Kinetics of Gaseous Reactions.

The Low Temperature Oxidation of Aliphatic Ethers.

Abstract of
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One of the most remarkable characteristics of the low-temperature, slow-oxidation of organic compounds is the influence of structure on the reaction rate. With the normal paraffin hydrocarbons, for example, the rate of oxidation, in strong contrast to the rate of pyrolysis, increases markedly with the length of the carbon chain (1). Structural sensitivity has recently been found to be quite general and any alteration in the molecule whether by branching or substitution of chloro, amino or carbonyl groups is reflected in the oxidation rate (2). The primary purpose of the present investigation is to determine the influence of R'O substitution (regarding an ether, R'O-R, as a hydrocarbon with an alkoxy substituent) upon oxidation.

It has been suggested that the sensitivity of oxidation reactions to the structure of the combustible substance may have, in part at least, a kinetic explanation (2). This hypothesis is reviewed in the thesis, and in its essentials it may be stated as follows. Low-temperature, slow oxidation takes place by a mechanism depending on the formation of a peroxide which slowly decomposes into radicals, thereby setting up branching chains. The peroxide forms by a series of reactions of the following type: $RH + O_2 \rightarrow R\text{-} + HO_2$; $R\text{-} + O_2 \rightarrow RO_2\text{-}$, and $RO_2\text{-} + RH \rightarrow ROOR''$ (where R'' may be H). Decomposition of the peroxide molecule leads to RO- and R''O-

which in general break down, for example, by the reaction $R_1CH_2O- \longrightarrow R_1-$ + HCHO. The smaller radical reacts further and may either continue the chain or terminate it.

Solution of the rate equations for the individual reaction steps shows that the rate of oxidation depends on the rate of initial attack of oxygen on the organic substance and also on the relative ease of splitting of the peroxide bond. Both factors may be influenced by the structure of the organic reactant, but because of the peculiar kinetics of the branching chain reaction, the oxidation rate gives a magnified and sensitive measure of the influence of the structure of R on the -O-O- linkage, the rupture of which is responsible for branching. The results of previous investigations indicate that the peroxide bond is weakened by substituents in R which are electron attractive (i.e. exert an inductive effect represented by -I) and is strengthened by the introduction of methyl groups which have a + I effect. This is in agreement with the view (3) that bonds between strongly electronegative elements should be strengthened by attachment of electron repelling groups since such groups facilitate the expansion of atomic orbitals and allow increased over-lap without the occurrence of nuclear repulsion.

The second factor on which the rate of oxidation depends is the rate of the chain-initiation process. Before taking part in the initiation reaction the attacking oxygen must be

changed, more or less completely, into the biradical form. In this change electrons must be drawn from the O=O bond, and the very initial stages of the re-distribution may well be helped by the action of a positive centre at the seat of reaction which would tend to draw electrons towards it. If this were so -I substituents would favour attack by creating the necessary positive centre, while +I substituents, such as the methyl group, would weaken the attack. Thus it appears that if the influence of substituents can be assessed in terms of the ease of approach of the attacking agent and the initiation of the requisite re-organisation, the effects of substitution on both the chain-branching and chain-initiating steps are in the same direction and tend to reinforce one another.

Apart from the influence of structure on the rate of oxidation, the most striking kinetic characteristics which this scheme summarises are:

(a) the autocatalytic nature of the reaction;

(b) the increase of the reaction rate with concentration of organic reactant;

(c) the independence, over a considerable range, of initial oxygen pressure and the reaction rate. In fact, an elaboration of the theory (4) predicts that oxygen in excess will have an inhibitory effect on the rate.

If the oxidation of ethers takes place according to a mechanism basically similar to that which has just been described, these kinetic features should be in evidence.

The object of the present investigation is to determine the extent to which the reactions of ethers are comparable in mechanism to those of other compounds previously studied, and where the mechanisms are comparable, what is the influence of the alkoxy group.

The experimental methods employed were similar to those used in previous work on the oxidation of paraffins, amines and ketones in this laboratory. Ether vapour and oxygen were admitted separately to a closed pyrex reaction vessel at constant temperature and the reaction was followed by the change in pressure and by chemical analysis.

In the kinetics of their slow oxidation dimethyl, methyl ethyl, methyl normal-propyl, diethyl, and di-normal-propyl ethers are generally similar to the other organic compounds which have been studied. During the combustion of ethers the pressure decreases at first and then increases, the rate passing through a maximum before the end of the reaction. The maximum rate of oxidation increases with the initial pressure of ether but is reduced by oxygen in excess. The length of time between the admission of the reactants to the reaction vessel and the establishment of the maximum rate (the induction period) is shortened by an increase in initial ether pressure but is lengthened by an increase in the initial pressure of oxygen in the range studied. In the low temperature region an increase in temperature favours

oxidation. The maximum in the concentration of peroxides of the ROOR" type during the slow reaction coincides with the maximum rate of pressure increase. The slow oxidation of ethers is insensitive to additions of inert gas, but the nature of the surface of the reaction vessel may influence the pressure change during the reaction, without greatly affecting the formation of peroxides. With standardization of experimental procedure reasonable reproducibility can be achieved.

Previous results on the maximum rate of oxidation of normal-pentane and the corresponding induction period having been generally confirmed in the present apparatus, the relative rates of oxidation of the ethers and pentane are as follows:

Compound	Relative Rate				
Pentane	1				
Dimethyl ether	25	1			
Methyl n-propyl ether	175	7	1		
Methyl ethyl ether	175	7	1.1	1	
Di-n-propyl ether	1300	50	7	7	1
Diethyl ether	2500	100	14	14	2

The rate of oxidation of di-iso-propyl ether is much lower than that of diethyl ether at 170°C.; in fact, it was not possible to make kinetic measurements with di-iso-propyl ether because no appreciable reaction occurs over a wide range of temperatures and pressures below those at which cool flames

are observed.

The similarity of the formal kinetics of the low-temperature oxidation of ethers to those of the unsubstituted paraffins, chloro-compounds, amines and ketons indicates that the oxidation of ethers occurs by the same basic mechanism proposed for the hydrocarbons. If the relative ease of oxidation of the ethers, compared to pentane, can be accounted for by the inductive effect of substituents according to the hypothesis outlined above, then the R'O group is electron attractive and exerts a -I effect. The inductive action of the alkoxy group deduced from oxidation measurements agrees with the -I effect of CH_3O determined by independent means. Furthermore, a comparison of the relative rates of oxidation of the ethers themselves shows that the -I effect of the ethoxy and propoxy group is greater than that of the methoxy.

The stabilising influence of methyl groups, and their inherent resistance to oxidation, so prominent in the behaviour of paraffins, are confirmed by the stability of dimethyl and di-iso-propyl ethers when compared with other ethers.

Ethers do not show the progressive and marked increase in the rate of oxidation with increasing length of the normal carbon chain which has been observed with the other organic compounds previously studied. It appears that the inductive action of the alkoxy group has to some extent saturated the response of the molecule, and the effect of the introduction

of -O- is not reinforced by lengthening of the carbon chain.

Early in the investigation it was found that relatively large quantities of peroxides were formed during the oxidation of ethers. According to current theories, compounds of this type play an important part, not only in the low-temperature, slow oxidation, but also in the cool flame reaction and it was thought that the oxidation reactions of ethers might be eminently suitable for a study of the cool flame mechanism. The most satisfactory hypothesis of cool flame formation postulates that peroxides play a dual role; on the one hand, they may dissociate and lead to the branching chain reaction characteristic of the slow oxidation, or on the other hand, above a critical temperature they may largely decompose by an alternate route which does not lead to branching but gives rise to the cool flame. This mechanism gives a satisfactory interpretation of the results on cool flames in butanone-oxygen mixtures (5).

Although the slow oxidation of ethers resembles that of other compounds, the cool flame reaction is quite different. In contrast to the precipitous decline in the concentration of peroxides of the ROOR" type previously observed after the cool flame in butanone-oxygen mixtures, the concentration of peroxides derived from ethers is practically unaffected by the passage of the cool flame. In fact, peroxides derived from diethyl ether exist at temperatures and pressures considerably

higher than those at which cool flames appear. Evidently peroxides of this type do not play the prominent part in the cool flame reaction of ethers that they seem to play in the butanone cool flame. A test of cool flame mechanisms with the ethers must await further information.

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INTRODUCTION

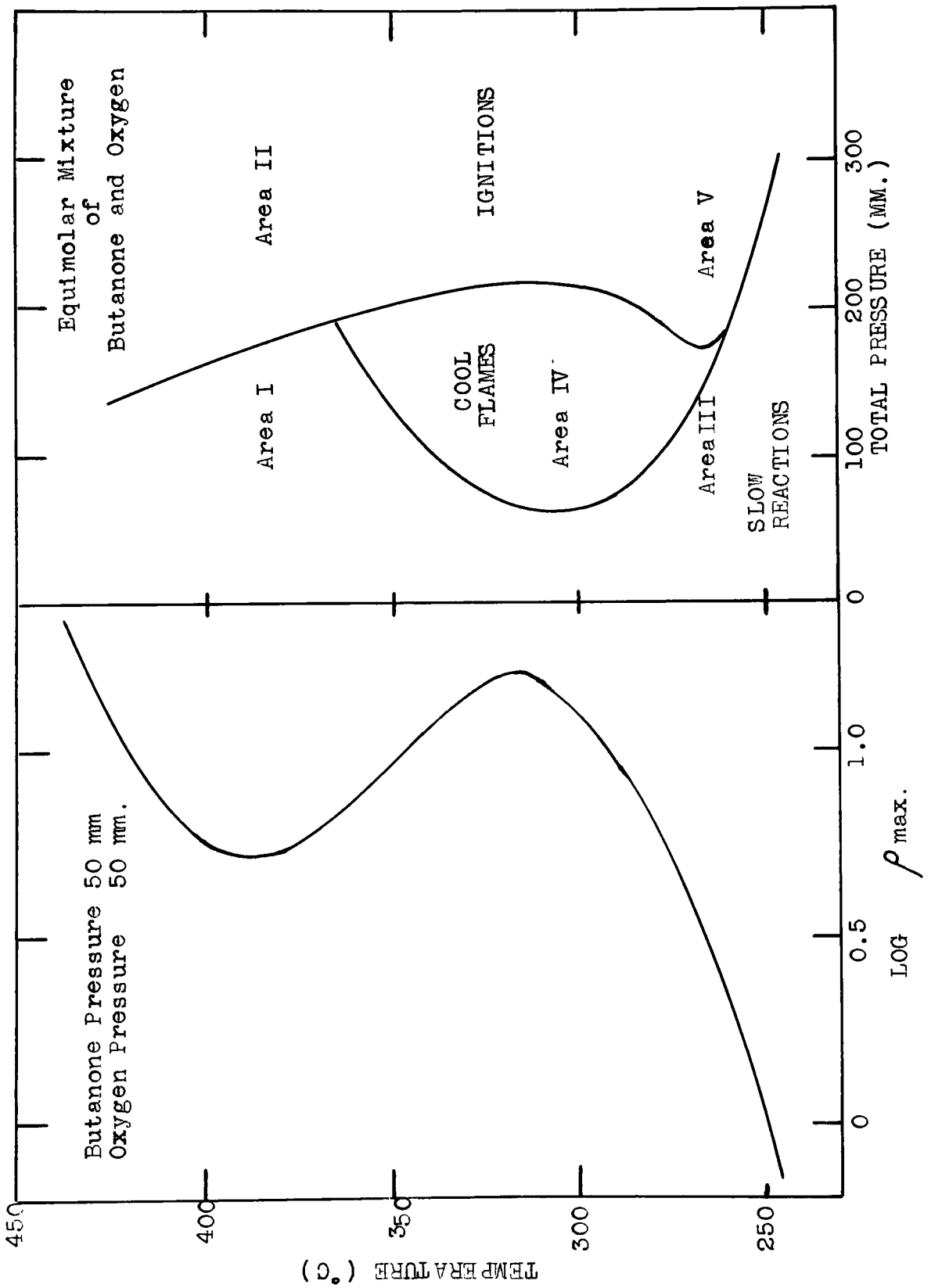
A study of the low temperature oxidation of gaseous organic compounds has proved to be a rewarding source of information about the influence of structure on the reactivity of molecules. With the normal paraffin hydrocarbons, for example, the rate of oxidation, in strong contrast to the rate of pyrolysis, increases markedly with the length of the carbon chain (1). Structural sensitivity has recently been found to be quite general and any alteration in the molecule whether by branching or substitution of chloro, amino or carbonyl groups is reflected in the oxidation rate (2, 3, 4, 5). A detailed discussion follows presently, but briefly the reason for the sensitivity is thought to lie, in part at least, in the reaction kinetics and besides being a useful method for investigating the relation between molecular structure and reactivity this approach leads to an increased understanding of the low temperature mode of oxidation.

The purpose of the present work is to determine the extent to which the mechanism of oxidation of ethers resembles that of other organic compounds, and where the mechanism is comparable to determine the influence of the oxygen atom in the molecular skeleton on the reactivity.

Structural sensitivity has only been observed in low temperature oxidations, one phase of a variety of behaviour exhibited in oxidations generally. If the conditions of temperature and pressure at which equimolar mixtures of a combustible gas and oxygen react are represented on a diagram, it is found that, except for the most primitive members of a homologous series, all compounds show five areas, each characterised by a distinct type of reaction (Figure 1) (6). At high temperatures slow reactions occur in Area I but give place abruptly to explosions in Area II as the temperature or pressure are increased. At lower temperatures there is an additional area; slow reactions in AreaIII are replaced by a special type of explosion or "cool flame" in Area IV with an increase of temperature or pressure. A further increase in pressure is required to give ignitions in Area V.

A distinction is made between slow reactions in Areas I and III because the rate of reaction does not increase steadily when the temperature is increased from one area to the other. Instead, there is often a transition range of temperatures between Area I and III where the rate is largely independent of temperature or may even be lowered by an increase in temperature. This type of behaviour has been observed with several compounds (5, 7, 8), and typical results obtained with butanone are shown in Figure I. To explain the abnormal dependence of the reaction rate on temperature it has been

FIGURE 1
The Effect of Temperature on the Maximum Oxidation Rate and the Pressure-Temperature Explosion Diagram for Butanone.



suggested that two modes of oxidation exist, one prevailing at high temperatures and the other at low, and that the blending of the two is responsible for the complexity shown in the transition region (6, 7). An intermediate may be involved in the low temperature type of reaction which, because of its low thermal stability, does not contribute to the high temperature reaction (9).

Methane is exceptional because it does not show a discontinuity in the temperature coefficient of the rate and, in fact, seems to oxidize entirely by the high temperature mechanism. The kinetics of its oxidation have been intensively investigated and the reactions involved are understood in broad outline (10). Propane (11), pentane (12) and di-iso-propyl ether (13) show similar kinetics in their respective high temperature oxidation ranges so it is perhaps not unreasonable to expect a common type of mechanism for all high temperature oxidations.

Regions II and V have also been carefully investigated and it appears that what occur in them are explosions of the thermal type (14) though doubtlessly involving chain reactions (15). The ignition at low temperatures often depends on the prior formation of a cool flame and appears to arise from the products of this primary step (14).

It is the slow reaction and cool flame areas (III and IV) at low temperatures that many of the interesting features of

oxidation are observed and these will be discussed more fully in the following sections.

The Low-Temperature Slow Reaction

The Salient Experimental Features.

Previous studies of a variety of organic compounds including straight and branched chain paraffins, chlorinated paraffins, amines and ketones have revealed the following kinetic features common to all:

a) Combustion is autocatalytic; if the progress of the reaction is followed by measurement of the pressure change it is observed that after a period of apparent quiescence (the induction period) the pressure increases to a maximum. The maximum rate of pressure change (ρ max.) is usually considered to be the most significant measure of the rate of reaction (1, 4, 7, 8, 17, 18).

b) The maximum rate of reaction increases with increasing pressure of the combustible gas but is largely independent of oxygen (1, 3, 4, 5, 8) or may actually be lowered by oxygen at high concentrations (5, 8).

c) The induction period is shortened by an increase in the pressure of the organic reactant but may depend on the oxygen pressure in a complex way (1, 2, 8, 16).

d) The maximum rate increases and the induction period is shortened by an increase in temperature (4, 7, 16).

e) Both the maximum rate and the induction period are sensitive to changes in the nature of the surface and an increase in the surface-volume ratio usually retards the reaction (1, 5, 19, 20, 21).

f) The addition of inert gases has no effect on the maximum rate of reaction and is usually without influence on the induction period (normal-pentane is exceptional among the compounds studied because the induction period is decreased by nitrogen additions) (1, 4, 5).

g) Many compounds are formed during combustion, some, such as carbon monoxide, acids and water reach their maximum concentration at the end of the reaction, others such as peroxides reach their maximum at the period of most rapid reaction (1, 5, 22, 23, 24, 25).

h) With paraffins, amines and ketones the rate increases with increasing length of the carbon chain but is very much lowered by the introduction of extra methyl groups into a hydrocarbon (1, 2, 4, 5).

The Low Temperature Reaction Mechanism

Oxidation reactions show so many complexities in spite of their general similarities that the theories that have been advanced from time to time usually only attempt to formulate a general mechanism and leave the details for resolution in particular examples.

Little need be said about the early theories of oxidation, such as the primary thermal decomposition and the hydroxylation theories (26, 27, 28, 29) for although they are important steps toward the understanding of oxidation phenomena they are not tenable in the light of more recent findings. The modern trend seems to stem from a suggestion by Egerton that peroxides initiate a chain reaction in the organic reactant-oxygen mixture (30). More detailed mechanisms of hydrocarbon oxidation applicable to the higher paraffins have been suggested by Ubbelohde (31) and by Lewis and von Elbe (9) in which it is proposed that combustion proceeds by a series of degradative steps involving chain carriers such as alkyl and alkoxy radicals. The outstanding features of the chain type reaction have been made clear by the work of Semenov (32).

Objections to the theories of oxidation at this stage in their development have been raised by Cullis and Hinshelwood and by Walsh. Cullis and Hinshelwood emphasise the general principle that the steps of a chemical reaction usually take place with the minimum disturbance of the existing configurations of the reactants, and point out that, as the theories stand, some of the postulated reactions involve improbable rearrangement (1). Walsh has objected to the early peroxide mechanisms because certain of the reaction steps are inconsistent with the known reactions of peroxides (33, 34, 35).

Modified theories which avoid these unlikely steps and

explain new experimental observations have therefore been advanced by Cullis and Hinshelwood and by Walsh. Both theories postulate a chain type of reaction which involves the formation of peroxides as essential intermediates. The autocatalytic nature of the reaction is thought to depend on chain branching arising from the decomposition of the peroxides, and both schemes account for the formation of formaldehyde by the decomposition of alkoxy radicals. Even though they have these features in common, the basis for the development of the theories is quite different and they will be developed separately. Since Walsh's treatment depends on observations of cool flames, as well as slow reactions, it will not be presented until the cool flame type of reaction has been described.

Cullis and Hinshelwood have postulated a mechanism which is not only consistent with the observed kinetics of the reaction but also leads to an understanding of the way in which the structure of the organic reactant can influence the rate (1). Since it is with this aspect that the present investigation is particularly concerned the theory will be considered in some detail.

Dialkyl peroxides (represented as ROOR) are considered to play an all-important role and are formed by the following reactions

$$RH + O_2 \longrightarrow R\text{-} + HO_2\text{-} \quad (1)$$

$$R\text{-} + O_2 \longrightarrow ROO\text{-} \quad (2)$$

$$ROO\text{-} + RH \longrightarrow ROOR \quad (3)$$

and $$ROO\text{-} + RH \longrightarrow \text{relatively inactive products} \quad (4)$$

RH represents the original organic molecule and R- is the radical derived from it by the removal of one hydrogen atom. The peroxide formed in (3) may be an alkyl hydrogen peroxide (represented as ROOH) without affecting the validity of the argument. The rate of the first reaction is ϕ and the rate constants of the subsequent reactions are designated as k_2, k_3, and so on, corresponding to the number of the reaction. The peroxide radical and RH might be expected to yield a number of different types of peroxide molecule in reaction (3) depending on the hydrogen atom removed; some of these may be relatively ineffective as far as continuing the reaction is concerned and are included in (4). The active ones, ROOR or ROOH, undergo further reaction, either branching

$$ROOR \longrightarrow 2\ RO\text{-} \quad (5)$$

or suffering non-chain degradation

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

The alkoxy radical may be written $R'CH_2O$- and decomposes further

$$R'CH_2O\text{-} \longrightarrow R'\text{-} + HCHO \quad (7);$$

if (7) is assumed to follow (5) immediately they can be written together as

$$ROOR \longrightarrow 2\ R'\text{-} + 2\ HCHO$$

The chain is continued by regeneration of R- from R'-

$$R'- + RH \rightarrow R- + R'H \qquad (8)$$

or R'- may react with oxygen

$$R'- + O_2 \rightarrow \text{less active products} \qquad (9)$$

The last step permits a simplification of the scheme by making use of the experimental fact that the rate of oxidation decreases with diminishing number of carbon atoms. From which it is inferred that the regeneration reaction (8) maintains the rate while (9) leads to peroxides which are less ready to undergo branching of the type (5).

