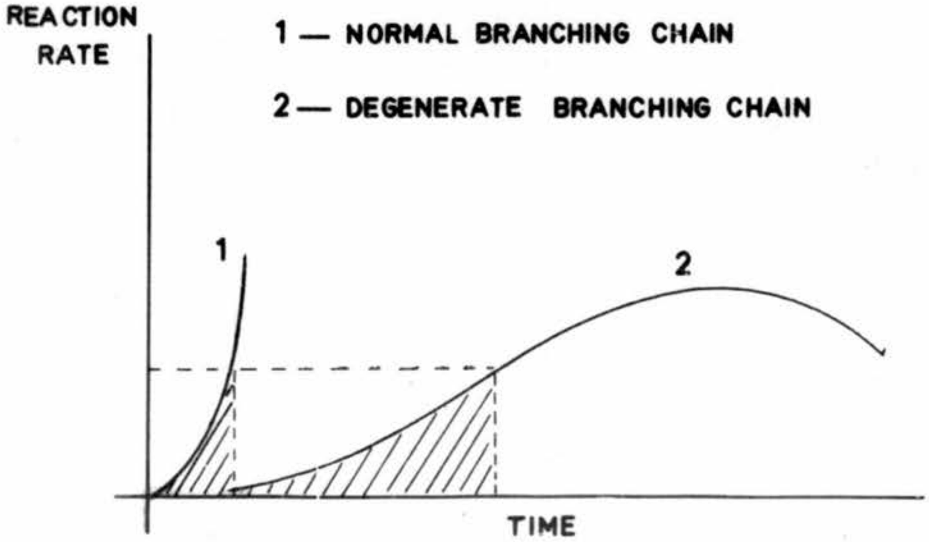
FIGURE A.



VARIATION OF CHAIN LENGTH WITH PRESSURE.

(SEMENOV – "CHEMICAL KINETICS & CHAIN REACTIONS.", 1935, p. 47.)

FIGURE B.



VARIATION OF REACTION RATE WITH TIME

(SEMENOV – "CHEMICAL KINETICS & CHAIN REACTIONS.", 1935, p. 73.)

The change over from stationary to non-stationary chains is extremely rapid for branching reactions (see Fig.A) but with degenerately branching reactions there is a more gradual increase in velocity. This tendency arises in the case of degenerately branching chain reactions from their being a greater amount of original substance reacted before the velocity reaches a certain value (see Fig. B).

At time t amount of substance reacted is given by the shaded areas $=\int w\,dt$. The greater the amount of original substance reacted then the more "dilute" the reaction mixture becomes and consequently the rate of chain branching will decrease until a point is reached where the rate of chain breaking will exceed that of branching and the reaction velocity will diminish.

As the general tendency for degenerately branching chain reactions is to show a gradual increase in reaction velocity it is difficult to distinguish whether non-stationary or stationary chains are operative, but as the rate curve for hydrogen combustions is concave and corresponds to the law $w = Ae^{\varphi t}$ then it is most probable that in hydrocarbon combustions we are dealing with degenerate non-stationary chains. (See Semenov "Chemical Kinetics and Chain Reactions", Oxford, Clarendon Press, 1935, pp166-167).

1. 4. The Branching Intermediate and Theories on Hydrocarbon Oxidation.

The intermediate responsible for degenerate branching in hydrocarbon oxidation has been the subject of a great deal of investigation and although it was generally agreed that aldehydes acted as the agents of degenerate branching in the high temperature oxidation (i.e. above 400°C) opinion was divided as to the nature of the intermediate in the low temperature region (i.e. below ca.350°C). There were two main schools of thought as to the identity of this low temperature intermediate viz. (a) those who thought it was a peroxide, (b) those who thought it was an aldehyde. The relative merits of these two viewpoints are discussed below.

(a) Peroxide Theories and Evidence for Peroxides in Oxidation Systems.

Ubbelohde(7) in 1935 was the first to assign peroxides to the role of degenerate branching agents in the low temperature oxidation of hydrocarbons. He was of the opinion that hydroperoxides were formed in the propagating steps of the oxidation and that these peroxides could subsequently decompose into free radicals with a resultant branching of the chain reaction.

$$RCH_2 + O_2 \quad = \quad RCH_2OO$$

Propagation ---

$$RCH_2OO + RCH_3 = RCH_2OOH \; + \; RCH_2$$

Branching -----$RCH_2OOH \quad = RCH_2O \quad + \quad OH$

Walsh[18] also considered that the agent of degenerate branching was a peroxide molecule which was capable of splitting at the O-O bond but he laid stress on the fact that subsequent rupture of the adjacent C-C bond was likely. Consequently the general scheme for the low temperature oxidation was considered to be:-

$$R + O_2 = RO_2$$

Propagation-------- $RO_2 + RH = ROOH + R$

Branching---------- $ROOH = RO + OH$

Degradation-------- $RO = R' + HCHO$

The radical R' could then enter into reaction with oxygen and thus the degradation of the fuel molecule was continued.

The peroxide theory was favoured by several other workers as it was thought that it provided an explanation as to why many of the products of hydrocarbon oxidation contained only one oxygen atom and why the rate of oxidation was dependent upon the structure of the molecule. This latter feature of the peroxide theory was suggested by Hinshelwood[19,20] and Cullis, Hinshelwood & Mulcahy[22], but it is to be noted that their conclusions were based upon a false assumption. They believed that the strength of the O-O bond in the peroxide molecule was dependent upon the substituent groups in the molecule and from this they considered that there was a correlation between the effect of the substituent groups on the strength of the O-O bond and the rate of oxidation. However it is now known that the strength of the O-O bond is independent of the structure of the peroxide.[22]

One obvious test of the peroxide theory is whether or not peroxides can be detected in oxidation systems. Certainly for oxidations in solution, where the temperature is low and the concentration of hydrocarbon or other reactant is extremely high, there is ample evidence for the existence of peroxides.[23] However for gas phase oxidations, where the temperature must of necessity be much higher, there is less evidence for their existence.

Gas phase oxidations have however been carried out at temperatures as low as 125-170°C by employing a catalyst such as hydrogen bromide. Rust & Vaughan[24] investigated the hydrogen bromide catalysed oxidation of iso-butane and they obtained yields of t-butyl hydroperoxide as high as 75% (based on oxygen consumed) with a 10:10:1 mixture of iso-butane : oxygen : hydrogen bromide. When these investigations were extended to straight chain paraffins it was found that only the hydroperoxides of the higher hydrocarbons could be isolated and when ethane and propane were oxidised no primary or secondary hydroperoxides were formed.[27,73] These results are of particular interest as it has recently been shown that this is also the case in the uncatalysed oxidations carried out at temperatures some 100°C or so higher. Cartlidge & Tipper[31,32] used paper chromotography to isolate and detect the hydroperoxides formed in the oxidation of propane at 327°, the oxidation of n-heptane between 250-270°, and the oxidation of n-butane between 315-345°C, and they found that with n-heptane and n-butane the peroxidic material isolated consisted of a mixture of hydroperoxides, hydrogen-peroxide, and hydrogen peroxide-aldehyde adducts, but with propane it consisted only of hydrogen peroxide and its derivatives. From these results they concluded that peroxides could not be the agents of degenerate branching in the lower hydrocarbon systems although it was possible that they were the agents of degenerate branching in the higher hydrocarbon systems. As this work supports the evidence of Kirk & Knox[33] that at 318°C the lifetimes of ethyl hydroperoxide and propyl hydroperoxide are too short for them to be the intermediates responsible for degenerate branching in ethane and propane oxidations it can be taken that peroxides are not the agents of degenerate branching in the oxidation of ethane and propane above ca.300°C.

With the higher hydrocarbons the evidence for or against hydroperoxides as the agents of degenerate branching is not so conclusive, and although hydroperoxides have been detected in the oxidation systems of higher hydrocarbons it is not possible to state definitely whether or not they are the agents of degenerate branching. A great deal of work has been carried out on the determination of hydroperoxides in hydrocarbon oxidation systems[28] but owing to the lack of suitable analytical techniques it was difficult to isolate and identify the hydroperoxides formed in the system. Batten, Gardner & Ridge[29] used polarography to analyse the peroxides formed in the oxidation of iso-butane between 250-270°C and even although this was one of the more refined analytical techniques available at that time they could not establish definitely that t-butyl hydroperoxide was formed. However through the development of paper chromotography it is now possible to isolate and establish conclusively the hydroperoxides formed in oxidation systems, and Taylor[30] by applying this technique to the oxidation of iso-butane was able to show that t-butyl hydroperoxide was in fact formed in the system up to a temperature of about 350°C. As has previously been stated this technique was used by Cartlidge & Tipper[31,32] to examine the peroxides formed in the oxidation of n-heptane between 250-270°C and n-butane between 315-345°C and in this case also the corresponding hydroperoxides were detected.

Although the presence of hydroperoxides in the oxidation systems of the higher hydrocarbons might be considered as providing indirect evidence that they are the agents of degenerate branching, there is also evidence to the contrary. Batten & Ridge[37] found that destroying the peroxides formed in the oxidation of iso-butane had no effect on the subsequent reaction. They withdrew the products of the reaction into a vessel containing mercury and no matter how long the product mixture remained in contact with the mercury the reaction continued at the same rate on re-entering the reaction vessel.

The destruction of the peroxides formed during the course of reaction has been used by other workers to demonstrate that they are not the agents of degenerate branching e.g. Shtern[35-36] used the above method in the oxidation of propane and propylene while Pease[34], also for propane, destroyed the peroxides by coating the reaction vessel with potassium chloride.

One factor which has to be borne in mind with regard to the experimental results given in the literature is that the methods used for the determination of the yields of peroxides e.g. liberation of iodine from potassium iodide, oxidation of ferrous ions, often make no distinction between hydrogen peroxide, hydroperoxides and other oxidising agents. When detailed examination has been made of the peroxidic material obtained from hydrocarbon oxidations it has been found in certain cases that hydrogen peroxide and its derivatives were the only constituents.[38, 39]

(b) Aldehyde Theory

The importance of aldehydes in hydrocarbon oxidation was realised by Pope, Dykstra and Edgar[40] as early as 1929. They suggested that hydrocarbons were oxidised via aldehydes which were degraded step by step to lower aldehydes.

$$RCH_2CHO + O_2 = RCHO + CO + H_2O = - - - - - = HCHO + CO + H_2O$$

This theory was rejected for various reasons e.g. the higher aldehydes were found in some cases and not in others, the suggested degradation does not produce formaldehyde in an excited state as required for cool flames. It was found in many cases that formaldehyde was the preponderant aldehyde in the products and this was explained by postulating a "non stop run" through the various aldehyde stages. This could not however explain why the higher aldehydes were formed in certain cases and not in others.

Lewis & von Elbe[42] overcame the objections to the "non stop run" theory by modifying the Pope, Dykstra, and Edgar scheme to one whereby radicals were degraded instead of molecules.

$$RCH_2CO + O_2 = RC\overset{O}{\cancel{H_2}} + CO + H_2O = - - - - = CH_3CO + CO + H_2O$$

By postulating a different reaction for CH_3CO than for the higher radicals viz. $CH_3CO + O_2 = HCHO + CO + OH$ they could explain the production of excited formaldehyde as this reaction is exothermic to the extent of some 110 k cal.

Norrish[44] also proposed a reaction scheme which was based on aldehydes and which included a degradative reaction involving the successive formation and destruction of RCH_2CO radicals, but this scheme differed from the above in that the RCH_2CO radical was regarded as having only a transitory existence.

Propagation -------------

$$RCH_2CH_3 + OH = RCH_2CH_2 + H_2O$$

$$RCH_2CH_2 + O_2 = RCH_2CHO + OH$$

Branching ---------------

$$RCH_2CHO + O_2 = RCH_2COOH + O$$

Degradation -------------

$$RCH_2CHO + OH = RCH_2 + CO + H_2O$$

$$RCH_2 + O_2 = RCHO + OH$$

$$RCHO + OH = R + CO + H_2O$$

$$CH_3CO + O_2 = CH_2O + CO + OH$$

Norrish suggested that the branching was due to the reaction of aldehyde with oxygen producing an oxygen atom capable of initiating fresh chains.

The difference between the peroxide theory of branching and the aldehyde theory lay in the stability of the peroxy radical formed from the reaction of an alkyl radical with oxygen. Norrish considered that this radical had a transient existence and decomposed rapidly into an aldehyde and a hydroxy radical, whereas Ubbelohde, Hinshelwood & Walsh etc., considered that the radical existed long enough to be able to abstract a hydrogen atom from the parent hydrocarbon.

$RCH_2 + O_2 = RCH_2OO = RCH_2OOH$ Peroxide Theory

$= RCHO + OH$ Aldehyde Theory

A suggestion by Lewis & von Elbe[42, 45, 46] combined the aldehyde theory and the peroxide theory. They suggested that the strength of the O-O bond of the peroxide molecule was reduced by condensation of an aldehyde with a molecule of peroxide, and thus the branching by means of peroxide would require the presence of aldehyde. However as the condensation product would be expected to give the normal tests for peroxide this theory could not explain the cause of branching in those oxidations where peroxides were absent.

As there is no doubt about the presence of aldehydes and of their ability to act as branching intermediates in the oxidation of hydrocarbons at temperatures about 300°C [29, 37, 38, 47] the aldehyde theory of branching is favoured to that of the peroxide theory. Nevertheless the amounts of aldehydes detected were small, generally less than 10% of the hydrocarbon consumed, and in order to explain this it was suggested that the aldehydes reacted as quickly as they were formed. Although the aldehydes may oxidise rapidly there is another possible explanation for the low yields of aldehydes viz. the existence of an alternative path for the reaction of alkyl radicals with oxygen.

$$\begin{tikzcd}R + O_2 \arrow[r] \arrow[dr, dashed] & R'CHO + OH \\ & \text{Other Products}\end{tikzcd}$$

The idea that alkyl radicals can react with oxygen in an alternative manner to either aldehyde or peroxide formation has come into prominence in recent years.

(c) HO_2 Radical Theory.

The high yields of olefins obtained from oxidations above 400°C has recently led to the conclusion that oxygen can abstract a hydrogen atom from an alkyl radical with the resultant formation of an olefin.[51-56] It was suggested that these high temperature oxidations proceeded by an HO_2 radical chain mechanism:-

$$C_nH_{2n-1} + O_2 = C_nH_{2n-2} + HO_2$$

$$C_nH_{2n} + HO_2 = C_nH_{2n-1} + H_2O_2$$

As yet there is no direct evidence for the existence of HO_2 radicals in hydrocarbon oxidation systems, but there is a great deal of indirect evidence. For example, hydroperoxy radicals have been detected mass-spectrometrically in the oxidation of methyl radicals[111], and appreciable amounts of hydrogen peroxide, formed by HO_2 radicals abstracting hydrogen, have been found in the products of methane[132] and propane[52,115] oxidations. Although most of the evidence for the existence of the HO_2 radicals comes from analytical work part also comes from kinetic work. Knox, Smith & Trotman-Dickenson[59] investigated the competitive oxidation of ethane, propane, and iso-butane, and they concluded that the HO_2 radical was probably the chain carrier from the fact that the ratios of the rate constants of the chain propagating steps showed remarkable constancy over a wide range of experimental conditions, and also from the fact that the HO_2 radical could explain satisfactorily the results of the high temperature oxidation. The close similarity which exists between the kinetics of the oxidation of these three hydrocarbons and of the three isomeric xylenes[57] suggests that the chain propagating radical is common to both systems, and as HO_2 is one of the radicals likely to be common to both systems this strengthens the view that the HO_2 acts as a chain carrier in these oxidations.

Postulation of HO_2 as a chain carrier derives indirect support from the work of Walsh and his collaborators[60] who identified the active anti-knock agent from tetra-ethyl lead as lead oxide and who suggested HO_2 as one of the likely chain carriers being destroyed

Owing to the earlier analytical techniques requiring relatively large amounts of products analysis could only be carried out for the later stages of reaction, and since oxygenated compounds and not olefins were found to be the major products in the later stages of the low temperature oxidations it was thought that the HO_2 radical chain did not operate in this temperature region. However through the development of gas chromatography the initial products of reaction can now be examined, and Knox[61] has shown for the low temperature oxidation of propane that about 75% of the propane initially consumed is converted to propylene. This indicates that the HO_2 radical chain also plays a part in low temperature oxidations.

Although it is now fairly well established that an HO_2 radical chain can operate in hydrogen oxidation systems the lifetime of the chain carrying HO_2 radical is not yet accurately known. Minkoff[58], who reviewed the earlier evidence for its existence in oxidation systems, suggested that it was a relatively long lived intermediate but he did not give a value for its lifetime, and it was not until Lewis & von Elbe[46] estimated its lifetime to be about one second in the hydrogen-oxygen reaction under conditions similar to those used in hydrocarbon oxidation that an idea as to how long it could exist in oxidation systems was obtained.

It has also been suggested that HO_2 radical chains play a part in alcohol oxidations[63,64,65] e.g. Cullis & Newitt[64] found for the oxidation of ethanol between 250-270°C that, under optimum surface conditions, acetaldehyde and hydrogen peroxide were produced in equivalent yields and they considered that this was in agreement with the following mechanism.

$$C_2H_6O + HO_2 = C_2H_5O + H_2O_2$$

$$C_2H_5O + O_2 = CH_3CHO + HO_2$$

2. THE SLOW OXIDATION OF ETHANE.

2.1. Review of Previous Work.

When interest was aroused in hydrocarbon oxidation in the early nineteen hundreds ethane being one of the simplest hydrocarbons was naturally chosen for investigation, and in this period a great deal of work, both analytical and kinetic, was carried out on its oxidation. As the analytical results obtained were explained on the basis of the "hydroxylation" theory, which has since been disproved, only the results of these investigations will be given. After the initial work ethane oxidation was less extensively investigated and workers in the field of hydrocarbon combustion tended to concentrate more on the higher hydrocarbons in order to solve the problem of the negative temperature coefficient and allied phenomena such as cool flames.

Ethane oxidation has been studied using two types of reaction system, the static system and the flow system. Both systems have their attendant advantages and disadvantages. The flow system has the advantage that it gives relatively large amounts of reaction products and is thus more amenable for analytical work, but it does not lend itself to kinetic investigation of the reaction. With the static system the reverse is true.

The kinetics of the low temperature oxidation were examined by Bone & Hill[66] over a wide range of experimental conditions and they drew up pressure-time curves for mixtures of different composition at various temperatures. These curves, along with those given by Kowalsky, Sadownikov & Chirkov[69] for the high temperature oxidation, were analysed by Semenov[17] and he showed that they could be made to coincide by suitable adjustment of the horizontal and vertical scales, and that when not more than 30-40% of the reactants had interacted they could be expressed by the mathematical form $\Delta p = Ne^{\phi t}$, where N and ϕ are constants, the latter being the acceleration constant.

From this expression the acceleration constant of the reaction could be calculated, and Semenov found that the values obtained using the results of Bone and of the Russian school were in good agreement even although the experimental conditions used by these workers were different.

He also demonstrated that the % reaction was given by :-

$$\xi = \frac{100}{1 + e^{-\theta'}} \quad \text{where } \theta' = \phi\,\theta$$

ϕ = acceleration constant

θ = time reckoned from moment of 50% reaction.

θ being positive when $\xi > 50$.

The pressure-time curves of Bone and of the Russian school were of sigmoid form, with a period of slow acceleration followed by a faster reaction increasing to a maximum rate and then a falling off to zero, and in order to account for the initial slow acceleration Semenov postulated that hydrocarbon combustion proceeded by a "degenerately" branching chain. This concept is now generally accepted but prior to this it was considered that the oxidations proceeded by "normal" chains. Early evidence for the existence of a chain reaction in ethane oxidation came from the work of Taylor & Riblett[68] who found that the reaction was preceded by an induction period, was sensitive to foreign substances, and exhibited a negative wall effect.

The kinetics of ethane oxidation, like those of other hydrocarbons, are markedly affected by the surface of the reaction vessel and normally it is only after numerous experiments in the same vessel that reproducible results can be obtained. Taylor & Riblett[68] using a pyrex vessel between 400-480°C found that if the reaction vessel was packed with pyrex glass coated with potassium chloride then the reaction was virtually stopped, and that if a silica vessel was substituted for the pyrex vessel then the kinetics were quite different. Kowalsky, Sadownikov & Chirkov[67] also noted the effect of surface on the kinetics of the high temperature oxidation. They used a quartz vessel at about 600°C and they found that the reaction vessel appeared to "age". However it was discovered that consistent results could be obtained if the reaction vessel surface was pre-treated with hydrofluoric acid.

The kinetics of the oxidation are also affected by the addition of small amounts of intermediates or other compounds.

Acetaldehyde was the intermediate most commonly added to ethane oxidation systems and although its effect in both the low and the high temperature regions was to reduce the induction period Bone & Hill[66] found that the addition of 1% to a 3:1 ethane to oxygen mixture at 316°C and 720 mms. Hg pressure not only reduced the induction period but caused the reaction mixture to explode. This marked effect of acetaldehyde in the low temperature region was also noted by Townend & Chamberlain[96]. They studied the effect of pressure on the ignition temperature of ethane-air mixtures and they observed that in the low temperature region the addition of 1% acetaldehyde greatly reduced the pressures at which the ignitions occurred whereas in the high temperature region the addition of acetaldehyde tended to retard the ignitions. The explanation put forward was that at the higher temperatures the acetaldehyde decomposed faster than it could oxidise.

Other additives do not have such a marked effect as acetaldehyde on the oxidation. For example, Bone & Hill found that the addition of 1% formaldehyde, iodine or nitrogen dioxide to ethane oxidation systems in the low temperature region eliminated the induction period but did not cause an explosion, whilst additives such as ethanol and water shortened the induction period. Similar results were obtained by Szabo & Gal[78] for the high temperature region but they also noted that the kinetics were dependent upon the initial oxygen concentration.

Szabo & Gal plotted the total pressure increase in the reaction and the time required for the reaction to reach maximum rate against the % oxygen in the reaction mixture and they found that a break always occurred in the plots in the region of 30% oxygen. This was taken as indicating that there were two possible types of oxidation and that whichever one was operative depended upon the initial oxygen concentration. However it is doubtful whether this is the case and confirmation by analytical experiments is necessary before it can be accepted.

The parameters which have been used in the interpretation of kinetic measurement are the induction period, maximum rate of reaction and the acceleration constant. Recently, however, Knox[79] has shown that the most reliable of these parameters is the acceleration constant, and by making certain simplifying assumptions with regard to the oxidation of ethane and propane at 318°C he derived a relationship between the acceleration constant and initial hydrocarbon concentration which agreed well with experiment. From this relationship the lifetime of the branching intermediate in ethane oxidation at 318°C was calculated and found to be approximately two minutes.

From a survey of the literature it is apparent that there is a dearth of systematic analytical studies covering the complete range of products from ethane oxidation. However, of the work which was carried out that of Bone and his school is outstanding. In one of the earlier papers Bone and Stockings[2], using a flow system, showed that the final products of the oxidation were carbon monoxide, carbon dioxide, and water. Later Bone and Hill[66] developed a method to determine the intermediate products.

In this work reaction was allowed to proceed for a given period, after which the reaction vessel was plunged into ice water and the products analysed. A series of such experiments with the reaction stopped at different time intervals allowed the construction of a graph showing the decrease in concentration of reactants and the increase in concentration of products with time. In this way it was shown for the low temperature oxidation that the concentration of aldehydes (consisting mainly of formaldehyde) passed through a maximum close to the maximum rate of reaction. The main products were carbon monoxide and water but small amounts of carbon dioxide, formic acid, and an unidentified peroxide were also found. No olefins, methane or alcohols were reported.

Ethylene was however reported in the high temperature oxidation by Steacie and Plewes[70]. They detected ethylene throughout the course of the whole reaction, and by suggesting that the main chain process in ethane oxidation was the oxidation of ethylene they stressed the importance of ethylene in the oxidation of ethane. This work was later confirmed by Gray[56] who, using a flow system instead of a static system as used by Steacie and Plewes, found that ethylene could be obtained in up to 80% yield (based on ethane consumed). He explained this high yield on the basis of an HO_2 radical chain and in doing so he was the first to postulate that this mechanism could operate in hydrocarbon oxidation systems.

$$C_2H_6 + HO_2 = C_2H_5 + H_2O_2$$

$$C_2H_5 + O_2 = C_2H_4 + HO_2$$

Methanol,[71] ethanol[71], hydrogen peroxide[84], and acetic acid[73] have also been detected in the products of ethane oxidation. The evidence for the formation of acetic acid comes from the hydrogen bromide catalysed oxidation of ethane at 220°C but as this temperature is much lower than that at which ethane normally oxidises it is doubtful whether it will be formed in the uncatalysed oxidation.

The products from the low temperature catalysed oxidation of ethane have also been examined and it has been shown that the primary product is ethyl hydroperoxide[74]. Although the evidence for its formation is fairly conclusive the mechanism whereby it is formed is still in doubt. Two mechanisms have been put forward for its formation. Gray[74] investigated the mercury photosensitised oxidation at 25°C and he suggested that the ethyl hydroperoxide was formed by the reactions:-

$$C_2H_5 + O_2 = C_2H_5OO$$

$$C_2H_5OO + C_2H_6 = C_2H_5OOH + C_2H_5$$

Watson and Darwent[88] disagreed with this on the basis that these reactions could not explain the kinetics of the oxidation and they proposed an alternative scheme :-

$$Hg.(^3P_1) + O_2 = O_2^* + Hg.(^1S_o)$$

$$O_2^* + C_2H_6 = C_2H_5OOH$$

Although ethyl hydroperoxide is the primary product of the low temperature catalysed oxidations it cannot be a major product in the uncatalysed oxidations as it has a very short lifetime at temperatures of 300°C and above.[33] Nalbandyan[50] did find however that a peroxide was the primary product in the mercury photosensitised oxidation at temperatures up to 310°C.

From the foregoing it can be seen that the kinetics of ethane oxidation have been fairly extensively investigated but that there is a lack of analytical data covering the range of products formed throughout the reaction. This is partly due to the fact that the earlier analytical techniques required relatively large amounts of product material for analysis and hence only the later stages of reaction could be investigated, and partly due to the fact that with the techniques available it was not possible to isolate and identify all the compounds present in the complex product mixture. However with the development of modern analytical techniques this situation can now be remedied.

2.2. Cool Flames and the Negative Temperature Coefficient in Ethane Oxidation.

It is well established that hydrocarbons containing three or more carbon atoms appear to react by two different degenerate branching mechanisms depending on the temperature. Above 400°C we have a 'high' temperature mechanism and below about 350°C we have a 'low' temperature mechanism. The transition between the two regions is generally associated with the phenomena of cool flames and negative temperature coefficients in the velocities of the slow reactions.

Until recently it was not known whether or not ethane exhibited these phenomena. It was found by certain workers that the oxidation of ethane, like methane, had different characteristics from the oxidation of higher hydrocarbons e.g. Mulcahy[80] found that the manner in which the maximum rate of reaction varied with hydrocarbon and oxygen pressure differed for ethane and butane oxidations, and Prettre[81] found, using a flow system, that he could observe cool flames for the higher hydrocarbons but never with methane or ethane. These results led to the belief that cool flames could not exist in ethane oxidation systems. However Townend[82] disagreed with this viewpoint and although he did not actually observe cool flames in ethane oxidation he was of the opinion that they would be obtainable under suitable experimental conditions. "Induced" cool flames were observed, however, by Gerber and Niemann[77] on addition of diethyl peroxide to ethane oxidation systems.

The question of whether or not the ethane oxidation system exhibited a negative temperature coefficient was partially answered by Chirkov and Entelis[76]. They found that the maximum rate of reaction increased in the regions 270-340°C and 400-480°C but remained constant between 340-400°C. However the existence of a negative temperature coefficient in the rate of the slow combustion of ethane was confirmed by Knox and Norrish[75] when they showed that the reaction rate, as measured both by the increase in reactant temperature and by increase in rate of pressure rise, decreased as the temperature increased between 350-400°C. They also observed that cool flames could be obtained if suitable experimental conditions were used viz. with sufficiently large reaction vessels between 300 and 380°C at pressures of 600 mms.Hg upwards and with ethane plus oxygen compositions ranging from 32/1 to 3/2.

These results of Knox and Norrish are of importance as they show that ethane exhibits the properties of the "low" temperature oxidation which had previously only been recorded for hydrocarbons containing three or more carbon atoms.

Gray[56] also observed cool flames in ethane oxidation using a flow system, but the temperatures at which they were observed were much higher than those characteristic of cool flames. This led Knox and Norrish to suggest that these cool flames were peculiar to flow systems and were caused by reaction starting off at the outlet end of the reaction tube and then sweeping back through the reaction mixture. This would leave the reaction tube full of reacted gas and another cool flame could only appear once the reacted gas had been swept out of the tube. In this way the periodicity of the cool flames could also be explained.

3. AIM OF THE RESEARCH.

In order to account for the existence of a negative temperature coefficient in the rate of hydrocarbon combustion it was supposed that hydrocarbons underwent oxidation by two distinct mechanisms viz. a "high" temperature mechanism above 400°C and a "low" temperature mechanism below ca. 350°C, and it was thought from analysis of the products in the later stages of reaction that olefins were the major products in the 'high' temperature region and that oxygenated compounds were the major products in the 'low' temperature region. However through the recent development of gas chromatography it is now possible to analyse the products from the initial stages of reaction, and it has been shown for propane oxidation that propylene was the major product in both the "high" and the "low" temperature oxidations. This was explained on the basis that the initial stages of propane oxidation involved an HO_2 radical chain mechanism which operated throughout the whole temperature range.

$$C_3H_8 + HO_2 = C_3H_7 + H_2O_2$$

$$C_3H_7 + O_2 = C_3H_6 + HO_2$$

The aim of the present work was to investigate the low temperature oxidation of ethane in order to determine whether or not the initial stages of ethane oxidation involved an HO_2 radical chain mechanism, and hence to confirm whether or not the initial stage oxidations were the same in the "high" and the "low" temperature regions. It was hoped to analyse, by means of gas chromatography, the products formed throughout the course of the reaction and to investigate the variation in product yields with mixture composition and temperature, and in this way to elucidate the mechanism of the complete reaction.

EXPERIMENTAL TECHNIQUE

1. APPARATUS

The apparatus was a conventional high vacuum system constructed of Pyrex glass (see figs. 1 and 2). Although it was essentially a unit it is convenient to divide its description into three sections (1) General Apparatus, (2) Kinetic Apparatus, (3) Analytical Apparatus.

1. 1. General Apparatus

(a) Pumping and Storage System

The pumping system consisted of a three stage mercury diffusion pump backed by a Hyvac rotary oil pump. With this system the pressure, which was measured on a vacuostat, could be reduced to $10^{-5} - 10^{-6}$ mms. Hg.

The purified reactants were stored in 5 litre bulbs, which were fitted with traps for degassing purposes, and any required mixture was made up by measuring the reactants into a 500 cc. mixing vessel. The sharing ratio between the mixing vessel and the reaction vessel plus Bourdon Spoon Gauge was known for different furnace temperatures, and any desired pressure in the reaction vessel was obtained by having the corresponding pressure of reactants in the mixing vessel.

(b) Reaction Vessel

A cylindrical Pyrex reaction vessel, 5.5 cm. in diameter and volume = 522 ccs., was used. It was housed in a furnace and surrounded by a copper jacket to promote uniform heating.

(c) Measurement of Temperature

The temperature of the furnace was measured by means of a thermocouple in conjunction with a Doran D.C. potentiometer. The thermocouple was constructed of T_1/T_2 thermocouple wire (British Driver Harris Ltd.) which was supplied with a calibration scale.

(d) Furnace

The furnace consisted of a silica tube, 66 cm. long by 9.2 cm. internal diameter, which was heated by means of three independent windings of nichrome wire, resistances 150, 100, and 150 ohms respectively, the whole being suitably lagged and insulated. The temperature along the reaction vessel was kept constant to within ± 1°C by having external variable resistances in parallel and in series with the windings (fig. 5). The power was supplied via a Variac transformer and the mean temperature of the reaction vessel was controlled by a Resistance Thermometer Controller Type RT2 (Sunvic Controls Ltd.).

1. 2. Kinetic Apparatus

The pressure change during the reaction was followed by means of a Bourdon Spoon Gauge made of Pyrex glass and fitted with an optical lever arrangement. The pointer deflection was thus magnified and could be read on a metre scale, a pressure change of 1 mm. mercury giving a deflection of 5.50 mm. on the scale. The deflection was linear with respect to pressure over the pressure range used. The gauge was connected to the reaction vessel by 2 mm. internal diameter capillary tubing which was wound with nichrome wire and heated to a constant temperature. This temperature was such that any product which might diffuse into the capillary tubing could not condense.

1. 3. Analytical Apparatus

(a) Sampling System

The sampling system is shown in fig. 2. It consisted of two sampling tubes connected to the reaction vessel system by 4 mm. O.D. tubing, with the whole heated to a constant temperature using nichrome heating wire. The temperature being such that no condensation of products occurred. One of the vessels could be connected to the Toepler pump by means of a two-way tap, whilst the other was removeable from the apparatus.

The sharing ratio between the reaction vessel and the sampling vessels was known for the various furnace temperatures.

(b) Toepler Pump

The volumes of the two bulbs were calibrated by weighing the amount of mercury required to fill them. The volumes were 24.09 mls. and 73.91 mls. giving total volumes of 24.09 and 98.00 mls. from the respective graduation marks to the tap.

(c) Injection System

The injection system consisted of a U tube trap fitted with two two-way taps which allowed the carrier gas to enter the U tube and pick up the sample or else by-pass the U tube completely. The gas then flowed along narrow capillary tubing to a specially constructed tap having one inlet and three outlets (fig. 3). The outlets were connected to three chromatography columns and hence the gas stream could be made to pass through any one of the columns. There was also a tap of the same construction at the outlet end of the columns. The advantage of these taps was that the "dead space" in the system was kept down to a minimum.

(d) Carrier Gas

Hydrogen was used as carried gas. It was preferred to nitrogen because it gave greater base line stability and, because of its high conductivity, it gave greater sensitivity for detection. Conductivity is $\propto \frac{1}{(M.W.)^{\frac{1}{2}}}$ and hence with hydrogen we have a greater difference between hydrogen conductivity and hydrocarbon conductivity than for nitrogen. However its higher H.E.T.P. value and explosion hazards are disadvantages to its use.

On leaving the cylinder the gas was dried by passing through successive tubes packed with calcium chloride and activated Linde Molecular Sieve. The carrier stream was then divided, part going to the injection system and dummy column, and part going to a series of water bubblers where a constant head of water ensured a constant gas pressure. Before going on to the injection system and dummy column the gas stream passed through a "buffering" vessel consisting of a series of narrow capillary tubes connected to wide bore tubing. This arrangement evened out minor fluctuations in the gas pressure. After passing through the "buffering' vessel the gas stream was again divided, part going to the injection system and part to the dummy column. After the injection system the carrier gas passed on to the chromatography columns and then on to the detection system.

(e) Columns

Four gas-chromatography columns were used to analyse for the reactants and most of the products. Details of the columns are given in table 1:

TABLE 1

Column No.	Column Container	Length ft.	Internal Diam. mms.	Column Packing	Stationary Phase	Column Temp. °C	Flow Rate mls/min.	Compounds Analysed
Dummy	Glass Tubing	5	5	Firebrick (40-60 mesh)	-	47	-	-
1	Glass Tubing	5	4	Linde Molecular Sieve Type 5A (60-80 mesh) + Charcoal (24-32)	-	Room Temp.	31	O_2, CH_4, CO
2	Coiled Copper Tubing	10	3	Celite (60-80 mesh)	20% Pet. Ether (140-160°C)	-80	32	CO_2 C_2H_4 C_2H_6
3	Glass Tubing	5	5	Celite (60-80 mesh)	20% Polyethylene Glycol 400	47	67	CH_3CHO, C_2H_4O CH_3OH, C_2H_5OH H_2O
4	Coiled Copper Tubing	5	3	Celite (60-80 mesh)	20% Polyethylene Glycol 400	0	73	CH_3CHO C_2H_4O

A "split" column technique was used with column 3. The carrier gas was allowed to flow through the full length of the column until the acetaldehyde, ethylene oxide, methanol, and ethanol peaks were eluted and then the column was "split" so that the carrier gas only went through the first half of the column. In this way the flow rate was approximately doubled and the column length halved and the water peak was thus eluted in a reasonable time.

Acetaldehyde and ethylene oxide came through as a single peak on column 3. This peak was trapped out by passing the gas stream through a cooled glass trap, containing glass beads (0.02 mm. diameter) cooled to -183°C, until the acetaldehyde plus ethylene oxide peak had been completely collected. This trap was then used as the injection system for column 4 on which the acetaldehyde and ethylene oxide were separated.

(f) Detector

The detector used was a thermal conductivity gauge. It consisted of a brass block (length = 7.5 cm., diameter = 7.5 cm.) with two cylindrical channels along which were stretched two tungsten filaments of approximately 10 ohm resistance. The filaments formed part of a Wheatstone bridge circuit (fig. 6). The carrier gas emerging from the chromatography columns flowed over one of the filaments whilst the carrier gas from the dummy column flowed over the other and a "steady state" existed in the Wheatstone bridge circuit until a product came through the chromatography column and passed over the filament. This caused a change in conductivity of the surrounding gas which in turn altered the temperature of the filament and hence its resistance. This change in resistance produced an "out of balance" current in the bridge circuit which was fed into a Honeywell Brown "Electronic" Strip Chart Recorder (0-1 mV Range) which both amplified and recorded the signal. As the amplified signal at times exceeded 1 m.V. three resistances of 2,000, 200, and 20 ohms were placed in parallel with the recorder so that the sensitivity could be altered (see fig. 6). When the recorder was connected to position A its range was close to 1 m.V. but when connected to positions B or C the range was increased to approximately 10 or 100 m.V. respectively.

The power to the Wheatstone bridge circuit was supplied by two 2 volt accumulators which, when fully charged, had an output of approximately 4.2 volts. The bridge voltage was kept constant at 4 volts by means of a variable resistance in series with the accumulators.

2. ANALYTICAL METHODS

2. 1. Gas Chromatography

Gas chromatography was used for the analysis of oxygen, methane, carbon monoxide, carbon dioxide, ethylene, ethane, acetaldehyde, ethylene oxide, methanol, ethanol, and water. The columns used are given in table 1.

By attaching a gas burette to the U tube trap of the chromatography system a known volume of gas at a known temperature and pressure could be introduced into the analysis system. In this way, by injecting a known amount of each compound on to the appropriate chromatography column and measuring the corresponding peak area calibration graphs of peak area vs. μ moles were constructed for each compound.

Peak areas rather than peak heights were used for the calibration as the latter are more dependent on the operating parameters.[48]

The peak areas were measured by planimeter. As in any one run there was liable to be as many as eleven peaks this method was less time consuming than the method of measuring areas by "trapeziums". The measurement of the areas by the formula - ½ peak width x peak height - was not used as this method tends to be inaccurate for tall narrow peaks.

2. 2. Other Methods

Formaldehyde was determined by the method of Bricker and Johnson.[83] 1 gm. of chromotropic acid (B.D.H. - sodium salt for formaldehyde determination) was dissolved in 5 mls. distilled water, and 1.5 mls. of the solution were then added to 0.8 mls. of the aqueous formaldehyde solution. Approximately 8.5 mls. of Analar concentrated sulphuric acid were then added and the solution was heated for half an hour in boiling water. The solution was cooled and made up to approximately 50 mls. in a standard flask with distilled water. On cooling to room temperature it was then accurately made up to the mark. The absorption of the coloured solution was compared to that of a blank determination using 10 mm. silica cells in an S.P. 600 Spectrophotometer at a wavelength of 5700Å. The concentration of the original formaldehyde solution could then be obtained from a previously constructed calibration graph.

As it is known that formaldehyde condenses with hydrogen peroxide in aqueous solutions[84,85,87] comparisons were made of the absorbances of aqueous solutions of formaldehyde and aqueous solutions of formaldehyde plus hydrogen peroxide. It was found, using ratios of formaldehyde to hydrogen peroxide similar to those observed in the oxidation products, that the solutions with the same formaldehyde concentration had the same absorbance whether or not hydrogen peroxide was present. Hence, under the conditions used hydrogen peroxide did not interfere with the formaldehyde determination.

Acetaldehyde. Tests were carried out to confirm whether or not the condensation of hydrogen peroxide with acetaldehyde affected the determination of the latter by gas chromatography. Two solutions were made up, both contained the same ratio of methanol to acetaldehyde but in the second solution hydrogen peroxide (of approx. the same concentration as that found in the oxidation products ~ 30%) instead of water was added. The methanol was present as a standard. On analysing these solutions on column 3 it was found that when hydrogen peroxide was present the area of the acetaldehyde peak was about $\frac{1}{7}$th of that when only water was present. This indicated that hydrogen peroxide interfered with the determination of acetaldehyde and that an acetaldehyde-hydrogen peroxide adduct was formed.

Various attempts were made to destroy this adduct in order to liberate the acetaldehyde and this was finally achieved by coating the surface of the sampling vessel with barium hydroxide. When the synthetic mixtures were allowed to react on this surface at the normal temperature of the sampling vessel about 95% of the acetaldehyde was recovered from the solution which contained the hydrogen peroxide. This method thus appeared satisfactory for the determination of acetaldehyde in the presence of hydrogen peroxide.

Using this method acetaldehyde determinations were carried out on a 1:1 mixture of ethane to oxygen at 362°C (see table 2), and the results are compared on fig. 10c with those obtained when the adduct was not previously destroyed. As it was at a rather late stage in the work when it was discovered that hydrogen peroxide interfered with the determination of acetaldehyde only three determinations were made but it can be seen that the values for when the adduct was destroyed are approximately 30% higher than those for when the adduct was not destroyed. Thus all the acetaldehyde values quoted in the tables to follow should be increased by about 30%.

<u>TABLE 2</u> (fig. 10c)

Series J. Ratio $C_2H_6:O_2$ = 1:1. Pressure = 442 mms. Hg.
Temp. = 362°C.

Run No.	Δp cms. Hg.	CH_3CHO mms. Hg.
1	4.73	0.37
2	7.70	0.31
3	2.68	0.17

Hydrogen Peroxide. Hydrogen peroxide was determined by the method of Egerton et al.[86] To a portion of stock solution of 15% w/v titanous sulphate in sulphuric acid, dilute hydrogen peroxide was added until the solution was a pale yellow colour. 1 ml. of this reagent was then added to 3 mls. of an aqueous solution of the reaction products and the absorbance of the resulting yellow solution determined using 10 mm. silica cells in an SP 600 Spectrophotometer at a wavelength of 4100Å. The concentration of hydrogen peroxide in the original solution was then determined from a previously constructed calibration graph.

Hydroperoxides if present in the reaction products will not affect the determination of hydrogen peroxide as Egerton et al. have shown that ethylhydroperoxide and di-ethyl peroxide do not give a colouration with titanous sulphate.

3. RUN PROCEDURE

3. 1. Pumping Procedure

Since the reaction rate was sensitive to the state of the walls of the vessel a standard pumping procedure was employed before each run was carried out. This consisted of pumping for fifteen minutes with no cold trap on the high vacuum side of the mercury diffusion pump, followed by fifteen minutes pumping with the cold trap present. The initial pumping had to be carried out without a cold trap in front of the mercury diffusion pump since any ethane present in the system would be retained in this trap and as ethane has a vapour pressure of the order 10^{-2} mms. Hg. at -183°C the apparatus could not then be pumped down below this value.

3. 2. Kinetic Procedure

The mixing vessel was evacuated and the reactants introduced in the order-additive, ethane, oxygen-by means of a "piling up" procedure. After the reaction vessel and Bourdon Spoon Gauge had been evacuated they were connected to the mixing vessel whence the entrance of the reactants into the reaction vessel registered as a "kick" on the Bourdon Spoon Gauge. The reactants were given fifteen seconds to equilibrate and then the connecting tap between the reaction vessel and mixing vessel plus mercury manometer was closed. The initial pressure of reactants in the reaction vessel could then be read on the mercury manometer. Thirty seconds after the entrance of the reactants the "shorting" tap on the Bourdon Spoon Gauge was closed and the pressure increase in the system could then be read off the metre scale at any desired time.

3. 3. Analytical Procedure

The sample for analysis was obtained by first isolating the Bourdon Spoon Gauge from the reaction vessel and then immediately opening the tap to the evacuated sampling system. After allowing thirty seconds for equilibration this tap was then closed, along with the taps on the two sampling vessels. The vessels were then cooled to $-183^{\circ}C$ in liquid oxygen. The products condensed in the detachable vessel were dissolved in a suitable volume of distilled water and the aqueous solution analysed for either formaldehyde or hydrogen peroxide.

The products uncondensable at $-183^{\circ}C$ viz. oxygen, methane, and carbon monoxide, which were contained in the other sampling vessel were then transferred to the gas burette by means of the Toepler pump, whence the temperature, pressure and volume of the fraction was measured. An aliquot of this fraction was then admitted to the gas chromatography injection system and subsequently analysed on column 1.

This procedure was repeated for those products uncondensable at $-80^{\circ}C$ viz. carbon dioxide, ethylene, and ethane, with the analysis being carried out on column 2.

The products condensable at $-80^{\circ}C$ viz. acetaldehyde, ethylene oxide, methanol, ethanol, and water were distilled over into the injection system of the chromatography unit and analysed on columns 3 and 4. For the first five minutes after the injection of fraction 3 into the gas stream the carrier gas from the outlet end of column 3 passed through a coiled glass trap containing glass beads (0.02 mm. diam.) cooled to $-183^{\circ}C$ and any acetaldehyde or ethylene oxide in the fraction was condensed out on the beads. After the five minutes the gas stream was by-passed round this trap and the pressure head in the water bubblers was adjusted so that the flow rate remained constant. After a further fifteen minutes, in which time methanol and ethanol were eluted, the column was split so that the carrier gas only flowed through the first half of the column. Finally the water peak was eluted.

Once the water peak had been completely eluted the carrier gas was diverted so that after leaving the injection system it passed through the coiled glass trap and then on to column 4. When this trap was warmed up the acetaldehyde and ethylene oxide were carried over on to column 4 where they were separated.

Owing to acetaldehyde and ethylene oxide having vapour pressures of approximately 1 mm. Hg. at -80°C part of these products were carried over into the gas burette along with fraction 2. The amount of each carried over was calculated by injecting an aliquot of fraction 2 on to column 4 and measuring the corresponding acetaldehyde and ethylene oxide peak areas.

3. 4. Calculation of Results

The results and calculations for a typical analysis are shown below:

Run No. 1(c) Ratio $C_2H_6:O_2$ = 3:1 Temp. = 362°C

Initial reading on Bourdon Gauge . . = 5.30

Final reading on Bourdon Gauge . . . = 26.15

$\therefore$ Pressure rise in reaction . . . . = 20.85 Bourdon cms.

= 5.38 cms. Hg.

Initial pressure of reaction mixture . = 29.58 cms. Hg.

$\therefore$ Final pressure of reaction mixture . . = 34.96 cms. Hg.

Volume of reaction vessel = 522 ccs. Temp. . . = 362°C

∴ No. of μ moles in reaction vessel on sampling . . = 4610

∴ μ moles in sampling vessel connected to Toepler pump = 355.8

∴ μ moles in detachable sampling vessel . . . . = 416.3

Fraction 1

Volume of fraction . . . . = 24.09 mls.

Temperature of fraction . . = 21.5°C

Pressure of fraction . . . = 3.62 cms. Hg.

∴ No. of μ moles in fraction . . = 47.5

Product	Peak Area	μ moles in aliquot
O_2	.019	0.38
CH_4	.039	0.90
CO	.031	5.87

Fraction 2

Volume of fraction . . . . . = 24.09 mls.

Temperature of fraction . . . = 21.0°C

Pressure of fraction . . . . . = 14.20 cms. Hg.

∴ No. of μ moles in fraction . . = 186.6

μ moles of CH_3CHO + C_2H_4O in fraction = 1.6

∴ Corrected μ moles in fraction . . = 185.0

Product	Peak Area	μ moles in aliquot
CO_2	.023	0.39
C_2H_4	.102	1.69
C_2H_6	.098	13.91

Fraction 3

Product		Peak Area	Total Peak Area	Flow Rate mls./min.	μ moles in fraction
CH_3CHO	(a)	.001	.001	74	0.12
	(b)	.0004	.0023		
C_2H_4O	(a)	.140	.140	74	6.94
	(b)	.007	.041		
CH_3OH		.149	.149	66	6.09
C_2H_5OH		.040	.040	66	1.44
H_2O		.852	.852	108	86.5

Peak areas (b) refer to the areas of the acetaldehyde and ethylene oxide peaks obtained on injection of an aliquot of fraction 2 on to column 4. They are converted into total peak areas by multiplying by a factor equal to

$$\frac{\text{Total amount of fraction 2}}{\text{Amount of fraction 2 injected on column 4}}.$$

Owing to changes in the ambient conditions the flow rates through the columns did not remain constant but varied by ±2% from the calibration flow rate. This could be ignored in the case of columns 1 and 2 as the flow rate term cancels out in the subsequent calculations but any variation in the flow rate through column 3 had to be taken into account:

$$\mu \text{ moles of product X in fr. 3} = \text{Pk. Area} \times \text{Calibration Factor} \times \frac{\text{Observed Flow Rate}}{\text{Calculated Flow Rate}}$$

The pressure of any product X in the reaction mixture is given by the formula

$$P = (\mu_x \times F \times M)/A \times T)$$

where μ_x = number of μ moles of product X in aliquot.

A = total number of μ moles in aliquot.

F = number of μ moles in fraction.

T = number of μ moles in sampling vessel.

M = final pressure of reactant mixture in reaction vessel.

In the case of either formaldehyde or hydrogen peroxide the pressure in the reaction mixture is given by:

$$P = R \times C \times V \times G/S$$

where R = absorbance of solution.

C = calibration factor.

V = volume of water added to sample.

G = factor converting a weight of formaldehyde or hydrogen peroxide into a pressure in the reaction vessel.

S = % of reaction mixture entering sampling vessel.

Applying the above formulae to Run 1(c) we obtain the results given in table 2.

TABLE 2

Product	Press. in R.V. mms. Hg.	Product	Press. in R.V. mms. Hg.
O_2	2.48	C_2H_4O	6.82
CH_4	5.88	CH_3OH	5.99
CO	38.3	C_2H_5OH	1.41
CO_2	4.39	H_2O	85.0
C_2H_4	19.3	HCHO	1.59
C_2H_6	158.1	H_2O_2	-
CH_3CHO	0.12		

Hydrogen peroxide yields were only determined for the 1:1 ratios of ethane and ethylene to oxygen at 362°C, and hence no value is given for hydrogen peroxide in the above table. However this does not affect the calculation of the element balances very considerably as the hydrogen peroxide decomposes into water either on the walls of the reaction vessel, in contact with the mercury of the Toepler pump or else on the chromatography columns, and the value for the water yield consequently includes that of hydrogen peroxide.

4. ELEMENT BALANCES

Element balances were constructed for Series L, M and N, see tables 13, 14, 18. The number of mm. atoms of carbon, hydrogen, and oxygen recovered did not vary in most cases by more than 5% from the amount initially used and was often much closer than this. However in the ethane oxidations since ethane was generally the major component of the reaction mixture the accuracy of the elements balance depended largely on the accuracy of the determination of ethane. In fig. 7 the experimental values for ethane in Series L are plotted alongside those values calculated from the carbon content of the products and it can be seen that the two lines, if drawn, would be more or less coincidental. A similar agreement held for oxygen.

These results indicate that the elements balance for the products was satisfactory and that no major product was unaccounted for.

5. PREPARATION AND PURIFICATION OF MATERIALS

5. 1. Column Packings

(a) Partition Chromatography. Graded commercial celite (60-80 mesh) was used as the solid support in all the columns.

Column 2 - Petroleum ether (140-160°C), 20% by weight of the celite to be used, was dissolved in a suitable volume of ether and then added, with continuous mixing, to the celite. The ether was drawn off at the water pump and the celite plus petroleum ether was then packed in a 10 ft. length of copper tubing which was subsequently coiled so as to fit inside a quart size thermos flask.

Columns 3 and 4 - Polyethylene glycol 400, 20% by weight of the celite to be used, was dissolved in acetone and then added, with continuous mixing, to the celite. The acetone was then evaporated off by heating the slurry to 100°C under vacuum. The dry celite plus polyethylene glycol was then packed in a 5 ft. glass tube for column 3 and in 5 ft. copper tubing for column 4. This latter column was also coiled so as to fit inside a quart size thermos flask.

(b) Adsorption Chromatography.

Column 1 - Active carbon (24-32 mesh - Sutcliffe and Speakman 27/c) was heated at 400°C under a vacuum for one hour to remove adsorbed gases.

Pellets of Linde Molecular Sieve Type 5A were crushed and sieved. A sample of mesh 60-80 was then roasted in a crucible over a meker burner for two hours.

The column was prepared by packing a 5 ft. glass column with the Linde Molecular Sieve to within 6 ins. of the end. The remaining 6 ins. were then packed with the activated charcoal.

5. 2. Reactants and Other Materials

Ethane. Analysis by gas chromatography showed that the ethane (B.O.G. cylinder) contained about 1.5% ethylene. This was removed by passing the gas slowly upwards through a 2.3 cm. O.D. column packed with activated charcoal which had been saturated with bromine. Any bromine carried over from the column was removed by passing the gas through a short tube filled with firebrick (40-60 mesh) plus 20% by weight of N:N dimethyl p - toluidine. This method of removing bromine had the advantage that the movement of the bromine front down the tube indicated when the absorbent had been saturated. The purified ethane emerging from the column was passed through a trap at -80°C and then collected at -183°C. It was then further purified in the apparatus by repeated distillations from -80°C to -183°C, the middle fraction being retained in each case.

Oxygen. Oxygen was taken directly from a B.O.G. cylinder and any condensibles present were removed by slowly passing the gas through two coiled glass traps maintained at -183°C. It was not purified further and generally contained about 0.3% nitrogen.

Ethylene. Ethylene was taken from a B.O.G. cylinder. On analysis by gas chromatography it was found to contain about 1.3% carbon dioxide.

Acetaldehyde. B.D.H. Laboratory Reagent. A few crystals of hydroquinone were added to each sample to decrease the polymerisation rate.

The gases used for the calibrations, apart from those mentioned above, were obtained as follows:

Carbon Dioxide - Commercial Cardice - Purified by distillation under vacuo, the middle fraction being retained.

Ethylene Oxide - B.D.H. Laboratory Reagent.

Methanol - Absolute methanol.

Ethanol - Absolute ethanol.

Methane - B.O.G. cylinder.

Carbon Monoxide - Carbon monoxide was prepared by dropping formic acid on to concentrated sulphuric acid heated to a 100°C in a vacuum. The carbon monoxide evolved was purified by passage through two traps at -183°C and then stored in the apparatus.

EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTS

The experimental results are divided into two sections (1) Analytical and (2) Kinetic. The main object of this research was to examine the products from ethane oxidation, both gaseous and liquid, over a wide range of experimental conditions, and consequently the majority of results listed are of an analytical nature. They are given in a logical rather than a chronological order, and their theoretical implications will be considered mainly in the Discussion.

1. ANALYTICAL RESULTS

The analysis were carried out on samples withdrawn from the reaction vessel after a desired pressure increase and the results were illustrated graphically by plotting the pressure of product in the reaction vessel against extent of reaction. The extent of reaction being measured either by the pressure increase in the system or else by the amount of water formed. The ethane and oxygen consumptions could not be used as a measure of the extent of reaction as they were obtained by the subtraction of two large numbers and were liable to be inaccurate. The reaction time was also considered too unreliable as the induction period tended to vary depending on the surface condition of the reaction vessel.

In the ethylene oxidation, where there was always an initial pressure decrease, the water formed was used as a measure of the extent of reaction. However, whether the pressure rise or water formed was taken, the ratios of the initial yields of products obtained from the plots remained the same.

1.1. Effect of Added Acetaldehyde

When oxidations were initially carried out the induction period for a I:I mixture of ethane to oxygen at an initial pressure of 444 mms.Hg. and at a temperature of 362°C was approximately four hours. This was inconveniently long and therefore 0.5% acetaldehyde was added to the reactant mixture. The induction period was then reduced to about four minutes. (The induction period being taken as the time required for the pressure in the reaction vessel to increase by 0.25 Bourdon cms. = 0.05 cms.Hg.)

A series of runs were carried out with the above mixture plus 0.5% acetaldehyde and the results are given in Table 3 and shown graphically on fig. 8.

After carrying out these runs it was found that the reaction vessel had become "aclimatised" and that when the same mixture was oxidised without acetaldehyde the induction period was now only about twenty-four minutes. The oxidation of ethane, without acetaldehyde initially present, was then investigated and the results are given in Table 4 and on fig. 8.

It can be seen from fig. 8 that in the initial stages the presence of acetaldehyde increased the yields of carbon monoxide, carbon dioxide, methanol, ethylene, and water. However when an amount of acetaldehyde equal to that added to the reactants was oxidised by itself i.e., by using the same mixture as above but with the ethane replaced by nitrogen, it was found that the carbon monoxide, carbon dioxide, and water produced were equivalent to the "extra" carbon monoxide, carbon dioxide, and water formed in the acetaldehyde initiated ethane oxidation. This is illustrated in table 5.

TABLE 5

Ratio $C_2H_6:O_2$ = 1:1 Pressure = 444 mms.Hg. Temp. = 362°C

Δp 0.9 mm.Hg	1:1 Mixture + 2 mm. CH_3CHO	1:1 Mixture	Δp due to oxdn. of CH_3CHO in mixt.	Oxdn. of 2 mm. CH_3CHO
O_2 Consumed	7.8	2.0	5.8	5.5
CO	2.8	0.0	2.8	3.7
CO_2	0.8	0.0	0.8	0.88
C_2H_4	3.9	2.4	1.5	0.0
CH_3OH	0.7	0.0	0.7	0.0
H_2O	5.3	2.2	3.1	3.1

The figures in table 5 show that the oxidation of acetaldehyde is superimposed on the oxidation of ethane with respect to carbon monoxide, carbon dioxide, water, and oxygen consumption. This effect however is not only confined to ethane oxidation and Cullis and Hinshelwood[89] concluded that the acetaldehyde added to benzene-oxygen and pentane-oxygen systems also oxidised more or less independently of the hydrocarbon.

The yields of ethylene and methanol are also increased by the addition of acetaldehyde. This suggests that the acetaldehyde on oxidising introduces radicals into the system which can then react with ethane to produce ethylene and methanol. If it is assumed that the initiation step in acetaldehyde oxidation involves the production of acetyl and hydroperoxy radicals, as suggested by McDowell and Thomas[93], then the formation of ethylene and methanol can be readily explained.

Initiation - - - - - $CH_3CHO + O_2 = CH_3CO + HO_2$

At the temperatures used the acetyl radicals will decompose into methyl radicals and carbon monoxide, and the methyl radicals will then most probably be converted to methanol by the following steps:-

$$CH_3 + O_2 = CH_2O + OH$$

$$OH + CH_3CH_3 = CH_3OH + CH_3$$

Although there is no direct evidence for this scheme the fact that the presence of ethane greatly increases the initial yield of methanol holds strongly in its favour.

The hydroperoxy radical produced in the initiation step will, as is shown later, probably abstract hydrogen from the ethane present to produce an alkyl radical, which on reaction with oxygen will give ethylene and another hydroperoxy radical.

$$C_2H_6 + HO_2 = C_2H_5 + H_2O_2$$

$$C_2H_5 + O_2 = C_2H_4 + HO_2$$

Hydrogen peroxide is also a product of this chain reaction, and although no analysis were carried out for hydrogen peroxide in this series of runs, evidence that the addition of acetaldehyde will increase the initial yield of hydrogen peroxide comes from the work of Kooijman[131] on the oxidation of ethane and propane. Kooijman found that with propane the yield of peroxide passed through maxima at 400° and 465°C but with ethane only the higher maximum could be observed. However the addition of 1% acetaldehyde to the ethane resulted in the appearance of the lower maximum. These results can be conveniently explained by supposing that the added acetaldehyde initiates the above chain and consequently increases the yield of hydrogen peroxide. If the acetaldehyde were to react as it was heating up in the reaction vessel then at the lower temperatures the HO_2 radical would probably be produced by the reactions

$$C_2H_5 + O_2 = CH_2O + CH_3O$$

$$CH_3O + O_2 = CH_2O + HO_2$$

since it has been shown in the present work that the first of these reactions has a lower activation energy than the reaction $C_2H_5 + O_2 = C_2H_4 + HO_2$. This latter reaction will however predominate as the temperature of the mixture comes up to the temperature of the surroundings.

It is envisaged that ethylene is formed by a chain reaction but since the yield of "extra" ethylene is much smaller than that which would be observed if each acetaldehyde molecule initiated a new chain there must be some factor which limits the increase in the ethylene yield. The most likely is that the acetaldehyde reacts as it is heating up in the reaction vessel and is mostly consumed by the time the hydrocarbon mixture has reached a temperature at which it can take part in reaction. Evidence for this comes from the fact that acetaldehyde is known to oxidise rapidly at temperatures below that at which the present oxidations were carried out[64], and that products were formed before the "shorting" tap on the Bourdon Spoon Gauge could be closed. This latter feature was indicated by there being products present at "zero" pressure rise. (See figs.8a and 8b).

Apart from the fact that most of the acetaldehyde may have reacted before reaction with the hydrocarbon can take place, the yield of "extra" ethylene will be small since the reaction $C_2H_5 + O_2 = CH_3O + CH_2O$ will predominate over the ethylene producing reaction $C_2H_5 + O_2 = C_2H_4 + HO_2$ at the lower temperatures.

There are two other possibilities for the small increase in the ethylene yield viz. that the chains consuming ethane are short in the initial stages, and that most of the acetaldehyde is destroyed at the walls of the reaction vessel. The first possibility is unlikely but the second may account for some of the acetaldehyde which is consumed before reaction with the hydrocarbon occurs.

The effect of adding acetaldehyde to oxidation systems has been studied by several workers. Townend and Chamberlain[96] noted that the addition of 1% acetaldehyde to ethane-air mixtures markedly decreased the pressure at which ignition occurred and also reduced the time of ignition lag from minutes or even hours to seconds. Pease[95] and Bone and Hill[3] also found that the addition of acetaldehyde to oxidation systems reduced the induction period and they observed that if too much acetaldehyde was added then the reaction mixture exploded.

Although the addition of acetaldehyde has a very pronounced effect on the induction period it does not greatly alter the maximum rate of reaction. Fig.18 shows the effect of added acetaldehyde on the pressure-time curves for ethane oxidation at 362°C, and it is clear that varying amounts of additive have little effect on the maximum rate of reaction. Similar results were also obtained by Mulcahy[80] for propane oxidation but in this case it was also shown that the temperature at which the acetaldehyde was added did not alter the effect of the acetaldehyde. These observations are not confined to acetaldehyde and it has been shown that other additives, such as formaldehyde, do not alter the maximum rate of reaction when added to hydrocarbon oxidation systems.[106]

Experiments were carried out to determine the products of acetaldehyde oxidation at 362°C and to determine how rapidly it was oxidised at this temperature. The results are listed in table 6.

TABLE 6 (Fig. 9)

Ratio $CH_3CHO:N_2:O_2$ = 1:20.4:20.4 Pressure = 442 mms.Hg.
Temp. = 362°C

Pressure in Reaction Vessel (mms.Hg)

Run No.	Time mins.	O_2	N_2	CH_3CHO	CO	CO	CH_3OH	H_2O	HCHO
1	3.0	203.7	210.4	-	11.2	4.80	1.33	13.9	1.20
2	2.0	202.4	211.4	-	9.60	4.10	1.30	12.0	1.50
3	1.0	202.8	210.4	1.32	9.80	4.10	1.00	10.5	2.02
4	3.0	196.5	210.4	1.00	11.3	4.42	1.34	11.7	1.58
5	0.5	202.1	210.0	1.72	8.50	3.97	1.00	11.2	2.40
6	0.25	209.8	206.7	2.22	9.53	3.54	1.13	11.0	2.49

N.B. "-" denotes not recorded.

It can be seen from fig. 9 that the acetaldehyde oxidises rapidly at 362°C and that after thirty seconds about 80% of the acetaldehyde had been converted to the end products, carbon monoxide, carbon dioxide, methanol, and water. Formaldehyde is also formed but its yield passes through a maximum indicating that it acts as an intermediate. These results are similar to those obtained by Newitt, Baxt and Kelkar[49] for the oxidation of acetaldehyde in a flow system at 360°C, but they found that the reaction was faster in their case, taking only ten seconds for 80% reaction, and that peracetic acid and traces of acetic and formic acids were also formed. However as there is no marked discrepancy in the carbon balance for the runs tabulated in table 6, the amounts of peracetic acid, acetic acid and formic acid, if formed, must be small.

According to McDowell and Thomas[93] the initiation step in acetaldehyde oxidation produces acetyl and hydroperoxy radicals.

$$CH_3CHO + O_2 = CH_3CO + HO_2$$

The hydroperoxy radicals formed will either be destroyed at the walls of the vessel or else abstract hydrogen to give hydrogen peroxide which on decomposing will give water and oxygen. On the other hand, the acetyl radicals will almost certainly decompose into methyl and carbon monoxide before further reaction can take place. The methyl radicals formed will then probably oxidise to give formaldehyde and hydroxy radicals, and the formaldehyde on oxidation will give carbon monoxide, carbon dioxide, and water. However the fate of the hydroxy radicals is not so certain.

It is suggested that these radicals will abstract methyl from the acetaldehyde to produce methanol and formyl radicals.

$$CH_3CHO + OH = CH_3OH + CHO$$

This reaction will probably have a lower activation energy than the reaction

$$CH_3CHO + OH = CH_3CO + H_2O$$

since the CH_3-CHO bond is weaker (75+-2 k,cal.) than the CH_3CO -H bond (about 85 k.cal.)

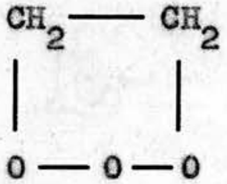
The view that the first of these reactions will be predominant receives support from the fact that when acetaldehyde oxidises in the presecence of ethane the yield of methanol is increased whereas the yield of water remains the same. This shows that the C-C bond in the ethane molecule is broken in preference to the stronger C-H bond, and that the reaction

$$CH_3CH_3 + OH = CH_3OH + CH_3$$

takes place in preference to

$$CH_3CH_3 + OH = CH_3CH_2 + H_2O$$

There are other possibilities for the formation of methanol but they are not so plausible as the above hydroxy radical reaction. Newitt and Baxt[91] suggested that the alcohol was formed by the breakdown of a peroxide of the following structure:-



$$= CH_3OH + CO_2$$

This requires a far reaching rearrangement of the molecule and is therefore unlikely. A more plausible reaction scheme was put forward by McDowell and Thomas[92]. They suggested that paracetic acid radicals were formed which on subsequent decomposition produced methoxy radicals which in turn formed methanol by hydrogen abstraction.

$$CH_3CO + O_2 = CH_3CO_3$$

$$CH_3CO_3 = CH_3O + CO_2$$

$$CH_3O + CH_3CHO = CH_3OH + CH_3CO$$

However as the present work was carried out some 200° or so higher than that of McDowell and Thomas the acetyl radicals produced will decompose rather than combine with oxygen.

It has been shown that methanol is formed in the oxidation of methyl radicals at temperatures of about 150°C. The suggested reactions are:-

a) $CH_3 + CH_3OO = HCHO + CH_3OH$ (Haedel, Ogg and Leighton[116])

b) $CH_3OO + CH_3OO = 2CH_3O + O_2$ (Raley, Porter, Rust and Vaughan[94])

$CH_3O + CH_3O = CH_3OH + CH_2O$

In their experiments on free methyl Raley, Porter, Rust and Vaughan concluded that methyl radicals were oxidised almost as quickly as they were formed and were present in much smaller concentrations than the methyl peroxy radicals. If this is the case the first of the above schemes will be unimportant as compared to the second. Although methanol may well be formed by means of this latter scheme under conditions of low temperature and high methyl peroxy radical concentration, it is unlikely that it will be formed by this mechanism in the present work since at the temperatures used the methyl peroxy radicals would be expected to decompose into HCHO + OH. Although it has been demonstrated that the reaction of methyl radicals with oxygen will produce methyl peroxy radicals at temperatures up to 200°C [117] it may be assumed that at 362°C the reaction will produce formaldehyde and hydroxyl radicals as this is the most likely manner in which formaldehyde can be formed in the oxidation of acetaldahyde.

From the above considerations, the following are the likely reactions whereby CO, CO_2, CH_3OH, HCHO, and $H_2O$are formed in the oxidation of acetaldehyde at 362°C.

a) $CH_3CHO + O_2 = CH_3CO + HO_2$

b) $CH_3CO = CH_3 + \underline{CO}$

c) $CH_3 + O_2 = \underline{CH_2O} + OH$

d) $OH + CH_3CHO = \underline{CH_3OH} + CHO$

e) $CH_2O + O_2 = \underline{CO}, \underline{CO_2}, \underline{H_2O}$

f) $CH_3CHO + HO_2 = CH_3CO + H_2O_2$

g) $H_2O_2 + \text{wall} = \underline{H_2O} + \frac{1}{2} O_2$

1. 2. Effect of Mixture Composition on Product Yields.

In order to determine the dependence of the yields of the various products on the oxygen concentration experiments were carried out with 3:1 and 1:2 mixtures of ethane to oxygen in addition to the 1:1 mixture. The results are shown in tables 7 and 8 and on fig. 10. To give a clearer picture of the relative yields, the products from the 1:1 mixture are plotted together on fig.11.

The initial yields of products for these mixtures along with those for other mixtures at different temperatures are summarised in table 9. The initial rate of formation of any product with respect to pressure rise or water formed was obtained by drawing a line tangential to the curve through the early points on the pressure vs. extent of reaction plot. (For illustration see fig.15.)

The results given in table 9, although only approximate, show that about 70-80% of the ethane consumed in the initial stages is converted to ethylene and that there is no marked oxygen dependence of any of the products, except perhaps formaldehyde, in the initial stages of reaction. This indicates that the reactions producing the initial products must all have the same kinetic dependence on oxygen.

The most striking feature of the later stage results is the sharp maxima exhibited by methanol, formaldehyde and ethylene with the 3:1 ethane to oxygen mixture. The maxima all occur after about 70% reaction and it is interesting to note that the yield of methane rises sharply at this point, presumably owing to methyl radicals in the system abstracting hydrogen when the oxygen concentration falls. This suggests that the maxima in the yields of methanol, formaldehyde and ethylene are due to the fall in oxygen concentration. Since they are produced via reactions involving oxygen their rate of production will fall as the oxygen is depleted and a point will be reached where the rate of removal exceeds the rate of production and a maximum will result. With the 1:2 ethane to oxygen mixture the methanol yield does not pass through a maximum presumably because the oxygen concentration is always sufficiently high to maintain its rate of production.

1. 3. Oxidation on an Ethane-Ethylene Mixture.

As about 75% of the ethane initially consumed was converted to ethylene, an ethane-ethylene mixture was oxidised in order to determine what effect the ethylene formed in the initial stages had on the subsequent reaction.

The total hydrocarbon concentration was the same as in the 1:1 mixture used previously but part of the ethane was replaced by ethylene in an amount equal to its stationary state concentration in the 1:1 ethane to oxygen mixture i.e. the initial ethylene concentration equalled that at the maximum rate of reaction in the 1:1 mixture. The results obtained are given in table 10 and on figs.12a and 12b.

Even although ethylene was initially present in substantial amounts its production in the early stages still exceeded its consumption and the ethylene concentration increased before passing through a maximum after about 10% reaction. This indicates that the radical removing ethane in the initial stages is considerably less reactive with respect to ethylene than the radical which removes it in the later stages. At the maximum in the ethylene yield the ratio ofethylene to ethane was approximately equal to the equilibrium ratio in the 1:1 ethane to oxygen mixture.

Table 9 shows that the effect of the added ethylene is to increase the initial yields of carbon monoxide, formaldehyde, and water, and since it can be seen from the experiments described in the next section that these are the major products from the oxidation of ethylene, it suggests that the ethylene formed in the course of ethane oxidation will be oxidised independently to these products.

1.4. Oxidation of Ethylene.

As ethylene is the major initial product from the oxidation of ethane at 362°C and as its concentration passes through a maximum close to the maximum rate of reaction, it is clear that ethylene plays an important role in ethane oxidation.

Consequently the oxidation of ethylene was investigated and the results are given in tables 11 and 12 and on figs. 13 (a) and 13 (b). The results given in table 11 are for the oxidation of a 1:1 mixture of ethylene to oxygen and those given in table 12 are for the initial stages in the oxidation of a 1:2 mixture.

The most obvious feature of these results is that in the early stages of reaction between 90-95% of the ethylene is converted to formaldehyde. However after about 3% reaction the yield of formaldehyde starts to fall showing that the formaldehyde itself is being oxidised, and since the yield of carbon monoxide rises as the formaldehyde yield falls it suggests that the degradation of the ethylene to carbon monoxide proceeds via formaldehyde as an intermediary.