The generalised kinetics of the branching chain type of reaction such as this had been discussed by Semenov (32) and he had pointed out that, if the intermediate formed is relatively stable, the reaction has special properties which he has embodied a theory of "degenerate branching". The distinguishing feature of this theory is that, because of the stability of the intermediate, the rate of formation of chain centres through the branching reaction can exceed the rate of destruction of centres without an explosion ensuing. There can be two types of degenerate branching, the stationary type where there is no possibility of explosion from developing chains because at any given moment the number of active centres formed is not as great as the number destroyed, or there is the non-stationary type where the number of centres formed

exceeds the number destroyed but the rate of reaction is not permitted to increase indefinitely because the stable intermediate intervenes.

Cullis and Hinshelwood consider the oxidation of pentane and hexane to be of the stationary type and obtain the following expression for the rate:

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

$$\text{where } \rho_{max.} = \frac{\left(\frac{2k_5}{k_5 + k_6}\right)\left(\frac{k_3}{k_3 + k_4}\right)\phi}{1 - k_5\left(\frac{2}{k_5 + k_6}\right)\left(\frac{k_3}{k_3 + k_4}\right)\left(\frac{k_8[RH]}{k_8[RH] + k_9[O_2]}\right)} \qquad (II)$$

$$\text{and } A = (k_5 + k_6) - 2k_5\left(\frac{k_3}{k_3 + k_4}\right)\left(\frac{k_8[RH]}{k_8[RH] + k_9[O_2]}\right) \qquad (III)$$

and they have found that, by giving suitable numerical values to the rate constants involved in (II), the predicted dependence of $\rho_{max.}$ on oxygen and hydrocarbon pressure is of the same form as that found experimentally. Furthermore, it will be shown in the next section that they were able to account for the observed effect of structure on the rate on the basis of the scheme.

The mechanism, in its essentials, has been found to be general and has been applied successfully to the oxidation of

amines (4) and ketones (5). In the latter case, however, the reaction is of the non-stationary type and the hydrogen atom (or alkyl radical) formed in (3) has been taken into account

$$ROO\cdot + RH \longrightarrow ROOR + H\cdot \qquad (10)$$

to permit increased formation of active centres. Also, to allow adequately for the inhibiting effect of oxygen at high pressure a decomposition reaction of the peroxide radical itself has been suggested

$$ROO\cdot \longrightarrow \text{less active products} \qquad (11).$$

The Influence of Structure

An outstanding feature of low temperature oxidation is the strong dependence of the rate of reaction on the molecular structure of the organic reactant. This fact may have, in part at least, a kinetic explanation (3, 36, 37). The expression for the rate of oxidation of a stationary type of reaction contains a factor of the form $\frac{\phi}{1 - ck_5}$ where ϕ is the rate of the initial attack of oxygen on the organic compound, k_5 is the velocity constant for the splitting of the peroxide molecule into radicals, and c is a constant (compare equations I and II). For a non-stationary reaction the factor takes the form $\frac{\phi}{ck_5 - 1}$. In either case ϕ is small and if the rate of oxidation is to be appreciable but not explosive,

ck_5 must not be far removed from unity. In these circumstances the term $1/[1 - ck_5]$ (or $1/[ck_5 - 1]$) changes rapidly with a change in k_5 itself and variations in the velocity constant of the decomposition reaction of the peroxide molecule therefore have a magnified effect on the rate. For this reason the rate of low-temperature oxidation gives a sensitive measure of the influence of the structure of R on the stability of the peroxide molecule, ROOR or ROOH. Another reason may well be that the -O-O- bond itself is specially responsive to the nature of the attached groups.

In principle, the structure of the organic reactant may influence both k_5 and ϕ, but the former is likely to be more important because its effect is enhanced in the manner described. Therefore, special attention has been directed toward the interpretation of the effect of changing the structure of R on the strength of the peroxide bond in the ROOR molecule.

The changes in the R group which have been studied by Hinshelwood and his students include variation of the length of the carbon chain and the introduction of various substituents. Before drawing conclusions about the influence of a particular group they first showed that the parent compound oxidized by the basic mechanism just outlined.

Briefly, their results have indicated that the introduction of methyl groups lowers the maximum rate of oxidation (1,2,3,36)

while chloro, amino or carbonyl substitution tends to increase the ease of oxidation (3,4,16). With each series of compounds, as with the straight chain hydrocarbons, lengthening the carbon skeleton favours oxidation. The first members of homologous series such as ethane and acetone were found to oxidize with extraordinary difficulty (8,16).

It has been concluded that the methyl group has two effects; in the first place, it appears to be inherently resistant to initial attack. Oxygen, like other electrophilic reagents attacks the organic molecule preferentially at the CH_2 or CH group. It is for this reason that ethane, acetone and other molecules without CH_2 or CH groups oxidize with difficulty (3). But quite apart from this, the methyl group exerts a specific effect in hindering the development of the branching chain.

Substitution of a chlorine atom or an amino radical for a primary hydrogen atom aids the initiation reaction by destroying methyl groups and thus more hydrogen atoms are made available for oxygen attack (3,4), but also have their own influence shown for example in the seconary chlorides (3).

These specific effects have been ascribed to the influence of the substituent on the strength of the peroxide bond, and the substituent may well act by electronic effects transmitted to the two oxygen atoms. It is pointed out that those

substituents which favour oxidation possess a capacity for electron-attraction, whereas the methyl group which has an unfavourable effect on oxidation is electron-repulsive (3,4,16,36,37).

According to the currently accepted views, the electronic factors responsible for the influence of molecular structure on the chemical and physical properties of organic compounds fall into two broad classifications (38). There is, on the one hand, the "tautomeric effect" which is of the utmost importance in conjugated systems, such as aromatic or alkyldiene molecules, but this effect cannot operate in the absence of conjugation. It is called the tautomeric effect because similar electron migrations are involved in a tautomeric change such as

$$CH_2 = CH-CH_2-COOH \longrightarrow CH_3-CH = CH - COOH.$$

This effect cannot be important in the oxidation of the compounds already referred to because a conjugated system is not available.

The other electronic mechanism depends on the "inductive effect". It is thought that certain groups have the ability to attract electrons in the outer shells of neighbouring atoms while other groups tend to allow their electrons to be strongly influenced by neighbouring nuclei. In a large molecule the resultant displacement need not be localized for there will be

a tendency for the electrons throughout the whole molecule to move in the same direction, but these secondary displacements will become increasingly less important as the number of intervening atoms increases. It is the shift of electrons in this manner that is responsible for the difference in acid strength of the aliphatic acids and the dipole moments of the halogeno-paraffins for example, and since these properties of the molecule can be measured directly and accurately a considerable body of quantitative information has been built up concerning this effect.

Hydrogen is the usual standard of reference; a group which, relative to hydrogen, repels electrons is said to have a +I effect, and a group which attracts electrons has a -I effect. Of the common substituents, the methyl group is outstanding as being the only one showing the +I effect while Cl and NH_2 are of the -I type, and the moment of the $\overset{+}{C}-\overset{-}{O}$ bond in the carbonyl group indicates that the shift of electrons in ketones is also likely to be toward the substituent.

Returning to the consideration of the influence of the structure of R on the strength of the peroxide bond in the ROOR molecule, it may be said that substituents of the -I type weaken the -O-O- bond while those with a +I effect strengthen it.

This conclusion is in agreement with a view expressed by

Walsh who has reconsidered the information about the strength of the peroxide linkage and the strength of bonds between electro-negative atoms in general (39,40). He points out that increased electronegativity of the two bonded atoms increases the strength of the bond between them, as for example with

I-I, Br-Br, Cl-Cl and F-F where the bond energies equal 36, 46 , 58 and 64 kcal./mole. However, there is a definite limit in this direction; beyond this the amount of overlap of atomic orbitals requisite for maximum bond strength cannot be established because the nuclei would be brought together so closely that repulsion would occur. In such cases a decrease in electronegativity in one of the bonded atoms increases the bond strength;

F-F and F-Cl with

bond energies of 64 and 87 kcal./mole are cited as an example. A similar situation is believed to arise with substituted organic peroxides. If the substituent is electron-repelling, as is the methyl group, the charge transfer to the oxygen atom of the -O-O- bond reduces its effective electronegativity, facilitates the expansion of the atomic orbitals and increases the amount of overlap with the net result that the peroxide bond is strengthened.

As previously mentioned, the maximum rate of oxidation

depends not only on the rate of the branching reaction but is also proportional to the rate of the initiation step:

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

The influence of this second factor on the maximum rate is less important for reasons already discussed, and is likely to be smaller, in any case, since the C-H bond exists between atoms with much less pronounced electrochemical characteristics than oxygen. Hinshelwood has pointed out the difficulty of forming an opinion about the effect which electron accession should have on this bond, but has suggested another possible approach to the problem (37). At the demand of the RH molecule the attacking oxygen probably takes the biradical form, more or less completely. In this change electrons must be drawn from the O=O. Therefore the very initial stages of the redistribution might be expected to be favoured by a positively charged centre which would tend to draw electrons toward it. Thus substituents which exert a -I effect would assist the attack while the methyl group, which exerts the opposite effect, would weaken the attack by causing a flow of electrons toward the seat of reaction. If the influence of substituents on the reactivity of organic molecules can thus be assessed in terms of the ease of approach of the reactants and the initiation of the requisite reorganization, then the effect of substituents is in the same direction in both the initiation and branching steps.

Cool Flames

The second type of oxidation in the low temperature region is the cool flame. Its relation to the other modes of oxidation has been shown in Figure 1.

Experimental Observations

The experimental facts about cool flames include the following:

a) The temperature rise accompanying a cool flame is less than that associated with ignitions in Area II or V in Figure 1 (41,12).

b) Cool flames do not produce a large total pressure change, but there is usually a decided pressure pulse during the passage of the flame(41).

c) Cool flames are not observed under any conditions with the first members of some homologous series. For example, methane, formaldehyde (42), glyoxal (43), ethylene (11), and methyl alcohol (44) do not form cool flames.

d) The emission spectrum of the cool flame is the same for all combustibles (45) and is identical with the fluoresence spectrum of formaldehyde (46,47). Since the temperature of the cool flame is too low for the formaldehyde to be thermally excited, the cool flame must be of the nature of chemiluminescence.

e) The kinetics of cool flame formation suggest that they are thermal explosions (14) or, at least partly so (15).

f) Several cool flames may occur at intervals in a suitable reaction mixture (17,48).

g) The cool flame area in the pressure-temperature diagram analogous to Figure 1 may show more than one lobe directed toward the temperature axis. With butanone, there is only one lobe (Figure 1), but with di-ethyl and di-iso-propyl ethers, for example, there is distinct evidence of two lobes at two different temperatures. Walsh has reviewed the available results (15).

h) Compounds such as aldehydes and peroxides are among the products of the cool flame reaction, indicating less complete combustion than takes place in ignitions (41).

i) Peroxides play an important role in cool flame formation; it has been found that additions of peroxides to reacting mixtures of hydrocarbons and oxygen may produce a cool flame (49), but the strongest evidence is the results of peroxide analysis during the cool flame reaction (48,50). With butanone the concentration of certain peroxides increases exponentially to a maximum coinciding with the appearance of the cool flame but they suffer practically complete destruction during the cool flame. If the conditions are suitable several more cool flames may occur and the peroxide concentration increases exponentially to a maximum each time.

The other instance where peroxides were measured during cool flame formation was with normal-propyl benzene. The peroxide analyses were incidental to a more extensive investigation of oxidation reactions and the results are not as decisive as those with butanone. Nevertheless, Burgoyne concludes that the propagation of cool flames in normal-propyl benzene is conditioned by the reactions of phenyl alkyl hydroperoxides.

j) With butanone the concentration of acetaldehyde and formaldehyde increases until the cool flame appears but is almost constant thereafter (48).

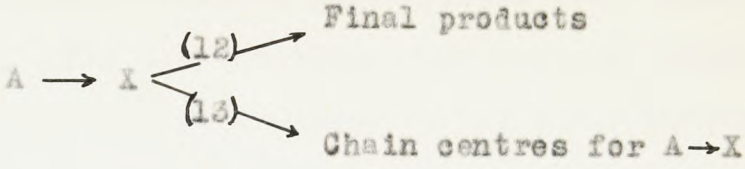
k) With normal-pentane, normal-hexane and butanone the relation between the induction period (the time for a cool flame or the maximum rate of slow reaction) (or its reciprocal) and the pressure of reactants is continuous from the area of slow reaction into the cool flame region. Also, the relation between the logarithm of the induction period (or its reciprocal) and the reciprocal of the absolute temperature is continuous in these regions (15, 16).

Theories of Cool Flame Formation

Several theories have been advanced to explain the complexities of the cool flame reaction, but recent experimental observations (48) are most satisfactorily explained by a suggestion originally made by Salnikov (51). In essence it

depends on two homogeneous consecutive reactions A→X→B, the temperature coefficient of the second being greater than that of the first. If the second reaction is also highly exothermic self-heating may occur as the reaction proceeds and the rate will increase until X is largely consumed; the rate of the second reaction will decline and the temperature will fall. If there is sufficient reactant the process is repeated.

Applied to butanone, it has been postulated that the reactions take the form



the intermediate, X, is thought to be a peroxide molecule capable of two reactions, one leading to branching (13) and the other (12) being useless for this purpose.

If, on the average, the regenerative reaction leads to the formation of ν molecules of X, the rate of its formation will be $v_o + k_{13}\nu x$ and its rate of destruction $(k_{13} + k_{12})x$ where v_o is the rate of initiation and x is the concentration of peroxide.

Then $$\frac{dx}{dt} = v_o + \left[k_{13}(\nu - 1) - k_{12}\right] x \qquad \text{(III)}$$

and $$x = \frac{v_o}{k_{13}(\nu - 1) - k_{12}} \left[e^{\left[k_{13}(\nu - 1) - k_{12}\right]t} - 1 \right] \qquad \text{(IV)}$$

The rate of oxidation is proportional to x, and the most important factor in determining its value at any point in the reaction is the net branching factor $A' k_{13}(\nu - 1) - k_{12}$. If k_{12} increases more rapidly than $k_{13}(\nu - 1)$ with increasing temperature, then at a certain temperature $k_{13}(\nu - 1) - k_{12}$ will fall to zero and an initially branching chain will fail to branch effectively.

The sequence of events leading to a cool flame start with an autocatalytic increase in the peroxide concentration. When the concentration exceeds a critical value, x_c, the heat produced by the exothermic reaction (12) exceeds that which can be conducted away from the reaction, self-heating occurs and eventually leads to a sharp decrease in the net branching factor. When A' passes through zero the peroxide concentration passes through a maximum, but the temperature rises further because accumulated peroxide continues to decompose. A' will be strongly negative because of the large increase in k_{12} and the peroxide concentration can fall to quite a low value. When it falls to a certain value (somewhat larger than x_c) self-heating stops, A' rises and the peroxide concentration passes through a minimum value. With further cooling A' eventually returns to normal and an exponential increase in x may occur provided sufficient reactants are available.

Thus the theory not only explains the peroxide behaviour

during periodic cool flames mentioned in paragraph (i) above, one of the most difficult points, but also is in agreement with the other observations including the thermal nature of cool flame explosions.

Considering the cool flame and slow oxidation reaction together, reaction (12) can be identified with (6) and (13) with (5) in the slow oxidation mechanism previously outlined. The intermediate, X, is of course, the peroxide ROOR. At temperatures where the slow reaction occurs the rate of (12) is not sufficiently great to produce self-heating even when the peroxide concentration is a maximum, and the branching chain reaction develops until the maximum rate is established. However, with increasing temperature a point will be reached when the maximum peroxide concentration will just equal x_c; the heat produced by (12) will exceed the amount that can be conducted away from the reaction and self-heating and the cool flames ensue. The time for the cool flame or the maximum rate will depend on the formation of the peroxides in the same way and it would therefore not be expected to be discontinuous on changing from the slow reaction to the cool flame area, in agreement with the experimental observations.

It was mentioned earlier than an alternative theory of low temperature oxidation has been advanced by Walsh (15,33,34,35). It has been developed largely from a consideration of the cool flame reaction and its basic postulate is that the cool flame

is an explosion (partly thermal and partly chain) initiated by the branching chains of the slow oxidation reaction. The explosion is soon quenched by the formaldehyde to which it gives rise; the mechanism of quenching will be discussed later. An analogy is drawn with the first pressure limit of explosion in hydrogen-oxygen mixtures but, in contrast to the "continuous" branching encountered with hydrogen and oxygen, "degenerate" branching, as postulated by Semenov (32), is thought to be the mode of reaction with the paraffins. The stable intermediate in the "degenerating" branching chains is identified with alkyl hydrogen peroxides and in this respect is similar to the theory of Cullis and Hinshelwood. Further development follows from Semenov's theories. A mechanism consistent with the general theoretical conclusions has been proposed and is as follows.

$$RH + O_2 \longrightarrow R\cdot + HO_2\cdot \qquad (14)$$

$$R\cdot + O_2 \longrightarrow ROO^{*}\cdot \qquad (15)$$

$$ROO^{*}\cdot + RH \longrightarrow ROOH + R\cdot \qquad (16)$$

(The asterisk on the product of the second reaction indicates that it must at first contain its own energy of formation).

$$ROOH + O_2 \longrightarrow OH\cdot \text{ and other products} \qquad (17)$$

including formaldehyde, acetaldehyde, simple olefins, simple ketones, OH radicals, methyl or ethyl radicals and relatively inert HO_2 radicals.

Other reactions of radicals follow:

$$OH\cdot + RH \longrightarrow R\cdot + H_2O \qquad (18)$$

$$OH\cdot + \text{surface} \longrightarrow \text{destruction} \qquad (19)$$

$$RO_2^{*}\cdot + \text{surface} \longrightarrow \text{destruction} \qquad (20)$$

$$ROOH \xrightarrow{RH} \text{destruction} \qquad (21)$$

This last reaction is assumed to be favoured by collision with RH, whereas collision with O_2 favours the branching reaction.

It will be noted that the only outstanding difference between this and the mechanism of Cullis and Hinshelwood is that the branching reaction is dependent on reaction with oxygen. This is postulated because the partial pressure of peroxide required for ignition in air is less than that required for explosion of the pure peroxide (52, 53) and also it offers an explanation of the complexity of the cool flame region mentioned in paragraph (g) above.

The lobes or peninsulae directed toward the temperature axis in cool flame diagrams such as Figure 1 are thought to be due to the attack of oxygen at different hydrogen atoms in the peroxide molecule. Since the dissociation energy of the tertiary C-H bond is less than that of a primary, oxygen attack on the former would be favoured at lower temperatures but at higher temperatures attack on the primary bond would occur. If the temperatures are far enough apart definite lobes would appear. It is pointed out that there is agreement

between the kinds of C-H bonds in the peroxide molecule and the lobes in the cool flame areas of a variety of compounds (15).

This theory breaks down, with butanone at least, in its interpretation of the behaviour of peroxides during cool flames, particularly recurrent cool flames. It was pointed previously that the cool flame is thought by Walsh to be a self-quenching type of explosion. The mechanism for this reaction and the periodicity of cool flames is ascribed to the inter-action of the intermediates and is a development of a general scheme proposed by Frank-Kamenetzki (54).

In outline, the reaction sequence put forward is

$$A + X \longrightarrow B + 2X \qquad (22)$$

$$X + Y \longrightarrow B + 2Y \qquad (23)$$

$$A + Y \longrightarrow B \qquad (24)$$

where A is a reactant molecule and B a product, X is identified with peroxides and Y with aldehydes, more specifically formaldehyde. In this series of reactions X increases autocatalytically until it reaches a critical concentration at which point sufficient Y forms by the autocatalytic reaction (23) to rapidly reduce the peroxide concentration to below the critical value. Thus the cool flame appears when the peroxide formation is very rapid and the peroxide concentration is approaching its maximum but is soon quenched by formaldehyde and the cool flames subsides. If sufficient reactant is

present the formaldehyde concentration will be reduced and the cycle of events can be repeated.

Previous Work on the Oxidation of Ethers

The danger of explosions with diethyl ether when used as an anaesthetic stimulated much of the early work on the vapour-phase oxidation of ether and the dependence of the explosion limits of ether-air and ether-oxygen mixtures on temperature, pressure, composition and other factors has been carefully investigated (14,41,42,55-60).

The pressure-temperature explosion diagrams for dimethyl and di-iso-propyl ether have also been determined and it was found that the cool flame limits of the former are very similar to Figure 1 (61), but that the limits for di-iso-propyl ether (and also diethyl ether) are more complex and may consist of two overlapping peninsulae directed toward the temperature axis (62).

These researches showed that diethyl ether produces easily detectable cool flames at convenient pressures and temperatures and is very suitable for studies of this type of oxidation. An extensive investigation of cool flames particularly in diethyl ether by Townend and his co-workers followed (14,41,56, 41,63). They first showed that there is no essential difference between cool flames initiated by sparks or hot filaments and cool flames initiated thermally. A technique was then developed which allowed them to maintain a stabilized

cool flame in a tube at room temperature and this work culminated in a series of experiments which showed that ignition is a two-stage process. The first stage leads to the cool flame and the second-stage appears in the cool flame products. The stationary flame technique also produced large samples for analysis and it was found that a much higher concentration of peroxides and aldehydes was produced by the cool flame than by the second-stage flame, thus emphasising the incomplete nature of cool flame combustion.

No information about the kinetics of the slow gas-phase oxidation of ethers in the low temperature range is available in the literature. The kinetics of the oxidation of dimethyl and di-iso-propyl ethers have been investigated but the former compound was studied in the transition range of temperatures between the high and low temperature type of reaction (61) while the latter was studied in the high temperature region (13).

The liquid phase auto-oxidation of ethers in the presence of dissolved oxygen has been studied by a number of workers (64-69). It is generally agreed that organic peroxides are involved but they are so unstable that purification and analysis is usually very difficult and the chemical constitution of the products is doubtful. It has been observed that, of the common ethers, di-isc-propyl ether forms peroxides most readily (69). Since ethyl butyl ether forms peroxides more readily than methyl butyl ether it has been suggested that the initial

oxygen attack is on a secondary hydrogen of a carbon atom adjacent to the ether-oxygen.

The only other comparison that might reflect the relative ease of oxidation of ethers is given by the ease of cool flame formation (14). The minimum ignition pressures required for cool flame propagation in equimolar mixtures of ethers and oxygen at constant temperature are given as:

Diethyl ether	80 mm.
Ethyl methyl ether	110 mm.
Ethyl propyl ether	110 mm.
Butyl methyl ether	120 mm.
Propyl methyl ether	190 mm.
Dimethyl ether	310 mm.

Since it is desirable to test the theories of low temperature oxidation as completely as possible and since the existing data do not permit such a test with the ethers an investigation toward this end was begun. The problems to be considered were to determine first, the extent to which the reactions of ethers are comparable in mechanism to those of the paraffins, amines and ketones and secondly, where the mechanism is comparable, what is the influence of the oxygen atom in the carbon skeleton. The experiments showed that large quantities of peroxides were produced during ether oxidations and therefore theories of cool flame formation could also be conveniently tested.

EXPERIMENTAL

The apparatus and experimental methods were similar to those used in previous work on oxidation in this laboratory. The ether vapour and oxygen were admitted separately to the hot reaction vessel, and the reaction was followed, in the first instance, by the pressure change. The partial pressure of peroxides in the reaction mixture at various times during the reaction was determined by chemical analysis of the products withdrawn from the reaction vessel.

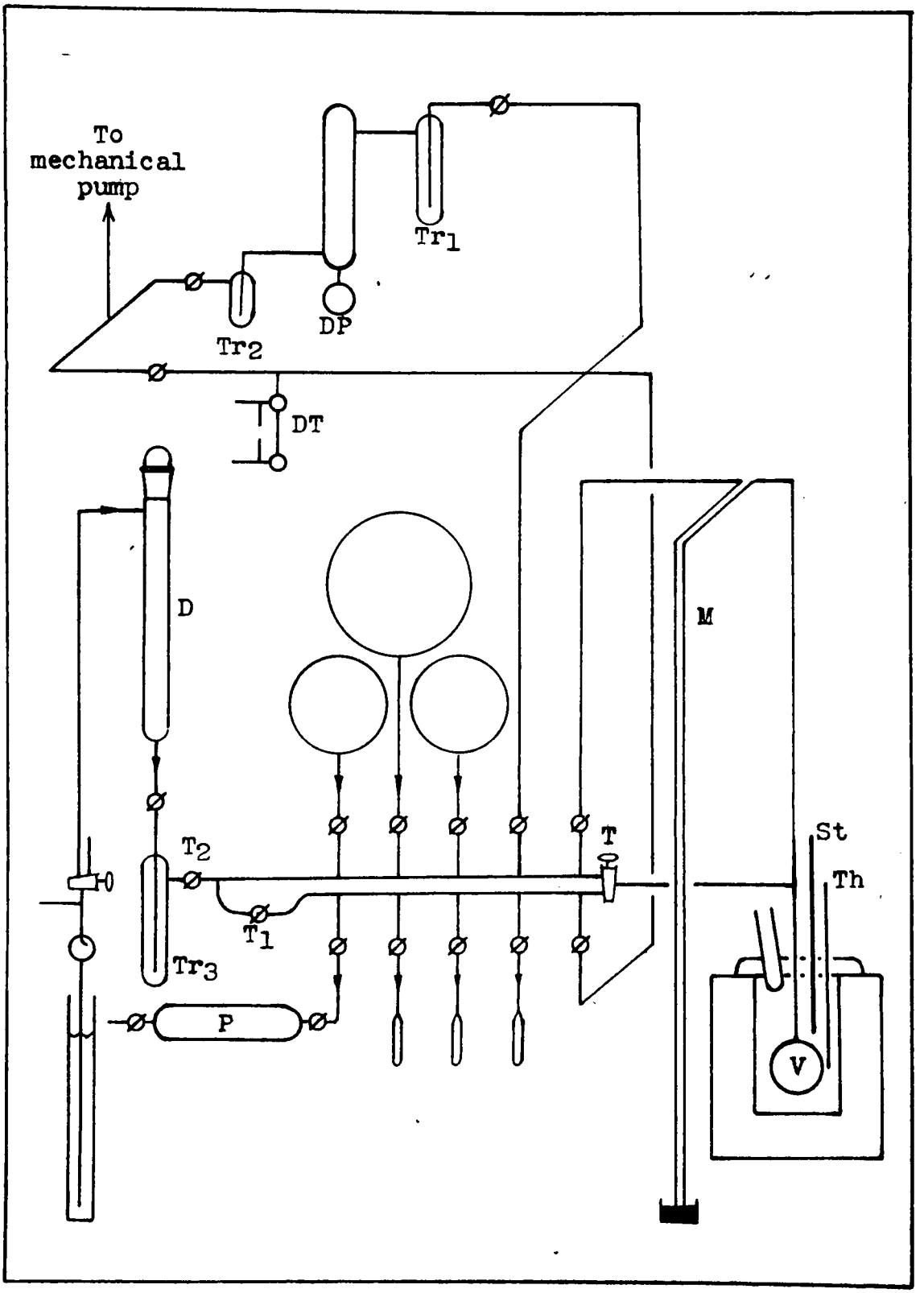
Apparatus.

The spherical, pyrex reaction vessel, V in Figure 2, of 250 ml. capacity was supported centrally in a thermostatically controlled furnace. The vessel was connected by capillary tubing to a mercury manometer, M, and a two-way tap, T, through which the reactants were admitted to the reaction vessel. When this tap was closed the vessel and its manometer were isolated from the rest of the system. To prevent condensation of the less volatile reactants and products the manometer and connecting tubing were wound with resistance wire and heated to 50°C.

The two-way tap connected the reaction vessel with two galleries to which were attached reservoirs of the reactants,

FIGURE 2

The Apparatus



the gaseous reactants on the upper gallery and the liquids on the lower. The upper and lower galleries were connected by a tap T_1. Gas purification equipment was provided on the upper gallery, although normally it was isolated by the tap T_2. The lower gallery had a tap and ground-glass joint for the attachment of a sampling pipette P. Each gallery was connected to the pumping system by an individual tap.

The apparatus was evacuated by a three-stage mercury diffusion pump, DP, backed by a mechanical rotary pump. The pumps were protected by the traps Tr_1 and Tr_2, and the former could be cooled if necessary. Since it was found that gaseous reaction products attacked hot mercury in the diffusion pump and produced solid material which interfered with its operation, a by-pass tube with appropriate taps was placed around the diffusion pump and was used for the initial evacuation. To give an indication of the pressure in the apparatus a high-voltage discharge tube, DT, placed in parallel with an air gap of about 7 mm. was provided on the manifold.

Liquid ethers, stored in bulbs on the lower gallery, were frozen and evacuated daily to remove air which may have been dissolved in them originally or which may have leaked in through the tap or ground-glass joint.

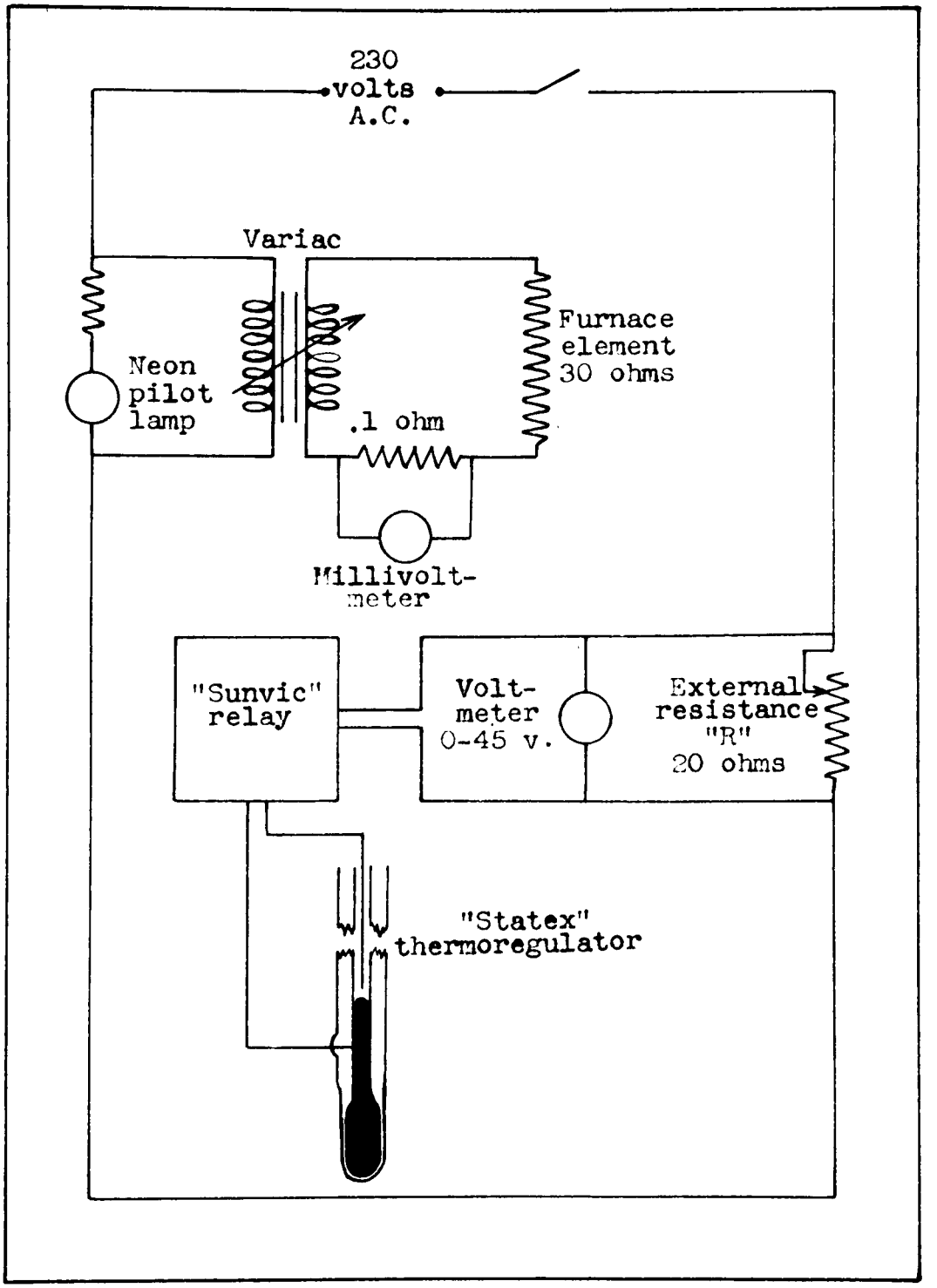
Gases, to be stored in the bulbs on the upper gallery, were first dried by passage through a bed of phosphorus pentoxide in the tube D. To ensure that no air leaked in

with the in-coming gas while the bulbs were being filled, the pressure in the tubing connecting the source of gas with the apparatus itself was kept above atmospheric. The "blow-off" tube immersed in water gave an indication of this pressure and also served as a safety valve. A 25 ml. trap on the "blow-off" tube was found to be a useful protection against a sudden rush of water into the phosphorus pentoxide when the pressure changed. Ethers with boiling points below room temperature were condensed in trap Tr_3 and were frozen and evacuated to remove dissolved air before they were vapourized into the storage bulbs. The bulbs were always thoroughly evacuated before they were filled, and, if possible, they were flushed several times with the gas to be stored.

The furnace in which the reaction vessel was placed was electrically heated and well insulated. The vessel itself could be observed through a glass window in the insulated cover. The temperature of the furnace was kept constant automatically by a "Statex" thermoregulator, St, and relay system. The heating circuit is shown in Figure 3. The operation was as follows: when the temperature of the furnace rises to a pre-selected value the mercury column in the "Statex" closes an electrical circuit and actuates the "Sunvic" hot-wire relay, which in turn places a small adjustable resistance, R, in series with the heating element. The heating current is thus reduced and the temperature of the furnace falls until

FIGURE 3

The Heating Circuit



the "Statex" breaks the relay circuit which shorts out the external resistance.

The temperature of the reaction vessel was measured with a calibrated thermometer, Th, the bulb of which was placed near the wall of the vessel. Alternatively, a chromel-alumel thermocouple and potentiometer were used. The temperature variation in the space normally occupied by the reaction vessel was found to be about $1^{\circ}C.$, and fluctuations arising from the operation of the temperature-controlling equipment were kept at less than $0.5^{\circ}C.$ by adjustment of the external resistance.

Experimental Procedure

The reaction vessel was evacuated by the diffusion pump for ten minutes immediately before an experiment was started, and then the required amount of ether was added, followed as quickly as possible by the oxygen. A stop-watch was started at this point. The pressure was read at suitable intervals and the change in pressure, Δp, was usually represented graphically as a function of time.

With ethers it was found that the pressure decreased at first and then increased, the rate passing through a maximum before the end of the reaction. The maximum rate of pressure increase and the time for its establishment were considered to be the most useful characteristics of the reaction to record in the preliminary general survey.

Under certain conditions cool flames or ignitions occurred and could easily be identified by the pressure pulse and light emission which accompanied them. A distinction between cool flames and ignitions can be made on the basis of a difference in the colour of the light emitted, but Maccormac and Townend have suggested a more reliable method (41). They found that cool flames invariably produce a smaller total pressure change than ignitions and so any sudden reaction which produced a pressure increase greater than 50% was termed an ignition.

Very early in the investigation of the oxidation of ethers it was found that the experimental procedure had to be strictly adhered to if reproducible results were to be obtained. Minor variations such as reversal of the order of admission of the reactants to the reaction vessel often produced marked changes in the maximum rate. The first experiments of the day were also not very reliable and were disregarded. This is a common observation in oxidation studies and is usually attributed to surface changes which have occurred overnight with the vessel in the evacuated condition (16,70).

With a subject as complex as oxidation simple manometric data are seldom sufficient, for although the pressure change has been found to parallel the disappearance of organic reactant in several instances (16,17,22) it may not reveal the formation and disappearance of intermediates. Since peroxides are believed to be important intermediates in both the cool flame

and slow reactions the reacting mixture was analysed for these compounds.

Peroxide Analysis

A number of analytical methods have been described in the literature. Many of them rely on the oxidation of the test reagent and yet it is known that some types of peroxides are such weak oxidizing agents that they do not react with hydriodic acid (71). Nevertheless, among the reducing agents that have been suggested are potassium iodide in neutral or acid solution (72) possibly with some differentiation among different types of peroxide by suitable choice of reaction time (50, 68) or catalysts (73), ferrous thiocyanate (74), stannous chloride (75,76), cymene hydrosulphide (77), and acetic acid solution of potassium iodide (78). Other methods involve hydrolysis followed by estimation of the hydrogen peroxide formed using either potassium iodide in acetic acid solution (79) or potassium permanganate (80). Colour reactions with titanic sulphate in dilute sulphuric acid solution (24), titanous chloride in dilute hydrochloric acid solution (73), potassium ferricyanide (73), and an ammoniacal solution of lead acetate alone (73) or with the addition of "tetra-base" (tetramethyl-diamino-diphenyl methane) and glacial acetic acid (73,81) have also been suggested.

All these tests have been objected to at various times;

those which involve the liberation of iodine because (a) they are not specific, acetaldehyde in acid solution, for example, will liberate iodine in the presence of oxygen (24), (b) in some systems iodine may be lost by addition to unsaturated compounds present (77,82), and (c) some peroxides such as di-alkyl peroxides and monohydroxy-dialkyl peroxides react incompletely or not at all (83).

Although ferrous salts are very sensitive to di-alkyl peroxides (73) they may (a) partly reduce and partly catalyse the decomposition of alkyl hydrogen peroxides, monohydroxy-dialkyl peroxides and aralkyl peroxides (such as the hydroperoxide of ethyl benzene) (83,84), (b) catalyse the dehydration of peroxides derived from compounds such as tetralin to form ketones (83) or (c) may not react with some peroxides, such as benzoyl peroxide (82). Kolthoff and Medalia (84) have made a detailed study of the reaction of ferrous ions with cumene hydroperoxide in organic solvents and have found that in the presence of oxygen a chain reaction is initiated which consumes more ferrous ions than would be expected from a simple oxidation-reduction reaction. In the absence of oxygen a somewhat similar chain consumes more hydroperoxide than would be expected from a simple non-chain reaction mechanism. This accounts for the complex effect of the ferrous ion in hydroperoxide systems and may be partly responsible for the diversity of the observations made with hydroperoxides and

ferrous thiocyanate in different solvents(74,82,85,86).

Stannous chloride has been objected to because it must be protected from oxygen and air, but more important, a brown colour forms during the titration and masks the end-point (74). The cymene hydrosulphide and hydrolytic methods are slow (74) and often incomplete (79), and the ferricyanide and tetra-base tests are only moderately sensitive (73), at least with alkyl hydrogen peroxide and dialkyl peroxides. The titanium test, although extremely sensitive with hydrogen peroxide is not reliable with alkyl hydrogen peroxides or dialkyl peroxides (73).

The influence of reaction conditions on the sensitivity of the potassium iodide method toward some of the types of peroxide that might be expected to form during hydrocarbon oxidation has been considered (50,72,73). It appears that a broad distinction can be made between different types of peroxides by selection of reaction conditions and the following conclusions were drawn:

a) potassium iodide in neutral solution reacts readily with acyl peroxides (peracids) of the type $R\text{-}C(=O)OOH$ derived from aldehydes (50,72) and with some products of the liquid phase oxidation of ethers (68). This group has been subdivided into two sections, those peroxides which react immediately and those which require 30 minutes, but the difference in constitution is not known (50).

b) potassium iodide in acid solution in an atmosphere of

nitrogen reacts within 30 minutes with hydrogen peroxide, and of course, members of group (a) (50). Acetic acid is suggested for acidification of the solution because it may increase the solubility of peroxides in the reagent.

c) potassium iodide under conditions similar to (b) reacts within 24 hours with aryl and alkyl hydrogen peroxides (50) and bis-di-hydroxy alkyl peroxides (83); members of this group will also appear to some extent in (b). The last two reactions can be made somewhat more specific by the use of selective catalysts:

d) potassium iodide in acid solution reacts rapidly with alkyl hydrogen peroxides if catalysed by molybdenum (73).

e) potassium iodide in acid solution in the presence of small amounts of ferrous sulphate reacts with dialkyl peroxides and it is stated that alkyl hydrogen peroxides are destroyed (73). It seems unlikely, from what has been said before about the reactions of the ferrous ions and this type of peroxide, that destruction is quantitatively complete.

The peroxides involved in the slow oxidation of normal-hexane (1) and the slow oxidation and cool flame reactions of normal-propyl benzene (50) were analysed by these methods with the results already stated in the introduction.

The ferrous thiocyanate method has been used in kinetic studies of the oxidation of amines and butanone (4,16,48) since it responds to di-alkyl peroxides, the type of peroxide thought

to be responsible for branching in the low temperature, slow oxidation reaction. Unfortunately, the reagent is not specific and reacts in an uncertain way with alkyl hydrogen peroxides, a type of peroxide which may also contribute to the branching reaction. When, however, the analyses of reaction mixtures are made under identical conditions it is likely that the ferrous thiocyanate method not only detects di-alkyl peroxides but also reflects relative changes in the concentration of alkyl hydrogen peroxides.

The ferrous thiocyanate method was used in the present investigation so that the results could be compared directly with results on butanone and amine oxidations. A few supplementary analyses of the cool flame reaction products were also made with the potassium iodide in neutral solution.