Another interesting feature of the results is the sudden increase in the yields of methane, ethane, and ethanol after about 80% reaction. This indicates that methyl and ethyl radicals are produced in the system and that when the oxygen concentration falls they are able to abstract a hydrogen atom to give the corresponding hydrocarbon. The increase in the yield of ethanol could be attributed to the reaction of ethyl and hydroxyl radicals.

In the oxidation of ethane the most plausible chain propagating steps are:-

$$C_2H_6 + HO_2 = C_2H_5 + H_2O_2 \quad - - - (1)$$

$$C_2H_5 + O_2 = C_2H_4 + HO_2 \quad - - - (2)$$

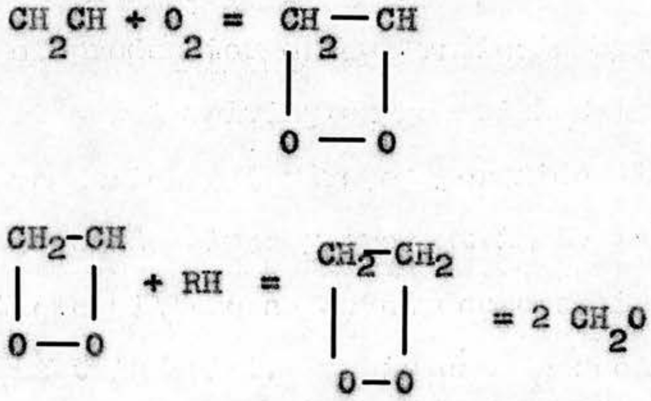
and it is likely that reaction (2) will be the source of the ethyl radicals formed in the oxidation of ethylene.

When the oxygen concentration is high the ethyl radicals produced will be oxidised back to ethylene and hydroperoxy radicals but as the oxygen is depleted the alkyl radicals will be able to abstract hydrogen to produce ethane, and at the same time the rate of production of HO_2 radicals by reaction (2) and by other reactions involving oxygen will fall. Consequently the rate of production of hydrogen peroxide will fall, and as the hydrogen peroxide already present in the system will decompose rapidly there will be a marked decrease in the yield of hydrogen peroxide at this point. This can be seen on fig.13a. It is interesting to note that the connection between the fall in oxygen concentration and the fall in the yield of hydrogen peroxide is shown up by the fact that the methane, ethane and ethanol yields increase at the point where the hydrogen peroxide yield decreases. (figs.13a and 13b).

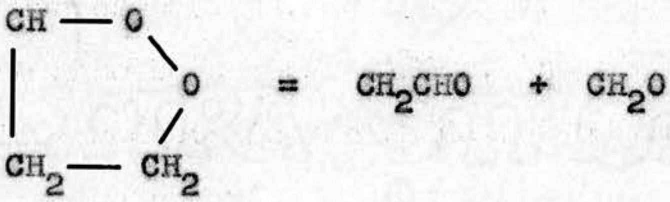
It can also be seen from figs.13a and 13b that the main degradation products in the oxidation of ethylene are carbon monoxide and water, with some carbon dioxide. This, and the fact that formaldehyde is the major intermediate product, is in agreement with other ethylene oxidation work.[97]

There was always a slight pressure decrease at the beginning of the reaction (see fig.17). The products whose formation would cause a pressure decrease are hydrogen-peroxide and ethylene oxide, but since in the initial stages their yields are too low to account for the observed decrease some other explanation has to be sought. Formaldehyde was the major product at this stage and the pressure decrease may be due to either polymerisation of the formaldehyde or else to the formation of a cyclic peroxy compound prior to the formaldehyde formation e.g.

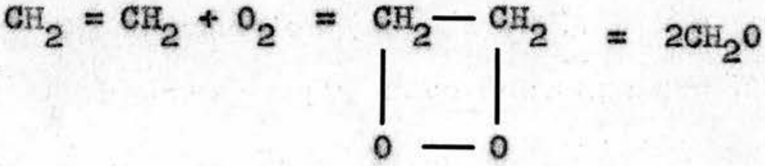
$$C_2H_4 + X = CH_2CH + HX$$



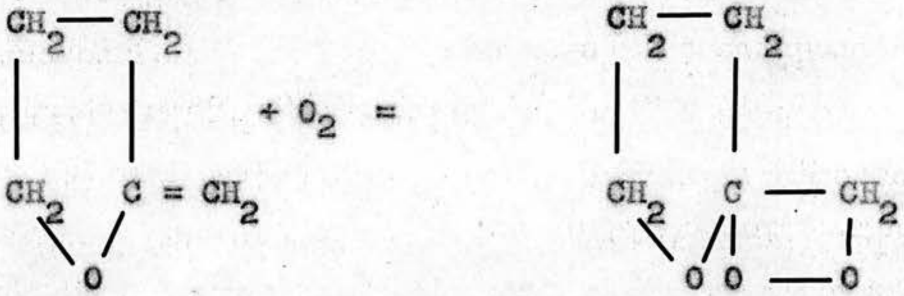
A similar mechanism to the above was proposed by McEwan and Tipper[99] for the slow combustion of cyclopropane, but in this case it was suggested that the cyclic peroxy radical formed split before hydrogen abstraction could occur.



According to these above schemes the formaldehyde is formed by means of a free radical mechanism but it is also possible that it is formed via a molecular addition reaction viz.



The view that oxygen could add across an ethylenic double bond was favoured by Dobrinskaya and Newmann[98]. They explained their observations on the oxidation of butene-2 in terms of two alternative modes of oxygen attack, one leading to hydroperoxide formation and the other to cyclic peroxide formation by addition across the double bond. However this was not the first time that this mechanism had been proposed for the formation of cyclic peroxides as Ubbelohde[7], in 1935, had suggested that they could be formed by the peroxidation of unsaturated oxygen ring compounds.



Several other workers have observed an initial pressure decrease in olefin oxidation but this has generally been attributed to either (1) radical polymerisation (2) hydroperoxide formation, or (3) the endothermicity of the initial step.

(1) Radical Polymerisation. The discovery by Burgoyne and Cox[100] that hydrocarbons with more than three carbon atoms were formed in the oxidation of ethylene at 515°C provided evidence that radical polymerisation could occur in oxidation systems. This would naturally cause a pressure decrease in the system, and it was suggested by Skirrow[130] and by Blundell and Skirrow[101] that this could partially account for the pressure decrease observed in the oxidation of hexene-1 at 263°C and of butene-2 between 290-395°C respectively. However as they did not analyse for the presence of higher hydrocarbons it is not possible to say definitely whether or not radical polymerisation does occur at these lower temperatures.

It is unlikely that radical induced polymerisation occurred in the present work on ethylene oxidation since there was no indication from the chromatograms that higher hydrocarbons were formed.

(2) Hydroperoxide Formation. The stoichimetric equation for the formation of hydroperoxides $RH+O_2 = ROOH$ requires a decrease in the number of molecules in the system which in turn requires a decrease of pressure in the system. This, plus the fact that Blundell and Skirrow[101] have shown for the oxidation of butene-2 between 290-395°C that the maximum in the yield of peroxide corresponds almost exactly to the minimum in the pressure-time curves, provides strong evidence that the pressure decrease in oxidation systems can be caused by the formation of hydroperoxides. Further evidence for this comes from the work of Lemay and Ouellet[102] who found that coating the reaction vessel surface with potassium chloride (known to decompose peroxides) eliminated the pressure decrease in the oxidation of ether.

Although the formation of hydroperoxides might be responsible for the pressure decrease in certain systems it is unlikely in ethylene oxidation as it is difficult to conceive of a scheme involving hydroperoxides which can explain both the pressure decrease and the formation of formaldehyde. A mechanism involving the formation of a cyclic peroxide does however fulfil both these requirements.

(3) The Endothermicity of the Initial Reaction. The initial step in hydrocarbon oxidation $RH+O_2 = R + HO_2$ is endothermic and Saloja[103] thought that the endothermicity of this step might be

such that it could cause a temperature drop in the system and hence cause a pressure drop in the system. He did in fact show for the oxidation of n-heptane/air mixtures in a flow system that in the initial stages the temperature fell by about 4-5°C, but as this effect could only be observed at the temperature at which the oxidation just commenced and not at higher temperatures, it is impropable that a decrease in pressure can be attributed to a temperature decrease in those systems maintained at temperatures well above that at which the oxidations just commence.

1.5. Effect of Temperature on Ethane and Ethylene Oxidations.

In the ethane oxidations carried out at 362°C the main initial products were ethylene and formaldehyde , and for the 1:1 ethane to oxygen mixture the ratio of the initial yield of ethylene to formaldehyde was 7.7. However the results given in table 13 for the oxidation of ethane at 318°C show that the initial ethylene to formaldehyde ratio is 0.96 and that formaldehyde is now the major initial product. This suggests that in the early stages of ethane oxidation there are two main competing reactions of different activation energies.

Experiments carried out at 318°C with mixtures of differing oxygen content (tables 13 and 14) show, as in the case of the oxidations at 362°C, that the yields of the initial products do not vary appreciably with oxygen content. This indicates that oxygen is not kinetically important in their formation and that they are formed via the ethyl peroxy radical or a transition complex of the formula C_2H_5OO. Thus the ratios of the initial products will depend upon the subsequent reactions of this radical or complex, and as ethylene and formaldehyde are the major initial products the main competing reactions in the early stages are likely to be:-

$$C_2H_5 + O_2 = C_2H_5OO \begin{array}{l} \nearrow C_2H_4 + HO_2 - - - - (a) \\ \searrow CH_2O + CH_3O - - - -(b) \end{array}$$

Oxidations were carried out at 340°C and 386°C with 1:1 ethane to oxygen mixtures in order to determine the initial ethylene to formaldehyde ratios at these temperatures. The yields of the initial products in these oxidations are given in tables 15 and 16.

From the variation in the initial ethylene to formaldehyde ratio with temperature (table 17) on activation energy plot was drawn up (fig.16) and the difference in activation energies of reactions (a) and (b) was calculated to be 21 ± 5 k.cal. The A factor ratio being approx. 10^8.

The continuous line on fig.16 represents the value for the initial ethylene to formaldehyde ratio when no acetaldehyde was added to the reactant mixture, and the dotted line represents the value when acetaldehyde was added.

The initial ethylene to formaldehyde ratio at 318°C when acetaldehyde was absent was calculated by adding to the value for the ratio when acetaldehyde was present the difference between the "acetaldehyde" and "non-acetaldehyde" values at 362°C.

The products from the oxidation of ethylene at 318°C were examined and the results are given in table 18 and on figs.13a. and 13b. The fall in pressure at the beginning of the reaction was about five times that observed at 362°C and the percentage conversion of ethylene to formaldehyde was about 65% as compared to about 90% at 362°C.

Since the formation of ethylene oxide and of the proposed intermediate cyclic peroxide both cause a decrease in the number of molecules in the system and hence a decrease in pressure, the increase in the pressure fall may be caused by increased yields of these compounds at the lower temperature. Table 9 shows that the ethylene oxide yield is almost doubled at the lower temperature but as this can only account for part of the decrease in pressure it suggests that the yield of the intermediate cyclic peroxide may also be increased at the lower temperature. The increase in the amount of peroxide present is probably due to its increased stability at the lower temperature.

The general features of ethylene oxidation at 318°C are the same as at 362°C, formaldehyde being the main intermediate product and carbon monoxide and water the main degradation products.

1.6. Hydrogen Peroxide in Ethane and Ethylene Oxidations.

Separate experiments were carried out to determine the hydrogen peroxide yields in 1:1 mixtures of ethane and ethylene to oxygen at 362°C. (tables 19 and 20 and figs.8b and 13a). With ethane the initial yield was about 30% that of water and with ethylene about 50%. In view of the rapid heterogeneous decomposition of hydrogen peroxide the percentage of hydrogen peroxide initially formed will be much higher than that actually detected, and as relatively large amounts are in fact detected it suggests that hydrogen peroxide is one of the major initial products in both ethane and ethylene oxidations. In the case of ethane oxidation this is in agreement with the theory that the chain propagating reactions are :-

$$C_2H_6 + HO_2 = C_2H_5 + H_2O_2$$

$$C_2H_5 + O_2 = C_2H_4 + HO_2$$

$$C_2H_5 + O_2 = CH_2O + CH_3O \xrightarrow{O_2} CH_2O + HO_2$$

With both the ethane and ethylene oxidation systems the yields of hydrogen peroxide passed through maxima after about 60% reaction, presumably owing to the depletion of the reactants and to the decomposition of the hydrogen peroxide itself.

The mechanism of hydrogen peroxide decomposition has been the subject of extensive study[107] and it has been shown that at temperatures below 420°C the decomposition is almost entirely heterogeneous whereas above 420°C homogeneous decomposition becomes significant. Thus at 362°C the hydrogen peroxide will decompose heterogeneously to give water and oxygen.

$$H_2O_2 + \text{wall} = H_2O + \tfrac{1}{2} O_2$$

2. KINETIC RESULTS

Pressure-time curves for various ethane-oxygen and ethylene-oxygen mixtures at differing temperatures are shown on fig.17. They have a typical sigmoid form, with a period of slow reaction followed by a faster reaction increasing to a maximum rate and then falling off to zero.

The most notable feature is the small total pressure increase in the oxidation of ethylene as compared to that in the oxidation of ethane. The major products at the end of the reaction, both with ethane and ethylene, were carbon monoxide and water, and as the formation of one molecule of carbon monoxide involves the consumption of half a molecule of ethane and half a molecule of oxygen without any resultant pressure change, the differences in the final pressures must be due to the amounts of water formed. With a 1:1 mixture of ethane to oxygen at an initial pressure of 444 mms.Hg. at a temperature of 362°C the final water pressure was approximately 220 mms.Hg. whereas in the corresponding mixture for ethylene the pressure was approximately 150 mms. This difference of approximately 70 mms. can account for the difference in total pressure increase between the ethane and ethylene oxidations.

Fig.17 shows that the maximum rate of reaction for ethane oxidation increases with temperature and that the initial pressure decrease observed in ethylene oxidation is much larger at 318°C than at 362°C.

As acetaldehyde was used in the early stages of the work to initiate the reaction between ethane and oxygen it was of interest to ascertain what effect its addition had on the kinetics of the reaction. The effect of adding various amounts of acetaldehyde to a 1:1 mixture of ethane to oxygen at 362°C is shown on fig.18. It can be seen that increasing the amount of acetaldehyde reduces the induction period but has little effect on the maximum rate of reaction. The addition of intermediates to oxidation systems can cause a "negative induction period", where the reaction starts off at a rate greater than the normal maximum rate of reaction and then slows down to give the normal maximum rate of reaction when no additive was introduced, but in this case the addition of up to 2% acetaldehyde to the reactant mixture did not produce this effect.

The three parameters commonly used in the interpretation of the kinetics of hydrocarbon oxidation are the induction period, the maximum rate of reaction, and the acceleration constant. The acceleration constant was taken to be the most reliable of these parameters since the induction period is affected by factors such as the reaction vessel surface and reactant concentrations, and since it is uncertain whether the maximum in the reaction rate is caused by destruction of the branching intermediate or by depletion of the reactants.

Semenov showed that the pressure increase in the early stages of hydrocarbon oxidation was given by the expression :-

$\Delta p = Ne^{\phi t}$ where $\phi =$ the acceleration constant.

Thus the acceleration constant can be obtained by plotting either $\ln \Delta p$. vs. t or $d\Delta p./dt.$ vs. Δp. The latter method is preferable as it eliminates any errors in Δp, but it also has the advantage that the acceleration constant can be obtained at any stage in the reaction from the slope of the line at that point.

A typical plot of rate vs. Δp is shown on fig. 19. It consists of four sections - an induction period in which the rate and acceleration of the reaction increases slowly, followed by a straight portion in which the rate accelerates exponentially, and then the acceleration falls off until at the maximum rate of reaction it is zero, and this is finally followed by a period in which the reaction decelerates. The rate of this deceleration varies with the oxygen content of the mixture, the less oxygen initially present the faster the rate of deceleration. The acceleration constant for the reaction was taken as the slope of the straight portion of the plot.

With the oxidations initiated by acetaldehyde the rate of reaction in the induction period was greater than when no acetaldehyde was added. However this is not the case for the later stages, and it can be seen from fig. 20 that with the mixture having an initial ethane pressure of 32.6 cms.Hg the value of the acceleration constant for when no acetaldehyde was added was, within the experimental error, the same as the value for when acetaldehyde was added. This shows that the addition of acetaldehyde did not alter the acceleration constant.

The variation of the acceleration constant with initial oxygen concentration is shown on fig. 23 and in table 21. The acceleration constant is dependent on the oxygen concentration for mixtures weak in oxygen but as has been observed for other systems[62,108] it is almost independent of oxygen in oxygen rich mixtures.

The effect of initial hydrocarbon concentration on the acceleration constant is shown on fig.20 and in table 21. In an investigation of the kinetics of ethane oxidation in a spherical reaction vessel at 318°C Knox[79] observed that the acceleration constant increased linearly with the initial ethane pressure. However it can be seen from fig. 20 that this relationship does not hold in a cylindrical reaction vessel at 362°C and that the dependence of the acceleration constant on initial ethane pressure is greater than unity. This suggests that the reaction is catalysed by some product from the oxidation. This product may be ethylene and it is perhaps significant that the rate of production of ethylene is much greater at 362°C than at 318°C, and that the substitution of ethylene for ethane in a 1:1 mixture at 362°C markedly increases the acceleration constant. (Table 24, fig. 23.)

Table 23 and fig. 22 show that the addition of "inert" gas viz. carbon dioxide, increases the acceleration constant of the reaction suggesting that the reaction chains are terminated on the walls of the reaction vessel and that the rate of termination is determined by the rate of diffusion of active particles to the walls. Thus the differences observed between this work and that of Knox could be due to the difference in reaction vessels and the consequent difference in wall effects.

Other workers have examined the variation of the acceleration constant with initial hydrocarbon pressure. Wright[57] studying the oxidation of the three isomeric xylenes at about 420°C observed that the acceleration constant increased linearly with the xylene pressure. This linear relationship was also found by Seakins[108] for the oxidation of propane at 290°C, but Bardwell[109] in the oxidation of butanone at 250°C showed that the increase in the acceleration constant with butanone pressure was of a higher order. The results of McEwan and Tipper[62] for the oxidation of cyclopropane between 380-430°C show that the effect of the cyclopropane pressure on the acceleration constant depends largely on the initial oxygen concentration. They found that the acceleration constant was dependent on oxygen concentration for oxygen weak mixtures but when the oxygen concentration was greater than a certain "critical" value it became independent of oxygen. Furthermore when the oxygen pressure in the mixture was below this "critical" value the acceleration constant increased linearly with the cyclopropane pressure, but when the oxygen pressure was above this "critical" value the acceleration constant increased with the square of the cyclopropane pressure. However this does not mean that a linear relationship only exists between the acceleration constant and the hydrocarbon pressure when the initial oxygen concentration is below the "critical" value as in this present investigation the oxygen pressure was well below that at which the acceleration constant became independent of oxygen.

The variation of the acceleration constant with initial ethane pressure was determined in order to confirm whether or not the kinetics of the oxidation were similar to those in a spherical reaction vessel at 318°C and to confirm whether or not the assumptions made for the latter case [Knox [79]] held for the conditions of this investigation. However the results obtained show that the kinetics are more complicated in a cylindrical vessel at 362°C, and there appears to be no simple relationship between the acceleration constant and hydrocarbon pressure under these conditions.

From an investigation of the high temperature oxidation of ethylene Harding and Norrish[106] suggested that ethylene oxide may be an agent for degenerate branching and as ethylene plays an important pole in the oxidation of ethane the effect of ethylene oxide on ethane oxidation was examined. The substitution of ethylene oxide for ethane (table 25, fig. 24) has no effect on the acceleration constant indicating that either the ethylene oxide oxidises at the same rate as ethane or else has an "inert" gas effect which balances the fall in the acceleration constant as the ethane is replaced. When ethylene oxide is added rather than substituted for the ethane in the mixture the acceleration constant increases linearly with the ethylene oxide pressure, (table 25, fig. 24). This suggests that either the oxidation of the ethylene oxide is superimposed on the oxidation of the ethane or else the ethylene oxide is acting as an "inert" gas. These results, plus the fact that the addition of the ethylene oxide did not reduce the induction period, show that ethylene oxide is not an agent of degenerate branching in the oxidation of ethylene at 362°C.

TABLE 3 (fig. 8)

atio C_2H_6: O_2 = 1:1   Pressure = 444 mms. Hg.   Temp. = 362°C
dded CH_3CHO = 0.5%

Pressure in Reaction Vessel (mms. Hg.)

un o.	Δp cms. Hg.	O_2	C_2H_6	CH_4	CO	CO_2	C_2H_4	CH_3 CHO	C_2 H_4O	CH_3OH	C_2H_5 OH	H_2O	HCHO
1	9.81	-	-	-	-	-	-	-	-	-	-	-	1.24
2	3.73	-	-	-	-	-	-	-	-	-	-	-	8.60
3	2.47	-	-	-	-	-	-	-	-	-	-	-	8.29
4	5.67	-	-	-	-	-	-	-	-	-	-	-	8.06
5	9.09	-	-	-	-	-	-	-	-	-	-	-	3.44
6	0.79	-	-	-	-	-	-	-	-	-	-	-	2.71
7	1.17	-	-	-	-	-	-	-	-	-	-	-	3.59
8	1.42	170.0	176.0	0.00	14.6	-	12.3	-	-	3.94	-	-	4.78
9	8.00	15.0	124.1	7.37	132.8	20.1	11.1	-	-	26.4	1.20	-	4.62
10	6.73	29.2	130.3	3.20	118.5	16.5	21.1	-	-	30.1	0.76	-	-
11	4.64	97.8	143.0	0.77	70.3	10.7	24.2	-	-	22.0	0.57	-	8.45
12	4.76	96.2	137.0	0.98	70.0	11.3	25.5	-	-	-	0.79	-	8.37
13	3.07	165.6	178.0	0.00	36.2	7.40	25.1	-	-	12.1	-	78.7	-
14	3.72	124.6	148.4	0.00	52.2	9.00	24.6	-	-	16.3	0.54	88.3	-
15	9.63	12.7	126.0	14.7	154.7	24.9	9.6	-	-	22.8	3.21	196.3	2.58
16	9.07	12.0	129.0	11.6	160.0	26.7	13.2	-	-	-	3.53	193.3	4.02
17	6.36	59.9	144.8	1.7	90.3	11.9	20.6	-	-	29.1	1.10	141.6	7.59
18	2.51	185.7	194.0	0.00	28.6	5.52	21.9	-	-	9.96	0.29	43.1	-
19	7.31	21.0	124.9	6.02	123.6	16.9	19.7	-	-	29.7	1.04	157.0	6.83
20	0.94	186.8	185.8	0.00	10.8	3.40	12.1	-	-	3.39	0.00	28.9	-
21	0.70	200.7	200.0	0.00	9.19	2.70	10.1	-	-	2.90	0.00	22.6	-
22	0.41	209.0	204.4	0.00	5.65	1.50	6.19	-	-	2.08	0.00	11.8	-
23	0.22	212.0	210.9	0.00	5.71	1.85	6.00	-	-	2.22	0.00	9.90	-
24	0.11	213.7	211.0	0.00	2.10	1.00	3.79	-	-	1.11	0.00	6.14	-
25	0.20	212.2	207.3	0.00	4.01	1.23	5.56	-	-	1.67	0.00	11.3	-
26	0.56	202.9	201.1	0.00	7.03	2.44	8.73	-	-	2.41	0.00	16.3	-
27	1.05	192.9	196.4	0.00	14.2	3.30	12.4	-	-	4.99	0.00	32.0	-
28	0.01	215.0	210.0	0.00	2.56	2.23	3.68	-	-	0.70	0.00	5.56	-
29	1.87	172.0	174.0	0.00	21.9	4.74	19.5	-	-	6.90	0.18	45.4	-
30	8.56	15.9	113.6	12.1	149.6	20.8	13.6	-	-	26.2	2.60	149.0	-

TABLE 4 (fig. 8)

Ratio C_2H_6:O_2 = 1:1   Pressure = 444 mms. Hg.   Temp. = 362°C

Pressure in Reaction Vessel (mms. Hg.)

un o.	Δp cms. Hg.	O_2	C_2H_6	CH_4	CO	CO_2	C_2H_4	CH_3 CHO	C_2H_4 O	CH_3 OH	C_2H_5 OH	H_2O	HCHO
1	1.87	177.5	168.7	0.00	16.5	3.83	28.2	-	-	5.34	-	43.2	-
2	5.50	82.0	134.5	1.75	94.0	11.1	24.4	-	-	25.8	0.82	134.0	-
3	8.34	16.2	113.2	9.30	125.1	19.4	14.8	-	-	26.3	2.30	161.5	5.94
4	0.55	212.0	202.0	0.00	3.06	0.63	12.5	-	1.16	0.40	0.00	14.2	1.89
5	0.46	203.9	197.0	0.00	2.30	0.31	9.44	-	0.30	0.66	0.00	9.40	1.26
6	0.67	207.0	201.0	0.00	3.94	0.25	11.5	-	1.00	1.37	0.00	16.7	1.77
7	0.74	208.0	198.0	0.00	4.63	0.42	13.3	-	1.22	1.36	0.00	18.5	1.87
8	0.36	214.8	208.0	0.00	1.32	0.10	7.64	-	0.35	0.23	0.00	7.90	1.36
9	0.92	199.3	195.5	0.00	7.10	0.67	15.3	-	1.15	2.15	0.00	24.1	3.29
0	0.01	219.8	219.3	0.00	0.00	0.00	2.40	-	-	0.00	0.00	2.20	0.35
1	0.28	217.0	208.0	0.00	1.10	0.30	7.20	-	0.28	0.37	0.00	7.00	1.19
2	1.29	196.0	191.1	0.00	11.2	1.20	18.1	-	1.90	3.65	0.00	33.4	3.87
3	2.14	174.7	178.0	0.00	25.1	3.27	22.5	-	-	7.48	0.35	60.3	5.97
4	3.04	145.0	157.0	0.04	39.0	5.60	26.7	-	-	12.9	0.50	78.3	7.08
5	4.56	105.5	141.5	0.80	67.0	9.40	26.7	-	-	21.2	0.70	126.0	7.33
6	7.22	18.3	109.1	5.76	120.0	16.3	24.0	-	-	29.2	1.10	180.0	6.55
7	9.47	10.6	101.0	13.4	136.2	23.3	8.03	-	-	22.4	3.60	211.2	4.42
8	9.09	13.5	119.3	10.9	137.8	20.1	12.0	-	-	25.9	3.10	214.0	3.61
9	0.20	218.0	214.6	0.00	1.00	0.25	5.03	-	0.08	0.13	0.00	-	0.96
0	4.33	-	-	-	-	-	-	0.26	4.95	-	-	-	-
1	7.89	-	-	-	-	-	-	0.25	9.09	-	-	-	-
2	0.64	-	-	-	-	-	-	0.0	0.50	-	-	-	-
3	6.39	-	-	-	-	-	-	0.23	8.16	-	-	-	-
4	5.47	-	-	-	-	-	-	0.24	7.00	-	-	-	-
5	11.00	-	-	-	-	-	-	0.22	9.90	-	-	-	-
6	2.00	-	-	-	-	-	-	0.10	3.30	-	-	-	-
7	3.45	-	-	-	-	-	-	0.21	5.94	-	-	-	-
8	11.00	-	-	-	-	-	-	0.24	9.70	-	-	-	-

TABLE 7 (figs. 10a and 10b)

Ratio $C_2H_6:O_2$ = 3:1 Pressure = 296 mms. Hg. Temp. = 362°C

Pressure in Reaction Vessel (mms. Hg.)

Run No.	Δp cms. Hg.	O_2	C_2H_6	CH_4	CO	CO_2	C_2H_4	CH_3CHO	C_2H_4O	CH_3OH	C_2H_5OH	H_2O	HCHO
1	5.38	2.48	159.4	5.88	38.3	4.52	19.4	0.12	6.80	5.81	1.37	84.9	1.59
2	1.31	55.7	191.2	0.28	5.00	1.30	20.6	0.02	2.58	0.77	0.00	30.4	1.59
3	2.40	24.7	159.9	0.89	16.9	3.62	26.1	0.00	2.80	2.75	0.05	43.0	-
4	2.19	39.4	179.8	0.74	12.4	3.55	24.6	0.08	2.68	4.25	0.09	46.3	3.28
5	0.43	73.3	210.0	0.17	0.49	0.21	5.61	0.00	0.04	0.16	0.00	7.29	0.41
6	2.88	9.72	153.1	2.52	28.8	7.34	29.1	0.20	5.04	8.06	0.52	77.3	4.89
7	1.82	35.5	165.3	0.72	12.1	2.62	23.1	0.07	2.50	3.11	0.00	44.2	4.69
8	3.19	5.79	162.9	3.32	33.9	4.45	24.1	0.12	5.01	7.60	0.83	79.8	3.34
9	3.46	3.24	165.4	5.85	40.2	4.71	17.6	0.05	5.22	6.88	1.08	79.1	1.86
10	2.86	9.71	164.5	1.96	31.2	4.35	29.5	0.13	3.86	9.06	0.31	76.3	4.89
11	2.20	-	-	-	-	-	-	-	-	-	-	-	4.86
12	0.24	80.3	215.5	0.00	0.00	0.17	1.48	0.00	0.00	0.00	0.00	0.98	0.02
13	0.63	68.9	206.7	0.02	1.75	0.54	9.69	0.00	0.44	0.43	0.00	13.0	1.10
14	0.93	65.7	200.0	0.21	2.08	0.38	10.7	-	-	-	-	14.9	0.96
15	2.65	11.1	166.4	2.20	28.3	3.94	26.8	0.11	3.55	9.47	0.27	74.0	4.94
16	1.55	52.2	190.5	0.34	7.52	2.16	16.7	0.00	0.80	2.61	0.00	37.0	-
17	2.44	-	-	-	-	-	-	-	-	-	-	-	5.62
18	2.43	-	-	-	-	-	-	-	-	-	-	-	5.48
19	2.91	-	-	-	-	-	-	-	-	-	-	-	4.39
20	2.04	-	-	-	-	-	-	-	-	-	-	-	3.95
21	1.07	62.0	201.4	0.09	3.16	1.18	13.0	0.00	0.48	-	-	19.6	1.94
22	0.87	-	-	-	-	-	-	-	0.64	-	-	-	-
23	1.27	-	-	-	-	-	-	-	1.34	-	-	-	-
24	0.71	-	-	-	-	-	-	-	0.71	-	-	-	-
25	0.44	-	-	-	-	-	-	-	0.27	-	-	-	-
26	1.18	-	-	-	-	-	-	-	1.20	-	-	-	-
27	2.37	-	-	-	-	-	-	-	-	8.82	-	61.4	-
28	2.54	-	-	-	-	-	-	-	-	9.34	-	63.1	-

TABLE 8 (figs. 10a and 10b)

Ratio $C_2H_6:O_2$ = 1.2 Pressure = 444 mms. Hg. Temp. = 362°C

Pressure in Reaction Vessel (mms. Hg.)

	Δp cms. Hg.	O_2	C_2H_6	CH_4	CO	CO_2	C_2H_4	CH_3 CHO	C_2H_4 O	CH_3 OH	C_2H_5 OH	H_2O	HCHO
1	10.1	42.7	32.3	2.90	150.4	39.8	7.26	0.18	7.51	15.0	0.0	244.2	-
2	1.84	263.8	116.8	0.00	15.6	3.86	18.3	0.08	2.20	2.90	0.08	49.2	3.15
3	3.66	197.7	88.1	0.00	54.9	19.1	19.1	0.14	4.20	9.25	0.32	105.6	5.48
4	2.74	177.6	93.3	0.00	27.1	7.12	20.5	0.21	3.96	5.24	0.21	77.6	4.85
5	0.90	285.1	134.2	0.00	4.16	1.65	11.80	0.00	0.47	-	-	17.3	1.63
6	1.33	268.3	122.6	0.00	8.18	2.66	15.4	0.00	1.52	-	-	33.1	3.13
7	5.45	164.7	69.2	0.00	77.0	13.6	19.1	0.16	6.14	9.68	0.18	143.2	4.97
8	6.38	129.9	61.2	0.58	100.7	19.2	16.5	0.17	6.34	14.6	0.31	160.0	4.97
9	7.31	112.8	55.2	1.21	113.3	22.6	14.7	0.19	7.05	14.5	0.26	179.8	5.28
0	8.18	80.1	45.6	1.29	118.0	27.4	11.1	0.18	6.82	14.2	0.20	208.0	4.33
1	9.09	55.2	40.7	1.99	147.1	39.5	9.05	0.12	7.08	15.5	0.21	209.8	4.58
2	0.59	282.3	141.3	0.00	2.82	1.75	9.63	0.00	0.55	0.22	0.00	29.2	1.61
3	4.37	176.0	77.3	0.00	60.9	12.1	19.2	0.25	5.10	11.7	0.29	120.0	5.49
4	0.27	284.7	138.0	0.00	0.93	1.27	6.75	0.00	0.22	0.00	0.00	-	0.85
5	0.42	286.7	134.5	0.00	1.78	1.32	8.73	0.00	0.32	0.07	0.00	15.5	1.35
6	0.71	275.8	129.2	0.00	5.73	1.05	13.2	0.01	0.94	0.63	0.00	20.9	2.44
7	0.07	295.8	145.5	0.00	0.00	0.00	3.50	0.00	0.00	0.00	0.00	3.40	0.24
8	0.18	286.5	141.9	0.00	0.21	0.00	5.83	0.00	0.00	0.17	0.00	5.40	0.72
9	0.14	293.9	145.6	0.00	0.00	0.00	3.91	0.00	0.00	0.00	0.00	-	0.41
	0.01	-	145.1	-	-	0.00	4.64	-	-	-	-	-	-

TABLE 9 (fig. 15[*])

Initial Yield of Products from the Oxidation of Ethane and Ethylene

	Mixture Composition - Oxygen:Ethane:Ethylene in mm. Hg.				
	74:222:0	222:222:0	296:148:0	296:130:19	222:0:222
emperature °C	362	362	362	362	362
ressure Rise (cm. Hg.)	1.00	1.00	1.00	1.00	-
xygen Consumed (cm.Hg.)	1.3	2.0	2.0	3.0	1.6
thane Consumed "	2.3	3.2	3.0	2.5	-
thylene Formed "	1.5	2.8	2.6	-	-
thylene Consumed "	-	-	-	-	-
rmaldehyde "	0.10	0.36	0.28	0.73	1.8
ater "	2.1	2.6	2.4	3.6	0.50
rbon Monoxide "	0.25	0.30	0.15	1.0	0.45
rbon Dioxide "	0.05	0.05	0.20	0.26	0.01
hylene Oxide "	0.06	0.14	0.10	0.11	0.06
thanol "	0.10	0.12	0.04	0.12	0.00
hanol "	0.00	0.00	0.00	0.00	0.00
etaldehyde "	0.00	0.00	0.00	0.01	0.00
thane "	0.02	0.00	0.00	0.00	0.00

Plots have not been drawn up for those products whose initial yields are low e.g. CO_2, C_2H_4O, CH_3OH, C_2H_5OH, CH_3CHO, CH_4

TABLE 9 (cont.)

Initial Yield of Products from the Oxidation of Ethane and Ethylene

Mixture Composition - Oxygen:Ethane:Ethylene in mm. Hg.					
222:0:111	222:222:0	74:222:0	221:0:221	222:222:0	222:222:0
362	318	318	318	340	386
-	1.00	1.00	-	1.00	1.00
1.6	3.0	2.9	1.3	2.9	2.4
-	1.5	2.1	-	2.5	2.4
-	1.2	1.1	-	2.0	2.8
0.40	-	-	2.0	-	-
1.9	1.3	1.4	2.5	0.60	0.26
0.50	2.2	1.7	0.60	3.9	2.7
0.55	0.27	0.40	0.60	0.21	0.20
0.00	0.22	0.00	0.02	0.15	0.00
0.06	0.00	0.00	0.28	0.04	0.00
0.01	0.17	0.24	0.02	0.18	0.04
0.00	0.01	0.00	0.00	0.00	0.00
0.00	0.10	0.06	0.02	0.00	0.00
0.00	0.06	0.00	0.00	0.00	0.00

TABLE 10 (figs. 12a and 12b)

Ratio C_2H_4: C_2H_6:O_2 = 1:13.6:14.6   Pressure = 444 mms. Hg.

Temp. = 362°C

Pressure in Reaction Vessel (mms. Hg.)