Technique of Peroxide Analysis

The partial pressure of peroxides in the reacting gases was determined by analysis of the products of combustion withdrawn from the reaction vessel into an evacuated pipette attached to the lower gallery. To prevent condensation of the less volatile reactants and products the tubing which connected the vessel with the pipette was heated to 50°C. The pressure in the reaction vessel was measured before and after the sample had been taken. The sample was analysed by the method described below and the peroxide pressure in the

reaction vessel was calculated from the gas laws with a correction for the connecting tubing.

The peroxides in the sampling pipette were estimated by absorption in benzene followed by reduction with ferrous thiocyanate. The concentration of ferric ions thus produced was determined by titration with standard titanous sulphate solution.

The benzene used was of "AnalaR" quality and fresh supplies were always tested before use by the ferrous thiocyanate method and found free of peroxides.

The reducing solution of ferrous thiocyanate had the following composition:

12.9	gm.	ferrous ammonium sulphate
5.0	gm.	ammonium thiocyanate
5.0	ml.	sulphuric acid (concentrated)
500	ml.	water
500	ml.	ethanol

It was usually pink when freshly prepared, either because of ferric impurities in the ferrous ammonium sulphate or oxidizing impurities in the other reagents (e.g. dissolved air); before use these were reduced with concentrated titanous sulphate solution until just colourless.

A solution of titanous sulphate 0.003N in reducing power in the reaction given below was prepared by dilution of a 15% solution with 4M sulphuric acid. It was stored over liquid

zinc amalgam and was vigorously shaken with the amalgam for five minutes before it was used. The solution was standardized with ferric chloride as directed by Treadwell and Hall (87).

The analytical procedure was as follows: after the pipette had been disconnected from the lower gallery its contents were extracted three times in a total of 10 ml. of benzene. The solutions thus obtained were combined in a 250 ml. glass-stoppered flask and exactly 10 ml. of ferrous thiocyanate solution was added. The mixture was thoroughly shaken for five minutes in a water bath at 60°C. The red solution produced was titrated until just colourless with standard titanous sulphate.

The peroxide concentration was calculated on the basis of the following reaction:

$$2\ Ti^{+3} + ROOR + 2\ H^{+} \longrightarrow 2\ Ti^{+4} + ROR + 2\ H_2O$$

where the peroxide is represented by ROOR.

This method is identical in all respects with the method used for the determination of peroxides in the oxidation of butanone (16,48) and the amines (4).

Preparation and Purification of Materials

High grade cylinder oxygen and nitrogen were dried before storage by passage through the column of phosphorus pentoxide attached to the upper gallery.

Diethyl, di-iso-propyl and di-normal propyl ethers were obtained from commercial sources. The first two were purified because they were found to contain peroxides. Dimethyl, methyl ethyl and methyl normal-propyl ethers were prepared by methods to be described.

The peroxides in diethyl ether were removed by a method suggested by Brandt (88). About 300 ml. of ether and a solution of 600 g. crystalline ferrous sulphate, 60 ml. sulphuric acid and 1,100 ml. water were shaken together at room temperature for nine hours. The ether was then washed with water, 5% sodium hydroxide solution and again with water. Next, it was shaken with 300 ml. of 0.5% potassium permanganate solution and washed several times with water. After it had been dried over calcium chloride and sodium the ether was distilled through a ten inch column; b.p. 34.0-34.5°C. No peroxides were detected in the product by the ferrous thiocyanate method after this treatment.

Di-iso-propyl ether was shaken with an equal volume of saturated sodium bisulphite solution for several hours at room temperature to remove peroxides (89). The ether was then washed with 5% sodium hydroxide solution and water. After it had been dried over calcium chloride and phosphorus pentoxide the ether was fractionated in an all-glass apparatus; b.p. 66.5-68°C.

Reagent quality di-normal-propyl ether was fractionated

and the middle portion which distilled between 89° and 91°C. was collected.

Dimethyl ether was prepared by the action of sulphuric acid on methanol (90). The gas evolved was absorbed in cold concentrated sulphuric acid and when production had ceased it was regenerated by dilution with water. The gaseous ether was dried by passage through the phosphorus pentoxide tube attached to the upper gallery and then condensed in a trap, Tr_3 in Figure 2, immersed in liquid air. While the ether was at liquid air temperature the apparatus was evacuated. The ether was then carefully fractionated and the middle portion was collected in the storage globes attached to the upper gallery.

Methyl normal-propyl ether was prepared by the reaction of sodium normal-propylate and methyl iodide (91). Normal-propyl alcohol, dried over anhydrous potassium carbonate, was fractionated and the portion which distilled at 97°C. was collected. Sodium (5.75 g.) was then dissolved in 149 ml. of the alcohol under reflux and 15.5 ml. of methyl iodide was added dropwise. When the addition was complete the ether formed was removed by distillation. The reaction and distillation were repeated twice more using the same alcohol. The crude ether yields were combined and refluxed several times with fresh sodium until no further reaction was observed. The product was then carefully fractionated; b.p. 39°C.

Methyl ethyl ether was prepared similarly by the reaction

of sodium methylate and ethyl iodide. A solution of 5 g. of sodium in 40 ml. of methanol was sealed in a glass tube with 16 ml. of ethyl iodide and heated for 6 hours at 60°C. The contents were then frozen and the tube was opened. The tube and its contents were immediately transferred to an all-glass distillation apparatus where the ether was permitted to distil. The product was dried over sodium for 24 hours in a bulb immersed in a dry ice-alcohol mixture. It was then sealed in a tube with more sodium and was heated for 9 hours at 60°C. The distillation and treatment with sodium were repeated until no further reaction with sodium occurred. The ether was finally distilled and stored over sodium in sealed tubes. Immediately before use it was transferred to a bulb attached to the lower gallery maintained at 0°C.

Iodides were shown to be absent from ethers prepared by the Williamson method. The test for impurities of this type was as follows: a sample of the ether was heated for 6 hours at 100°C. in a sealed tube with sodium ethylate dissolved in ethanol. The tube was then opened and its contents were dissolved in water. After the solution had been neutralized with nitric acid the test for iodides was made by addition of silver nitrate.

RESULTS

CONDITIONS FOR EXPLOSION

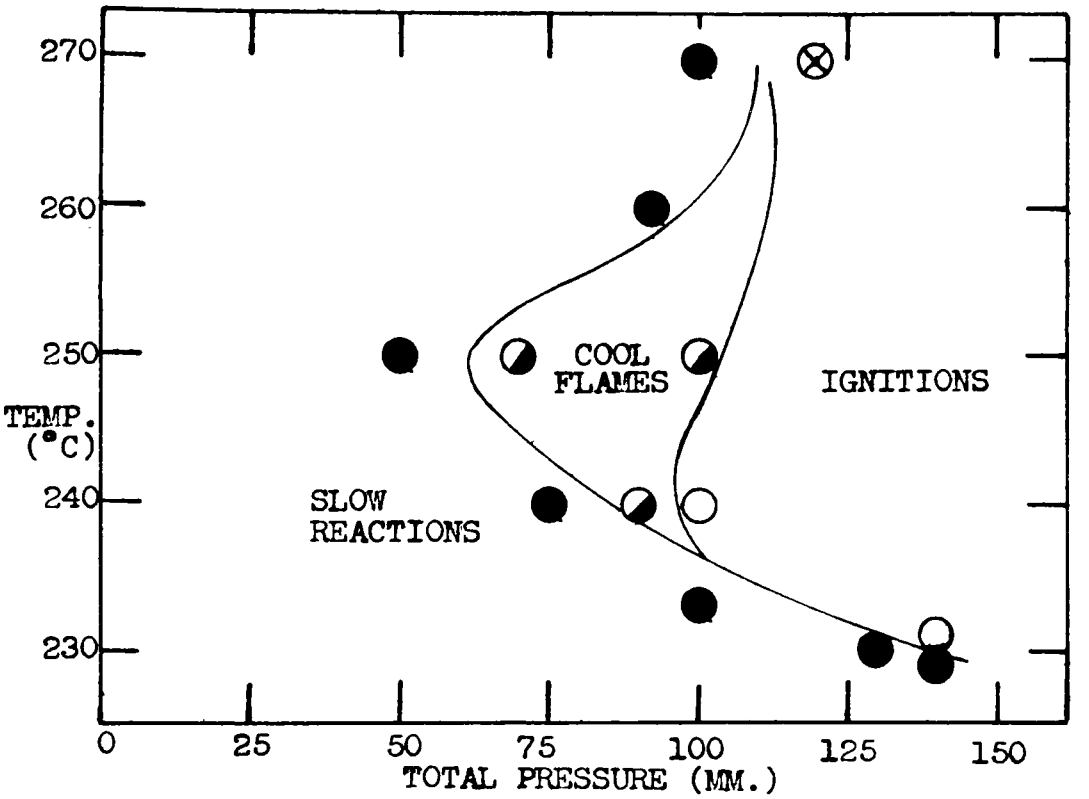
Although pressure-temperature explosion diagrams for a few ethers have been published already by other investigators (60,61,62) the appropriate experiments were repeated so that all the ethers studied could be compared under the same reaction conditions. These diagrams, moreover, are useful because they show the cool flames in proper perspective in the complete range of oxidative behaviour.

The experimental points for determining the boundaries of the slow reaction, cool flame and ignition zones are plotted in Figures 4-9 (for equimolar mixtures of ether and oxygen). The limits could not be determined more accurately because it was found that the transition from one area to another was not quite sharp, especially at low pressures (20 mm. or less) where the pressure pulse or luminosity accompanying the cool flame is very faint. At higher temperatures the reaction became so rapid that the products expanded into the connecting tubes before the oxygen could be completely added, but since the low temperature zone is of the most interest in the present investigation experiments were confined to this region.

Di-iso-propyl ether was found to be unique in two respects; the boundary between cool flames and ignitions was above 300 mm. and could not be determined in the apparatus because at these

FIGURE 4

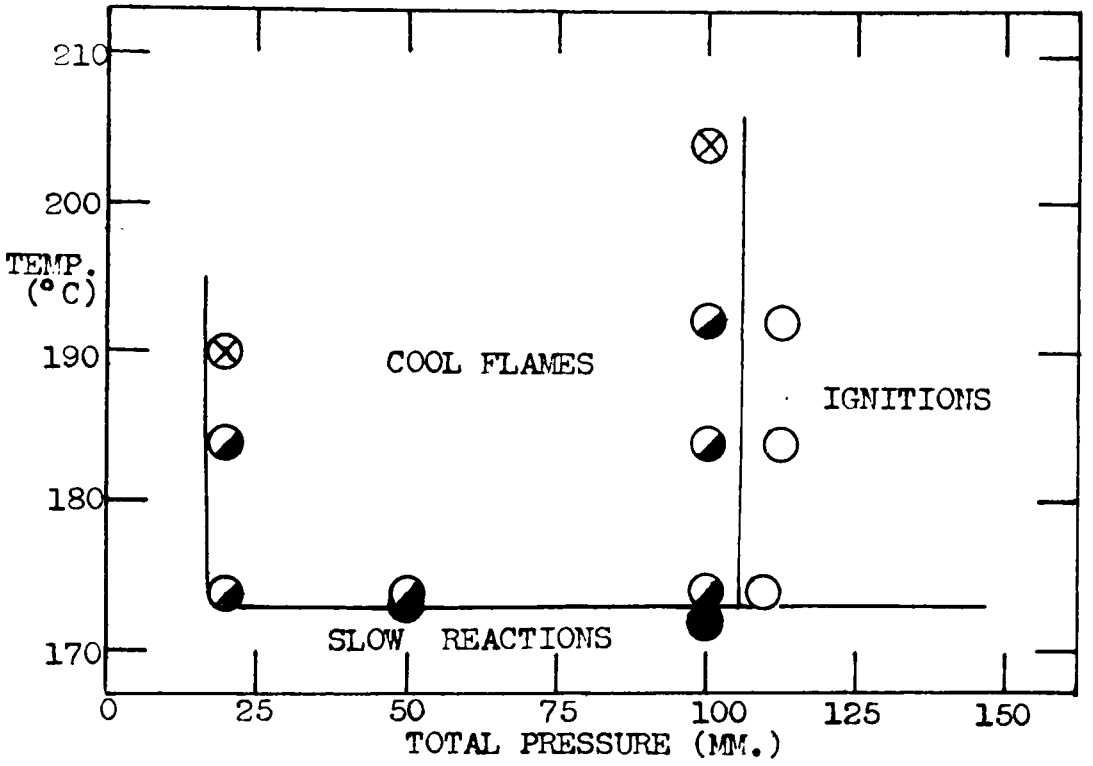
The Pressure-Temperature
Explosion Diagram for Dimethyl Ether



Slow reaction - - - - - - - -
Cool flame - - - - - - - - -
Ignition - - - - - - - - - -
Explosion during oxygen addition

FIGURE 5

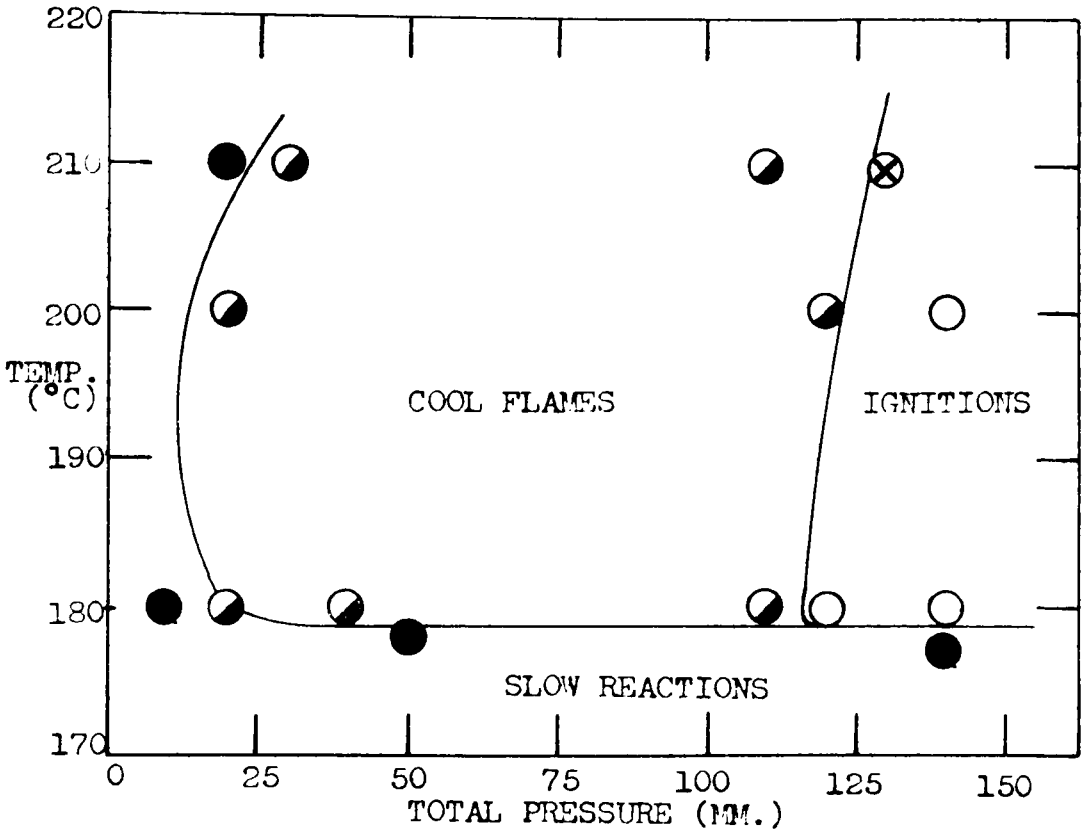
The Pressure-Temperature
Explosion Diagram for Diethyl Ether



Slow reaction - - - - - ●
Cool flame - - - - - - ◐
Ignition - - - - - - - ○
Explosion during oxygen addition - - - ⊗

FIGURE 6

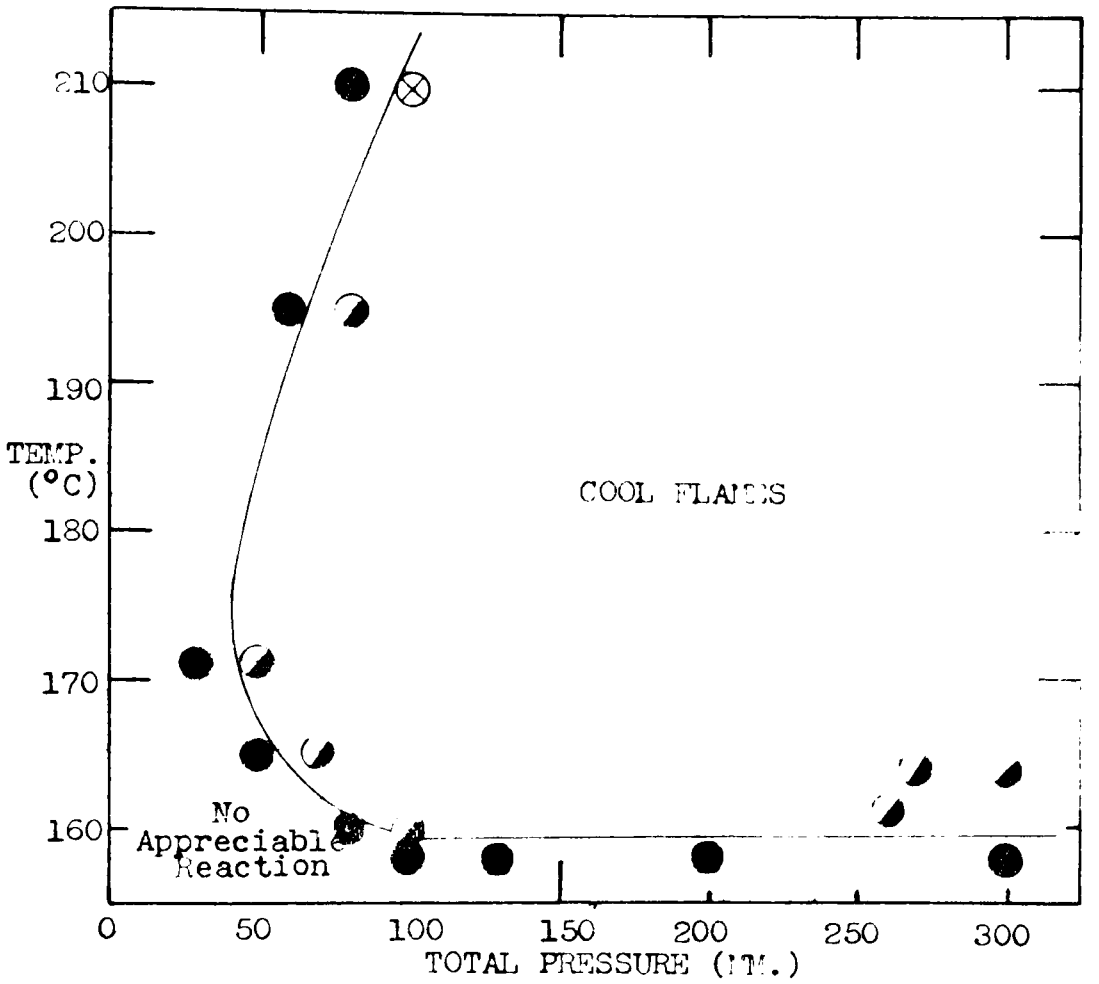
The Pressure-Temperature
Explosion Diagram for Di-normal-Propyl Ether