Δp cms. Hg.	O_2	C_2H_6	CH_4	CO	CO_2	C_2H_4	CH_3CHO	C_2H_4O	CH_3OH	C_2H_5OH	H_2O	HCHO
1.87	168.1	155.2	0.00	26.0	4.86	35.2	0.13	2.15	4.45	0.00	56.0	7.26
9.42	9.92	106.2	14.9	145.6	24.4	7.11	0.26	4.22	15.3	2.09	206.1	2.66
7.87	13.6	102.6	9.19	137.1	23.8	16.7	0.27	4.80	18.6	2.18	154.5	-
2.77	134.0	141.5	0.61	44.0	7.79	32.6	0.24	2.77	10.3	0.70	83.2	7.51
3.68	117.0	136.9	0.36	63.7	9.72	35.5	0.25	3.48	13.6	0.33	105.8	8.80
4.57	75.9	123.1	0.47	85.9	13.3	31.3	0.33	4.83	-	-	-	9.18
5.40	52.8	114.4	1.74	97.9	15.3	29.1	0.24	3.47	20.8	0.56	146.1	7.91
1.55	185.6	163.1	0.00	14.7	4.05	35.2	0.00	1.05	2.75	0.06	45.7	5.93
6.60	19.4	103.7	3.73	127.4	19.9	28.0	0.25	5.33	22.8	0.89	168.6	7.57
0.76	200.0	173.7	0.00	9.24	2.28	31.8	0.00	0.95	1.52	0.00	27.4	3.21
0.55	206.1	178.6	0.00	6.26	1.63	33.4	0.00	0.62	1.39	0.00	22.4	3.92
0.36	211.3	181.6	0.00	4.28	1.87	30.0	0.00	0.96	0.45	0.00	14.2	2.88
0.16	218.6	185.7	0.00	0.91	1.67	30.0	0.00	0.44	0.11	0.00	7.37	1.56
0.06	221.9	190.5	0.00	0.38	1.22	28.8	0.00	0.22	0.00	0.00	4.52	0.82

TABLE 11 (figs. 13a and 13b)

Ratio C_2H_4:O_2 = 1:1   Pressure = 441 mms. Hg.   Temp. = 362°C

Pressure in Reaction Vessel (mms. Hg.)

Δp cms. Hg.	O_2	C_2H_4	CH_4	CO	CO_2	C_2H_6	CH_3 CHO	C_2H_4 O	CH_3 OH	C_2H_5 OH	H_2O	HCHO
1.95	35.0	122.5	0.79	135.4	15.2	0.00	0.66	-	7.37	0.48	106.6	14.9
2.78	18.9	93.4	2.76	150.0	21.3	4.77	0.42	11.7	8.00	5.40	124.1	7.36
0.94	86.5	141.1	0.36	86.4	10.4	0.00	0.72	8.72	4.63	0.21	80.5	17.8
0.54	126.3	163.0	0.00	58.5	5.60	0.00	0.51	7.25	3.33	0.10	56.3	17.3
0.18	155.2	177.6	0.00	32.2	2.62	0.00	0.20	6.70	-	-	35.5	17.7
4.24	7.95	42.5	12.3	184.4	33.3	22.9	0.62	10.9	4.76	3.96	147.1	2.35
-0.06	219.7	218.8	0.00	1.73	0.00	0.00	0.00	0.35	0.00	0.00	2.40	8.13
-0.11	212.1	193.6	0.00	3.68	0.00	0.00	0.00	0.46	0.00	0.00	3.30	9.23
-0.10	189.7	197.1	0.00	14.0	0.78	0.00	0.07	1.54	0.23	0.00	13.4	15.0
-0.11	179.5	191.6	0.00	21.6	0.00	0.00	0.00	1.75	0.46	0.00	20.4	15.6
3.33	12.9	72.7	7.12	173.1	24.8	11.6	0.66	11.9	6.64	5.10	132.4	3.79
2.60	-	-	-	-	-	-	-	-	7.42	4.62	120.0	-
0.00	219.2	-	0.00	0.54	-	-	0.15	0.16	0.00	0.00	0.74	4.11

TABLE 12 (figs. 13a and 13b)

Ratio $C_2H_4:O_2$ = 1.2   Pressure = 335 mms. Hg.   Temp. = 362°C

Pressure in Reaction Vessel (mms. Hg.)

Run No.	Δp cms. Hg.	O_2	C_2H_4	CH_4	CO	CO_2	C_2H_6	CH_3CHO	C_2H_4O	CH_3OH	C_2H_5OH	H_2O	HCHO
1	0.06	213.3	110.0	0.00	2.85	0.00	0.00	0.00	0.43	0.00	0.00	3.20	6.24
2	0.10	210.7	110.6	0.00	2.79	0.00	0.00	0.00	0.36	0.00	0.00	2.10	6.41
3	0.00	187.8	93.4	0.00	19.0	0.50	0.00	0.00	1.63	0.34	0.00	18.7	7.63
4	0.16	180.6	87.8	0.00	24.9	1.16	0.00	0.07	2.42	0.84	0.00	22.6	7.46
5	0.29	167.4	82.5	0.00	38.4	2.54	0.00	0.21	3.20	1.02	0.00	34.7	9.42
6												0.50	1.76
7												0.75	4.06
8												1.02	8.10

TABLE 13 (figs. 14a and 14b)

Ratio $C_2H_6:O_2$ = 1:1 Pressure = 444 mms. Hg. Temp. = 318°C
Added acetaldehyde = 0.1%

Pressure in Reaction Vessel (mms. Hg.)

Δp cms. Hg.	O_2	C_2H_6	CH_4	CO	CO_2	C_2H_4	CH_3CHO	C_2H_4O	CH_3OH	C_2H_5OH	H_2O	HCHO
0.35	212.0	214.0	0.00	2.25	1.41	2.79	0.20	0.00	0.55	0.00	7.20	5.09
1.24	195.2	204.6	0.00	12.7	2.57	4.91	0.74	0.00	7.24	0.31	29.2	8.73
2.66	154.6	181.0	0.00	37.0	5.91	7.02	0.71	0.00	18.0	1.06	60.5	8.85
6.27	39.6	133.9	1.03	110.1	18.4	8.63	0.30	1.37	37.3	1.67	168.0	6.51
0.14	220.4	221.6	0.00	0.32	0.76	1.81	0.24	0.00	0.19	0.00	3.10	0.79
0.78	198.8	207.5	0.00	7.07	1.39	4.51	0.63	0.15	2.39	0.18	17.6	7.43
1.84	172.1	199.7	0.00	26.8	4.30	6.88	0.75	0.17	10.0	0.58	44.8	8.51
0.04	217.9	220.8	0.00	0.00	0.00	0.38	0.04	0.00	0.00	0.00	2.03	0.89
4.26	94.7	152.0	0.27	71.8	10.4	8.67	0.63	0.65	29.2	1.53	118.2	9.23
7.70	10.3	114.3	3.03	129.4	23.5	5.08	0.29	1.91	38.1	1.96	200.1	3.37

terial Balance

(mm. atoms)

Run No.	C	H	O
1	444	1332	444
1	444	1323	442
2	452	1346	455
3	449	1333	447
4	465	1357	441
5	450	1338	448
6	443	1327	436
7	466	1378	444
8	443	1332	439
9	447	1333	441
10	444	1299	443

TABLE 14 (figs. 14a and 14b)

Ratio C_2H_6:O_2 = 3:1 Pressure = 292 mms. Hg. Temp. = 318°C

Added acetaldehyde = 0.1%

Pressure in Reaction Vessel (mms. Hg.)

Δp cms. Hg.	O_2	C_2H_6	CH_4	CO	CO_2	C_2H_4	CH_3CHO	C_2H_4O	CH_3OH	C_2H_5OH	H_2O	HCHO
2.29	7.53	177.5	0.33	32.4	3.00	8.04	0.36	0.42	18.2	0.60	51.8	7.70
2.34	4.93	177.8	0.64	36.5	3.12	7.81	0.36	0.50	18.6	0.83	-	5.81
0.16	66.5	218.4	0.00	0.89	0.38	1.90	0.10	0.00	0.60	0.00	2.52	2.19
0.52	56.6	211.3	0.00	4.75	1.15	3.97	0.21	0.00	2.61	0.03	10.2	6.29
0.84	49.5	207.4	0.00	8.86	1.44	5.72	0.29	0.00	5.44	0.19	17.2	8.65
1.57	29.2	192.6	0.05	19.5	2.10	6.74	0.39	0.02	13.3	0.58	39.7	8.39
0.04	71.9	228.0	0.00	0.05	0.00	0.39	0.02	0.00	0.15	0.00	1.21	0.36
0.09	69.5	220.2	0.00	0.33	0.00	0.88	0.05	0.00	-	0.00	1.69	1.83
1.57	29.7	192.7	0.00	20.2	1.80	6.77	0.51	0.00	14.0	0.39	38.0	8.22
1.87	-	-	-	-	-	-	-	-	17.7	0.63	43.4	-
2.08	-	-	-	-	-	-	-	-	18.9	0.83	47.5	-

terial Balance

(mm. atoms)

	C	H	O
	438	1314	146
1	435	1294	133
2	439	1299	134
3	445	1331	140
4	446	1368	150
5	446	1360	142
6	444	1335	145
7	447	1342	144
8	444	1332	143
9	447	1362	143

TABLE 15 (fig. 15)

Ratio $C_2H_6:O_2$ = 1:1   Pressure = 445 mms. Hg.   Temp. = 340°C

Pressure in Reaction Vessel (mms. Hg.)

un o.	Δp cms. Hg.	O_2	C_2H_6	CH_4	CO	CO_2	C_2H_4	CH_3CHO	C_2H_4O	CH_3OH	C_2H_5OH	H_2O	HCHO
	0.22	218.9	216.2	0.00	1.43	0.82	5.65	0.00	0.17	0.34	0.00	8.78	1.41
	0.06	216.6	213.4	0.00	0.37	0.60	3.00	0.00	0.00	0.00	0.00	3.50	0.57
	0.44	204.8	200.2	0.00	2.35	0.83	8.78	0.00	0.27	1.40	0.10	12.5	2.21
	0.56	207.6	203.8	0.00	4.66	0.63	10.7	0.19	0.58	1.36	0.00	17.3	2.73
	0.10	231.1	220.8	0.00	0.00	0.22	1.69	0.00	0.00	0.00	0.00	1.37	0.45
	0.08	221.1	217.1	0.00	0.00	0.25	1.77	0.00	0.00	0.00	0.00	4.83	0.82
	1.15	199.6	197.5	0.00	7.24	2.02	11.4	0.12	0.47	2.03	0.11	23.9	4.41
	0.10	221.7	218.1	0.00	0.00	0.21	1.85	0.00	0.00	0.00	0.00	1.95	0.73
	0.20	222.0	218.3	0.00	0.00	0.25	2.70	0.00	0.00	0.00	0.00	3.30	0.69
	0.10	222.3	218.0	0.00	0.00	0.34	1.74	0.00	0.00	0.00	0.00	1.30	0.31
	0.11	224.3	220.1	0.00	0.00	0.25	1.75	0.00	0.00	0.00	0.00	1.40	0.27
	0.06	224.3	220.1	0.00	0.00	0.36	1.44	0.00	0.00	0.00	0.00	0.80	0.22

TABLE 16 (fig. 15)

Ratio $C_2H_6:O_2$ = 1:1   Pressure = 450 mms. Hg.   Temp. = 386°C

Pressure in Reaction Vessel (mms. Hg.)

un o.	Δp cms. Hg.	O_2	C_2H_6	CH_4	CO	CO_2	C_2H_4	CH_3CHO	C_2H_4O	CH_3OH	C_2H_5OH	H_2O	HCHO
	0.37	217.2	214.3	0.00	1.01	0.00	8.60	0.00	0.02	0.21	0.00	8.60	1.06
	0.90	202.8	202.6	0.00	4.93	0.00	17.1	0.00	0.05	0.82	0.00	24.5	2.34
	0.01	226.1	225.0	0.00	0.00	0.00	0.52	0.00	0.00	0.00	0.00	0.75	0.19
	0.06	225.2	223.0	0.00	0.00	0.00	2.10	0.00	0.00	0.00	0.00	2.20	0.15
	0.15	224.5	221.6	0.00	0.00	0.00	4.48	0.00	0.00	0.00	0.00	3.75	0.32
	0.60	214.5	210.9	0.00	2.57	0.00	13.9	0.04	0.54	0.56	0.00	15.9	1.59
	0.22	220.5	216.5	0.00	0.33	0.00	5.79	0.00	0.00	0.11	0.00	6.50	0.68
	0.10	222.4	218.9	0.00	0.00	0.00	2.98	0.00	0.00	0.00	0.00	2.60	0.34
	0.04	227.3	225.1	0.00	0.00	0.00	0.97	0.00	0.00	0.00	0.00	0.78	0.06

TABLE 17 (fig. 16)

Ratio $C_2H_6:O_2$ = 1:1

Temp. °C	$\frac{1}{T^{o}A} \times 10^3$	$\frac{C_2H_4}{HCHO}$	$\log \frac{C_2H_4}{HCHO}$	Error
318(a)	1.692	0.96	$\bar{1}$.982	0.090
340	1.631	3.4	0.531 ✓	0.095
362(a)	1.574	3.5	0.544	0.044
362	1.574 ✓	7.7	0.886 ✓	0.100
386	1.517 ✓	10.8	1.033 ✓	0.064

(a) refers to added acetaldehyde

TABLE 18 (figs. 13a and 13b)

Ratio $C_2H_4:O_2$ = 1:1 Pressure = 442 mms. Hg. Temp. = 318°C

n .	Δp cms. Hg.	O_2	C_2H_4	CH_4	CO	CO_2	C_2H_6	CH_3 CHO	C_2H_4O	CH_3 OH	C_2H_5 OH	H_2O	HCHO
	0.58	109.1	157.6	0.00	81.0	8.75	0.00	0.67	14.2	5.44	0.49	67.6	21.8
	0.08	146.7	175.2	0.00	52.3	4.75	0.00	0.69	11.3	3.24	0.31	45.1	16.8
	1.30	15.9	115.3	0.00	163.8	17.2	2.20	0.55	22.9	10.8	2.63	103.5	14.4
	-0.14	214.8	216.9	0.00	2.41	0.00	0.00	0.04	0.47	0.00	0.00	2.42	7.46
	0.93	74.1	126.7	0.00	124.9	14.4	0.00	0.39	19.7	9.27	0.88	87.9	17.2
	-0.20	200.3	198.2	0.00	10.0	0.59	0.00	0.25	3.64	0.87	0.00	9.10	15.6
	-0.18	182.0	186.2	0.00	29.8	1.87	0.00	0.52	6.87	1.00	0.05	22.3	20.1

aterial Balance

Run No.	C	H	O
1	442	484	442
1	463	894	427
2	452	887	433
3	493	862	484
4	445	889	442
5	461	868	427
6	428	861	441
7	430	863	448

TABLE 19 (fig. 8b)

Ratio $C_2H_6:O_2$ = 1:1 Pressure = 442 mms. Hg. Temp. = 362°C

Run No.	Δp cms. Hg.	H_2O_2 mms. Hg.	H_2O mms. Hg.
1	2.62	14.3	69.0
2	0.80	6.00	21.0
3	3.86	16.1	102.0
4	0.40	2.54	10.0
5	0.20	2.34	5.0
6	4.78	21.3	125.0
7	0.19	0.98	4.5
8	9.14	10.9	211.0
9	5.84	23.8	149.0
10	6.82	17.2	172.0
11	5.86	23.4	150.0
12	6.45	20.1	164.0
13	6.85	18.1	193.0

N.B. The values quoted for water in the above table were taken from the plot of water pressure vs. Δp. (fig. 10a).

TABLE 20 (fig. 13a)

Ratio $C_2H_4:O_2$ = 1:1   Pressure = 442 mms. Hg.   Temp. = 362°C

Run No.	Δp cms. Hg.	H_2O_2 mms. Hg.	H_2O mms. Hg.
1	1.96	31.1	109.0
2	2.74	21.2	115.0
3	1.15	25.6	85.0
4	0.60	18.8	63.0
5	-0.10	2.00	8.5
6	3.54	8.14	136.0
7	1.60	29.6	101.0
8	2.07	31.2	112.0
9	0.23	12.4	39.0

N.B. The values quoted for water in the above table were taken from a plot of water pressure vs. total pressure change where the total pressure change equalled the actual pressure increase plus twice the pressure decrease.

TABLE 21 (fig. 20)

Run No.	O_2 cms. Hg.	C_2H_6 cms. Hg.	Φ min.^{-1}
1	7.66	21.79	0.18
2		10.39	0.05
3		29.71	0.40
4		36.31	0.80
5		25.57	0.25
6		15.35	0.08
7		32.63	0.57
8		32.60	0.62
9		5.86	0.02
1	15.28	28.61	0.52
2		8.50	0.05
3		24.12	0.30
4		16.32	0.14
5		19.34	0.18
6		12.82	0.09

N.B. 0.3% Acetaldehyde was added to all the mixtures except to that of run 8.

TABLE 22 (fig. 21)

Run No.	C_2H_6 cms. Hg.	O_2 cms. Hg.	ϕ min.$^{-1}$
1	25.60	16.04	0.41
2	"	6.06	0.20
3	"	19.72	0.41
4	"	11.82	0.34
5	"	3.21	0.11
6	"	7.66	0.25

N.B. 0.3% Acetaldehyde added to all the mixtures.

TABLE 23 (fig. 22)

Run No.	C_2H_6 cms. Hg.	O_2 cms. Hg.	CO_2 cms. Hg.	ϕ min.$^{-1}$
1	21.84	7.67	16.22	0.22
2	"	"	0.00	0.19
3	"	"	5.84	0.21
4	"	"	11.57	0.21

N.B. 0.3% Acetaldehyde added to all the mixtures.

TABLE 24 (fig. 23)

Run No.	C_2H_6 mms. Hg.	O_2 mms. Hg.	C_2H_4 mms. Hg.	Φ min.$^{-1}$
1	190.5	221.8	26.4	0.39
2	219.2	223.8	0.00	0.30
3	156.4	222.7	62.2	0.53
4	127.9	222.2	90.4	0.75
5	173.8	222.8	45.1	0.45
6	202.9	222.4	15.5	0.35
7	138.6	223.0	80.4	0.65

TABLE 25 (fig. 24)

Run No.	C_2H_6 mms. Hg.	O_2 mms. Hg.	C_2H_4O mms. Hg.	Φ min.$^{-1}$
1	188.1	222.1	30.1	0.31
2	156.4	221.9	61.4	0.29
3	217.8	221.8	24.5	0.43
4	206.0	209.7	45.9	0.47
5	219.2	223.8	0.00	0.30

DISCUSSION

In the part of the thesis which follows the experimental results recorded in the previous sections are discussed and a reaction mechanism which can account for them is suggested.

In the first section the thermal data used for evaluating the heat changes in the various reactions are given along with the source of the data.

The second section deals with the initial stages of ethane oxidation. The main products are ethylene and formaldehyde, and proposals are made for the mechanisms whereby they are formed.

The next section is concerned with the oxidation of ethylene and formaldehyde. Particular attention is paid to the initial products of ethylene oxidation and a mechanism is put forward for the initial stages in the oxidation. A simplified form of the scheme postulated by Lewis & von Elbe is adopted for formaldehyde oxidation.

In the fourth section the degenerate branching reaction is discussed and the conclusion reached that the branching occurs through formaldehyde. The possible branching reactions are examined and a decision made as to which one is the most feasible.

In the next section the series of reactions which are considered to represent the slow combustion of ethane are listed, and this is then followed by the final section which is concerned with the relationship between the negative temperature coefficient in the rate of oxidation and the mechanism of oxidation.

1. THERMAL DATA.

The enthalpy changes occurring in the majority of reactions advanced in the following sections have been calculated from the values of the heats of formation given in the table below. Although the free energy change and not the enthalpy change involved in a reaction is a more accurate criterion of whether or not a reaction will occur, the enthalpy change is a much more easily obtainable quantity and is generally taken as a rough approximation of the free energy change. However which of a number of possible reactions will take place in a given system will not depend on either the enthalpy change or the free energy change but on the activation energy as this determines the rate of reaction. Polanyi[110] has demonstrated for the reaction of sodium atoms with halides that the activation energy is proportional to the exothermicity of the reaction and although this does not apply to other reactions it suggests that the enthalpy change in a reaction gives some estimate of the possibility of the reaction occurring. In a system where there is a number of possible reactions the most exothermic is generally preferred.

The heat data which are given in the table below have been taken from the following sources:-

Heats of Formation of Molecules - "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds" by Rossini et al.

- "Circular 500 Selected Values of Chemical Thermodynamic Properties, 1952."

Heats of Formation of Radicals - "Gas Kinetics" by Trotman-Dickenson.

Heats of Formation of H_2O_2, HO_2 - Foner & Hudson. J.C.P. 1955, 23, 1364.

Heats of Formation in K-cals./mole at 25°C and 1 atmos. pressure.

Compound	Heat of Formation	Radical	Heat of Formation
C_2H_6	-20.2	C_2H_5	25.2
C_2H_4	+12.5	CH_3	32.5
CH_4	-17.9	OH	10.1
CH_3CHO	-44	HO_2	5
C_2H_4O	-12.2	CH_3O	-1
CH_3OH	-48.3	CHO	+6
C_2H_5OH	-56.7	CH_3CO	-6
CO	-26.4	C_2H_5OO	11
CO_2	-94	CH_3OO	19
H_2O_2	-32.6	CH_2OH	-16
H_2O	-57.8		
HCHO	-27.7		
O_2	0		

2. THE MECHANISM OF THE REACTION.

Early work on the oxidation of hydrocarbons concentrated mainly on the products, especially the oxygenated products, from the later stages of reaction. This was partly due to the lack of suitably sensitive analytical techniques and methods had to be used which required large quantities of product material, and partly because it was considered that oxygenated compounds provided the key to oxidation mechanisms. However, through the recent development of gas chromatography small amounts of products can now be detected in large amounts of reactants and the early stages of reaction can be examined. Furthermore it has been shown that olefins play an important part in this early stage reaction. Consequently the discussion on ethane oxidation is divided into two main parts:- (1) the initial stage reaction (2) the later stage reaction, and the role played by olefins and oxygenated compounds in these two stages is examined.

The numbers that are given to the reactions which follow are those from the complete reaction scheme which is given later.

2.1. Initial Stages of Reaction.

In the oxidation of ethane between 318-386°C the major initial products were ethylene and formaldehyde, and as the relative yields varied with temperature the reactions producing them must have different activation energies. It was found that in the initial stages oxygen was removed as fast as ethane and since at the higher temperatures ethylene was the only major product its formation must have involved oxygen. This, and the fact that about 80% of the ethane consumed in the initial stages was converted to ethylene can be explained by an HO_2 radical chain.

(1) $C_2H_6 + HO_2 = C_2H_5 + H_2O_2 \quad \Delta H = +8$ kcals.

(2) $C_2H_5 + O_2 = C_2H_4 + HO_2 \quad \Delta H = -8$ kcals.

Apart from formaldehyde, the yields of the initial products were found to be independent of the oxygen concentration indicating that the reactions forming them must all have the same kinetic dependence on oxygen. Consequently they will be formed, in the same manner as ethylene, by the reaction of alkyl radicals with oxygen e.g. ethylene oxide will be produced by:-

(4) $C_2H_5 + O_2 = C_2H_4O + OH \quad \Delta H = -27$ Kcals.

Although the initial yield of formaldehyde was dependent upon the oxygen concentration formaldehyde, like ethylene, will be formed by the reaction of alkyl radicals with oxygen:-

(3) $C_2H_5 + O_2 = CH_3O + CH_2O \quad \Delta H = -54$ Kcals.

The methoxyl radicals formed in this reaction will react rapidly with oxygen to produce more formaldehyde and thus as part of the initial formaldehyde is produced by means of a two stage reaction, each stage involving oxygen, the initial yield of formaldehyde would be expected to have a greater dependence on oxygen than the yields of those products which are formed by reactions which only involve oxygen in one step. The fact that only small amounts of methanol are formed in the initial stages shows that the reaction of oxygen with methoxyl is faster than hydrogen abstraction by methoxyl. Most of these radicals will therefore be oxidised to formaldehyde, and consequently the dependence of the initial formaldehyde yield on oxygen will only be observed in oxygen weak mixtures where hydrogen abstraction can become of importance. It can be seen from table 9 that in the oxidation of ethane at 362° the initial yield of formaldehyde with a 3:1 ethane to oxygen mixture is appreciably lower than with a 1:1 mixture. However with the same mixture at 318°C the initial yields are practically the same. This is presumably due to the activation energy required for methoxyl radicals to abstract hydrogen being greater than the activation energy for the reaction of methoxyl radicals with oxygen with the effect that at the lower temperature the latter reaction is predominant even in oxygen weak mixtures.

It is generally agreed that the first step in hydrocarbon combustion is the abstraction of a hydrogen atom from the fuel molecule with the production of an alkyl radical. The alkyl radicals formed will combine with oxygen giving alkyl peroxy radicals. Although the work of Ingold & Bryce[111] on the reaction of alkyl radicals with oxygen provides the only direct evidence for this association there is much indirect evidence e.g. the formation of hydroperoxides in oxidation systems $ROO + RH = ROOH + R$[32]; the decomposition of di-t-butyl hydroperoxide in the gas phase proceeds by $(CH_3)_3\ COOC\ (CH_3)_3 = 2\ (CH_3)_3\ CO = 2(CH_3)_2\ CO + 2\ CH_3$ and in the presence of oxygen no methane or ethane was detected indicating that all the methyl radicals reacted with oxygen[112]; the results of Hoare & Walsh[117] on methyl radical oxidation could only be explained by the formation of CH_3OO radicals.

The ethyl peroxy radicals formed by combination of oxygen with ethyl radicals can either decompose or abstract a hydrogen atom to produce a hydroperoxide. Recent work[32] suggests that the hydroperoxides of the lower hydrocarbons viz. ethane and propane, are not formed at the temperatures used in this work (> 315°C) and that any peroxide material recovered will consist of hydrogen peroxide or a mixture of hydrogen peroxide and aldehyde - hydrogen peroxide adducts. Thus we have to consider the decomposition of the ethyl peroxy radical. There are four possible ways for the decomposition, each involving isomerisation in the first instance:-

(a) $CH_3CH_2OO \longrightarrow CH_2CH_2OOH \longrightarrow C_2H_4 + HO_2$

(b) $CH_3CH_2OO \longrightarrow CH_2CH_2OOH \longrightarrow C_2H_4O + OH$

(c) $CH_3CH_2OO \longrightarrow CH_3OOCH_2 \longrightarrow CH_3O + OCH_2$

(d) $CH_3CH_2OO \longrightarrow CH_3CHOOH \longrightarrow CH_3CHO + OH$

(a) In this case the oxygen free valency attacks a C-H bond in the methyl group and the resulting radical splits into two halves giving ethylene and an HO_2 radical. The first stage involving the breaking of a C-H bond (98 k.cal.) and the formation of an OO-H bond (~90 k.cal.) will be endothermic, and like all isomerisations will involve a substantial activation energy ~20 k.cal. The second stage involves the split of a C-O bond (~ 90 k.cal.) and the formation of the second link of an olefinic C=C bond. (~ 70 k.cal.)

Whether the ethylene is produced by rearrangement of the alkyl peroxy radical in this manner or whether it is formed by direct abstraction of hydrogen by the oxygen molecule is open to question. The formation of ethyl radicals in the later stages of ethylene oxidation presumably takes place by the reaction

$$C_2H_4 + HO_2 = C_2H_4OOH = C_2H_5 + O_2$$

and this suggests that the radical C_2H_4OOH can in fact be formed. Nevertheless the simplicity of the reaction in which ethylene is formed by direct hydrogen abstraction holds strongly in its favour.

(b) Here the intermediate radical is the same as for (a), but in this case split of the radical at the O-O bond with subsequent formation of a C-O bond produces ethylene oxide and a hydroxyl radical. The first stage i.e. formation of the intermediate radical, is endothermic whereas the second stage is exothermic (O-O bond broken and C-O bond formed.)

Although ethylene oxide is not a major initial product it is produced in appreciable amounts and thus reaction (b) is of importance in the early stages.

(c) Here the split of the C-C bond (85 k.cal.) and the formation of a C-O bond (~90 k.cal.) produces a radical which on decomposition gives formaldehyde and a methoxyl radical. The first step is almost thermoneutral but the second step is exothermic since an O-O bond (40-50 k.cal.) is broken and a C=O bond formed (~75 k.cal.

(d) The shift of a hydrogen atom from the carbon to the oxygen results in a radical which on decomposing gives a hydroxyl radical and acetaldehyde. The first step is endothermic as it involves the breaking of a C-H bond (98 k.cal.) and the formation of an O-H bond (~90 k.cal.) whereas the second step is exothermic, an O-O bond (40-50 k.cal.) is broken and a C=O bond (~75 k.cal.) formed.

Analysis of the reaction products throughout the course of the reaction show that acetaldehyde is only formed in trace amounts, suggesting that reaction (d) does not play an important part in the consumption of ethane. However experiments on the oxidation of acetaldehyde have shown that under the conditions used it is rapidly oxidised to formaldehyde and the low yield might possibly be explained by the rapid conversion of the acetaldehyde to formaldehyde. If this reaction were the only source of formaldehyde the initial yield of carbon monoxide would greatly exceed that of formaldehyde but as can be seen from table 9 the yields in the oxidation of ethane at 362°C are approximately the same, and at 318°C the initial yield of formaldehyde exceeds that of the carbon monoxide. Thus the contribution of reaction (d) to the production of formaldehyde must be small.

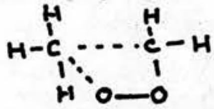
From the above considerations the main reactions consuming ethane in the initial stages are probably:-

(1) $C_2H_6 + HO_2 = C_2H_5 + H_2O_2 \quad \Delta H = + 8$ k.cals.

(2) $C_2H_5 + O_2 = C_2H_4 + HO_2 \quad \Delta H = - 8$ k.cals.

(3) $C_2H_5 + O_2 = C_2H_5OO = CH_3O + CH_2O \quad \Delta H = - 54$ k.cals.

Reaction (3) being the most exothermic would be expected to have the lowest activation energy and to predominate at the lower temperatures, while reaction (2) will become important at the higher temperatures. The ratio of the A factors and the difference in the activation energy for these two reactions, obtained by plotting the log. ratio of the initial yields of ethylene to formaldehyde against the reciprocal of temperature (fig.16), were $\frac{A_2}{A_3} \approx 10^8$ and $E_2 - E_3 = 21 \pm 5$ k.cal. respectively. This large difference in the activation energies is rather surprising considering that the ethylene and formaldehyde are both produced by the reaction of alkyl radicals with oxygen. The ratio of A factors is also much higher than one might expect but this could be explained if the steric factor for reaction (3) was abnormally low.

In the isomerisation step of reaction (3) the intermediate complex will have the form  and as there is a greater restriction to movement in the complex than in the original radical, due to the increase in the number of bonds, the formation of the complex will be accompanied by a large decrease in entropy. This will result in a low A factor.

If this intermediate complex is considered as analogous to a four membered ring compound then a rough estimate of the decrease in entropy on its formation from the ethyl peroxy radical may be obtained by comparing the standard entropies of cyclobutane and butene-1. The difference between the entropies of cyclobutane (62 e.u.) and butene-1 (73.5 e.u.) at 298°K is 11.5 e.u. and by comparison with the difference between the entropies of cyclopentane and pentane at 298 and 600°K viz. 13 e.u. and 19 e.u. respectively, this difference would be expected to be about 18 e.u. at 600°K. This value is rather less than the calculated value for the difference in the entropies of activation of reactions (2) and

(3). With an A factor ratio of approx. 10^8 for these reactions the difference in the entropies of activation will be about 37 e.u. However the change in entropy on formation of the transition complex is not the only factor which can contribute to a high A factor ratio. The ethyl peroxy radical will be in an excited state as it contains the energy released from the association reaction of ethyl radicals with oxygen, and the probability of its dissociation back into ethyl and oxygen before further reaction can take place is high. This will also cause reaction (3) to have a low A factor and the combined effect of the dissociation of the peroxy radical and of the decrease in entropy on formation of the transition complex may well lead to an abnormally low A factor ratio for reaction (3) and hence to a very high A factor for reactions (2) and (3).

Reactions (2) and (3) are reminiscent of the cis-trans isomerisation reactions of ethylene derivatives, where the specific reaction rates for compounds such as maleic acid and butene-2 are given approximately by the equation:-

$$k \approx 10^{4} e^{-25,000/RT} \ \mathrm{sec}^{-1}$$

and for compounds such as methyl cinnamate, stilbene by the equation

$$k \approx 10^{11} e^{-45,000/RT} \ \mathrm{sec}^{-1}$$

In other words one group is characterised by a low frequency factor and a low energy of activation whereas in the other these quantities are high.

Since the reaction of propyl radicals with oxygen appears to be similar to that of ethyl radicals with oxygen the above results may be compared with results on the oxidation of propane.

Satterfield & Reid[54] calculated that the activation energy difference between the reaction producing propylene and that producing oxygenated products was approximately 19 k.cals, with an A factor ratio for the two reactions of approximately $10.^6$ According to Shtern[36] the value for the activation energy difference is nearer 13 k.cal. It has to be noted, however, that these results were based on the yields of products in the later stages of reaction and therefore do not bear direct comparison with those given above for the initial stages of ethane oxidation. Nevertheless if the equilibrium concentrations of ethylene and formaldehyde which are attained in the later stages of reaction, were used to calculate the activation energy difference between reactions (2) and (3) a value fairly close to that found for the initial stage reaction is obtained. Thus the values quoted by Shtern and Satterfield & Wilson may also apply to the initial stages of propane oxidation.

Ethylene oxide is produced in the early stages of reaction and, as considered earlier, it will probably be formed by the reaction:-

$$(4) \quad C_2H_5 + O_2 = CH_2CH_2OOH = C_2H_4O + OH \quad \Delta H = -27 \text{ k.cal.}$$

It was not possible to obtain the activation energy of this reaction relative to the activation energy of either reactions (2) or (3) as the inaccuracy in the determination of the small amounts of ethylene oxide initially produced rendered any activation energy plot valueless.

Reactions (1) and (2) explain the relatively high yield of hydrogen peroxide observed in the initial stages of the reaction (fig. 8b). Although the yield does not equal that of the ethylene as predicted by the reaction scheme it has to be remembered that the hydrogen peroxide will decompose rapidly on the surface of the reaction vessel, and it has been shown[34] that the amount of hydrogen peroxide isolated depends inversely upon the efficiency of the reaction vessel surface in catalysing its heterogeneous decomposition.

Evidence that hydrogen peroxide can be produced by the reaction of hydroperoxy radicals with hydrocarbons in the gas phase comes from the work of Geib & Harteck[113]. They found that under conditions where atomic hydrogen alone does not react with hydrocarbons, atomic hydrogen plus oxygen will give a rapid reaction. This suggests that the reaction $RH + HO_2 = R + H_2O_2$ occurs. Further evidence for the occurrence of this reaction in the gas phase is supplied by Lacomble.[114] He carried out propane oxidations in a spherical shell by introducing the reactants tangentially at the outer circumference and then withdrawing the products from the centre whereupon he found that hydrogen peroxide was formed in relatively high yield.

It is suggested that methoxyl radicals are formed in the system by means of reaction (3). As decomposition of the radicals is unlikely, having an activation energy of at least 25 k.cal., they will either abstract hydrogen or else react with oxygen.

(20) $CH_3O + C_2H_6 = CH_3OH + C_2H_5$ $\Delta H = -2$ k.cals.

(10) $CH_3O + O_2 = CH_2O + HO_2$ $\Delta H = -24$ k.cals.

The analytical results have shown that the initial yield of methanol is low and hence the methoxyl radicals must mostly be removed by reaction with oxygen. This reaction being the more exothermic would be expected to predominate at the lower temperatures. However as the temperature increases the yield of methanol does not correspondingly increase since the rate of production of methoxyl radicals falls as the temperature increases.

It has been suggested that[115] that methoxyl radicals can react with oxygen forming carbon monoxide, water and a hydroxyl radical.

$CH_3O + O_2 = CO + H_2O + OH$ $\Delta H = -75$ kc.

This appears to be too complex a process to occur in a single stage and a more likely scheme would be :-

$CH_3O + O_2 = CHO + H_2O_2$ $\Delta H = -26$ kc.

$CHO + O_2 = CO + HO_2$ $\Delta H = -27$ kc.

Even although these reactions could explain the initial formation of carbon monoxide the most plausible mechanism for the reaction of methoxyl radicals with oxygen is that of reaction (10) whereby formaldehyde is produced.