Slow reaction ●
Cool flame ◪
Ignition ○
Explosion during oxygen addition ⊗

FIGURE 7

The Pressure-Temperature
Explosion Diagram for Di-iso-propyl Ether



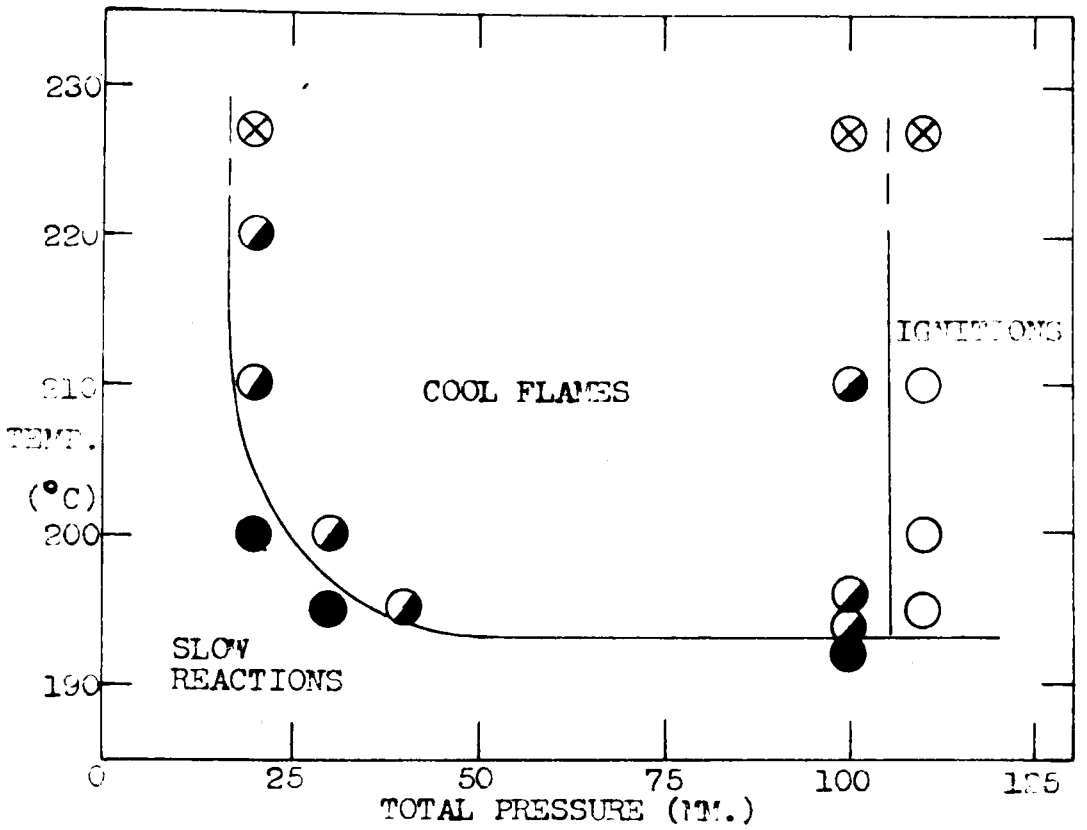
Slow reaction ●

Cool flame ◑

Explosion during oxygen addition ⊗

FIGURE 8

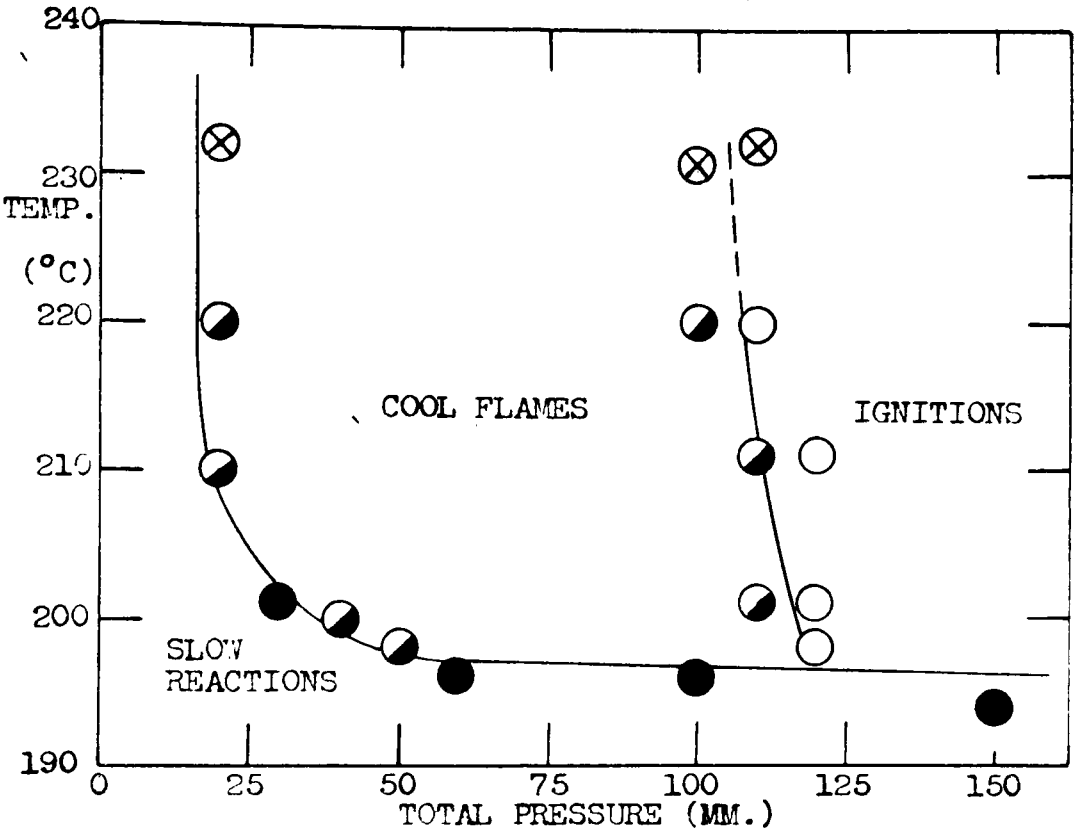
The Pressure-Temperature
Explosion Diagram for Methyl Ethyl Ether



Slow reaction - -
Cool flame - - -
Ignition - - - -
Explosion during oxygen addition

FIGURE 9

The Pressure-Temperature
Explosion Diagram for Methyl normal-Propyl
Ether



Slow reaction
Cool flame
Ignition
Explosion during oxygen addition

pressures the pulse accompanying the cool flame exceeded atmospheric pressure and some of the products escaped through the manometer tube. Since an undetermined amount was lost the final pressure after the cool flame was not known and the usual criterion of a cool flame, namely at total pressure change of less than 50%, could not be used, but since the light emission was predominantly blue in colour there can be little doubt that cool flames occurred.

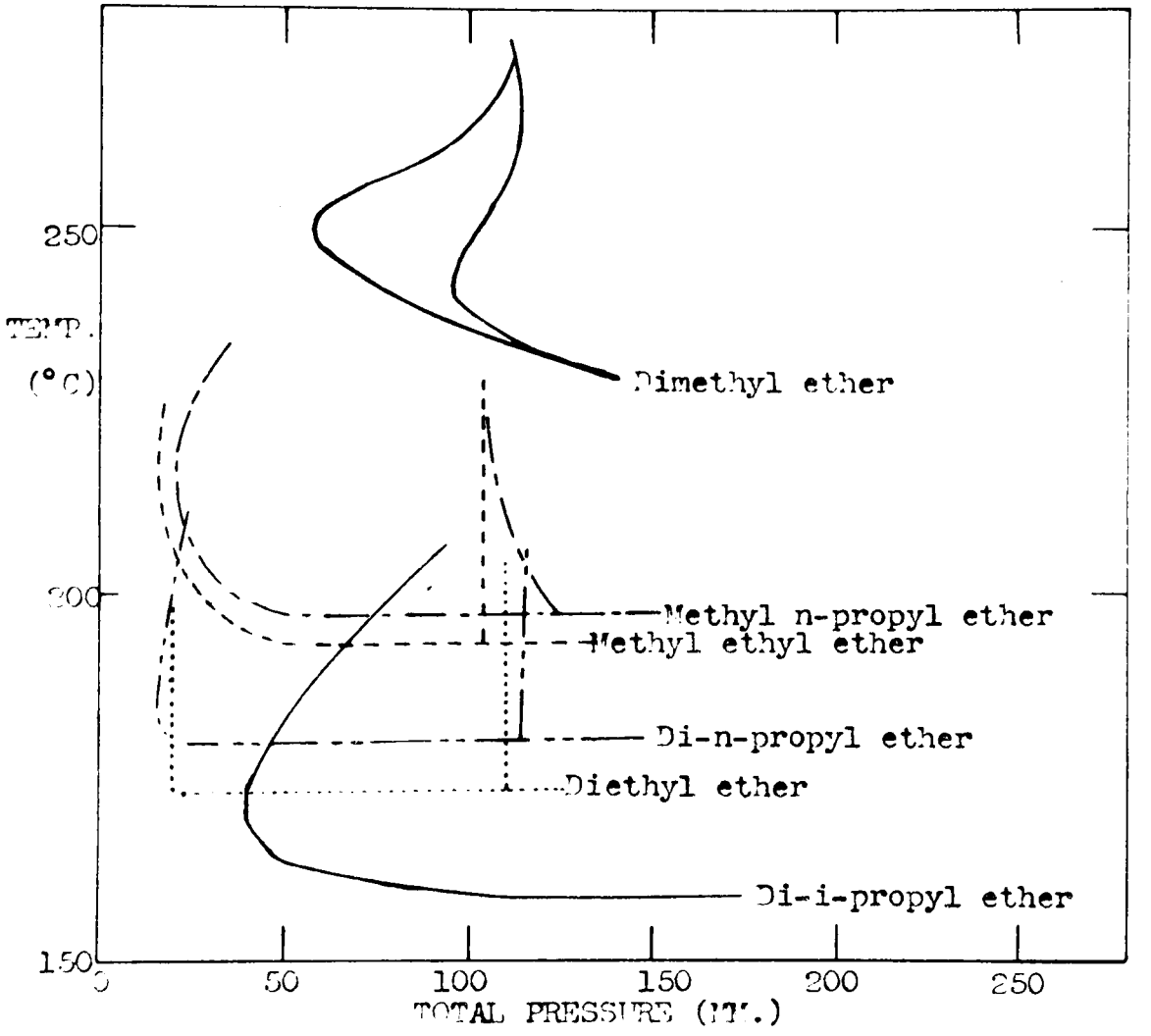
It was also found that outside the cool flame area for di-iso-propyl ether there was no appreciable pressure change in 24 hours. This might mean that two reactions occur, one giving a pressure increase and the other a pressure decrease and that they exactly equal one another, but analytical experiments to be mentioned later show that there is, in fact, no significant reaction under these conditions. Therefore, it has not been possible to make kinetic measurements with this ether. Under the conditions of the present investigation the cool flame with di-iso-propyl ether always appears within 30 seconds of the admission of the reactants to the reaction vessel.

No conditions were found where any of the ethers studied gave repeated cool flames.

For comparison, the limits of reaction for all the ethers studied have been plotted in Figure 10, and it will be noted that, except for dimethyl ether, they all lie in the same region of temperature and pressure.

FIGURE 10

The Pressure-Temperature
Explosion Diagram for Equimolar Ether-Oxygen Mixtures.



KINETICS OF THE LOW-TEMPERATURE SLOW OXIDATION

Factors Influencing the Maximum Rate

A study of the influence of the reaction variables on the maximum rate of pressure change, $\rho_{max.}$, has been found to be a useful basis for comparison of experiment and theory (1,3,5). The significance of simple pressure measurements is increased by the discovery that for many combustible gases the disappearance of reactants parallels the pressure change, Δp (16,17). The maximum rate probably indicates a steady state in the reaction where intermediates are formed and destroyed at an equal rate. If appreciable reaction has occurred before the attainment of the maximum rate the interpretation of this measurement becomes complicated because the reactant concentrations are somewhat lower than their initial values. This is especially true for the ethers and higher hydrocarbons where a pressure decrease precedes the establishment of the maximum rate of pressure increase. Nevertheless, the maximum rate probably remains a significant measure of the reaction and the effect of the reaction variables on the maximum rate of pressure increase will now be considered.

The Influence of Temperature

The influence of temperature on the maximum rate of reaction was studied with equimolar mixtures of diethyl and

dimethyl ether at a total pressure of 300 mm. and with diethyl, di-normal-propyl, and methyl normal-propyl ether at 100 mm.; the results are shown in Figures 11-14. The maximum variation in the temperature of the reaction mixture ($\pm 0.5^{\circ}$C.) is indicated in the figures and also points on the graphs for duplicate experiments giving the same result are marked '2'.

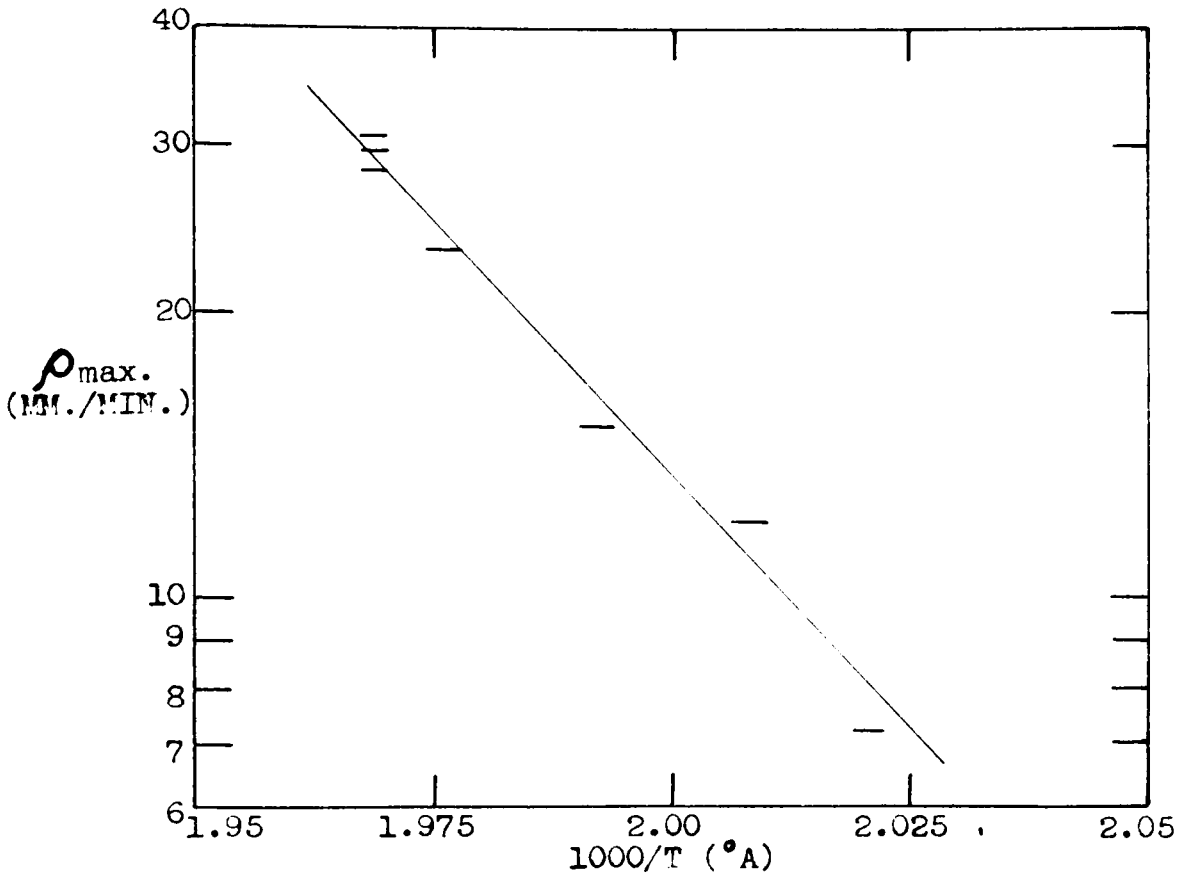
It was impossible to obtain a similar diagram with methyl ethyl ether because even though reaction occurred, the rate never showed the well-defined maximum observed with the other ethers under similar conditions; instead the pressure increased very slowly to its final value without discontinuity except for the initial pressure decrease. Further experiments, to be reported in the next section, show that this is due to oxygen inhibition.

An estimate of the reproducibility of the experiments can be formed from Figure 13 which includes the results of three groups of observations with diethyl ether; between the first and last groups over 600 experiments were made with other ethers giving all types of reaction, i.e. slow reactions, cool flames or ignitions.

Since the temperature coefficients of the rates have all been measured below the temperature at which cool flames appear, they are all well within the low temperature reaction region and would not be expected to show the negative temperature coefficient characteristic of the transition temperature region.

FIGURE 11

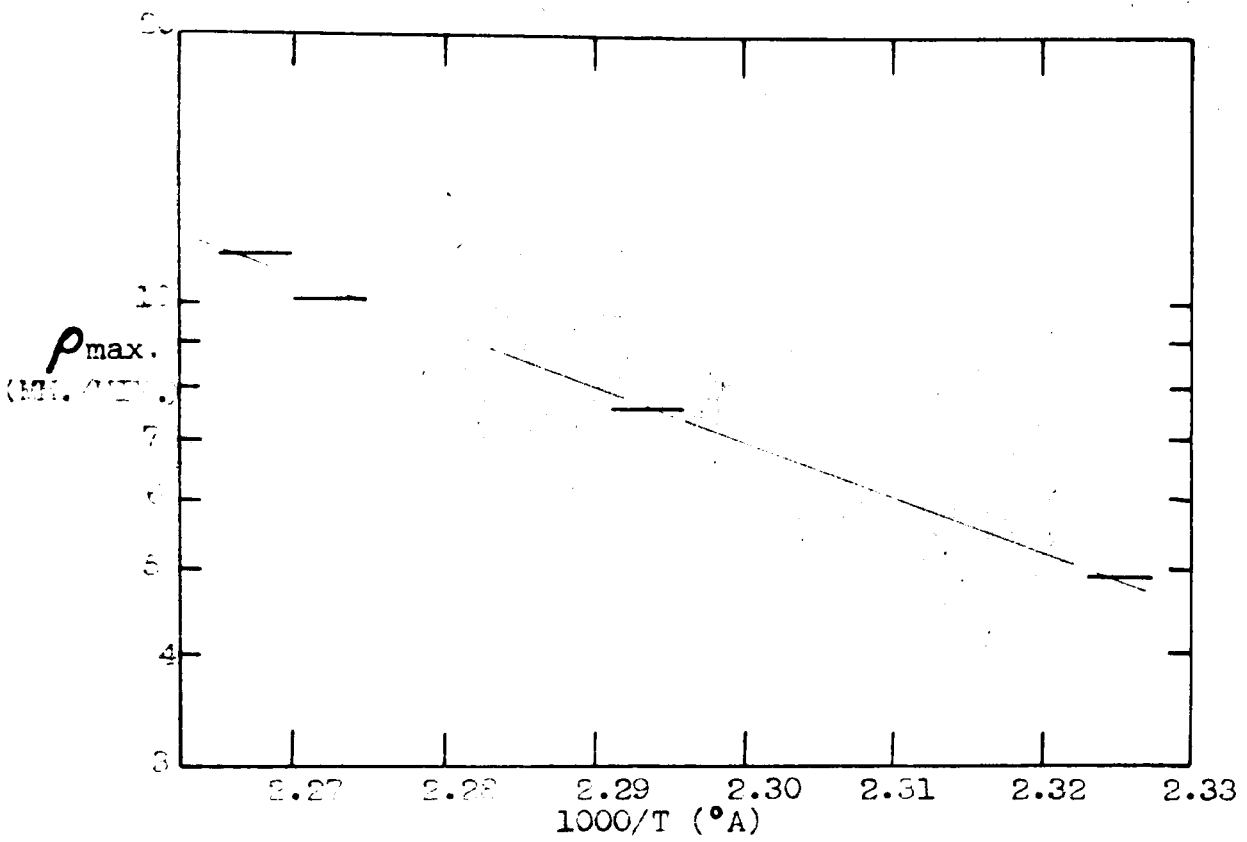
The Effect of Temperature
on the Maximum Oxidation Rate of Dimethyl Ether



Dimethyl ether pressure 150 mm.
Oxygen pressure 150 mm.