The formation of carbon monoxide could be explained by the oxidation of acetaldehyde and formaldehyde. As seen previously the amount of acetaldehyde formed in the system is small and therefore formaldehyde is the more likely source of the carbon monoxide. The reaction of oxygen with formaldehyde if it occurred in the gas phase would be a branching reaction but the slow development of the reaction rate suggests that the branching intermediates initially formed are destroyed on the walls of the reaction vessel. Thus the carbon monoxide will most probably be formed initially by surface oxidation of the formaldehyde.

The replacement of ethane by ethylene increased the yield of carbon monoxide indicating that the ethylene was oxidised via formaldehyde to carbon monoxide. It is thus possible that by the time the first analysis was made in the ethane oxidations part of the ethylene initially formed may have been oxidised to carbon monoxide. Consequently one cannot conclude whether or not the value quoted for the initial carbon monoxide yield represents its rate of formation by surface oxidation of formaldehyde which is formed directly from ethane, or by surface oxidation of formaldehyde produced from ethylene as well as from ethane.

Small amounts of methanol are formed in the early stages of the oxidation. The methanol may be formed in two ways, (a) hydrogen abstraction by methoxyl radicals or (b) oxidation of methyl radicals.

(a) Methoxy radicals are produced in equivalent yield to formaldehyde by reaction (3), but as the initial yield of methanol is much lower than the initial yield of formaldehyde the oxidation of the methoxy radicals must exceed hydrogen abstraction. Consequently the reaction :-

$$CH_3O + C_2H_6 = CH_3OH + C_2H_5 \quad \Delta H = -2 \text{ kc.}$$

will not be an important source of methanol.

(b) The addition of acetaldehyde to the oxidation system increased the initial yield of methanol, and as the oxidation of acetaldehyde will introduce methyl radicals into the system it suggests that the methanol was formed by the oxidation of these radicals

It has been shown by several other workers[94,116] that methanol can be formed by the oxidation of methyl radicals. However these experiments were generally carried out under conditions of low temperature and high radical concentration whereas in the present work the temperature was relatively high and the concentration of radicals would be relatively low. Although various different mechanisms were proposed for the formation of the methanol they were all similar in that they postulated the intermediate formation of methyl peroxy radicals and methoxy radicals e.g. Raley, Porter, Rust & Vaughan[94] investigated the oxidation of methyl radicals between 120-160° and they concluded that the following scheme could explain the methanol formation:-

$$CH_3 + O_2 = CH_3O_2$$

$$2CH_3O_2 = 2CH_3O + O_2$$

$$CH_3O + CH_3O = CH_3OH + CH_2O$$

Although this mechanism may well explain the formation of methanol under the conditions used by Raley et al., it is unlikely that methanol will be formed in the same manner under the conditions used in the present work. Here the concentration of methyl peroxy radicals will probably be low, and rather than produce methoxy radicals they would be expected to decompose into formaldehyde and hydroxyl. Apart from this, the experimental evidence points to the fact that methoxy radicals, if formed, will be oxidised before they can abstract hydrogen.

Nevertheless the experiments with added acetaldehyde show that under the conditions used in the present work methanol can in fact be formed by the oxidation of methyl radicals. The most likely mechanism is :-

$$(22) \quad CH_3 + O_2 = CH_2O + OH \quad \Delta H = -50 \text{ kc.}$$

$$(23) \quad OH + CH_3\overset{c}{\cancel{O}}H_3 = CH_3OH + CH_3 \quad \Delta H = -6 \text{ Kc.}$$

This scheme envisages that the methyl radicals are oxidised to formaldehyde and hydroxyl radicals, and that the hydroxyl radicals then abstract methyl from the ethane to produce methanol and methyl radicals. The methyl radicals can then continue the chain.

Evidence for this scheme comes from the following :-

(1) The oxidation of acetaldehyde produces formaldehyde and the most plausible reaction is :- $CH_3 + O_2 = CH_2O + OH$

(2) The yield of methanol from the oxidation of acetaldehyde is increased when ethane is present in the system, presumably due to the occurrence of the reaction $OH + CH_3CH_3 = CH_3OH + CH_3$

(3) Methanol is formed in the early stages of ethane oxidation even although none of the products present at this stage could give rise to methyl radicals. However hydroxyl radicals will be formed in the early stages by the reaction $C_2H_5 + O_2 = C_2H_4O + OH$ and if they were to initiate the above chain the formation of methanol could be explained.

It has to be noted that the above scheme for the formation of methanol implies that hydroxyl radicals abstract methyl from ethane in preference to abstracting hydrogen, and that even although the former reaction is less exothermic than the latter the activation energy is smaller.

Water, in addition to ethylene and formaldehyde, is a major product of the initial stage reaction, and for a 1:1 mixture of ethane to oxygen at 362°C about 60% of the oxygen initially consumed is converted to water. The water will be produced partly by decomposition of hydrogen peroxide and partly by hydroxyl radicals abstracting hydrogen.

(18) $H_2O_2 + \text{wall} = H_2O + \frac{1}{2} O_2$

(23) $OH + C_2H_6 = H_2O + C_2H_5$

The possibility of the hydrogen peroxide decomposing to give hydroxyl radicals is excluded by the high activation energy required for this dissociation (ca. 54 k.cal.) and by the evidence[107] that the decomposition of hydrogen peroxide is almost entirely heterogeneous below 420°C.

Summarising the foregoing conclusions. The main reactions in the initial stages of ethane oxidation between 318 and 386°C are those producing the intermediates ethylene and formaldehyde. It is suggested that ethylene is formed by oxygen abstracting hydrogen directly from the ethyl radical and that formaldehyde is formed by the decomposition of the radical CH_3OOCH_2. This radical is produced by the isomerisation of the ethyl peroxy radical which is itself formed by the association of an alkyl radical with oxygen. Alternative isomerisations of the ethyl peroxy radical accompanied by the decomposition of the radicals formed can produce ethylene oxide and acetaldehyde. Acetaldehyde is only formed in trace amounts throughout the course of the oxidation and even although it is oxidised rapidly under the conditions used it is considered that little or no acetaldehyde is produced in the initial stages.

Hydrogen peroxide is formed by an HO_2 radical chain mechanism whilst the other products viz. carbon monoxide, water and methanol, are produced by side reactions.

The reactions which are considered to occur in the initial stages of ethane oxidation are listed overleaf.

$$(1)\quad C_2H_6 + HO_2 = C_2H_5 + H_2O_2 \qquad \Delta H = +\ 8\text{kcal.}$$

$$(2)\quad C_2H_5 + O_2 = C_2H_4 + HO_2 \qquad \Delta H = -\ 8\ \text{k.cal.}$$

$$(3)\quad C_2H_5 + O_2 = C_2H_5OO = CH_3O + CH_2O \qquad \Delta H = -54\ \text{k.cal.}$$

$$(4)\quad C_2H_5 + O_2 = C_2H_5OO = C_2H_4O + OH \qquad \Delta H = -27\ \text{k.cal.}$$

$$(20)\quad CH_3O + C_2H_6 = CH_3OH + C_2H_5 \qquad \Delta H = -\ 2\ \text{k.cal.}$$

$$(10)\quad CH_3O + O_2 = CH_2O + HO_2 \qquad \Delta H = -24.\text{k.cal.}$$

$$(21)\quad OH + CH_3CH_3 = CH_3OH + CH_3 \qquad \Delta H = -\ 6.\text{k.cal.}$$

$$(22)\quad CH_3 + O_2 = CH_2O + OH \qquad \Delta H = -50\ \text{k.cal.}$$

$$(23)\quad OH + C_2H_6 = H_2O + C_2H_5 \qquad \Delta H = -73\ \text{k.cal.}$$

$$(18)\quad H_2O_2 + \text{wall} = H_2O + \tfrac{1}{2}O_2$$

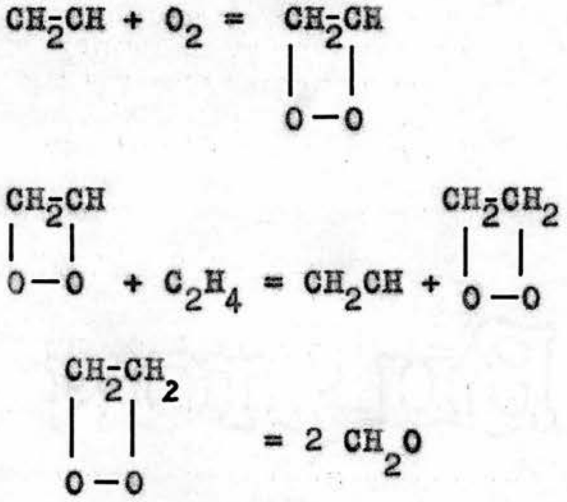
$$HCHO + O_2 + \text{wall} = CO + HO_2$$

2.2. Later Stages of Reaction

In the later stages of ethane oxidation the yields of ethylene and formaldehyde pass through maxima indicating that they themselves are oxidised throughout the course of reaction. Thus any discussion on ethane oxidation must include the oxidation of ethylene and formaldehyde.

Analysis of the products from the oxidation of ethylene has shown that formaldehyde is the major initial product. This, and the fact that there was always an initial pressure decrease was explained earlier by postulating that a cyclic peroxy compound was formed prior to the formation of formaldehyde.

$$C_2H_4 + X = CH_2CH + HX$$



$$CH_2CH + O_2 = \begin{array}{c} CH_2\text{-}CH \\ | \quad\; | \\ O - O \end{array}$$

$$\begin{array}{c} CH_2\text{-}CH \\ | \quad\; | \\ O - O \end{array} + C_2H_4 = CH_2CH + \begin{array}{c} CH_2\text{-}CH_2 \\ | \quad\; | \\ O - O \end{array}$$

$$\begin{array}{c} CH_2\text{-}CH_2 \\ | \quad\; | \\ O - O \end{array} = 2\ CH_2O$$

As no acetylene was detected in the reaction products the vinyl radicals, if formed, must react with oxygen in a different manner to the ethyl radicals produced in ethane oxidation. Hence it is feasible that they will react with oxygen to give a cyclic peroxy radical.

The same mechanism was proposed by Henley, Schiffries & Barr[118] to explain the high yields of aldehydes from the radiation of ethylene-water solutions at room temperature. However no attempt was made to identify the intermediate cyclic peroxide and until the existence of this compound in oxidation systems has been proven any mechanisms involving its formation will naturally be hypothetical.

The above scheme envisages that radicals abstract hydrogen from ethylene. This appears to be contradictory to the work of Brinton[119] and Mandelcorn & Steacie[120] which suggested that radicals would add to olefins rather than abstract hydrogen. Nevertheless as this scheme can explain both the initial pressure decrease and the high initial yield of formaldehyde it appears plausible. However it is not the only scheme whereby formaldehyde could be produced from ethylene. An alternative would be :-

$$C_2H_4 + HO_2 = CH_2CH_2OOH$$

$$CH_2CH_2OOH = CH_2O + CH_2OH$$

$$CH_2OH + O_2 = HO_2 + CH_2O$$

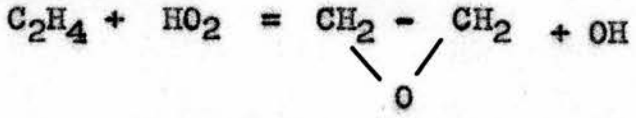
This mechanism is in accord with the viewpoint that radicals will add to olefins but it cannot explain the initial pressure decrease observed in the oxidation of ethylene.

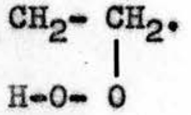
Hydrogen peroxide is a major initial product in the oxidation of ethylene indicating that hydroperoxy radicals are present in the early stage reaction. Oxidation of the formaldehyde already present in the system is the most likely source of these radicals.

$$HCHO + O_2 = CHO + HO_2 \qquad \Delta H = +39 \text{ kc.}$$

$$HCHO + CHO + O_2 = CO + H_2O_2 + CHO \Delta H = -31 \text{ kc.}$$

Ethylene oxide is also produced in the early stages of ethylene oxidation, presumably via the addition of an oxygenated radical to the ethylene molecule. As the oxidation of formaldehyde produces hydroperoxy radicals in the initial stages, the ethylene oxide will probably be formed by the reaction:-


$$C_2H_4 + HO_2 = \underset{\diagdown\, O\, \diagup}{CH_2 - CH_2} + OH$$

The initial step in the reaction will be the addition of the hydroperoxy radical to ethylene producing the radical  $CH_2-\underset{\overset{|}{H-O-O}}{CH_2}$.

On splitting at the O-O bond the oxygen free valency in the remaining radical skeleton will combine with the free valency on the terminal carbon atom forming a C-O bond.

By analogy with the ethyl peroxy radical in ethane oxidation the radical CH_2CH_2OOH will be expected to isomerise in the ethylene oxidation system. There are three possible ways of isomerisation:-

a) $CH_2CH_2OOH \quad = \quad HOCH_2CH_2O \quad = HOCH_2 + CH_2O$

b) $CH_2CH_2OOH \quad = \quad CH_3CHOOH \quad = CH_3CHO + OH$

c) $CH_2CH_2OOH \quad = \quad CH_3CH_2OO \quad = C_2H_5 + O_2$

(a) Here transfer of the -OH group to the terminal carbon atom produces a radical which on subsequent decomposition gives formaldehyde and a hydroxy methyl radical. This method of isomerisation was considered in connection with the high yield of formaldehyde in the initial stages of ethylene oxidation but was rejected on the grounds that it could not explain the pressure decrease which accompanied the formaldehyde formation. However part of the formaldehyde may be produced by this reaction.

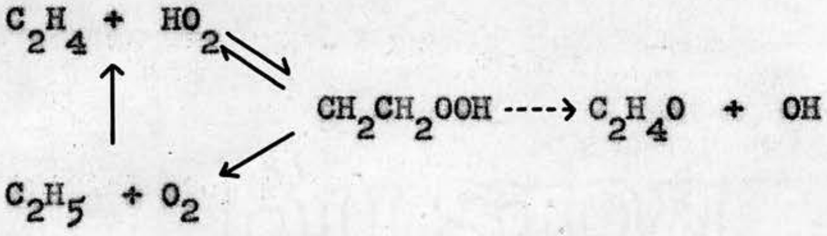
(b) In this case isomerisation and decomposition of the subsequent radical produces acetaldehyde and a hydroxyl radical. As acetaldehyde was only detected in small quantities this reaction will probably only have a minor role in ethylene oxidation.

(c) Shift of the hydrogen atom from oxygen to the terminal carbon atom produces the ethyl peroxy radical which on decomposing will give an ethyl radical and oxygen. Evidence for the formation of ethyl radicals in ethylene oxidation comes from the presence of ethane in the latter stages of the oxidation. Towards the end of the reaction the concentration of oxygen is low and the ethyl radicals produced instead of reacting with oxygen will abstract hydrogen to form ethane.

The radical CH_2CH_2OOH is formed in the oxidation of ethane by reaction of alkyl radicals with oxygen and as with ethylene oxidation it may split at the O-O bond producing ethylene oxide and a hydroxyl radical. If the radical could also split at the C-O bond a hydroperoxy radical and ethylene would be formed. Thus in a system of ethane - ethylene - oxygen the following reversible reaction scheme would exist :-

$$\begin{tikzcd}
C_2H_4 + HO_2 \arrow[r, shift left] & CH_2CH_2OOH \arrow[l, shift left] \arrow[r, shift left] \arrow[d, dashed] & C_2H_5 + O_2 \arrow[l, shift left] \\
 & C_2H_4O + OH &
\end{tikzcd}$$

However if it were assumed that ethylene was formed in the oxidation of ethane by oxygen abstracting hydrogen directly from an ethyl radical and not via the formation of the radical CH_2CH_2OOH, then the reactions occurring in a system of ethane - ethylene - oxygen could be represented by :-



It is a matter of opinion as to which of the above schemes is taken as representing the reactions occurring when a mixture of ethylene and ethane is undergoing oxidation. In the author's view the simplicity of the ethylene forming reaction in the second scheme holds in its favour.

The rapid rise in the production of ethane in the later stages of ethylene oxidation is accompanied by a rapid rise in the production of ethanol and methane, suggesting that their formation is also associated with the fall in oxygen concentration. The ethanol yield rises in a similar manner to that of ethane indicating that the ethanol may also be produced from ethyl radicals i.e. by the reaction

$$(25) \quad C_2H_5 + OH = C_2H_5OH \qquad \Delta H = -92 \text{ k.cal.}$$

However as this is a radical-radical reaction as opposed to a radical-molecule reaction for the formation of ethane, the yield of ethanol will be less than that of ethane.

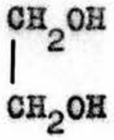
Methane and ethane will almost certainly be formed by methyl and ethyl radicals abstracting hydrogen, and it is interesting to note that as the yields of methane and ethane rise that of methanol decreases. This, plus the fact that methanol is the only product present which will donate hydrogen indicates that the methyl and ethyl radicals abstract from methanol.

$$CH_3 + CH_3OH = CH_4 + CH_2OH \quad \Delta H = -18 \text{ kc.}$$

$$C_2H_5 + CH_3OH = C_2H_6 + CH_2OH \quad \Delta H = +27 \text{ kc.}$$

The fate of the hydroxymethyl radicals which are produced in the above reactions is uncertain. If they had been formed in mixtures containing oxygen they would most probably have been oxidised to formaldehyde. However they are produced in the latter stages of reaction where the oxygen concentration is low and thus they must be removed by some other reaction. Ethylene glycol has been detected in the products of ethylene oxidation[121] and it is possible that the radicals will dimerise. Evidence that the CH_2OH radicals can dimerise comes from the work of Takezaki & Takeuchi[133]. They studied the decomposition of methanol induced by methoxyl radicals and they found that ethylene glycol was formed. The suggested reactions were :-

$$CH_3O + CH_3OH = CH_3OH + CH_2OH$$



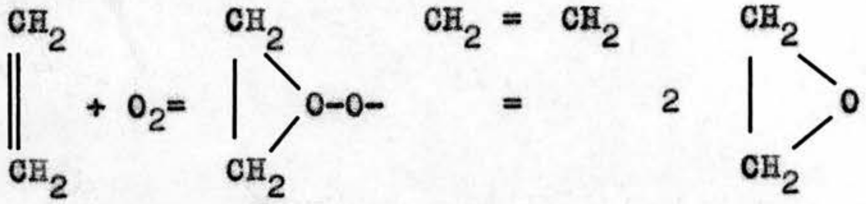
$$2\ CH_2OH = \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

Methanol is formed throughout the course of the reaction and as in the oxidation of ethane it is probably formed by hydroxyl radicals abstracting methyl, although in the case of ethylene oxidation the source of methyl radicals is uncertain.

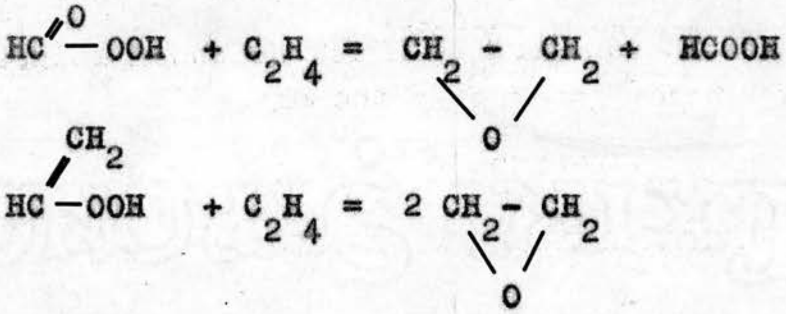
The yield of hydrogen peroxide falls sharply at the point where the rates of production of methane and ethane increase. (figs. 13a and 13b). This indicates that owing to the depletion of the oxygen the rate of formation of the hydrogen peroxide falls below that of its rate of decomposition. The maximum in the yield of hydrogen peroxide occurs after the maximum rate of reaction which shows that the hydrogen peroxide is an end product of the oxidation and not an active intermediate.

In the foregoing the formation of the products in ethylene oxidation has been considered, but before dealing with the next stage in the oxidation process viz. formaldehyde oxidation, it is worthwhile considering the various theories on the formation of ethylene oxide in ethylene oxidation, especially as a new viewpoint is now put forward.

Lenher[97] was one of the first workers to study ethylene oxidation and he found that in the oxidation between 360-410°C ethylene oxide was produced in fairly high yield. He postulated that oxygen activated the olefinic double bond in such a manner that the oxygen molecule added across the bond with the formation of a radical which on subsequent reaction with ethylene formed ethylene oxide.



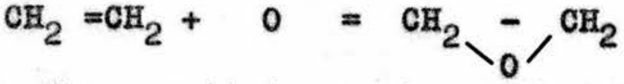
An alternative mechanism was put forward by Lewis & von Elbe[46]. They considered that ethylene hydroperoxide was formed in the oxidation of ethylene and that this compound would react in an analogous manner to peracids which are known to produce olefin oxides and normal acids on reaction with olefins.



However the evidence for the reaction of peracids with olefins comes from experiments in solution and like other peroxide reactions is probably not applicable to the gas phase where the temperatures are of necessity much higher.

Harding and Norrish's view[97] was that the chain branching reaction in ethylene oxidation produced oxygen atoms which on addition across the ethylene double bond formed ethylene oxide.

$HCHO + O_2 = HCOOH + O$



However it is now known that hydrogen peroxide is formed in the oxidation of ethylene and as the most likely source of hydroperoxy radicals (precursors of hydrogen peroxide formation) is the reaction $HCHO + O_2 = CHO + HO_2$ it suggests that the oxygen atom theory of Harding & Norrish is incorrect.

The thermal oxidation of formaldehyde has been investigated by several workers viz. Bone & Gardner[5], Spence[122], Snowdon & Style[123], and Axford & Norrish.[124] Although their findings were contradictory on certain points the results were correlated by Lewis & von Elbe[46] in 1951 and a mechanism put forward to explain the oxidation. The choice of possible reactions was restricted by the following:-

a) The rate of reaction was proportional to the square of the formaldehyde concentration and independent of the oxygen concentration.

b) The reaction was independent of vessel diameter which indicated that both the chain breaking and chain initiation reactions were either gas phase or surface processes.

c) The reaction was inhibited by inert gas. This showed that the chain breaking reaction occurred in the gas phase and hence the chain initiation reaction also.

d) Initiation may involve either decomposition of the formaldehyde or homogeneous reaction between formaldehyde and oxygen. The high activation energy for the dissociation of formaldehyde rules out the former possibility and the evidence is that the initiation step in aldehyde oxidation is a bimolecular reaction between the aldehyde and oxygen.

e) The inhibiting effect of inert gases pointed to the chain breaking reaction being a ternary process involving a chain carrier, inert gas, and one of the reactants.

A simplified form of the Lewis & von Elbe scheme, which takes into account the above considerations, is given below:-

Initiation --------

$$HCHO + O_2 = CHO + HO_2$$

$$HO_2 + HCHO = CHO + H_2O_2$$

Chain Propagation ------

$$CHO + HCHO + O_2 = \underset{\substack{\downarrow \\ CO + H_2O_2}}{HCOOOH} + CHO$$

Termination

$$CHO + O_2 + M = CHO_3$$

$$CHO_3 + \text{wall} = \text{destruction}$$

$$HCOOOH + \text{wall} = CO_2,\ H_2O$$

This scheme envisages that performic acid is the primary product of the chain reaction and that carbon monoxide and hydrogen peroxide are produced by the decomposition of this acid. This was partly suggested by the fact that Bone & Gardner[5] found that performic acid was formed in high yield in the initial stages of reaction, and partly by the fact that the kinetics of the reaction require the chain propagating reaction to be termolecular.

Although a detailed analysis of the initial products is required to determine conclusively the role of performic acid in the oxidation of formaldehyde, the fact that the above scheme can explain both the kinetic and analytical data holds strongly in its favour, and in the absence of a more plausible mechanism it will be taken as representing the oxidation of formaldehyde.

The most likely alternative to the above chain propagating reaction is :-

$$CHO + O_2 = CO + HO_2$$

$$HO_2 + HCHO = CHO + H_2O_2$$

This chain can explain the high yields of carbon monoxide and water but it cannot explain the rate of reaction being proportional to the square of the formaldehyde concentration and independent of the oxygen concentration. Apart from this, if this chain were operative it would have to be postulated that carbon dioxide was formed by a reaction such as :-

$$CHO + O_2 = CO_2 + OH$$

The occurrence of this reaction would require the yield of carbon dioxide to increase linearly throughout the course of the reaction, in a similar manner to the carbon monoxide yield, whereas in fact its rate of production increases markedly towards the end of the reaction. (see fig.13a.). This was also observed by Bone & Gardner[5] in their experiments on formaldehyde oxidation, and since the increase in the carbon dioxide yield was accompanied by a decrease in the yield of performic acid they suggested that the carbon dioxide was formed by surface decomposition of the acid.

It is to be noted that the association reaction between formyl radicals and oxygen must be extremely fast as McKellar & Norrish[128] detected both OH and CHO radicals in the explosive combustion of formaldehyde but only OH radicals in the slow combustion.

In conclusion, it appears that the later stages of ethane oxidation involve primarily the oxidation of the intermediates ethylene and formaldehyde. Ethylene is oxidised mainly to formaldehyde and the formaldehyde is oxidised to the final degradation products carbon monoxide and water. The reactions which will be common to the ethane, ethylene, and formaldehyde oxidation systems are listed below:-

(6) $C_2H_4 + O_2 = 2\ CH_2O$

(7) $C_2H_4 + HO_2 = C_2H_4OOH = C_2H_4O + OH$

(8) $C_2H_4 + HO_2 = CH_3CHOOH = CH_3CHO + OH$

(9) $C_2H_4 + HO_2 = CH_3CH_2OO = C_2H_5 + O_2$

(10) $CH_2O + O_2 = CHO + HO_2$

(12) $CH_2O + HO_2 = CHO + H_2O_2$

(14) $CHO + O_2 + HCHO = HCOOOH + CHO$

$= CO + H_2O_2 + CHO$

(15) $CHO + O_2 + M = CHO_3 + M$

(16) $CHO_3 + \text{wall} = \text{destruction}$

(17) $HCOOOH + \text{wall} = CO_2, H_2O$

(18) $H_2O_2 + \text{wall} = H_2O + \frac{1}{2} O_2$

(19) $HO_2 + \text{wall} = \text{destruction}$

2.3. Mechanism of Degenerate Branching

The slow oxidation of ethane is characterised by an induction period in which little or no pressure rise occurs, followed by an acceleration to the maximum rate of reaction. According to Semenoff these characteristics are due to the build up by a primary chain of an intermediate which can survive long after the primary chains have ended and then react to produce radicals which are capable of initiating new chains.

Various theories have been put forward as to the nature of the branching intermediate and there arose two schools of thought (1) those who thought that it was peroxidic in nature (2) those who thought it was aldehydic in nature. The difference between the two theories lay in the fate of the alkyperoxy radical produced in the oxidation system. Those in favour of the peroxide theory considered that this radical was fairly stable and could exist in the reaction system long enough to enable it to abstract hydrogen and form a peroxide, whereas those in favour of the aldehyde theory considered that it was unstable and would decompose into an aldehyde and a free radical before it had time to abstract hydrogen. Branching by peroxides was considered to occur by the split of the molecule at the O-O bond producing two free radicals, whilst aldehyde branching was thought to take place by the reaction of the aldehyde with oxygen producing free radicals.

$ROOH = RO + OH$ Peroxide branching.

$RCHO + O_2 =$ Free Radicals Aldehyde branching.

Peroxides have been detected in the products of hydrocarbon oxidation in solution, and evidence that they can act as agents of degenerate branching comes from the work of Medvedev[28]. He found that the addition of tetralin hydroperoxide to tetralin caused the reaction to start off at a rate greater than the normal maximum rate and then slow down to the normal maximum rate.

Hydroperoxides have also been detected in the oxidation of hydrocarbons in the gas phase but it appears that only the hydroperoxides of higher hydrocarbons are produced and that those of the lower hydrocarbons viz. ethane and propane, are not readily formed under the conditions of hydrocarbon oxidation e.g. Cartlidge & Tipper[32] obtained hydroperoxides from the oxidation of n-butane, cyclohexane and n-heptane between 310-386°C but with propane at 327°C only hydrogen peroxide was detected. Even at temperatures below those at which hydrocarbons normally oxidise the lower hydroperoxides are not produced Bell, Dickey, Raley, Rust & Vaughan[25] investigating the hydrogen bromide catalysed oxidation of iso-butane between 100-160°C found that t-butyl hydroperoxide was produced but no secondary or primary hydroperoxides.

The expected lifetime of the branching intermediate in hydrocarbon oxidation is of the order of minutes (Semenoff, 1935, p.68) but Kirk & Knox[33] have shown from a study of the thermal decomposition of hydroperoxides that the lifetimes of ethyl and propyl hydroperoxides are approximately 3.7 secs. at 318°C. This provides further evidence that hydroperoxides are not the agents of degenerate branching in the oxidation of ethane and propane above 300°C.

In general the rate of hydrocarbon oxidations indicate that the pressure of intermediate responsible for degenerate branching must be of the order of mms. e.g. for an intermediate of lifetime 60 secs. and for a maximum rate of 0.2 mm. hydrocarbon oxidised per second the maximum pressure of intermediate will be 12 mm. Pressures of this order have been observed for aldehydes in several oxidation systems and it can be seen from fig. 8a that in the oxidation of ethane at 362°C the maximum formaldehyde pressure is 7 mms. Furthermore the maximum in the formaldehyde pressure occurs at the maximum rate of reaction as required if formaldehyde were the branching intermediate in ethane oxidation.

The effect of light on methane and ethylene oxidations in the high temperature region provides interesting evidence for aldehyde branching. Norrish & Reagh[125] found that on illuminating the oxidation system with U.V.light of wavelength 3800-2400 A° (known to dissociate formaldehyde into hydrogen atoms and carbon monoxide) the reaction immediately accelerated, and that when the light was excluded the reaction decelerated. Examination of the kinetics both in the light and in the dark showed that the effect of the light was merely to augment that of the thermal reaction, and while the rate of the dark reaction was given by:-

$$R_D = k_1 (Hy.)(O_2) + K_2(Hy)^2 (O_2) P$$

the rate in the light was given by:-

$$R_L = k_1 (Hy)(O_2) + k_1^1(Hy) I + K_2 (Hy)^2 (O_2) P + K_2^1 (Hy)^2 IP$$

where P = total pressure, I = intensity of light.

The effect of light was to introduce the term k_1^1 (Hy)I + K_2^1 $(Hy)^2$ IP in the rate expression. Thus the augmented reaction due to irradiation followed a similar law to the dark reaction, with the light intensity replacing the oxygen pressure. As the effect of light was to accelerate the reaction without altering the kinetics and as the incident light was not absorbed by the hydrocarbon or oxygen, the photochemical effect must have been exerted through the branching intermediate:-

$$RCH_2CHO + I = H + CHO$$

These results show that the branching reaction in the thermal oxidation is one in which oxygen attacks an intermediate compound which is capable of absorbing light i.e. the branching reaction is of the form:-

$$RCH_2CHO + O_2 = \text{free radicals}$$

This is further supported by the fact that aldehydes absorb light of the wavelength used in the experiments of Norrish & Reagh.

Thus the initiation reaction in aldehyde oxidation i.e. the branching reaction in hydrocarbon oxidation will be bimolecular. This is in agreement with the ideas of Hoare & Walsh[126] and McDowell & Thomas[92, 93] who, from an investigation of methane and acetaldehyde oxidations respectively, suggested that the initiation reactions in formaldehyde and acetaldehyde oxidations were:-

$$HCHO + O_2 = CHO + HO_2 \quad \Delta H = +39 \text{ Kc.}$$

$$CH_3CHO + O_2 = CH_3CO + HO_2 \quad \Delta H = +37 \text{ Kc.}$$

Harding & Norrish[97] have demonstrated that formaldehyde is the branching intermediate in the high temperature oxidation of ethylene, and the evidence presented in this thesis suggests that it is also the branching intermediate in the low temperature region 318-386°C. As ethylene and formaldehyde are the major initial products from ethane oxidation formaldehyde will also be the agent of degenerate branching in ethane oxidation.

The activation energy for the branching reaction i.e. the activation energy for the initiation reaction in formaldehyde oxidation, has been determined by several workers. Axford & Norrish[124] estimated the value to be about 21 k.cal./mole in the temperature range 325-370°C and about 39 k.cal./mole in the temperature range 450-470°C. However this apparent rise in activation energy could be due to a change in chain length rather than a change in the initiation reaction (Lewis & von Elbe 1951) and the activation energy for the initiation step may be taken as 21 k.cal./mole. The initiation reaction proposed by Axford & Norrish involved the formation of formic acid and an oxygen atom:-

$$HCHO + O_2 = HCOOH + O$$

However the high yield of hydrogen peroxide in the initial products of ethylene oxidation suggests that a more likely reaction would be :-

$$HCHO + O_2 = CHO + HO_2$$

This reaction was favoured by Hoare & Walsh[126] and by Markevitch & Filippova[127]. They gave values of 25 and 26 k.cal./mole respectively for the activation energy.

Lewis & von Elbe[46] considered that the initiation reaction in formaldehyde oxidation could be represented by either

$HCHO + O_2 = CHO + HO_2$ or

$HCHO + O_2 = CHOO + OH$

These two possibilities were considered by Hoare & Walsh[126] and they concluded from an investigation of the inhibiting effect of lead tetra-ethyl on the oxidation of methane that the production of OH radicals could not explain their experimental findings whereas they could be explained if HO_2 radicals were produced in this step.

Thus the branching reaction in the oxidation of ethane and ethylene, may be taken as :-

$HCHO + O_2 = CHO + HO_2$ $E \sim 24$ k.cal./mole.

As this reaction has a high activation energy the rate of branching will be markedly affected by temperature, and although in ethane oxidation relatively more formaldehyde is produced at the lower temperatures the rate of branching, and hence the overall rate of reaction, will be lower at these temperatures. As well as this, the degradation reactions undergone by formaldehyde being more exothermic than the branching reaction will presumably have lower activation energies and hence will become relatively more important with respect to the branching reaction as the temperature is decreased.

Branching	$HCHO + O_2 = CHO + HO_2$	$\Delta H = +39$ kc.
Degradation	$HCHO + HO_2 = CHO + H_2O_2$	$\Delta H = -10$ kc.
	$HCHO + OH = CHO + H_2O$	$\Delta H = -34$ kc.

2.4. The Mechanism of the Complete Reaction.

In the foregoing sections of the Discussion the initial stages in ethane oxidation and the oxidation of ethylene and formaldehyde have been considered separately. Although these oxidations will be interlinked throughout the course of ethane oxidation the basic mechanisms will remain the same and the complete reaction scheme for ethane oxidation will embody the basic schemes of ethylene and formaldehyde oxidation.

It is suggested that the following series of reactions represents the slow combustion of ethane in the temperature range 318-386°C :-

Propagation

(1) $C_2H_6 + HO_2 = C_2H_5 + H_2O_2 \quad \Delta H = +8$ kc.

(2) $C_2H_5 + O_2 = C_2H_4 + HO_2 \quad \Delta H = -8$ kc.

(3) $C_2H_5 + O_2 = CH_3O + CH_2O \quad \Delta H = -54$ kc.

(4) $C_2H_5 + O_2 = C_2H_4O + OH \quad \Delta H = -27$ kc.

(5) $C_2H_5 + O_2 = CH_3CHO + OH \quad \Delta H = -59$ kc.

(6) $C_2H_4 + O_2 = 2\ CH_2O \quad \Delta H = -68$ kc.

(7) $C_2H_4 + HO_2 = C_2H_4O + OH \quad \Delta H = -20$ kc.

(8) $C_2H_4 + HO_2 = CH_3CHO + OH \quad \Delta H = -51$ kc.

(9) $C_2H_4 + HO_2 = C_2H_5 + O_2 \quad \Delta H = +8$ kc.

(10) $CH_3O + O_2 = CH_2O + HO_2 \quad \Delta H = -22$ kc.

Branching

(11) $CH_2O + O_2 = CHO + HO_2 \quad \Delta H = +39$ kc.

Degradation

(12) $CH_2O + HO_2 = CHO + H_2O_2 \quad \Delta H = -10$ kc.

(13) $CH_2O + OH = CHO + H_2O \quad \Delta H = -34$ kc.

(14) $CHO + O_2 + CH_2O = HCOOOH + CHO$
$= CO + H_2O_2 + CHO \; \Delta H = -31$kc

Termination

(15) $CHO + O_2 + M = CHO_3 + M$

(16) $CHO_3 +$ wall = destruction

(17) $HCOOOH +$ wall $= CO_2 + H_2O$

(18) $H_2O_2 +$ wall $= H_2O + \frac{1}{2} O_2$

(19) $HO_2 +$ wall = destruction

Other Reactions

(20) $CH_3O + C_2H_6 = CH_3OH + C_5H_5$ $\Delta H = -2$ kc.