FIGURE 12

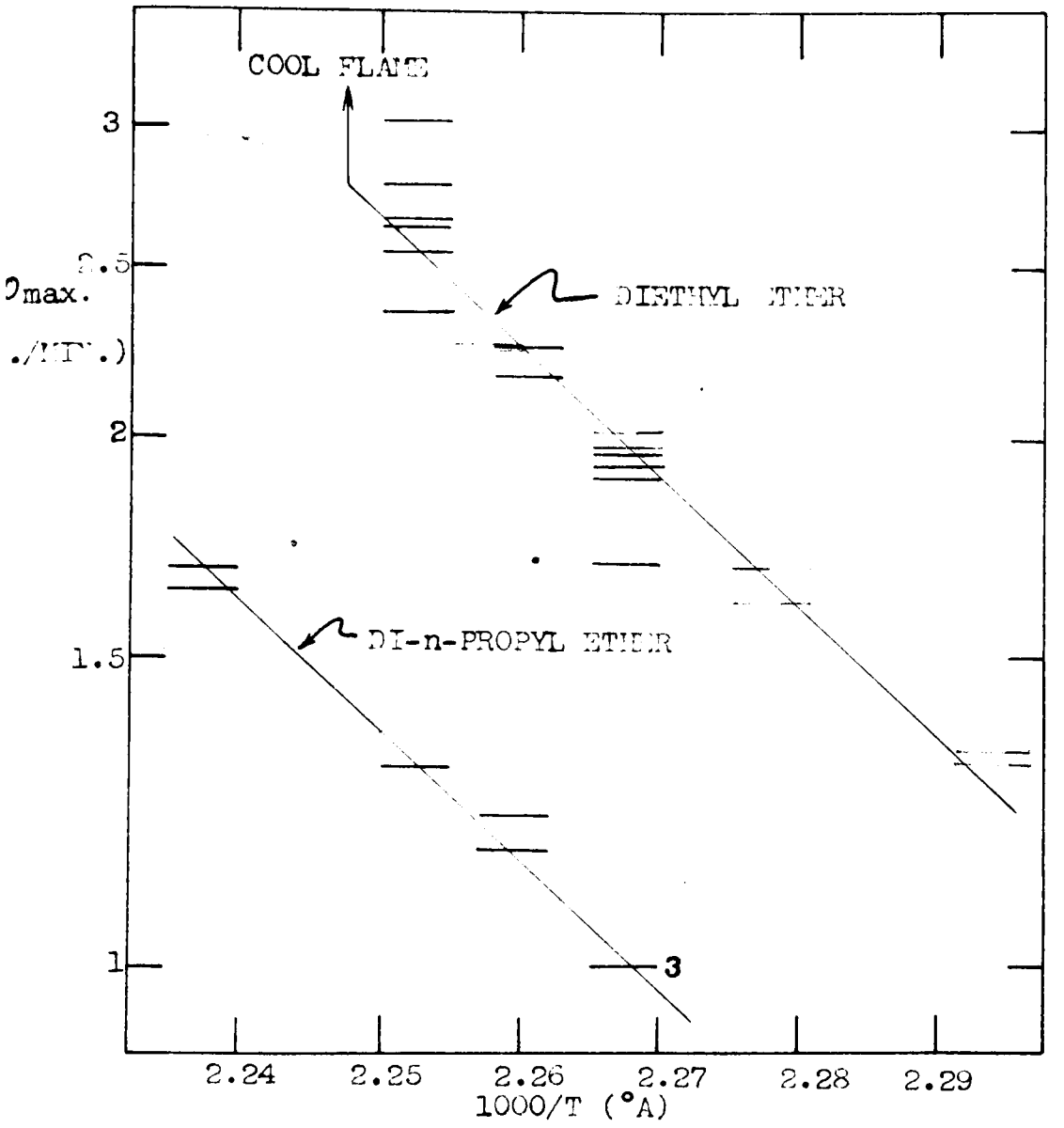
The Effect of Temperature
on the Maximum Oxidation Rate of Diethyl Ether



Diethyl ether pressure 150 mm.
Oxygen pressure 150 mm.

FIGURE 13

The Effect of Temperature
on the Maximum Oxidation Rate of Diethyl Ether
and Di-normal-Propyl Ether



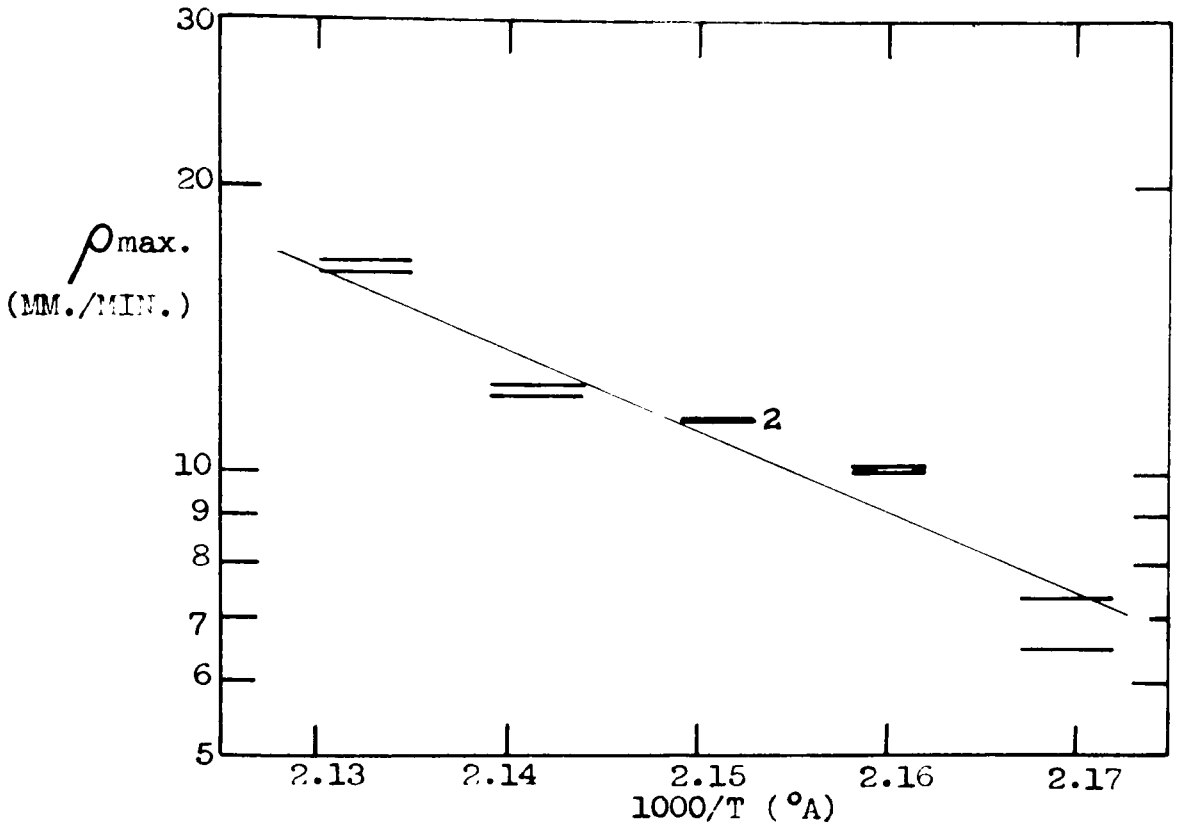
Diethyl ether pressure 50 mm.
Oxygen pressure 50 mm.

Experiments in
Group 1 ——
Group 2 ——
Group 3 ——

Di-n-propyl ether 50 mm.
Oxygen pressure 50 mm.

FIGURE 14

The Effect of Temperature on
the Maximum Oxidation Rate of Methyl n-Propyl Ether



Methyl n-propyl ether pressure 50 mm.
Oxygen pressure 50 mm.

However, the linear temperature dependence does contrast with the upward curvature observed with butanone in a range of about 5°C. below the cool flame temperature (16).

The range over which the temperature coefficient could be measured is very small, because on the one hand the reaction is too slow and the maximum rate blends into the slow pressure rise, while on the other, a cool flame appears. The absolute values of the slopes are therefore not very significant; they correspond to an activation energy of about 35 kcal. per mole. The data are useful for comparing ethers which do not oxidize at measurable rates at the same temperature, and for this purpose the results have been re-plotted in Figure 15.

To establish a link with other compounds already studied in this laboratory a few experiments were first made with normal-pentane, a frequently used reference substance. The results are also given in Figure 15.

The relative rate of oxidation deduced from this figure are:-

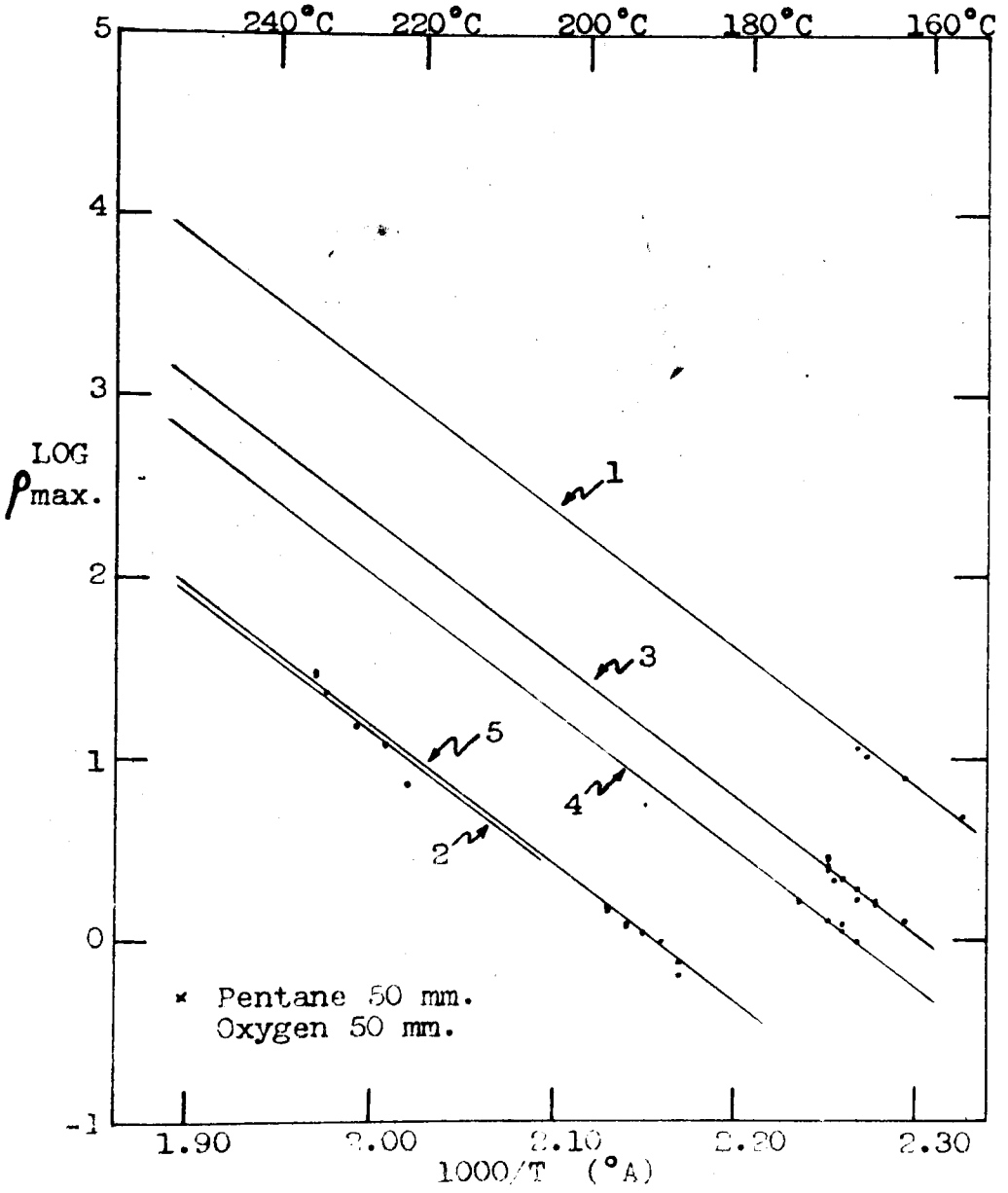
TABLE I

Relative Rates of Oxidation of the Ethers and Pentane.

Compound	Relative Rate			
Pentane	1			
Dimethyl ether	25	1		
Methyl n-propyl ether	175	7	1	
Di-n-propyl ether	1300	50	7	1
Diethyl ether	2500	100	14	2

FIGURE 15

The Effect of Temperature
on the Maximum Oxidation Rate of the Ethers.



1. Diethyl ether 150 mm. Oxygen 150 mm.
2. Dimethyl ether 150 mm. Oxygen 150 mm.
3. Diethyl ether 50 mm. Oxygen 50 mm.
4. Di-n-propyl ether 50 mm. Oxygen 50 mm.
5. Methyl n-propyl ether 50 mm. Oxygen 50 mm.

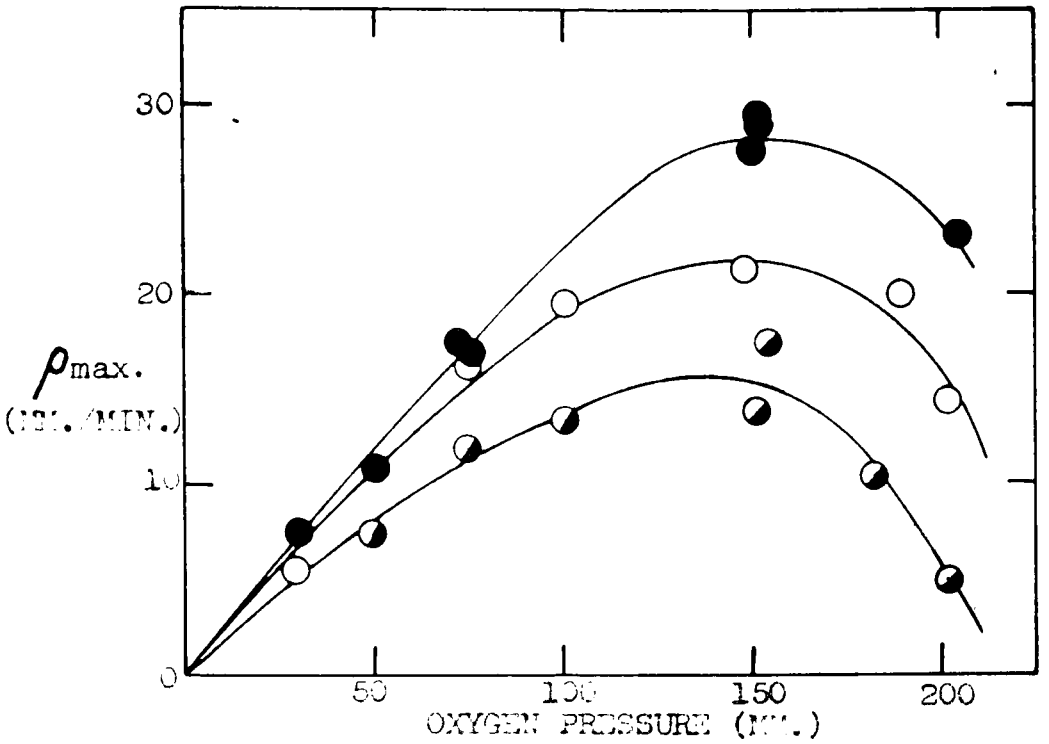
Direct comparison at the same temperature was possible with di-normal-propyl ether and diethyl ether and the results are given in Table II where the ratio of $\rho_{max.}$ for diethyl ether and $\rho_{max.}$ for di-n-propyl ether is shown at different temperatures and ether-oxygen mixtures. It is clear that none of the reaction variables reverse the order in which these compounds appear in Table I, although the ratio of the rates does change when oxygen is in excess.

Influence of Oxygen Pressure.

The dependence of maximum rate on oxygen concentration for a constant pressure of each of the ethers is shown in Figures 16-18. At first increased oxygen pressure favourably affects the rate but further increase produces inhibition and the rate declines to a very small value. Still further increase gives immeasurably low rates. The inhibition is even greater than has previously been observed with butanone and butane (5,8). The dependence is the same throughout the low temperature region with di-methyl and di-ethyl ether (Figures 16 and 17), but the curves at the higher temperatures studied are incomplete because ether-rich mixtures give rise to cool flames while the oxygen-rich mixtures give ignitions.

FIGURE 16

The Variation of the Maximum Oxidation Rate with Initial Oxygen Pressure

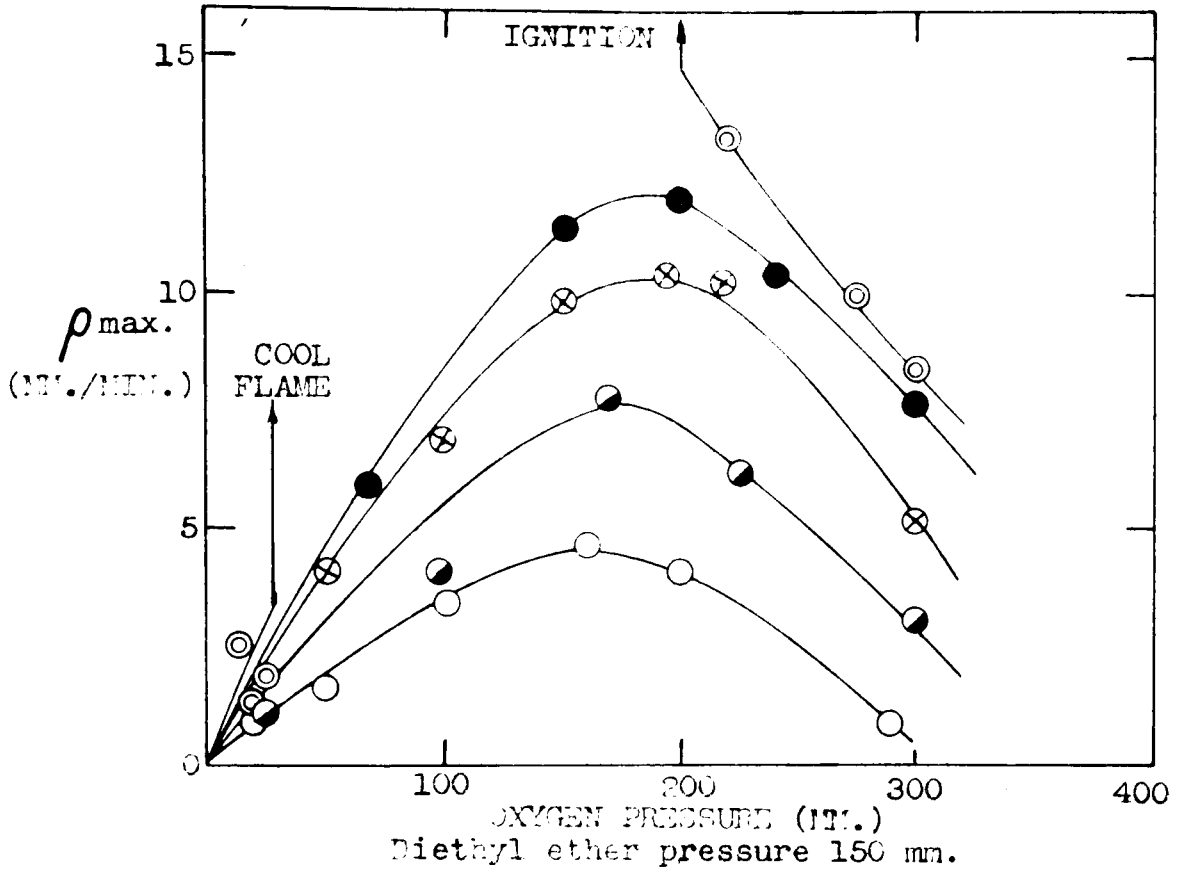


Dimethyl ether pressure 150 mm.

Temperature
229°C ◕
233°C ○
235°C ●

FIGURE 17

The Variation of the
Maximum Oxidation Rate with Initial Oxygen Pressure

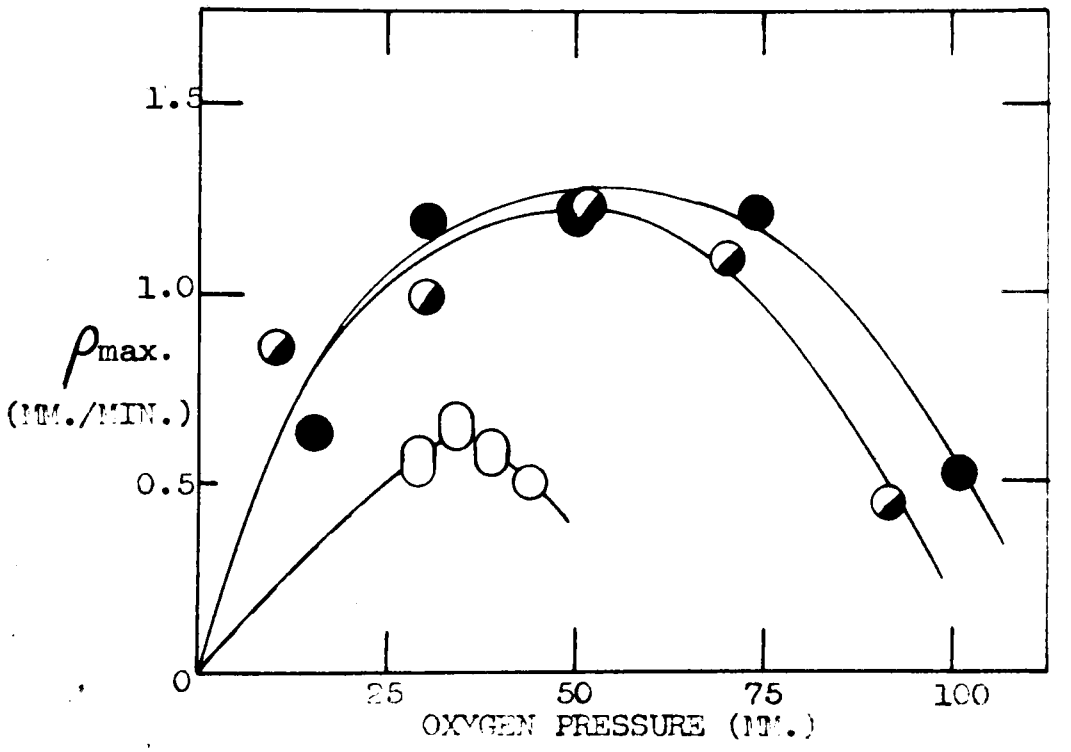


Diethyl ether pressure 150 mm.

Temperature	
173°C	◎
168°C	●
167°C	⊗
162°C	◪
157°C	○

FIGURE 18

The Variation of the Maximum
Oxidation Rate with Initial Oxygen Pressure



Di-n-propyl ether (50 mm. 171°C) - - - -
Methyl ethyl ether (50 mm. 190°C) - - -
Methyl n-propyl ether (50 mm. 194°C) - -

TABLE II

The Influence of the Reaction Variables on the Ratio of Maximum Oxidation Rates of Diethyl and Di-n-propyl Ethers.

Influence of Temperature

Ether 50 mm.
Oxygen 50 mm.

Temperature (°C)	Ratio of Maximum rates
168.0	1.9
169.5	1.9
171.0	2.1

Influence of Initial Oxygen Pressure

Ether 50 mm.
Temperature 171°C.

Oxygen pressure (mm.)	Ratio of Maximum rates
10	1.7
30	1.9
50	2.1
70	3.0
90	4.7

Influence of Initial Ether Pressure

Oxygen pressure 50 mm.
Temperature 171°C.

Ether pressure (mm.)	Ratio of Maximum rates
30	2.1
50	2.3
65	2.3

The accuracy of the results for methyl ethyl ether, as indicated by the size of the points in Figure 18, is poor because the rates are low and the maximum rate is not well defined. This figure shows that the temperature coefficient could not be measured with a reaction mixture of 50 mm. of methyl ethyl ether and 50 mm. of oxygen because, under these conditions, oxygen inhibits the reaction.

The relation between rate and oxygen concentration was studied in detail with dimethyl and diethyl at 233° and 162°C. respectively, and Figures 19 and 20 show the effect of oxygen at several initial ether pressures. The curves are incomplete because ignitions set in at high dimethyl ether pressures.

Further experiments were made with normal-pentane in the present apparatus to compare the effect of oxygen with that observed previously by Cullis (Figure 21) (1).

The general agreement is immediately apparent, the discrepancy in temperature is probably connected with the difference in shape, size and surface characteristics of the reaction vessels.

Influence of Ether Pressure

The results show that for each of the ethers studied the maximum rate of reaction increases with increasing concentration of ether, oxygen pressure being constant (Figures 22-24). This observation is in qualitative agreement with the

FIGURE 19

The Variation of the
Maximum Oxidation Rate with Initial Oxygen Pressure

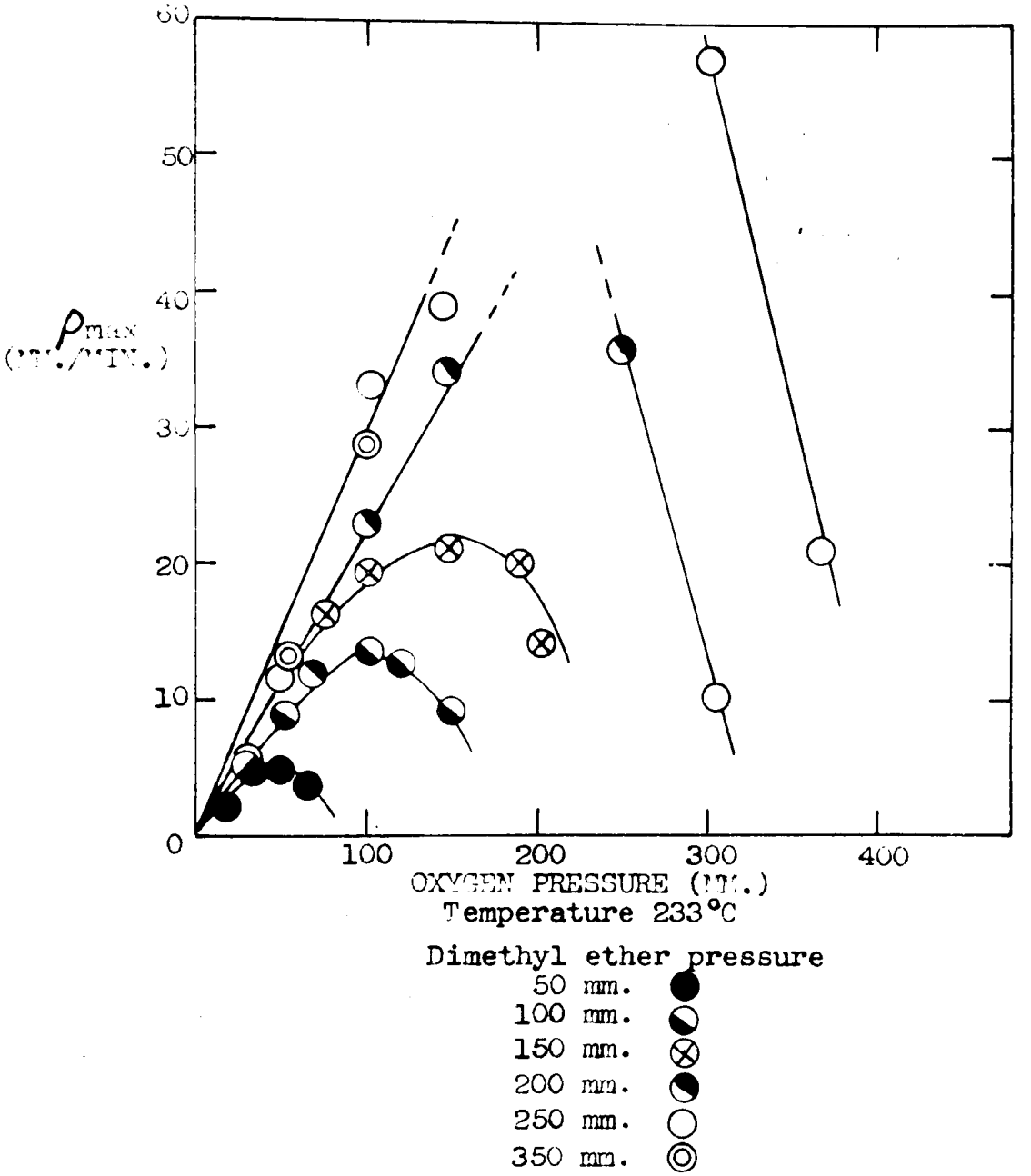
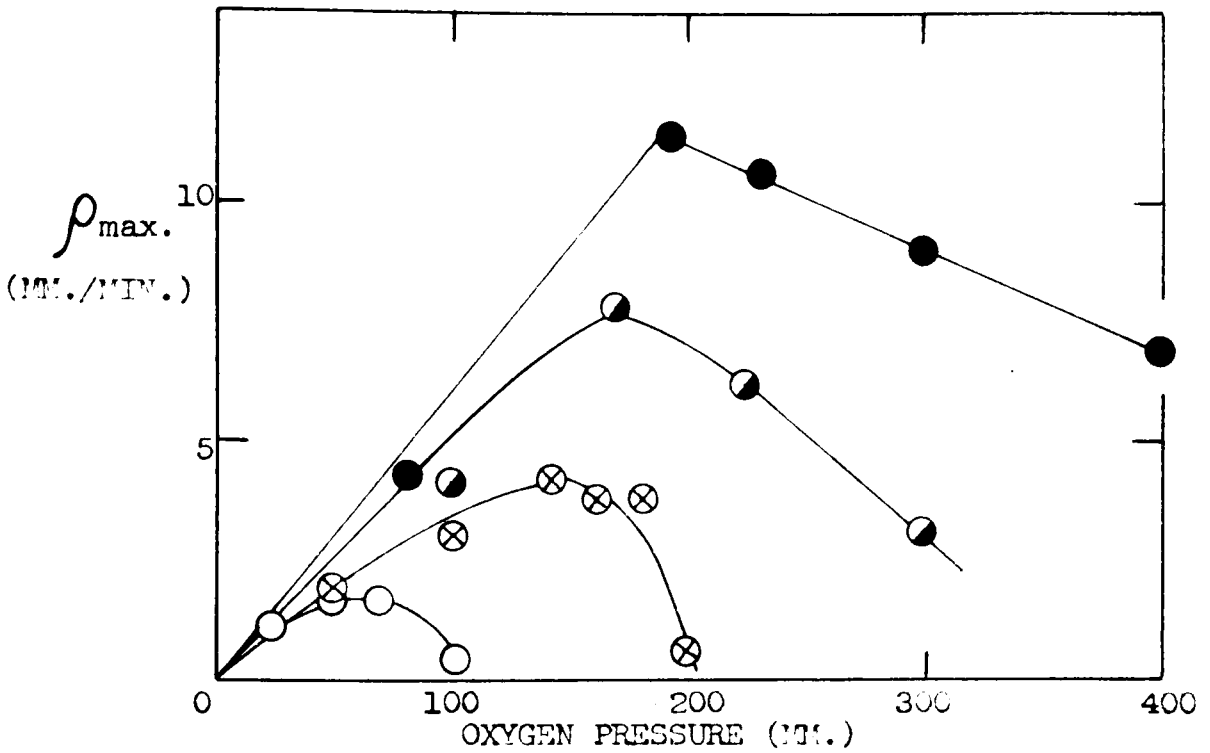


FIGURE 20

The Variation of the
Maximum oxidation rate with Initial Oxygen Pressure



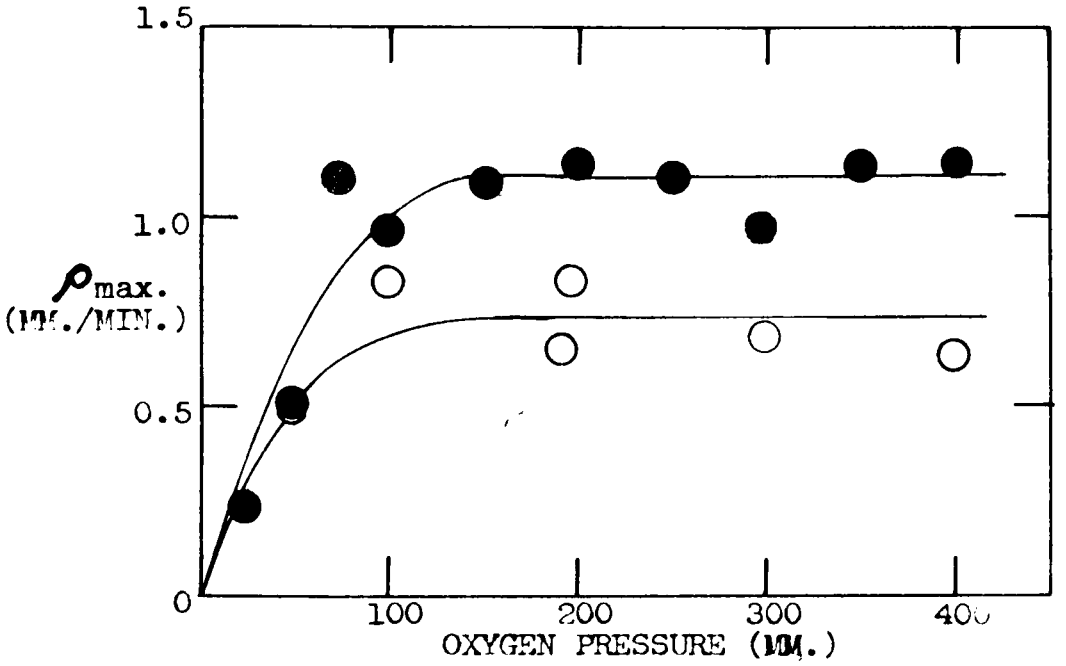
Temperature 162°C

Diethyl ether pressure

50 mm. ○
100 mm. ⊗
150 mm. ◪
200 mm. ●

FIGURE 21

The Variation of the Maximum
Oxidation Rate with the Initial Oxygen Pressure



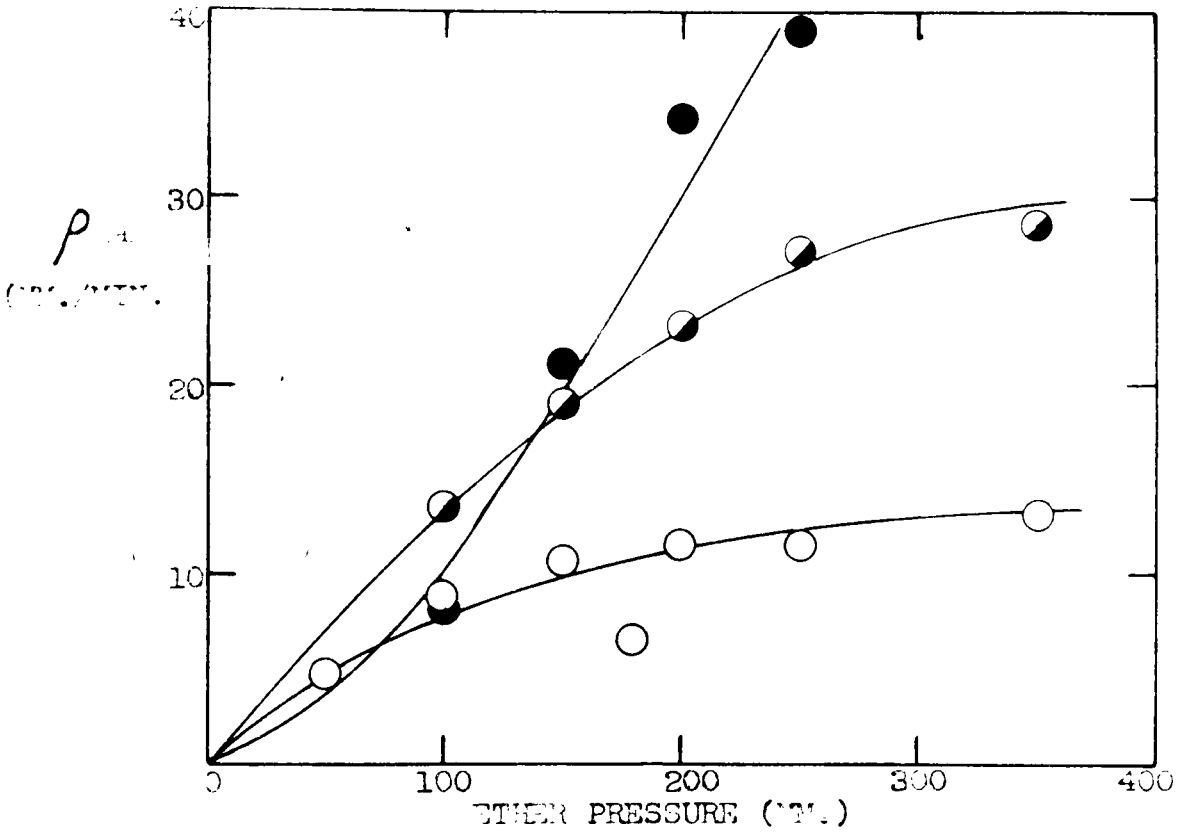
n-Pentane pressure
50 mm.

Results from reference (1) (227°C) ●

Comparison results (254°C) - - - - ○

FIGURE 22

The Variation of the Maximum Oxidation
Rate with Initial Pressure of Dimethyl Ether

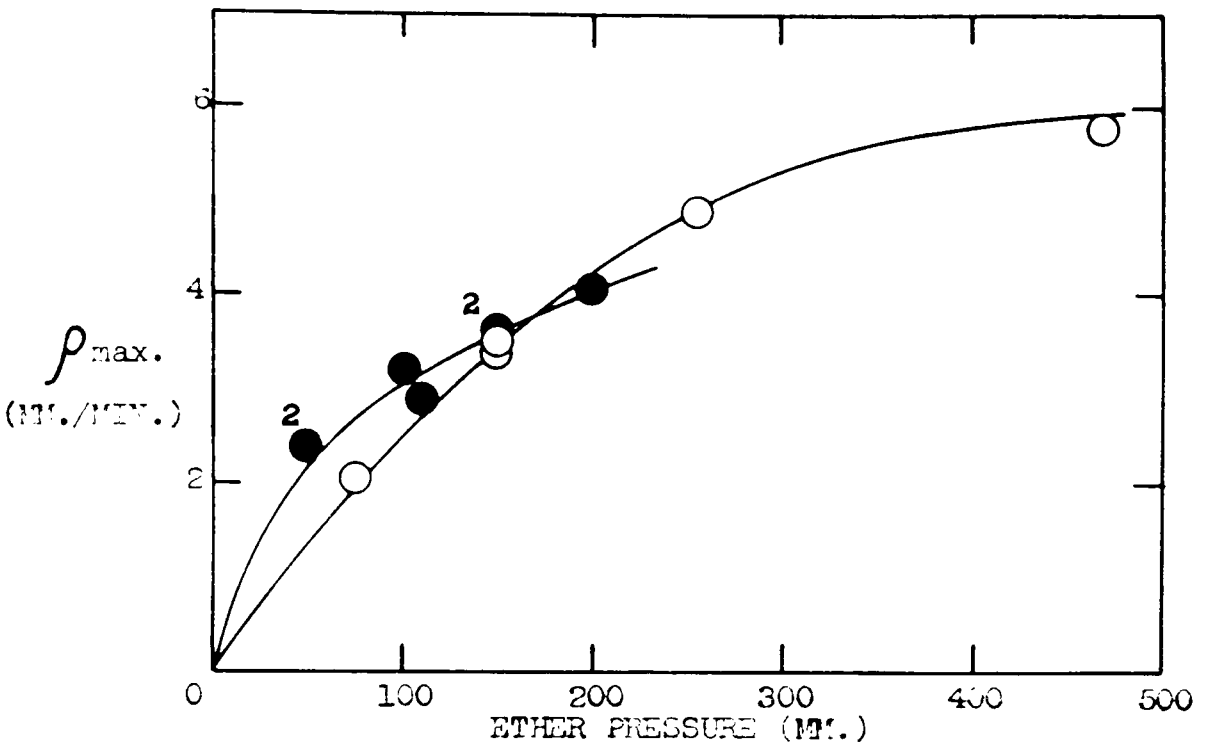


Temperature 233°C

Oxygen pressure
50 mm. ○
100 mm. ◐
150 mm. ●

FIGURE 23 .

The Variation of Maximum Oxidation Rate with Initial Pressure of Diethyl Ether

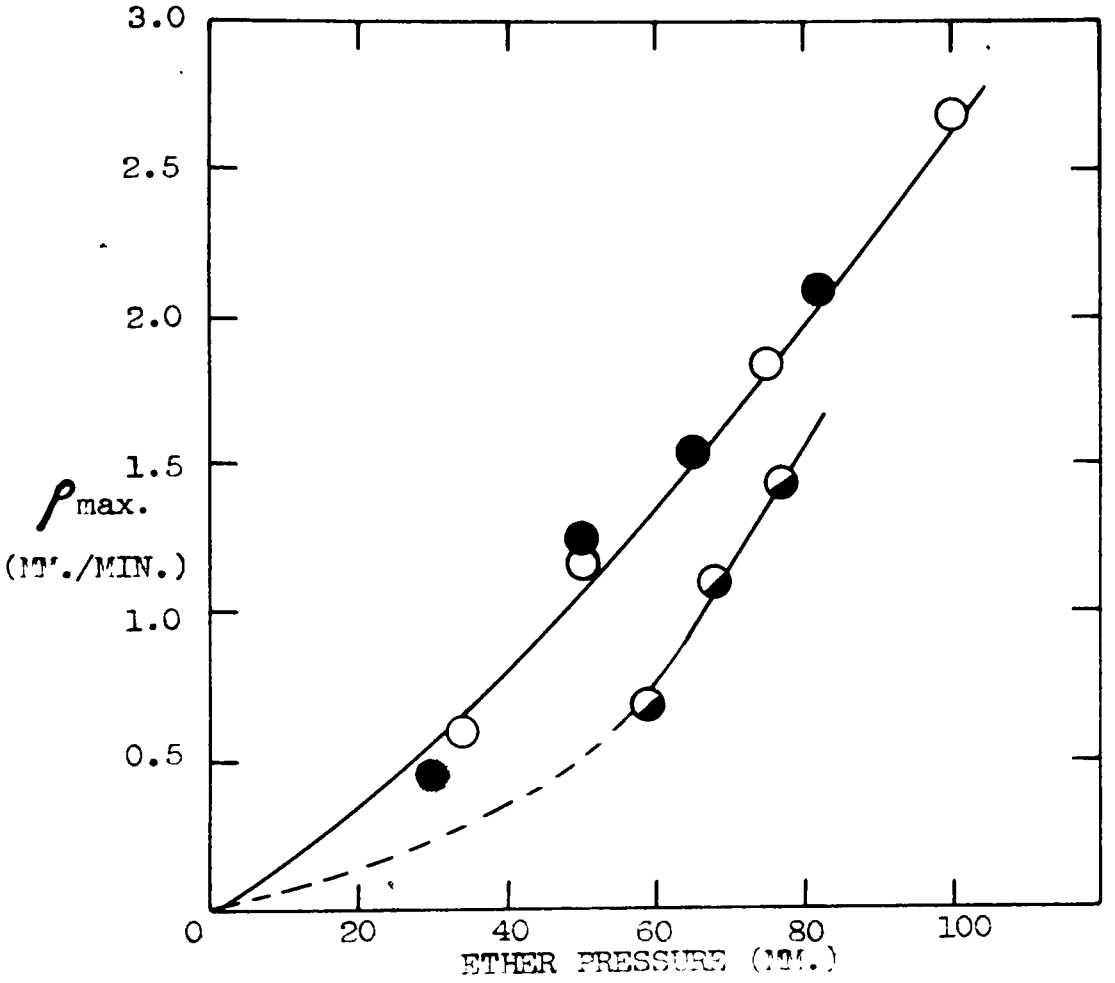


Temperature 157°C

Oxygen pressure
100 mm. ●
50 mm. ○

FIGURE 24

The variation of the Maximum
Oxidation Rate with Initial Pressure of Ether



Oxygen pressure 50 mm.