(21) $OH + CH_3CH_3 = CH_3OH + CH_3$ $\Delta H = -6$ kc.

(22) $CH_3 + O_2 = CH_2O + OH$ $\Delta H = -50$ kc.

(23) $OH + C_2H_6 = C_2H_5 + H_2O$ $\Delta H = -73$ kc

(24) $CH_3 + C_2H_6 = CH_4 + C_2H_5$ $\Delta H = -5$ kc.

(25) $C_2H_5 + OH = C_2H_5OH$ $\Delta H = -92$ kc.

Reactions (5) and (8) are considered to be of minor importance and the possible reactions of acetaldehyde are not included in the above scheme. However if acetaldehyde were produced in appreciable amounts and was then rapidly oxidised to end products, the following additional reactions would have to be introduced into the above scheme.

(26) $CH_3CHO + O_2 = CH_3CO + HO_2$ $\Delta H = +43$ kc

(27) $CH_3CHO + HO_2 = CH_3CO + H_2O_2$ $\Delta H = 0$ kc

(28) $CH_3CO = CH_3 + CO$ $\Delta H = +12$ kc.

2.5. The Negative Temperature Coefficient in Hydrocarbon Combustion.

The existence of a negative temperature coefficient in the rate of hydrocarbon combustion between ca. 350-400°C led to the suggestion that hydrocarbons oxidised by two distinct mechanisms viz. a "high" temperature mechanism above ca. 400°C and a "low" temperature mechanism below ca. 350°C, and it was considered that the region of the negative temperature coefficient represented the temperature range in which the oxidation changed over from the "low" to the "high" temperature mechanism. Owing to the earlier analytical techniques requiring relatively large amounts of products analysis could only be carried out for the later stages of reaction, and it was found that olefins predominated in the products of the "high" temperature oxidation whereas oxygenated compounds predominated in the products of the "low" temperature oxidation. This was explained on the basis that the alkyl radicals produced from the fuel molecule reacted with oxygen in different ways dependent upon the temperature.

"High" Temp. $\text{Alkyl} + O_2 \longrightarrow \text{Olefin} + HO_2$

"Low" Temp. $\text{Alkyl} + O_2 \longrightarrow \text{Aldehyde or Peroxide} \rightarrow \text{Oxygenated Compounds.}$

Through the recent development of gas chromatography the initial products of reaction can now be examined and it has been observed in the present work on ethane oxidation and in previous work on propane oxidation that olefins are produced in high initial yield in the "low" temperature oxidation, and in fact with ethane the initial yield of aldehyde only exceeds that of the olefin at temperatures below ca.320°C. Consequently the previous views on the negative temperature coefficient in the rates of ethane and propane oxidations have to be modified and the region of the negative temperature coefficient regarded as the temperature range in which the change over occurs from a mechanism in which aldehydes and olefins are initially produced to one in which only olefins are initially produced.

To confirm this viewpoint experiments would have to be conducted over a temperature range extending from the "low" to the "high" temperature region and analysis of the initial products carried out in order to determine whether or not there was a correlation between the reaction rate and the initial yields of aldehyde and olefin. During the course of this work experiments were carried out with temperatures up to 386°C and it was found that the initial yield of formaldehyde decreased with increasing temperature whilst the initial ethylene yield increased with temperature, but as the reaction rate increased continuously with temperature up to 386°C no conclusions can be drawn as regards the connection between the negative temperature coefficient and the initial yields of formaldehyde and ethylene. It is to be noted, however, that the kinetics of the reaction rate will vary with the conditions used. ~~since~~ Knox & Norrish[75] observed a negative temperature coefficient in the rate of ethane oxidation between 350-410°C whereas in the present work the rate increased continuously with temperature up to 386°C.

SUMMARY

The oxidation of ethane like that of other aliphatic hydrocarbons, apart from methane, can proceed by two distinct mechanisms. One operates above and the other below ca. 400°C. Analytical work on ethane oxidation has shown that in the later stages of the high temperature oxidation ethylene is the major product whereas in the low temperature region oxygenated compounds are the major products. Through the development of gas chromatography it is now possible to analyse the products in the early stages of reaction. The aim of the present work was to apply this technique to the analysis of the products in the initial stages of ethane oxidation and to determine the relative importance of ethylene and of oxygenated compounds in the early stages. At the same time analysis of the products formed throughout the course of the whole reaction would provide valuable analytical data for the elucidation of the oxidation mechanism.

The oxidations were carried out in a static system between 318-386°C using mixtures of different composition. The relative yields of the initial products did not change appreciably when the ethane:oxygen ratio was altered by a factor of six. However the initial yields changed with temperature, and at the higher temperature ethylene was the main initial product whereas at the lower temperatures formaldehyde predominated. A value is given for the difference in activation energy between the reactions producing ethylene and formaldehyde. The kinetics of the oxidation at 362°C

were investigated and the variation of the acceleration constant with oxygen, ethane, "inert" gas, and ethylene oxide pressure was determined.

Ethylene oxidations were carried out at 318 and 362°C with mixtures of different composition and the products from both the early and later stages of reaction were examined. The oxidation of acetaldehyde at 362°C was also investigated and a mechanism for the oxidation has been put forward.

In the latter part of this thesis the experimental results were discussed. It appears that the degradation of the ethane molecule is a stepwise process involving the intermediate formation of ethylene and formaldehyde. It was concluded that the ethylene was formed by oxygen abstracting hydrogen directly from ethyl radicals, and that the formaldehyde was formed by isomerisation and decomposition of ethyl peroxy radicals. In the later stages of reaction the ethylene and formaldehyde are themselves oxidised, ethylene mainly to formaldehyde, and formaldehyde to the final oxidation products carbon monoxide, carbon dioxide, and water. A mechanism involving the intermediate formation of a cyclic peroxide has been proposed for the oxidation of ethylene to formaldehyde. As no experiments were carried out on the oxidation of formaldehyde the scheme proposed by Lewis & von Elbe for formaldehyde oxidation has been adopted. A reaction scheme, which can explain the formation of the products of ethane oxidation and which embodies the basic schemes of ethylene and formaldehyde oxidations, has been put forward for the oxidation of ethane.

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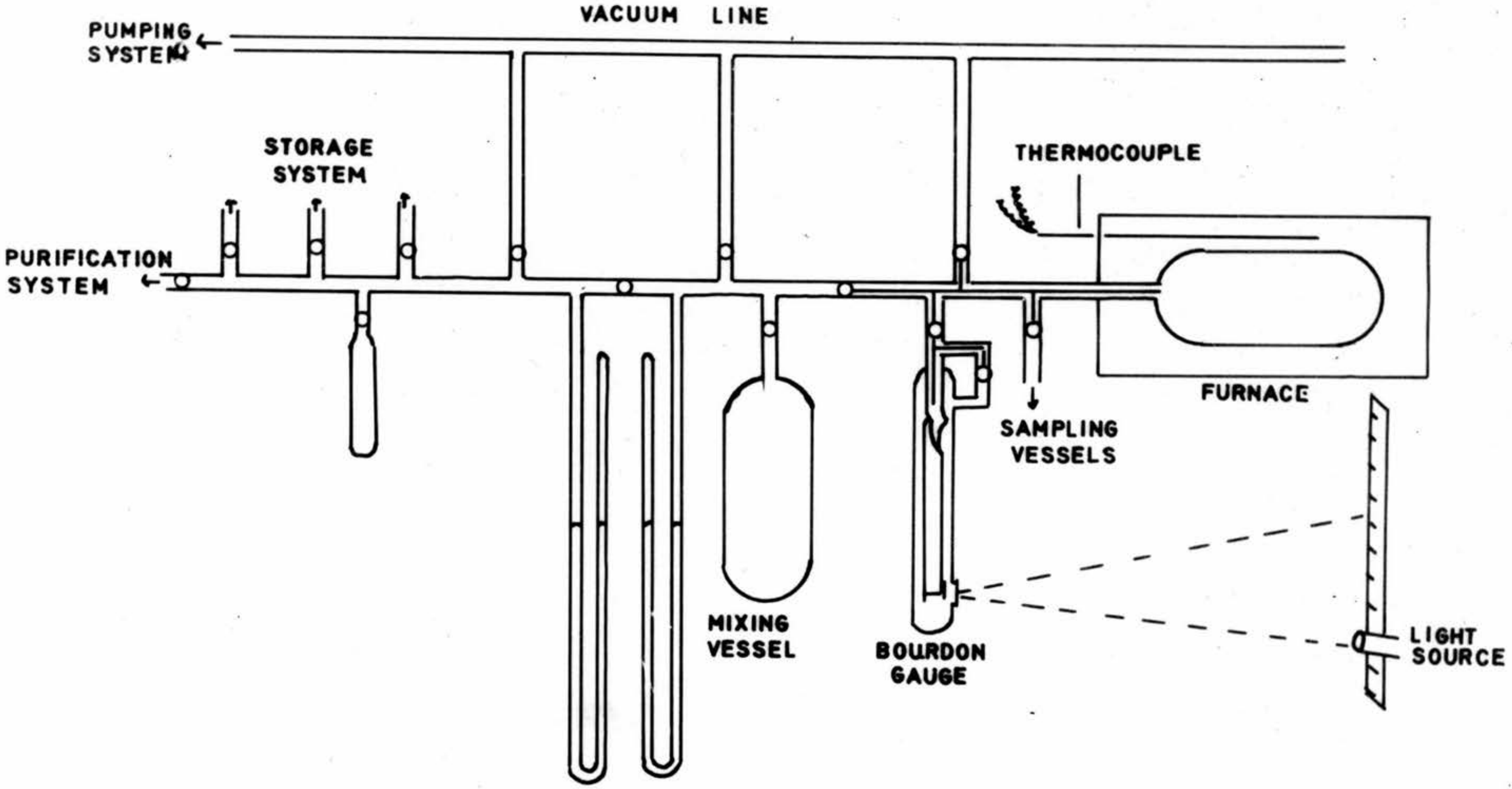
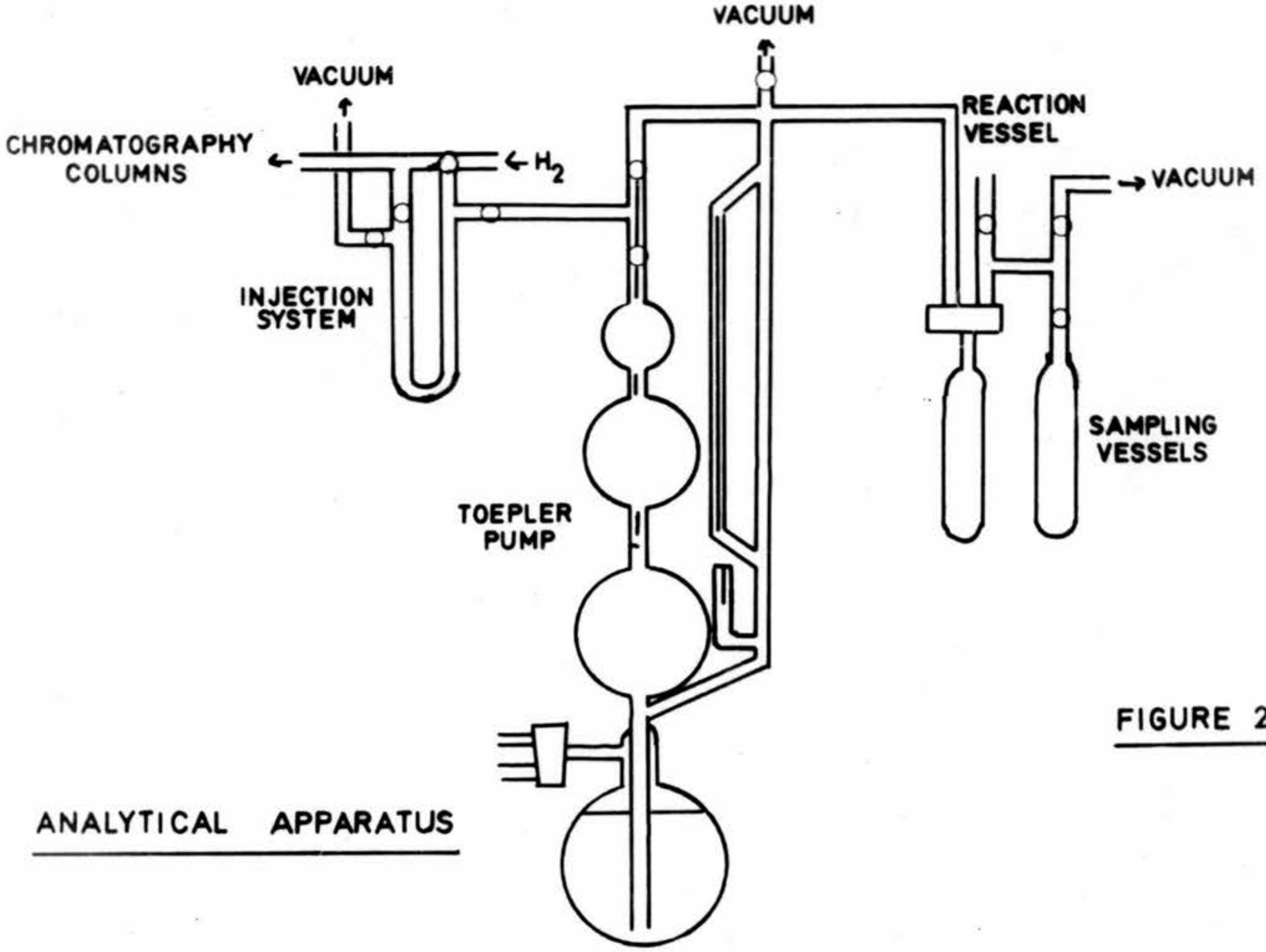


KINETIC APPARATUS

FIGURE 1.



ANALYTICAL APPARATUS

FIGURE 2.

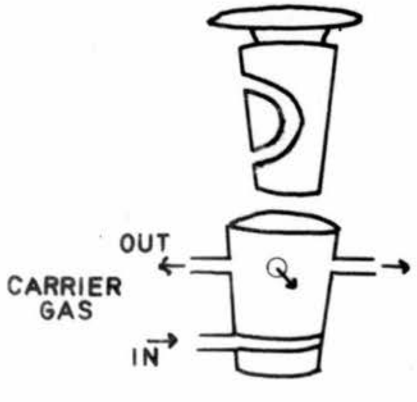


FIGURE 3.

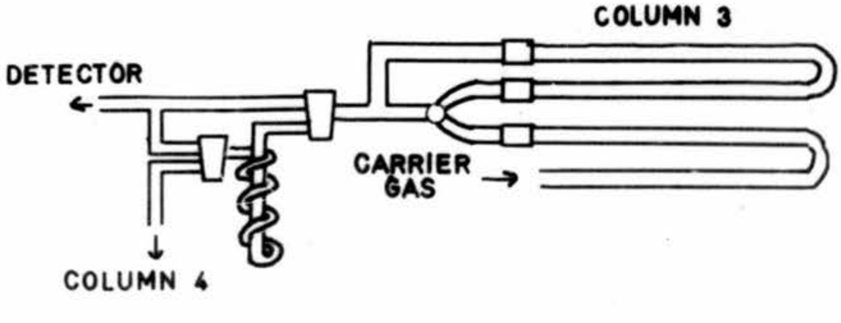
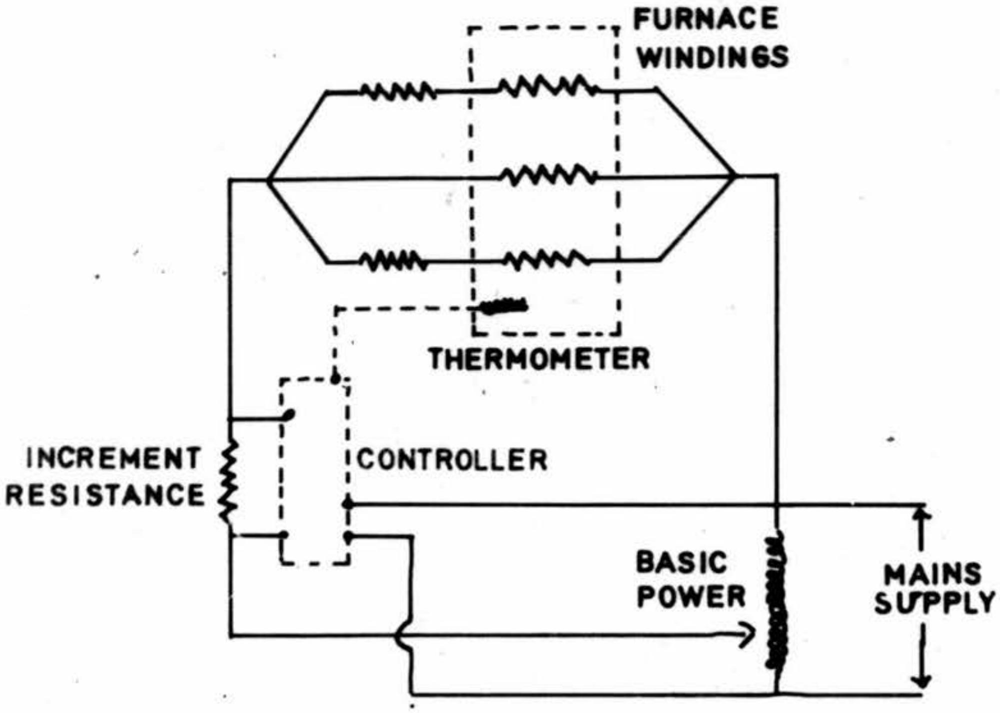


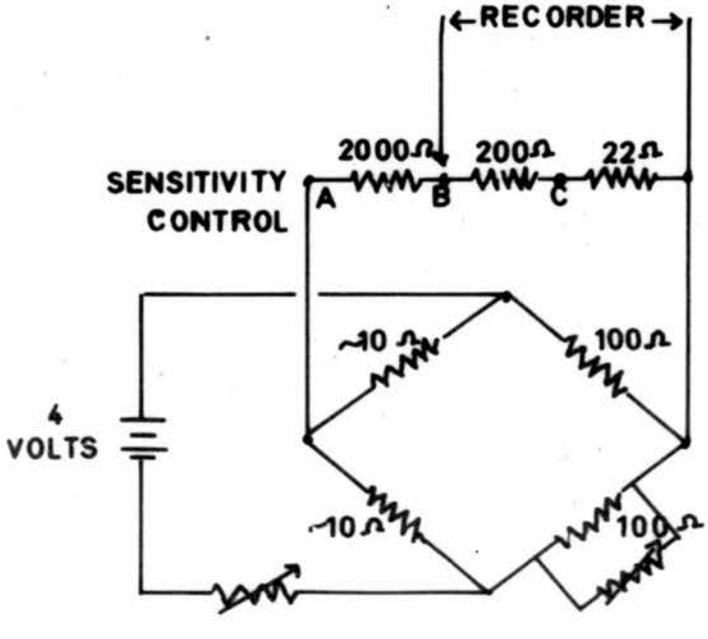
FIGURE 4.

FIGURE 5.



FURNACE CIRCUIT.

FIGURE 6.



DETECTOR CIRCUIT.

FIGURE 7.

ETHANE MATERIAL BALANCE

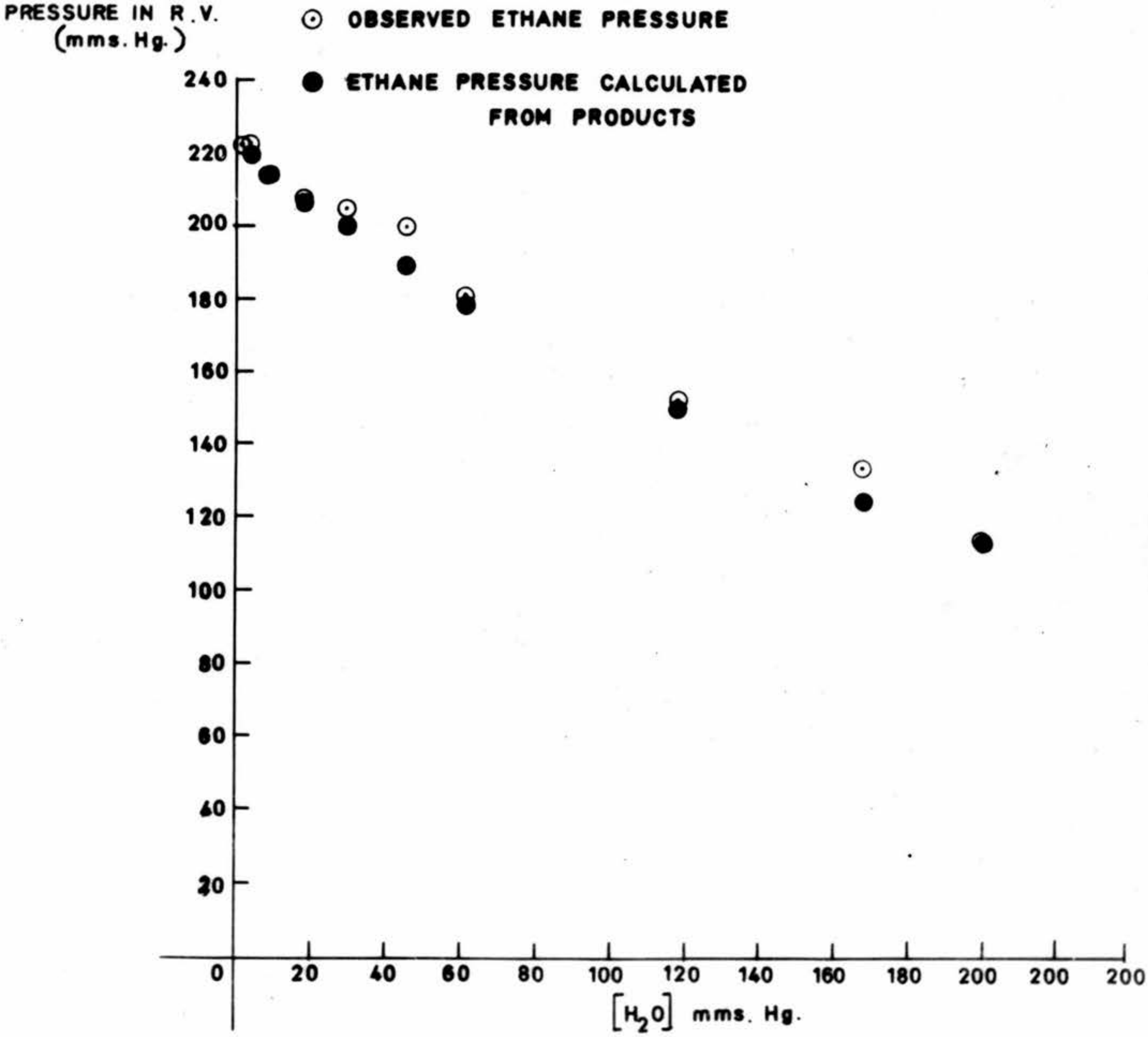
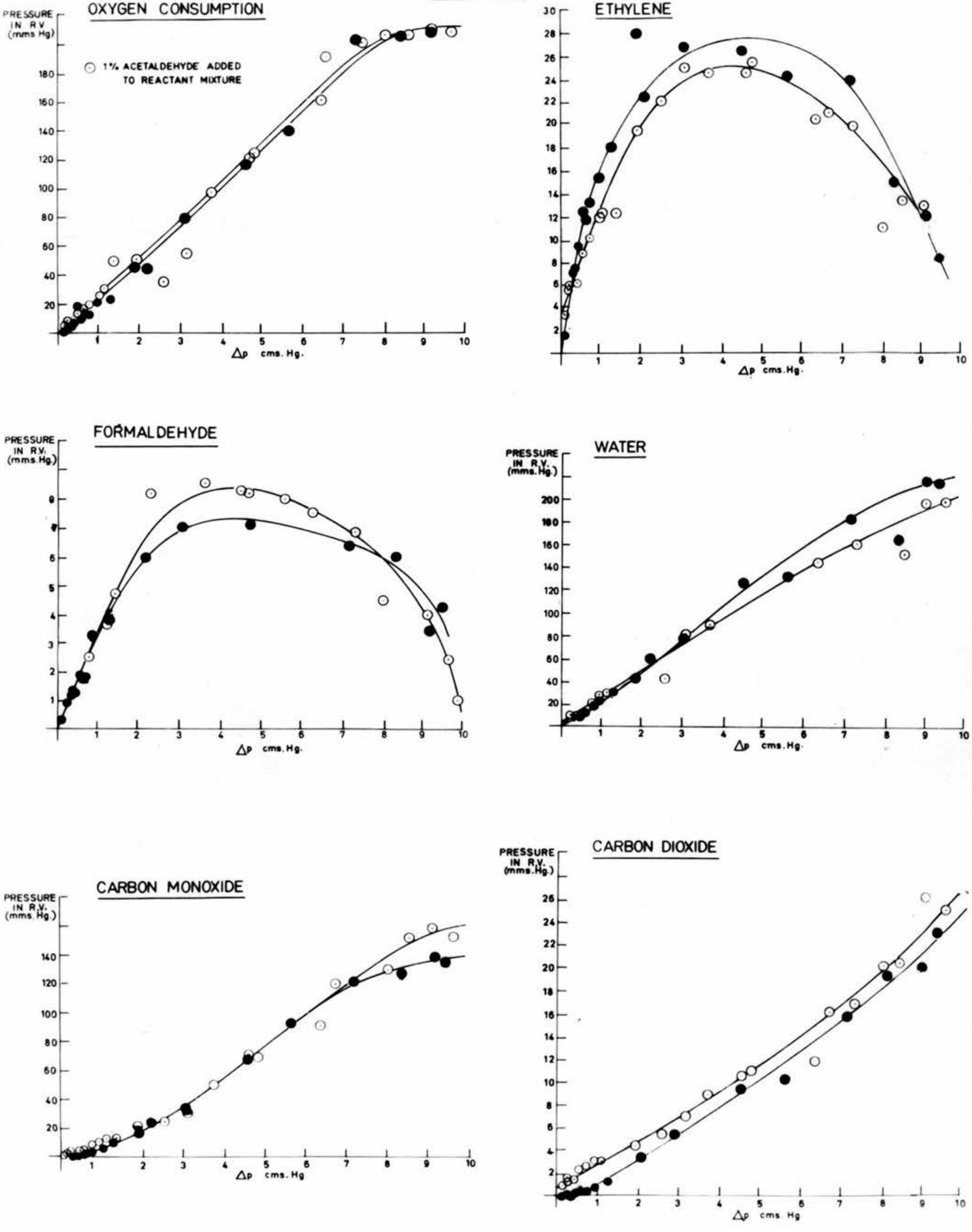
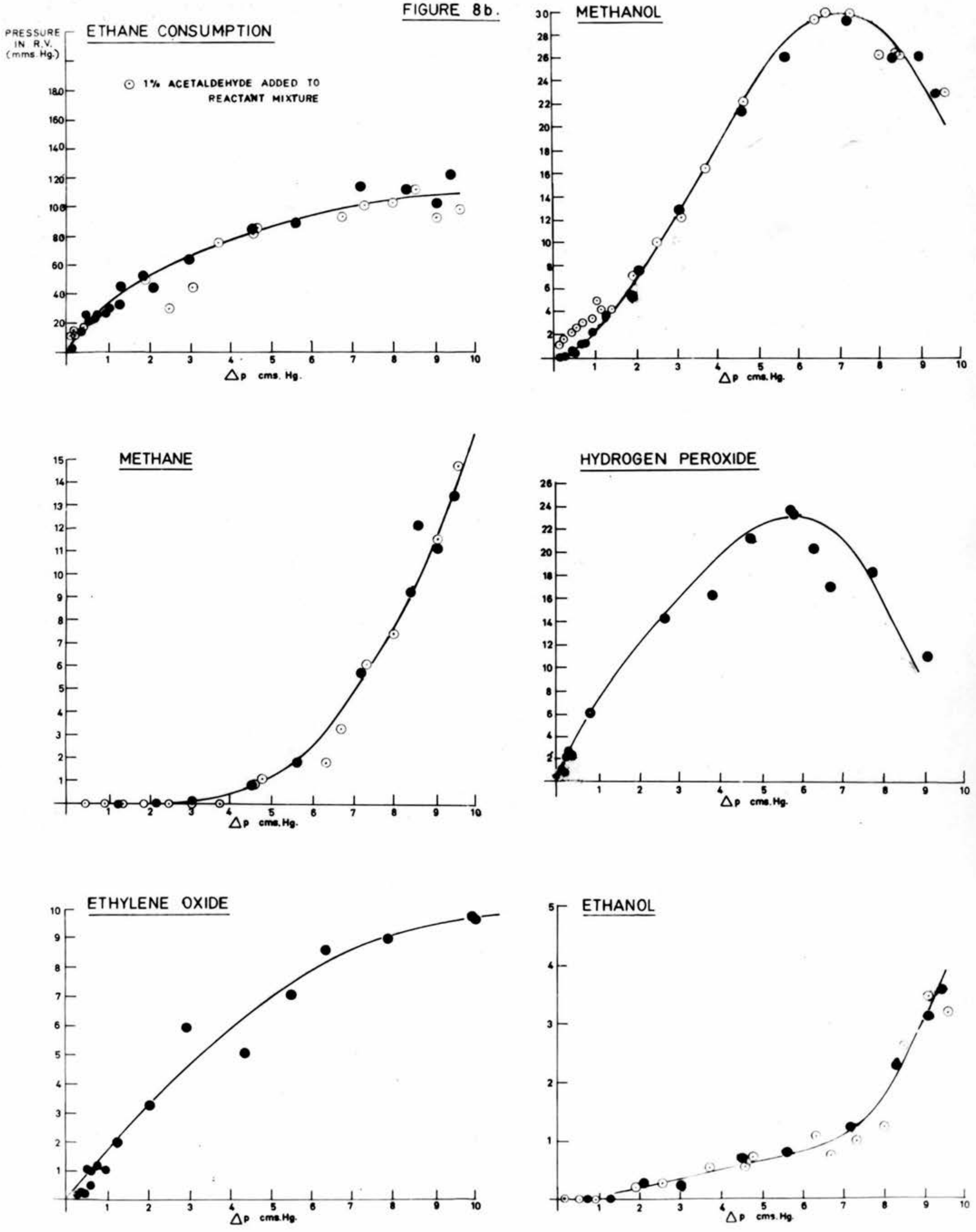


FIGURE 8a.



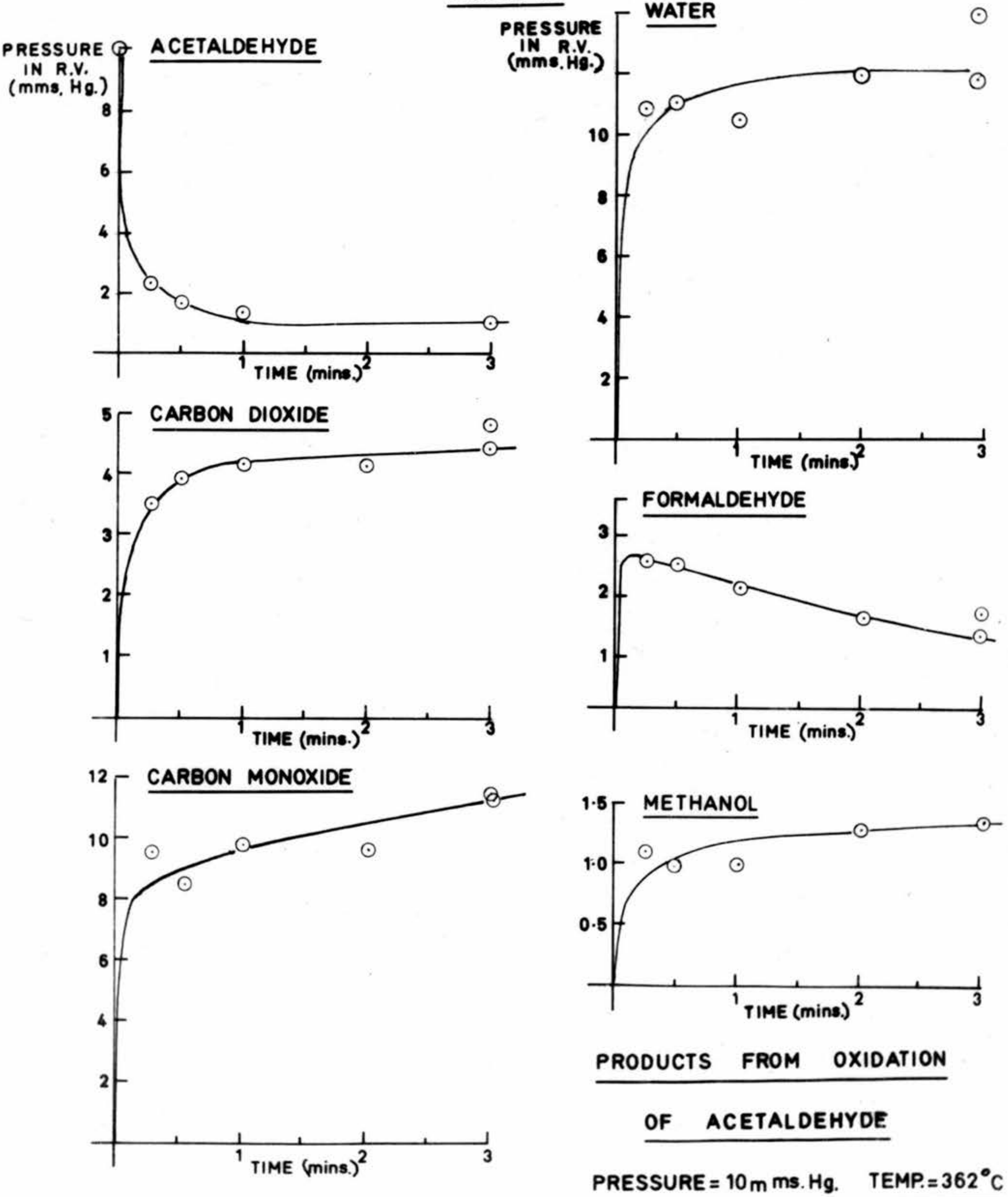
PRODUCTS FROM 1:1 MIXTURE ETHANE - OXYGEN. PRESSURE = 444 mms. Hg. TEMP. = 362 °C.

FIGURE 8b.



PRODUCTS FROM 1:1 MIXTURE ETHANE – OXYGEN. PRESSURE = 444 mms. Hg. TEMP. = 362°C.

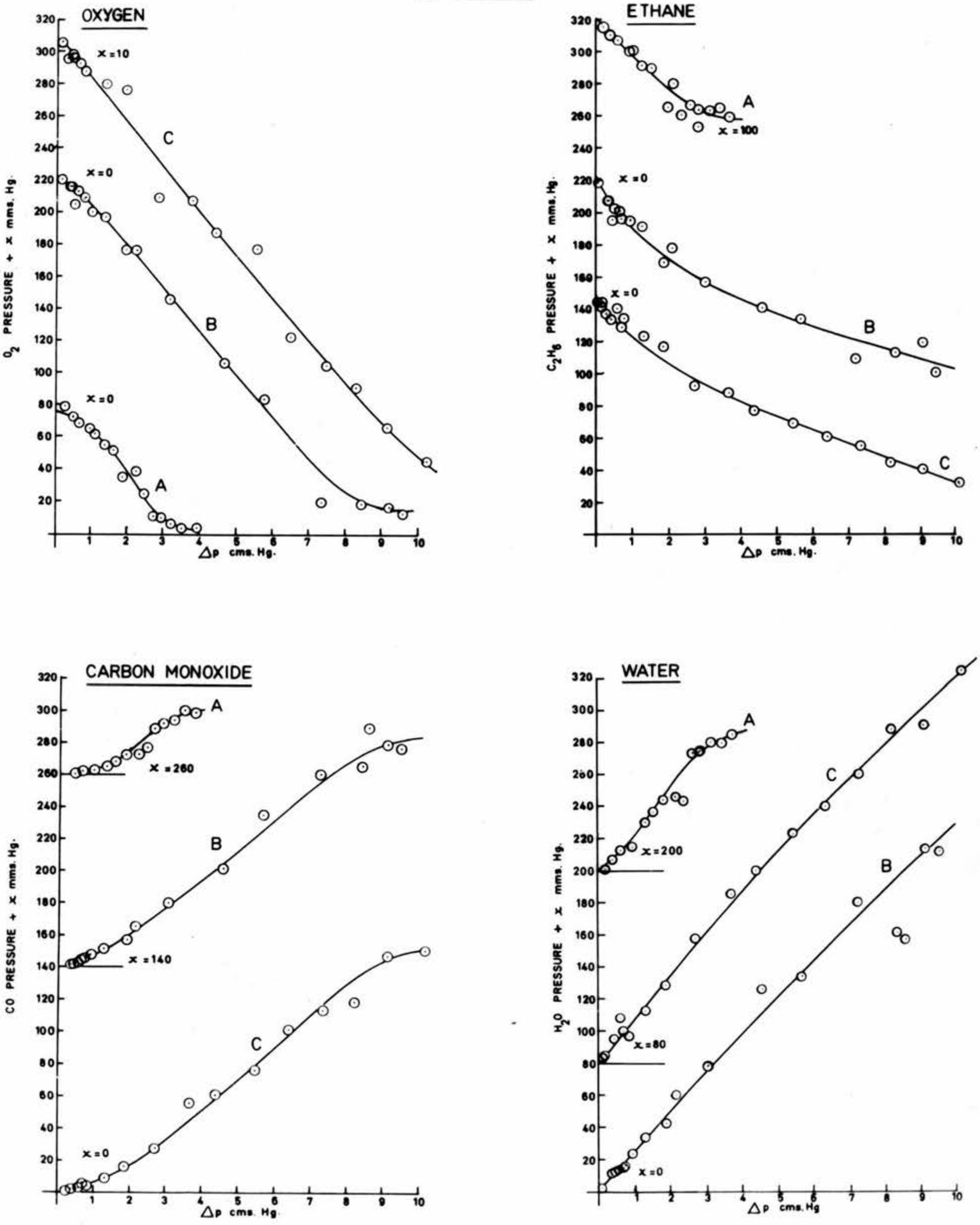
FIGURE 9.



PRODUCTS FROM OXIDATION OF ACETALDEHYDE

PRESSURE = 10 mms. Hg. TEMP. = 362°C

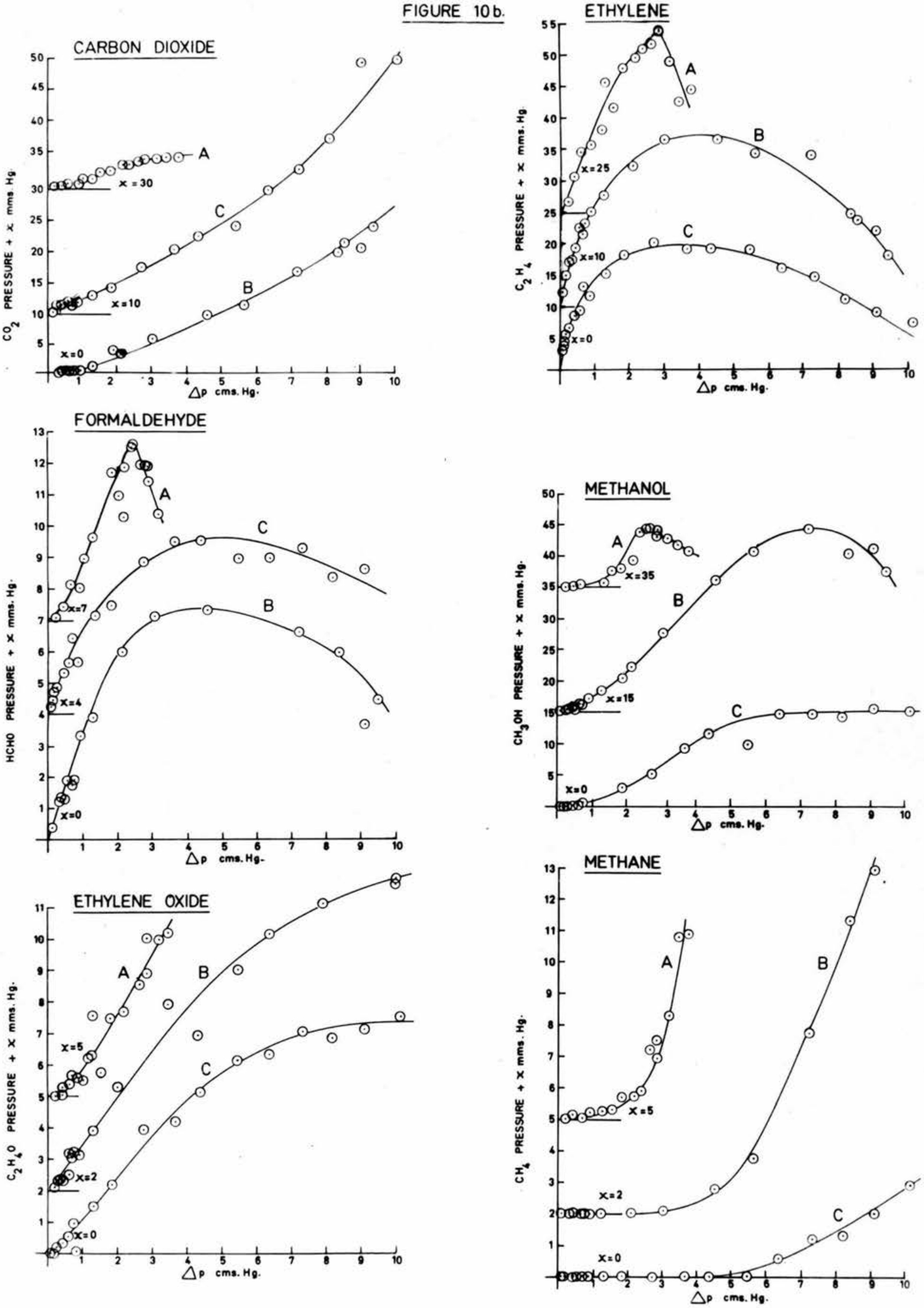
FIGURE 10 a.



EFFECT OF MIXTURE COMPOSITION ON THE YIELDS OF PRODUCTS.

A = 3:1 ; B = 1:1 ; C = 1:2 MIXTURE ETHANE - OXYGEN. TEMPERATURE = 362°C.

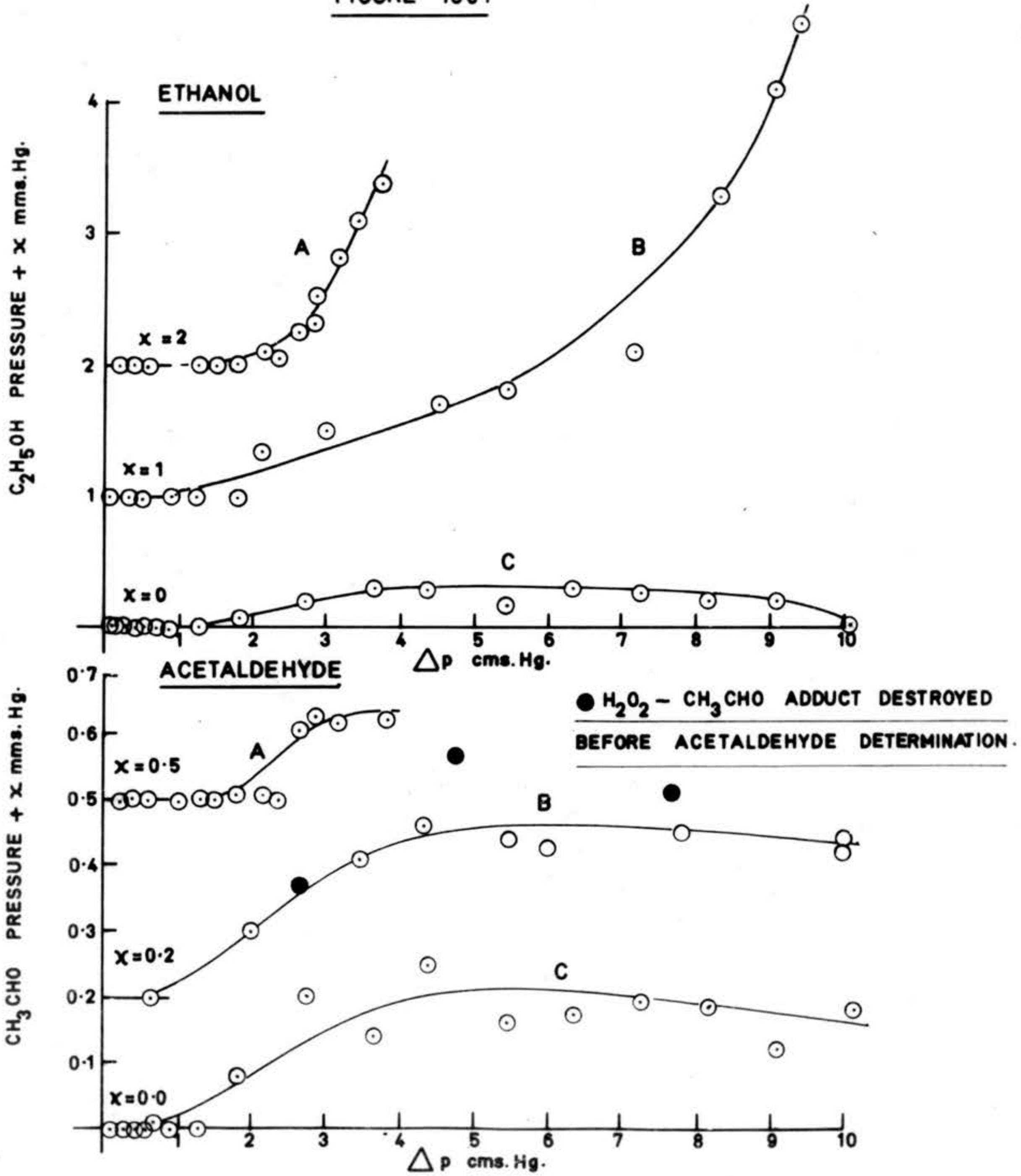
FIGURE 10b.



EFFECT OF MIXTURE COMPOSITION ON THE YIELDS OF PRODUCTS.

A = 3:1 ; B = 1:1 ; C = 1:2 MIXTURE ETHANE - OXYGEN. TEMPERATURE = 362°C

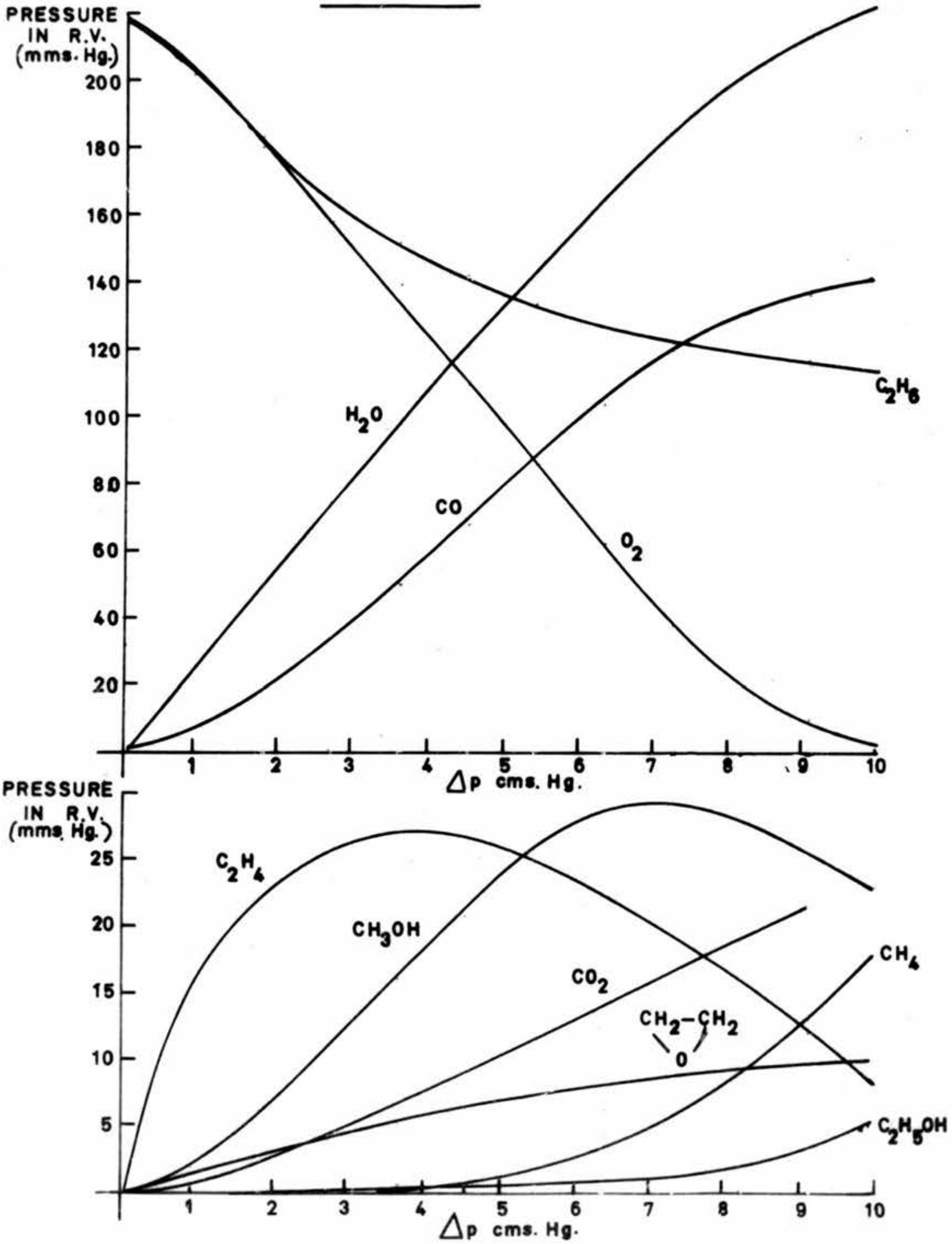
FIGURE 10c.



EFFECT OF MIXTURE COMPOSITION ON THE YIELDS OF PRODUCTS.

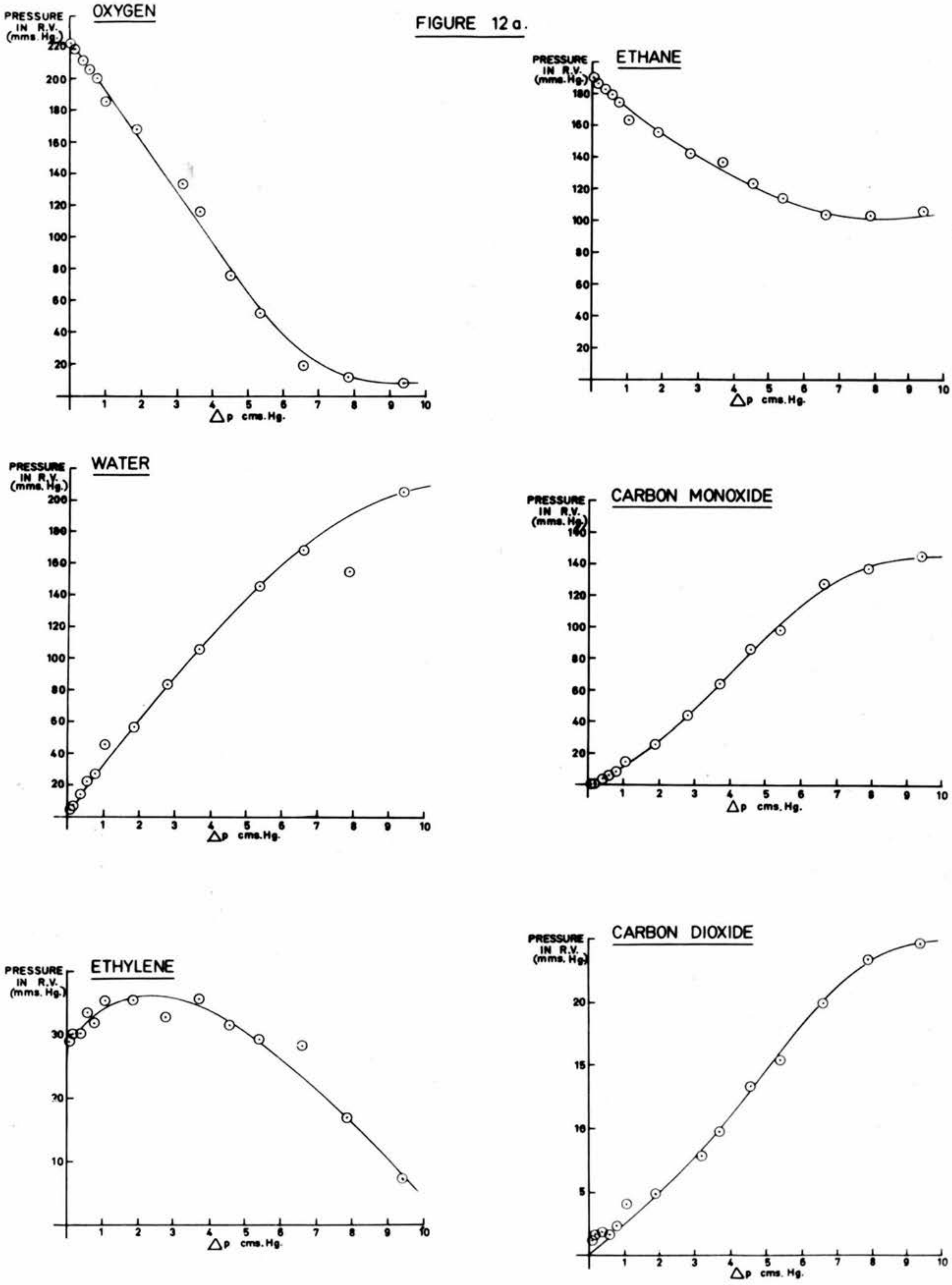
A = 3:1 : B = 1:1 : C = 1:2 MIXTURE ETHANE—OXYGEN. TEMPERATURE = 362 °C.

FIGURE 11.



PRODUCTS FROM 1:1 MIXTURE ETHANE-OXGEN. PRESS.= 444 mm.Hg.
TEMP = 362°C

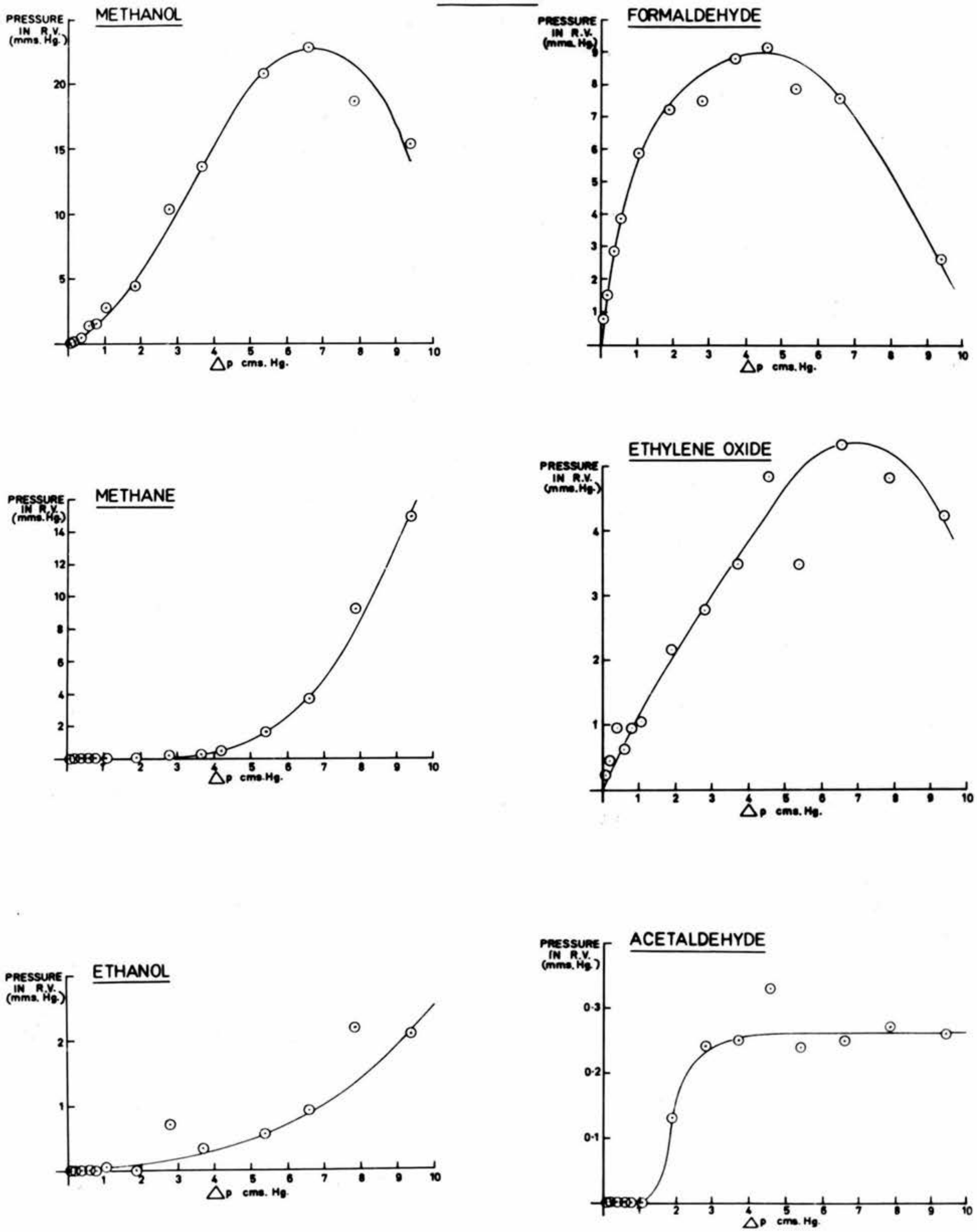
FIGURE 12 a.



PRODUCTS FROM 1 : 13·6 : 14·6 MIXTURE ETHYLENE : ETHANE : OXYGEN.

PRESSURE = 444 mms. Hg. TEMPERATURE = 362 °C.

FIGURE 12b.



METHANOL

FORMALDEHYDE

METHANE

ETHYLENE OXIDE

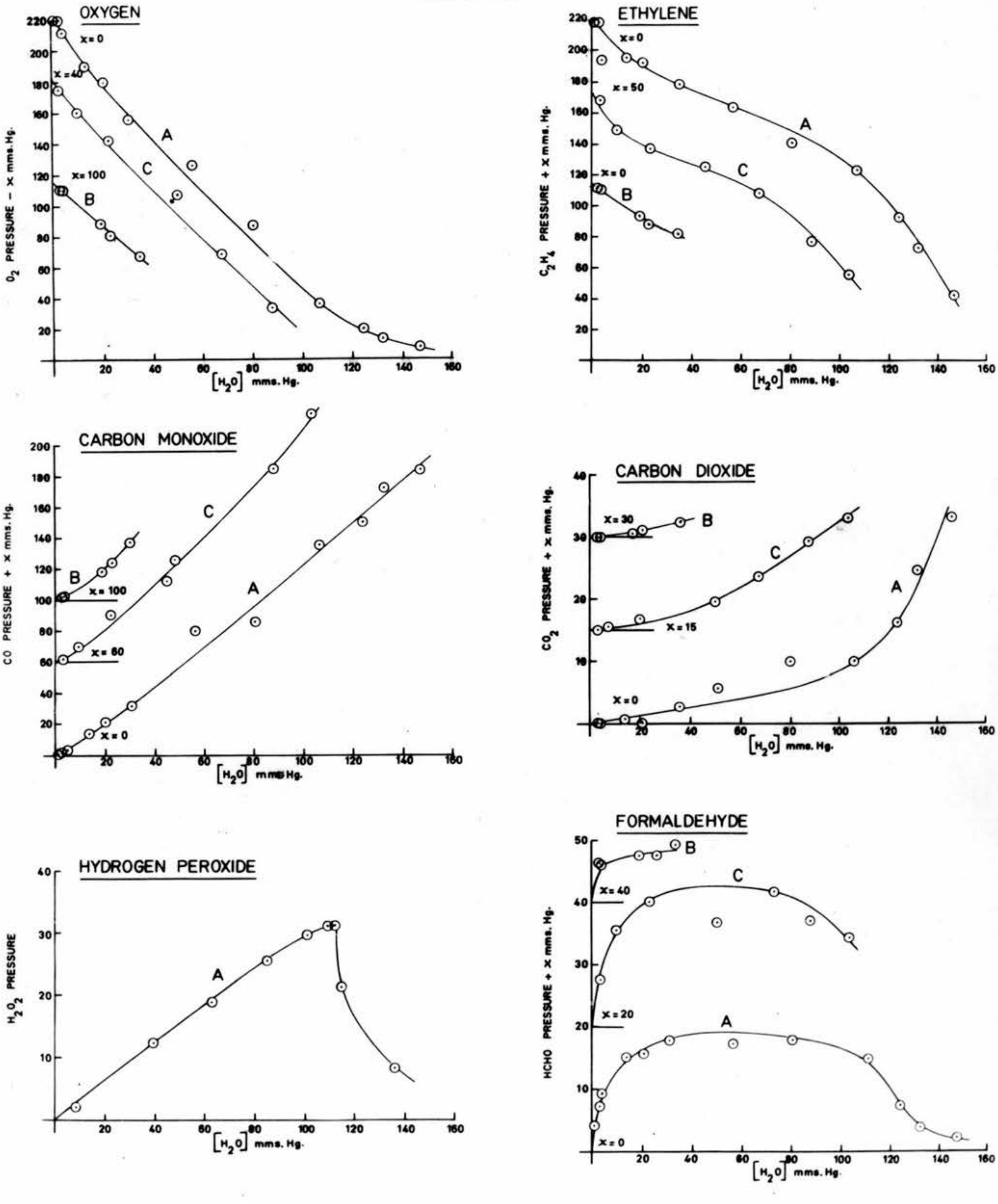
ETHANOL

ACETALDEHYDE

PRODUCTS FROM 1:13·6:14·6 MIXTURE ETHYLENE : ETHANE : OXYGEN.

PRESSURE = 444 mms. Hg. TEMPERATURE = 362 °C.

FIGURE 13a.

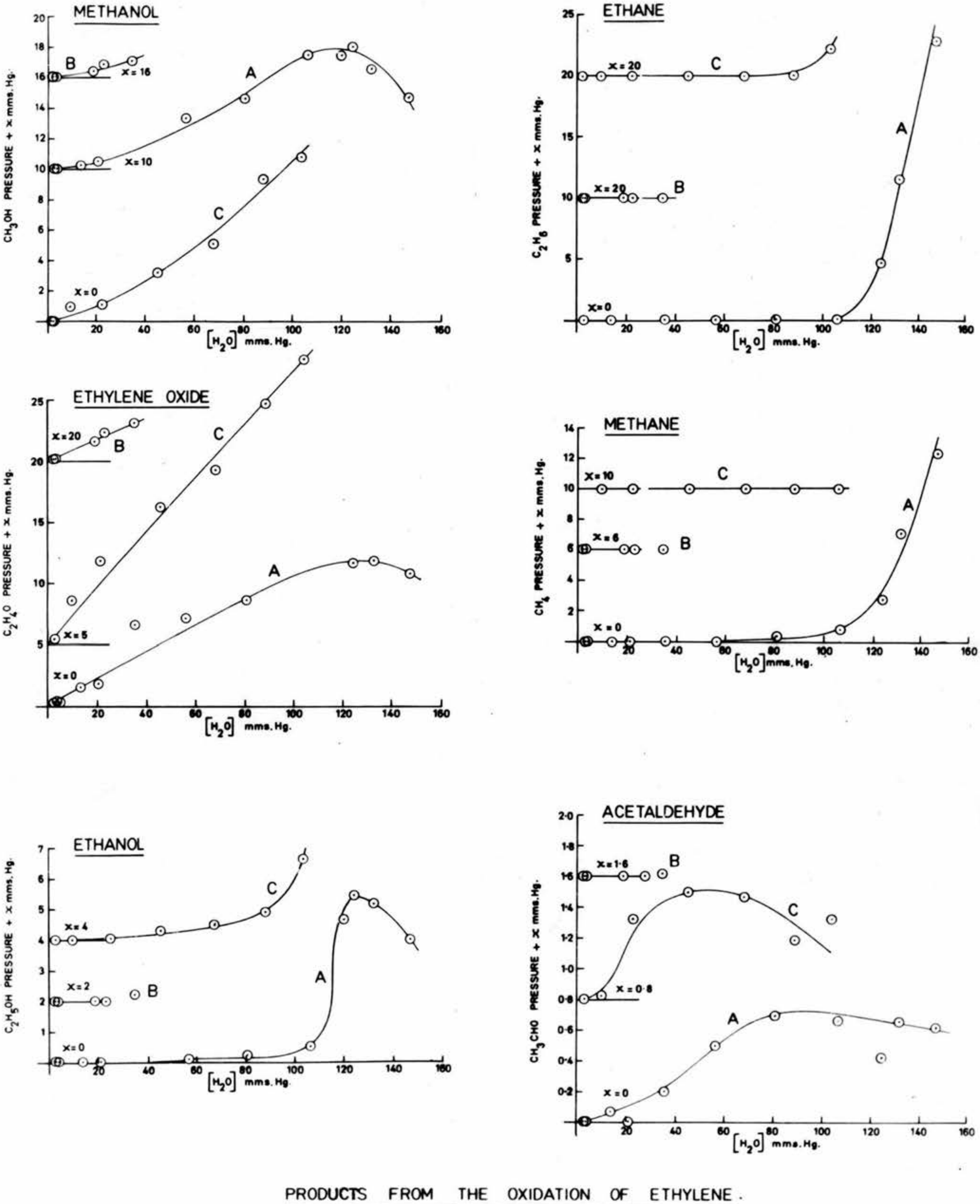


PRODUCTS FROM THE OXIDATION OF ETHYLENE.

A = 1:1 ; B = 1:2 MIXTURE ETHYLENE-OXYGEN. PRESSURE = 442 ; 335 mms.Hg. TEMP. = 362 °C

C = 1:1 MIXTURE ETHYLENE-OXYGEN. PRESSURE = 442 mms. Hg. TEMP. = 318 °C.

FIGURE 13b.

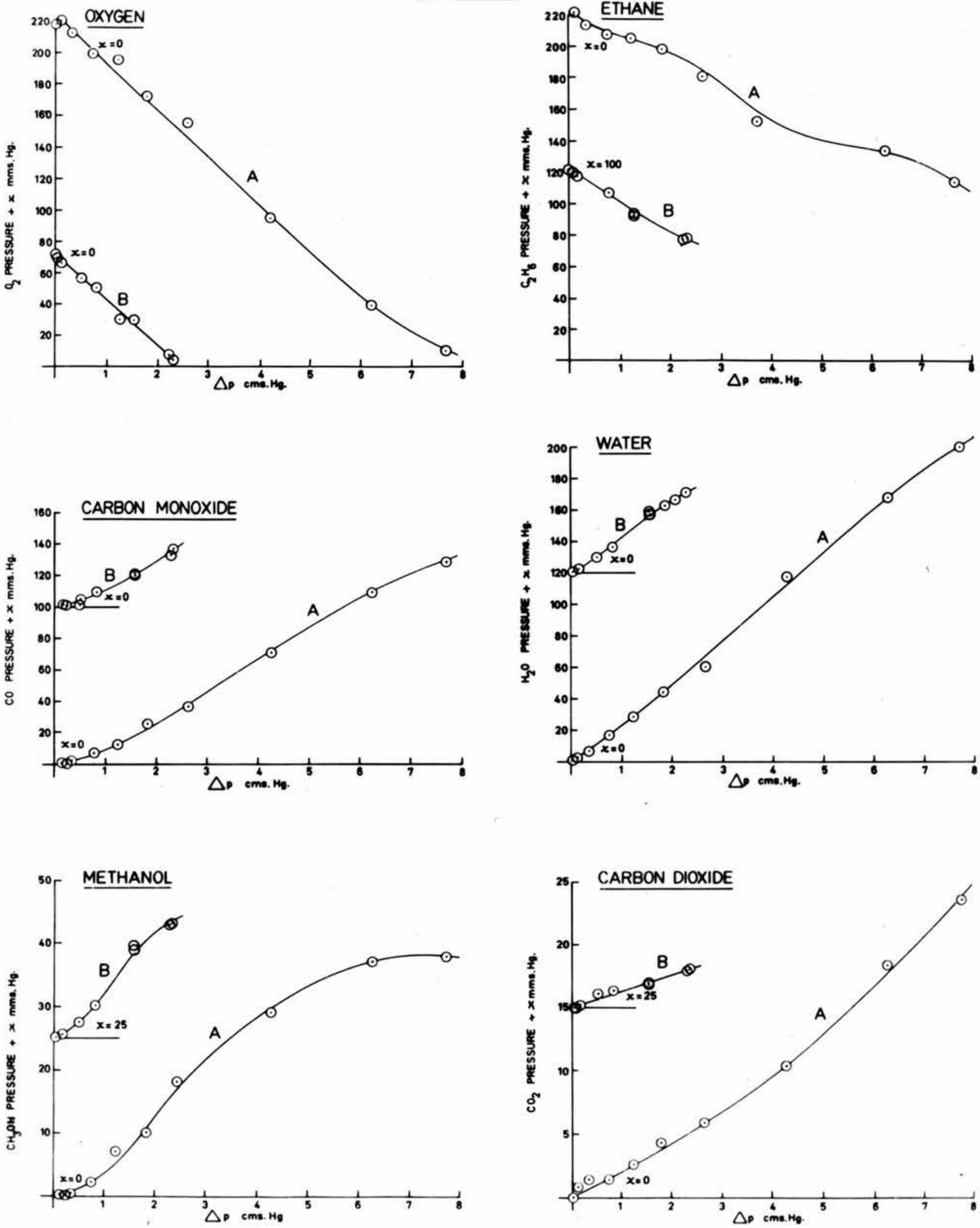


PRODUCTS FROM THE OXIDATION OF ETHYLENE.

A = 1:1 ; B = 1:2 MIXTURE ETHYLENE - OXYGEN. PRESSURE = 442 ; 335 mms. Hg. TEMP. = 362 °C.

C = 1:1 MIXTURE ETHYLENE - OXYGEN. PRESSURE = 442 mms. Hg. TEMP. = 318 °C.

FIGURE 14a.



OXYGEN

ETHANE

CARBON MONOXIDE

WATER

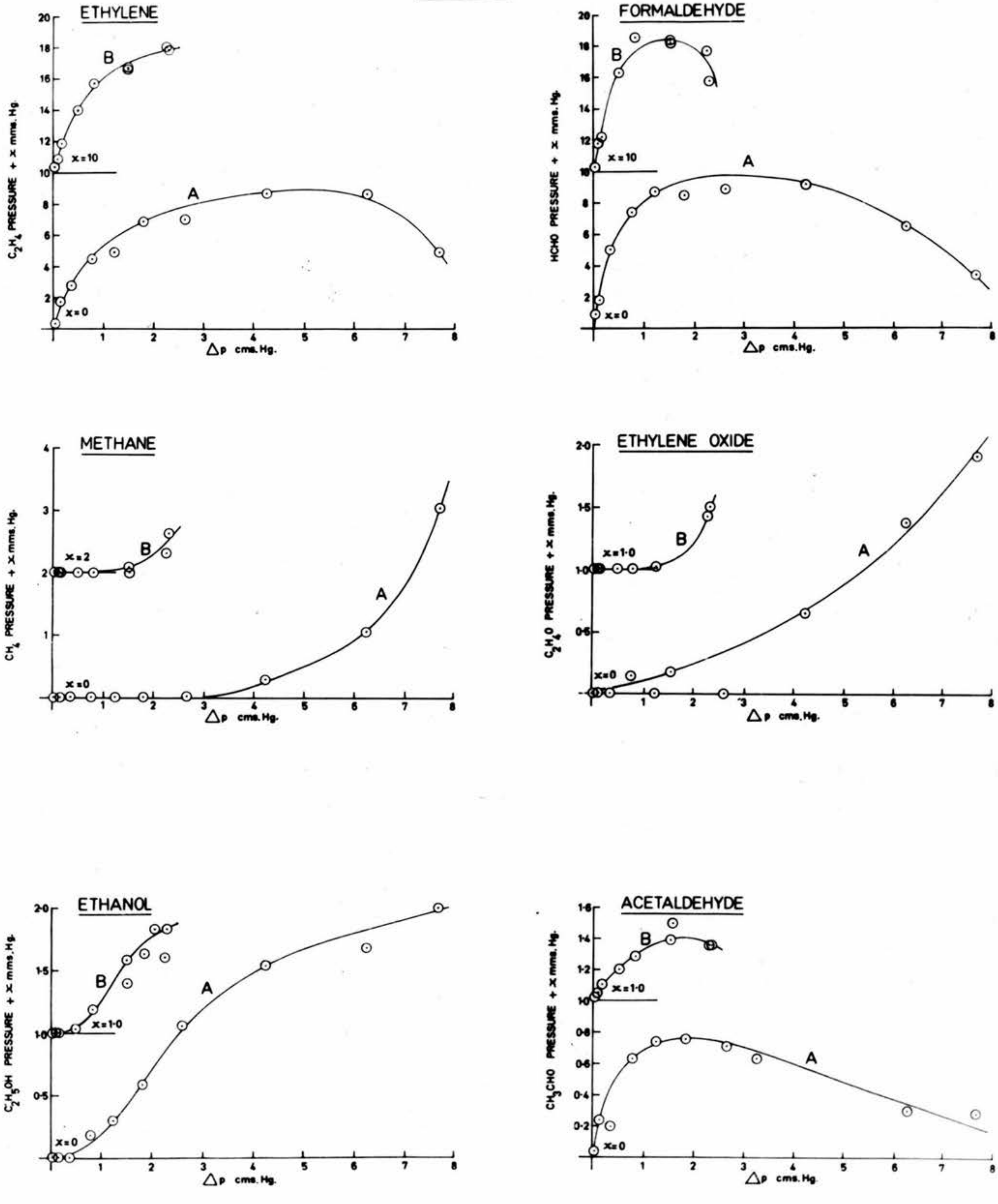
METHANOL

CARBON DIOXIDE

EFFECT OF MIXTURE COMPOSITION ON THE YIELDS OF PRODUCTS.

A = 1:1 ; B = 3:1 MIXTURE ETHANE - OXYGEN. PRESSURE = 444 ; 292 mms.Hg. TEMP. = 318 °C.

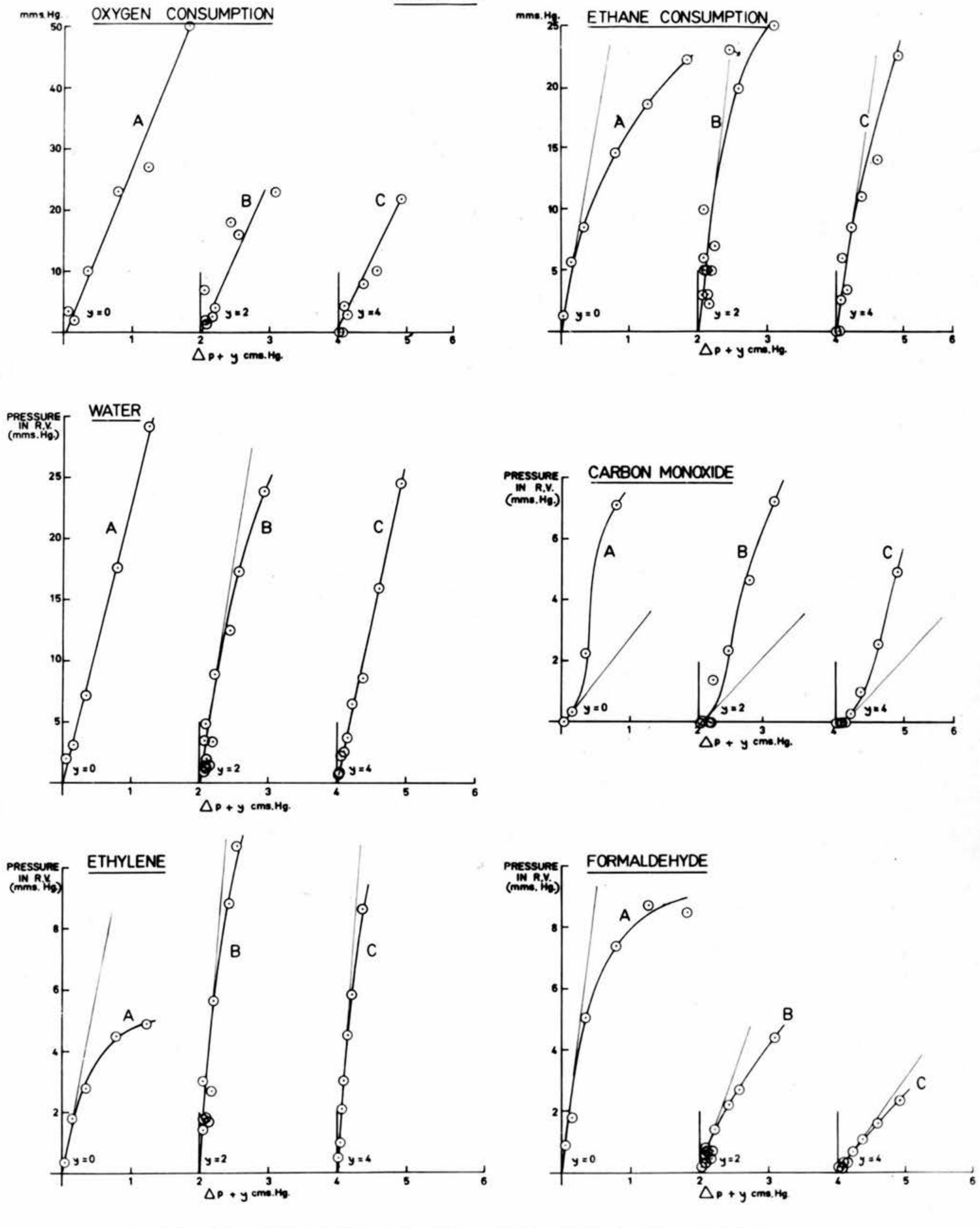
FIGURE 14b.



EFFECT OF MIXTURE COMPOSITION ON THE YIELDS OF PRODUCTS.

A = 1:1 : B = 3:1 MIXTURE ETHANE-OXYGEN. PRESSURE = 444 : 292 mms. Hg. TEMP. = 318°C.

FIGURE 15.

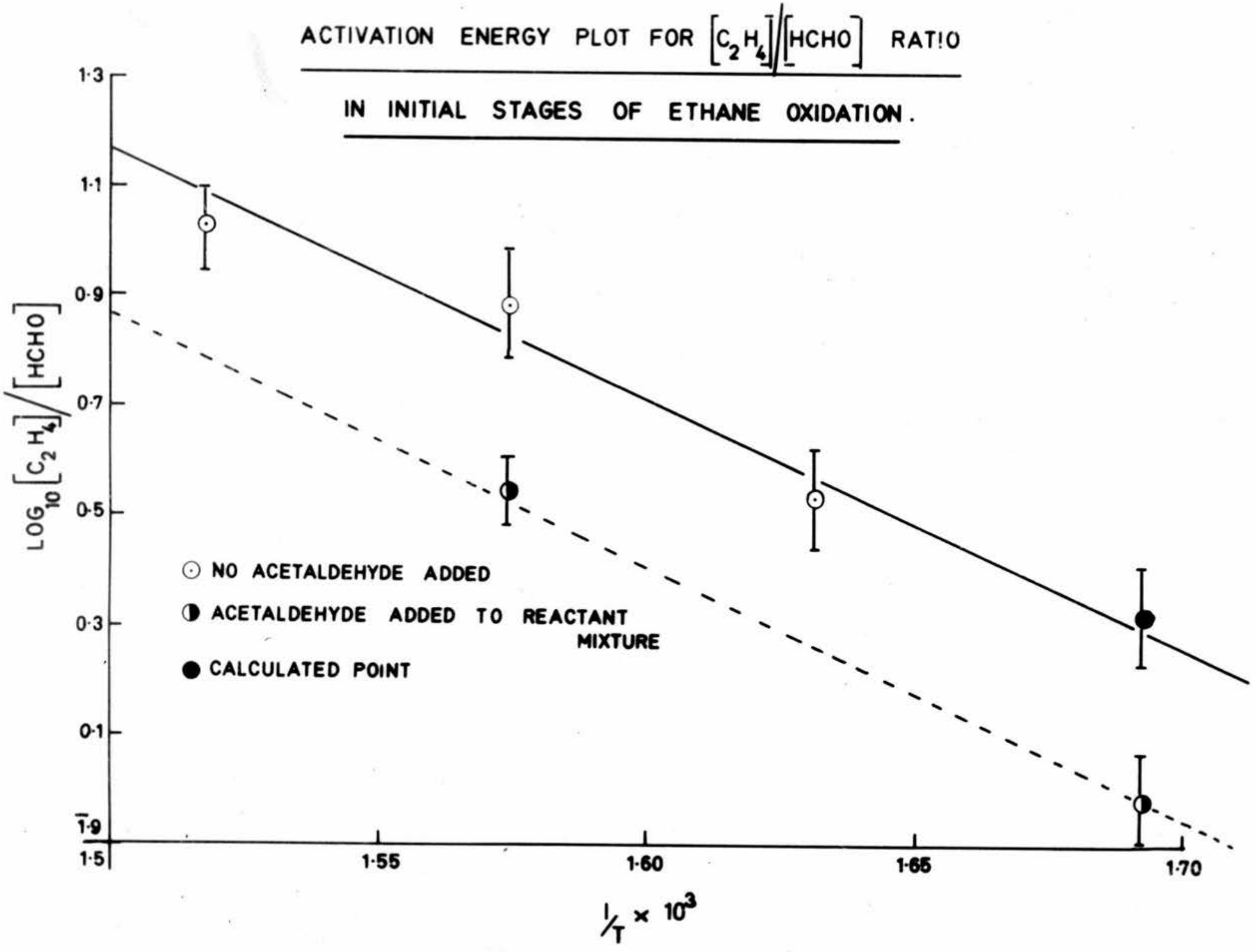


EFFECT OF TEMPERATURE ON THE INITIAL YIELDS OF PRODUCTS.

1:1 MIXTURE ETHANE-OXYGEN. PRESSURE = 444 mms.Hg.

A = 318 °C. B = 340 °C. C = 386 °C.

FIGURE 16.

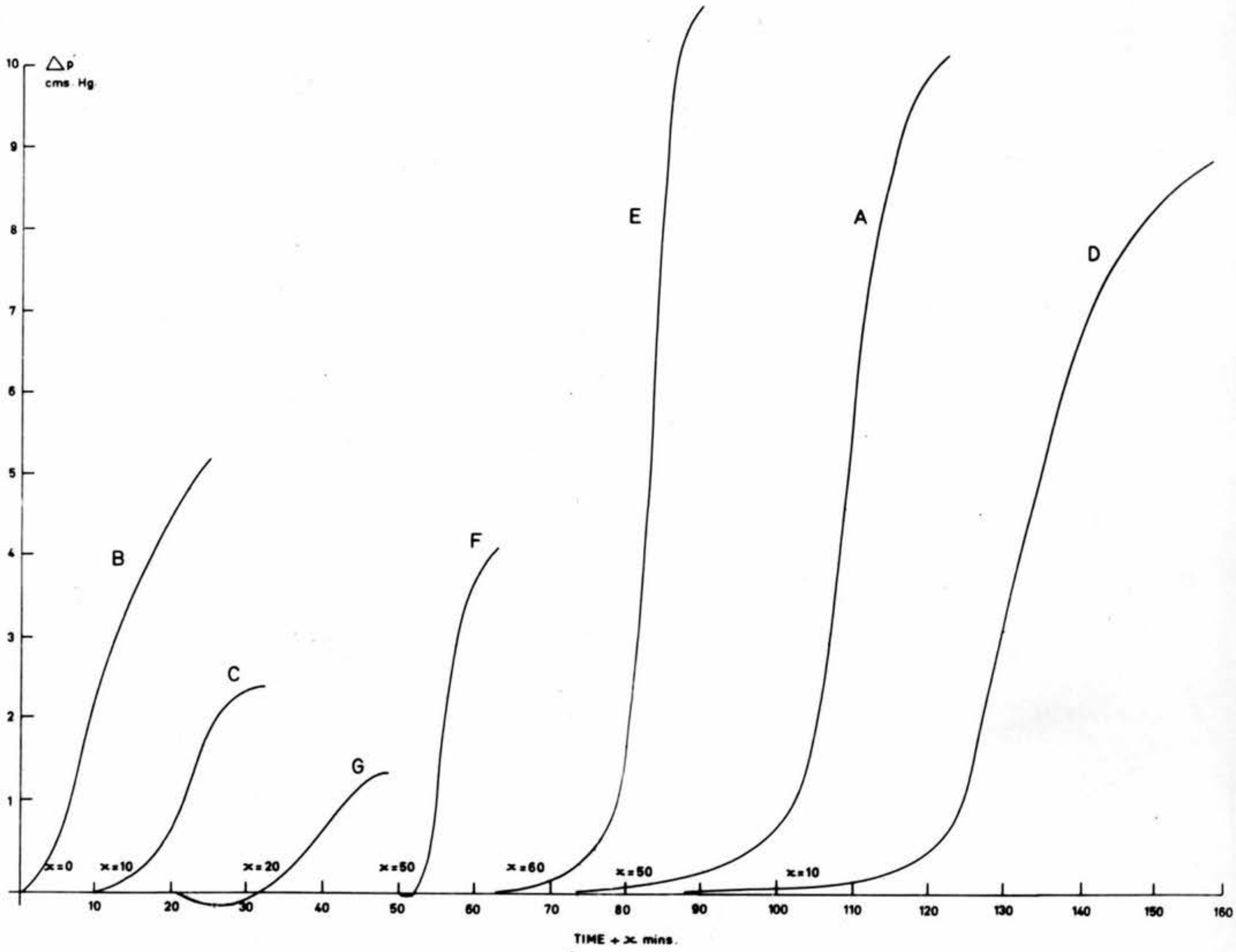


ACTIVATION ENERGY PLOT FOR $[C_2H_4]/[HCHO]$ RATIO

IN INITIAL STAGES OF ETHANE OXIDATION.

FIGURE 17

PRESSURE — TIME CURVES FOR ETHANE AND ETHYLENE OXIDATIONS.



A — 1:1 MIXTURE ETHANE-OXYGEN. PRESSURE = 444 mms.Hg. TEMPERATURE = 362 °C. NO ACETALDEHYDE ADDED.

B 1:1 MIXTURE ETHANE-OXYGEN. PRESSURE = 444 mms.Hg. TEMPERATURE = 318 °C. 0·1% ACETALDEHYDE ADDED.

C 3:1 MIXTURE ETHANE-OXYGEN. PRESSURE = 292 mms.Hg. TEMPERATURE = 318 °C. 0·1% ACETALDEHYDE ADDED.

D 1:1 MIXTURE ETHANE-OXYGEN. PRESSURE = 442 mms.Hg. TEMPERATURE = 340 °C. NO ACETALDEHYDE ADDED.

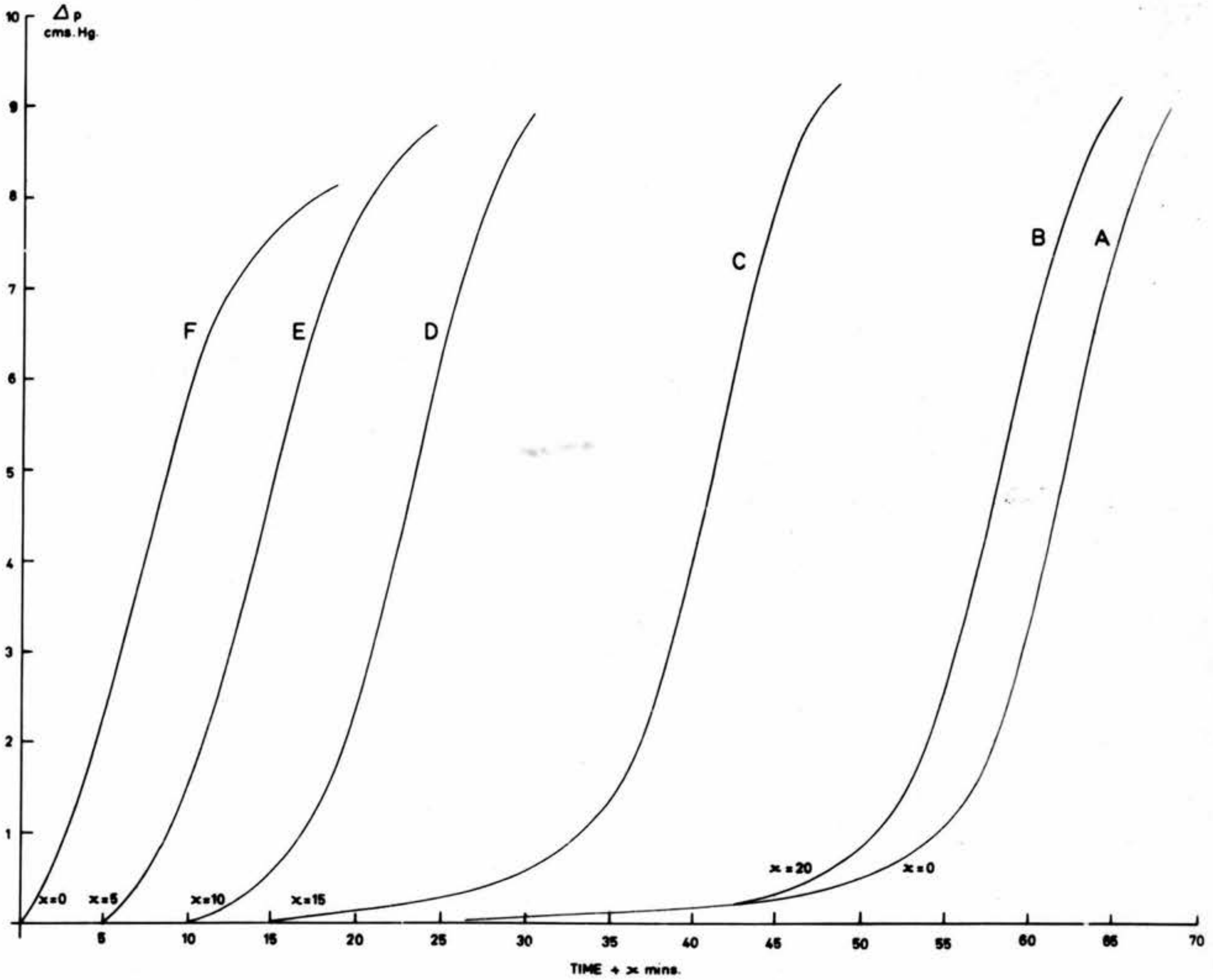
E 1:1 MIXTURE ETHANE-OXYGEN. PRESSURE = 444 mms.Hg. TEMPERATURE = 386 °C. NO ACETALDEHYDE ADDED.

F 1:1 MIXTURE ETHYLENE-OXYGEN. PRESSURE = 442 mms.Hg. TEMPERATURE = 362 °C. NO ACETALDEHYDE ADDED.

G 1:1 MIXTURE ETHYLENE-OXYGEN. PRESSURE = 442 mms.Hg. TEMPERATURE = 318 °C. NO ACETALDEHYDE ADDED.

FIGURE 18.

EFFECT OF ACETALDEHYDE ON PRESSURE-TIME CURVES FOR ETHANE OXIDATION.

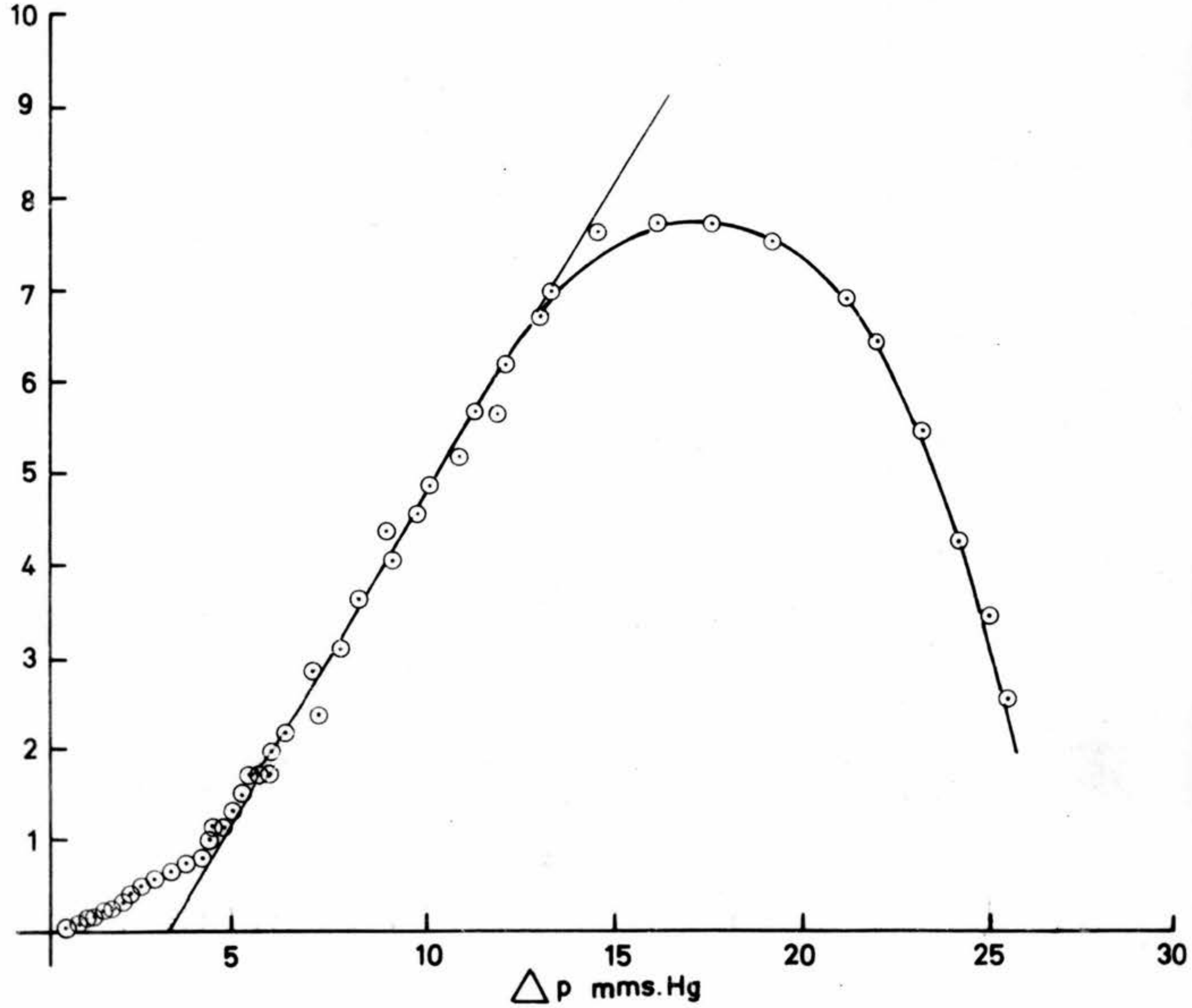


1:1 MIXTURE ETHANE-OXYGEN. PRESSURE = 444 mms. Hg. TEMPERATURE = 362 °C.

ADDED ACETALDEHYDE :-

A – 0·0 mms. ; B – 0·4 mms. ; C – 1·1 mms. ; D – 2·1 mms. ; E – 4·3 mms. ; F – 8·3 mms.

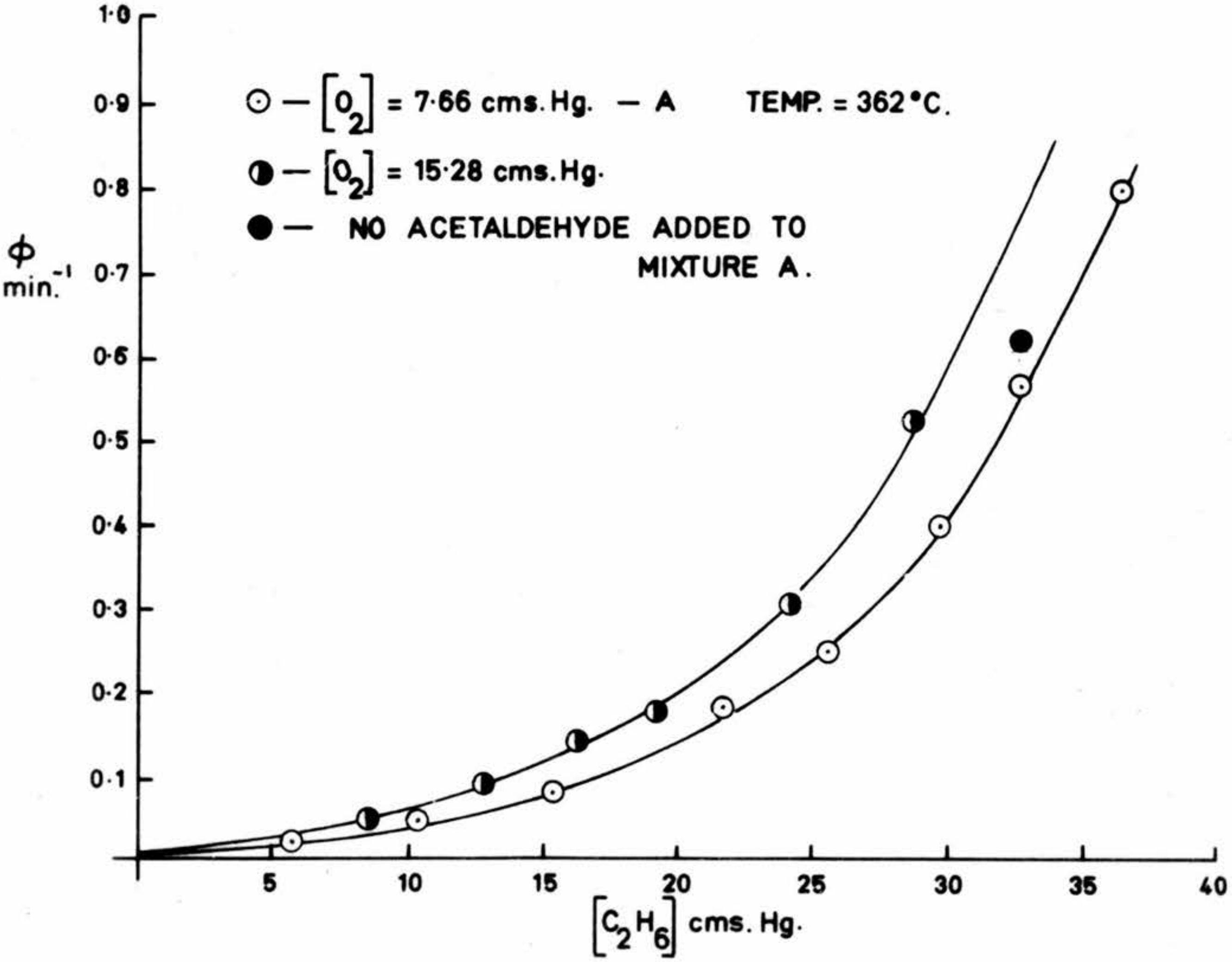
FIGURE 19.



TYPICAL PLOT OF RATE AGAINST PRESSURE RISE.

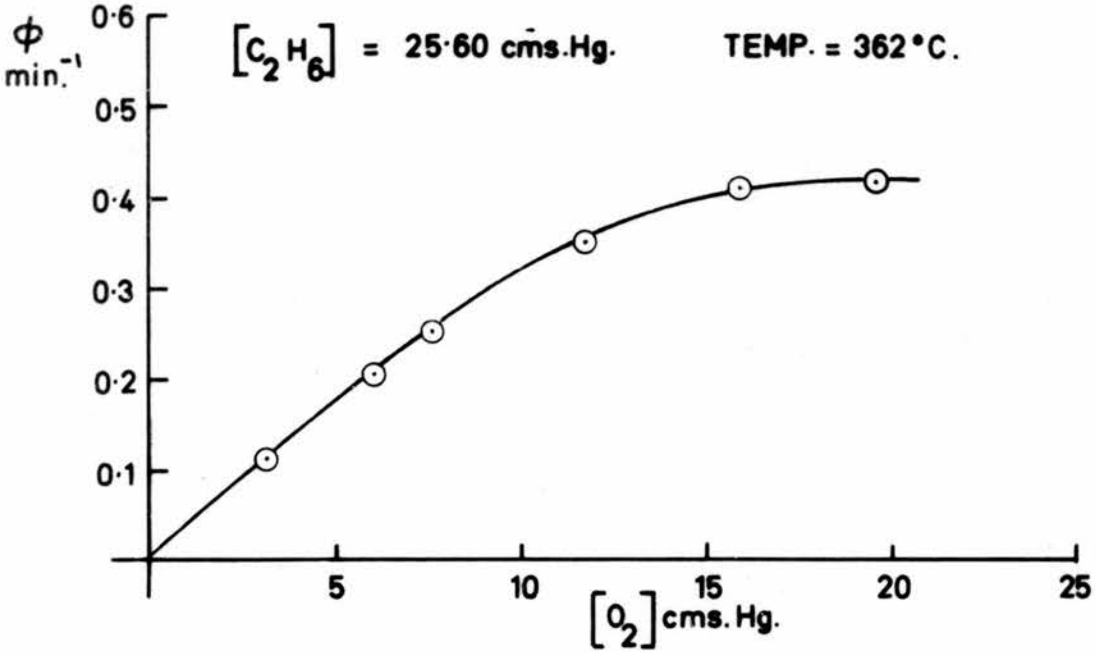
4:1 MIXTURE ETHANE-OXYGEN. PRESSURE = 444 mms. Hg. TEMP. = 362 °C.

FIGURE 20.



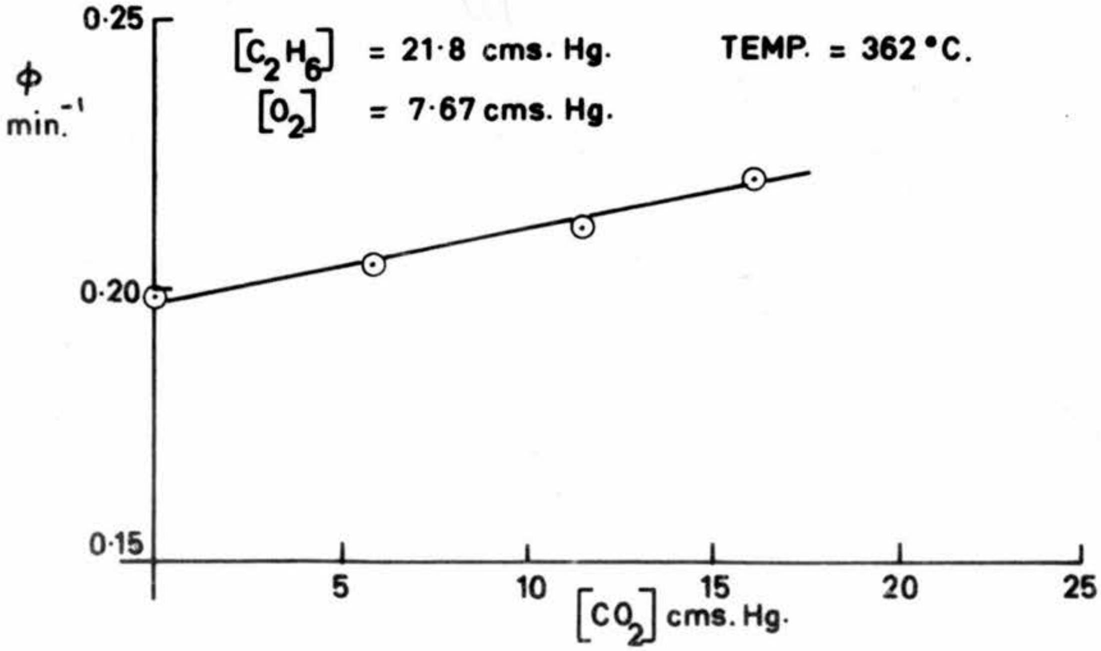
PLOT OF ACCELERATION CONSTANT vs. INITIAL ETHANE CONCENTRATION.

FIGURE 21.



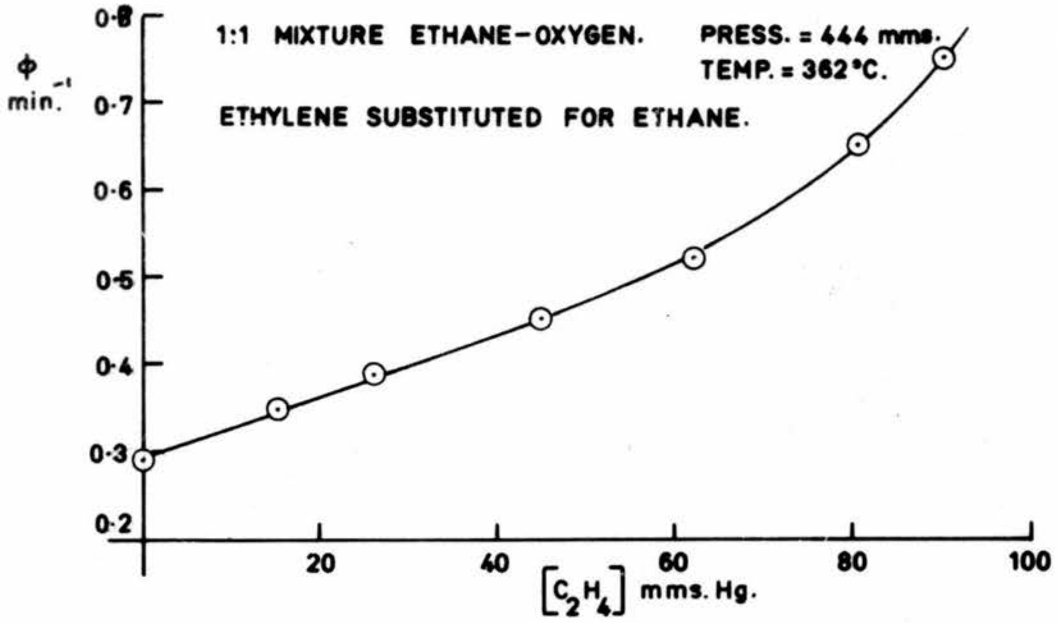
PLOT OF ACCELERATION CONSTANT vs. INITIAL OXYGEN CONCENTRATION.

FIGURE 22.



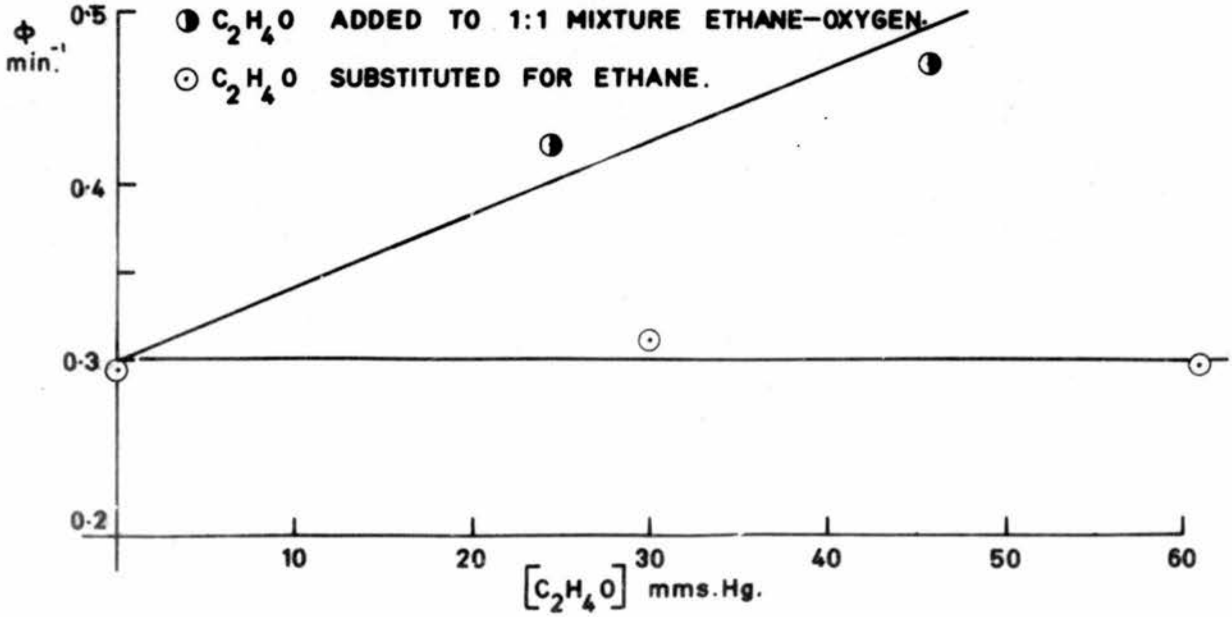
PLOT OF ACCELERATION CONSTANT vs. INERT GAS PRESSURE.

FIGURE 23.



PLOT OF ACCELERATION CONSTANT vs. PRESSURE OF SUBSTITUTED ETHYLENE.

FIGURE 24.



PLOT OF ACCELERATION CONSTANT vs. ETHYLENE OXIDE PRESSURE.