Di-normal-propyl ether (171°C) ●
Methyl ethyl ether (190°C) ◪
Methyl n-propyl ether (194°C) ○

previous investigations on oxidation of other substances (1,2,3,4,5). Closer comparison indicates that, in contrast to the other compounds for which information is available, the "apparent order" of reaction with respect to ether is unity or less. This is clear from Table III, but it should also be noted that the comparison is made at widely different reactant ratios. With ethers it is impossible, because of the strong inhibiting influence of excess oxygen already mentioned, to extend the measurements to low ether-oxygen ratios. At such low ratios the pressure change is slow and steady, and never shows a well-defined maximum. However, at the lowest ratios at which it was possible to make measurements (Figures 22 and 24) the relation between ether pressure and maximum rate is linear and extrapolation to lower reactant ratios (lower ether pressures) does indicate that the trend is toward an "apparent order" greater than one, in agreement with the behaviour of the other combustible gases.

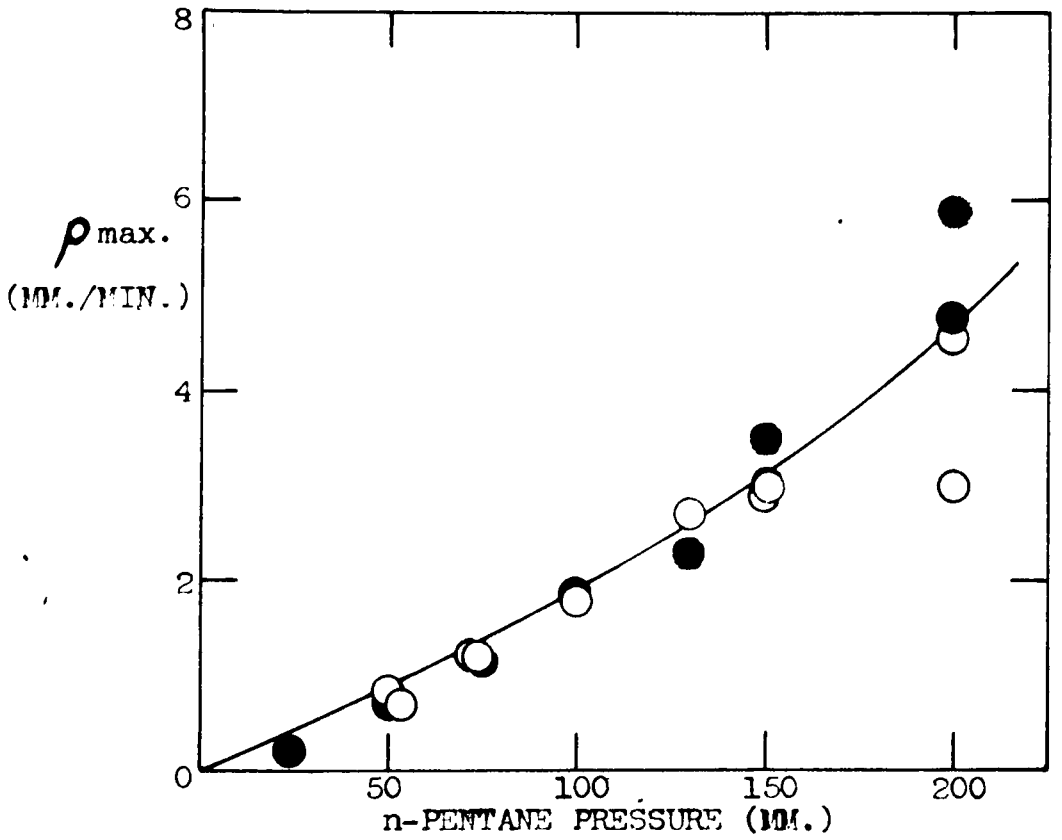
The rates of oxidation of methyl ethyl and methyl normal-propyl ether can now be compared: assuming that the temperature coefficient is the same at an ether-oxygen ratio of 77:50 as it is at a ratio of 50:50, the maximum rate for methyl normal-propyl ether at 190°C. from Figure 14 would be about 1.26 compared to 1.43 measured with methyl ethyl ether at the same temperature and reactant ratio. Thus these two ethers react at about the same rate, and methyl ethyl ether should appear

between methyl normal-propyl and di-normal-propyl ether in Table I.

The results of additional experiments with normal-pentane are shown together with those of Cullis in Figure 25; once again the general agreement is good except for the temperature difference.

FIGURE 25

Variation of Maximum Oxidation Rate
with Initial Pressure of normal-Pentane



Oxygen pressure 100 mm.

Results from reference (1) (227°C) - - - ●
Comparison Results (254°C) - - - - - - - ○

TABLE III

The Dependence of the "Apparent Order" of the Rate with respect to Organic Reactant on the Reactant Ratio

Compound (RH)	Range of RH pressure (mm.)	O_2 press. (mm.)	RH/O_2 ratio	Order of rate with respect to (RH)	1/e dependence on (RH) pressure
Butane	25-125	250	0.1-0.5	>1	linear
Pentane	25-225	100	0.25-2.3	>1	>linear
Hexane	20-170	100	0.2-1.7	>1	>linear
2-methyl pentane	20-150	200	0.1-0.75	>1	linear
1-chloro-propane	30-90	102	0.29-0.88	>1	
2-chloro-propane	30-95	250	0.12-0.38	>1	
1-chloro-3-methyl butane	25-140	200	0.12-0.70	>1	
2-chloro-butane	25-150	200	0.12-0.75	>1	
Ethylamine	20-200	200	0.1-1.0	>1	
Propylamine	10-100	200	0.05-0.5	>1	
Butanone	75-160	400	0.19-0.4	>1	>linear
Dimethyl ether	50-360	50	1-7.2	<1	<linear
	100-360	100	1-3.6	<1	<linear
	100-250	150	0.67-1.7	1	linear
Diethyl ether	50-200	50	1-4.0	<1	<linear
	75-470	100	0.75-4.7	<1	<linear
Di-n-propyl ether	30-80	50	0.6-1.6	1	linear
Me.ethyl ether	58-77	50	1.2-1.4	1	linear
Me.n-propyl ether	34-100	50	0.67-2.0	1	linear

The Influence of an Added Inert Gas

Addition of nitrogen to diethyl ether-oxygen mixtures is shown by the results in Table IV to have no significant effect on the maximum rate.

TABLE IV

The Influence of Added Nitrogen on the Maximum Oxidation Rate and the Induction Period.

Diethyl ether pressure 150 mm.
Oxygen pressure 150 mm.
Temperature 168°C.

Nitrogen added (mm.)	Maximum rate (mm/min.)	Induction period (min.)
0	7.5	15.0
0	7.4	15.0
0	7.2	15.5
0	7.2	15.0
10	7.0	15.5
50	6.8	16.0
160	7.3	14.5
300	7.0	15.0

- - - - - - -

Diethyl ether pressure 150 mm.
Oxygen pressure 50 mm.
Temperature 168°C.

Nitrogen added (mm.)	Maximum rate (mm/min.)	Induction period (min.)
0	3.0	4.75
100	2.8	5.0
200	2.9	5.0
300	2.4	5.0

Factors Influencing the Induction Period

To make the comparison of the kinetic relations of the ethers and other compounds as complete as possible the influence of the reaction variables on the induction period was determined. Several definitions for the induction period, θ, are in current use; one, for example, is the time elapsed between the admission of reactants and the attainment of the maximum rate (16) and another is the time for the establishment of a standard rate (e.g. 0.5 mm. per minute)(8). Since it was found that the reaction with ethers accelerates very quickly from 0.5 mm. per min. to its maximum rate either of the two definitions give the same form to the relationships to be described. The former definition is more convenient in practice, and therefore it was used.

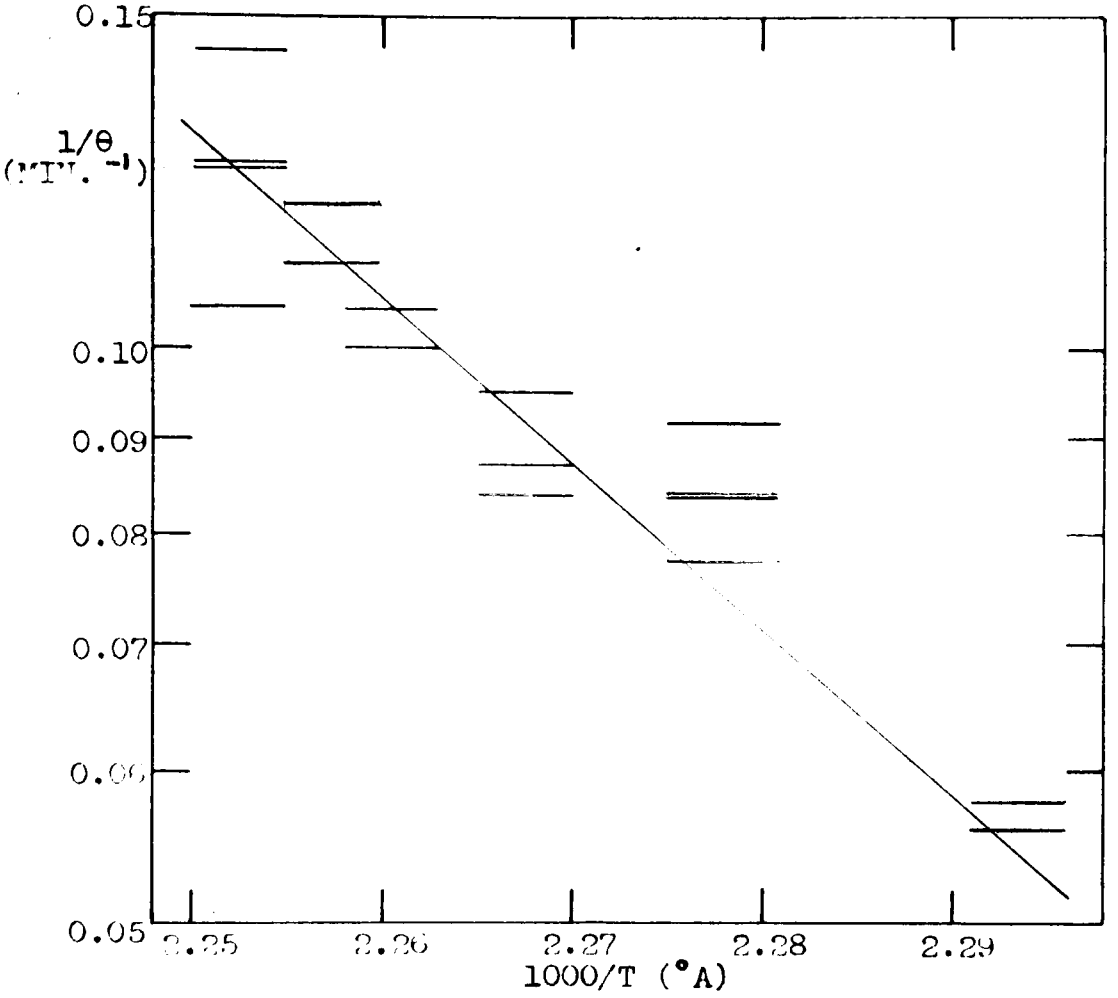
The Influence of Temperature.

Temperature increase always produces a shortening of the induction period and a plot (Figure 26) of the logarithm of the reciprocal induction period and the reciprocal of the absolute temperature for diethyl ether is linear in the low temperature region. The "activation energy" is about 40 kcal. per mole.

The reproducibility of the induction period is not as good as that obtained with the maximum rate. This is not uncommon with oxidation reactions (1,16) and several reasons

FIGURE 26

The Effect of Temperature
on the Induction Period with Diethyl Ether.



Diethyl ether pressure 50 mm.
Oxygen pressure 50 mm.
Experiments in
Group 1 ——
Group 2 ——
Group 3 ——

have been suggested. The induction period may be more sensitive to surface changes than the maximum rate or, since oxidations depend on a chain mechanism, small and variable amounts of impurities in the reactants may act as "inhibitors" or "promotors" and influence the induction period by hindering or helping the development of the chain. Results to be discussed in a later section on the effect of surface indicate that the former reason is likely to be the less important.

In contrast to the results with butanone, the linear relation between log $1/\theta$ and $1/T$ does not continue from the low temperature into the cool flame region. The period between the admission of the reactants and the appearance of the cool flame at 172°C. ($1/T(^{\circ}K) = 2.24 \times 10^{-3}$) is 25 seconds ($1/\theta = 2.4$ min.$^{-1}$) which on the scale of Figure 26 would appear about 9 inches above the upper margin.

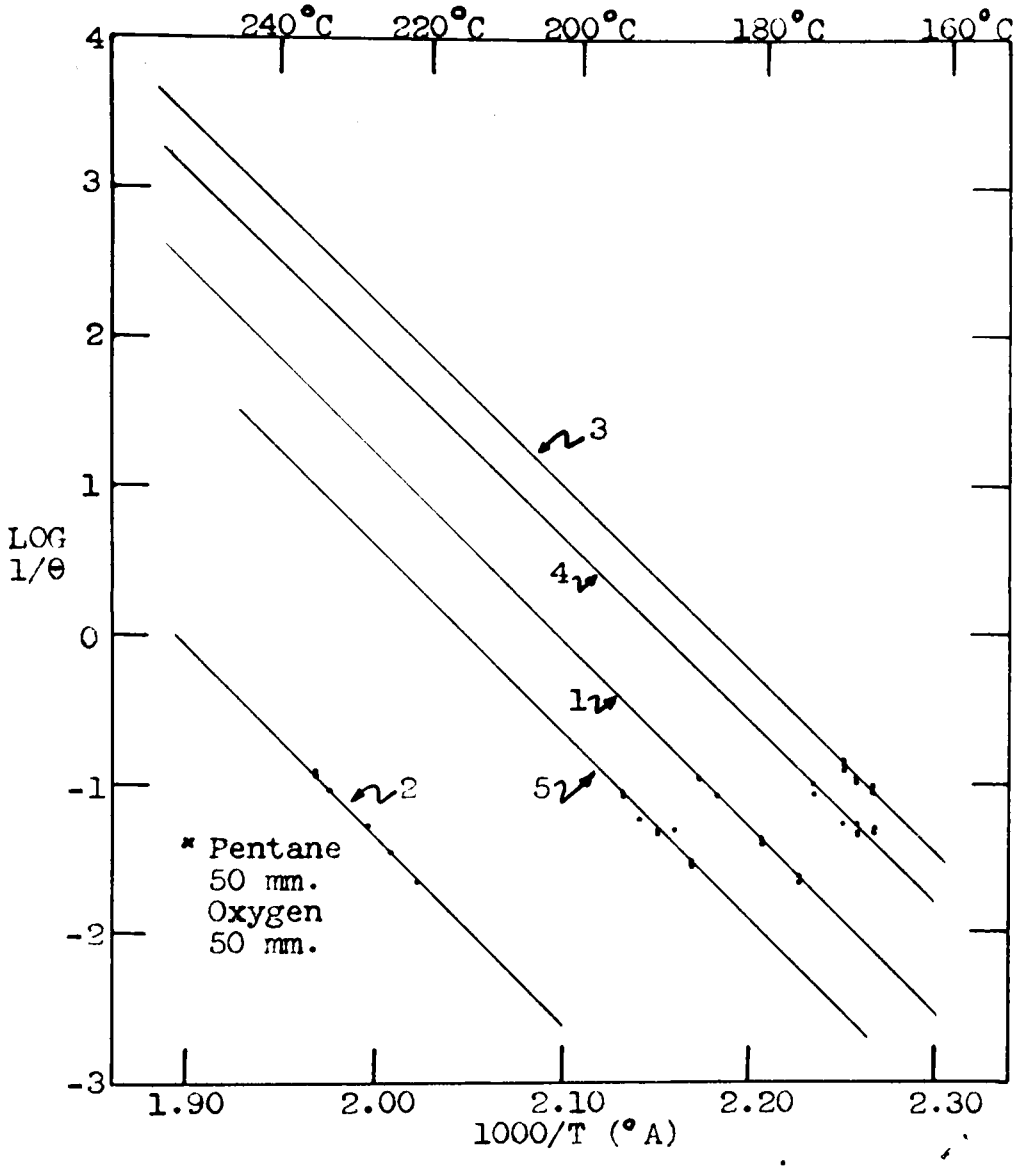
Similar results have been obtained with each of the other ethers and for comparison they are plotted together in Figure 27.

The Influence of Oxygen Pressure

The induction period lengthens as the initial pressure of oxygen is increased, the ether pressure being constant. The reciprocal of the induction period ($1/\theta$ min.$^{-1}$) is plotted against oxygen pressure in Figures 28-30 and it appears that the effect of oxygen is just the opposite of that observed with hydrocarbons. However, it is reminiscent of the butanone

FIGURE 27

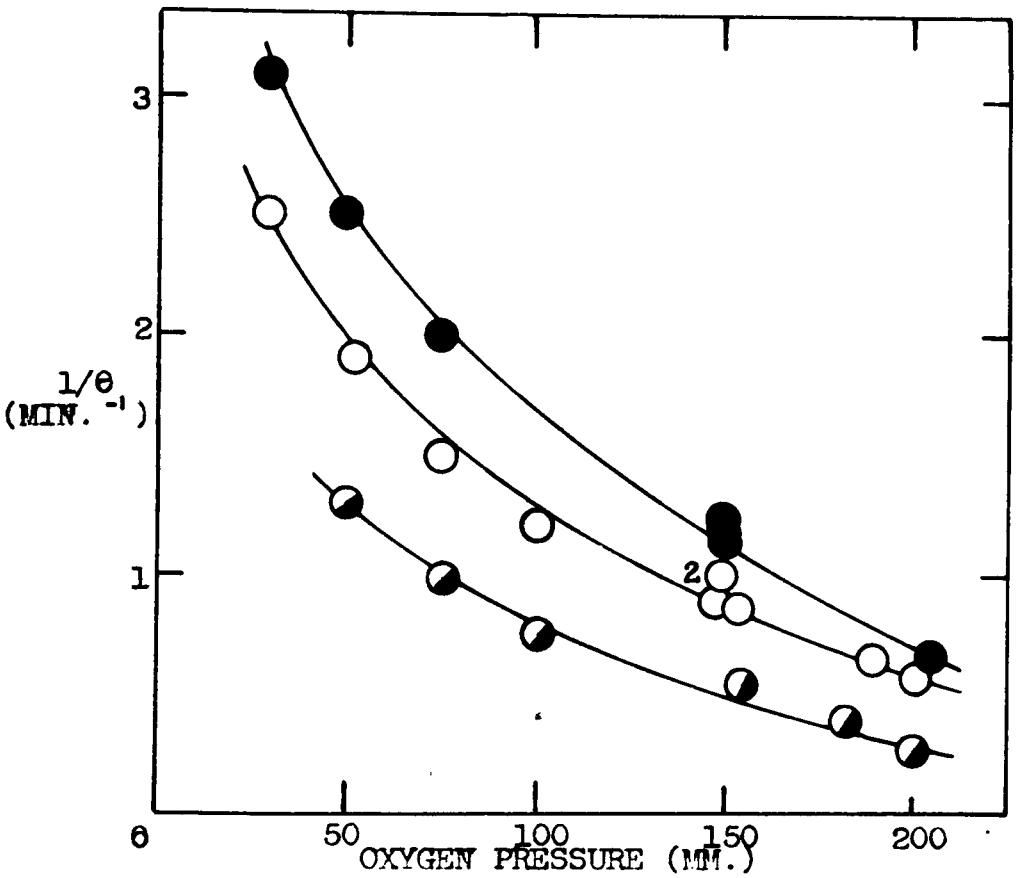
The Effect of Temperature
on the Induction Period with the Ethers



1. Diethyl ether 150 mm. Oxygen 150 mm.
2. Dimethyl ether 150 mm. Oxygen 150 mm.
3. Diethyl ether 50 mm. Oxygen 50 mm.
4. Di-n-propyl ether 50 mm. Oxygen 50 mm.
5. Methyl n-propyl ether 50 mm. Oxygen 50 mm.

FIGURE 28

The Variation of the
Induction Period with Initial Oxygen Pressure



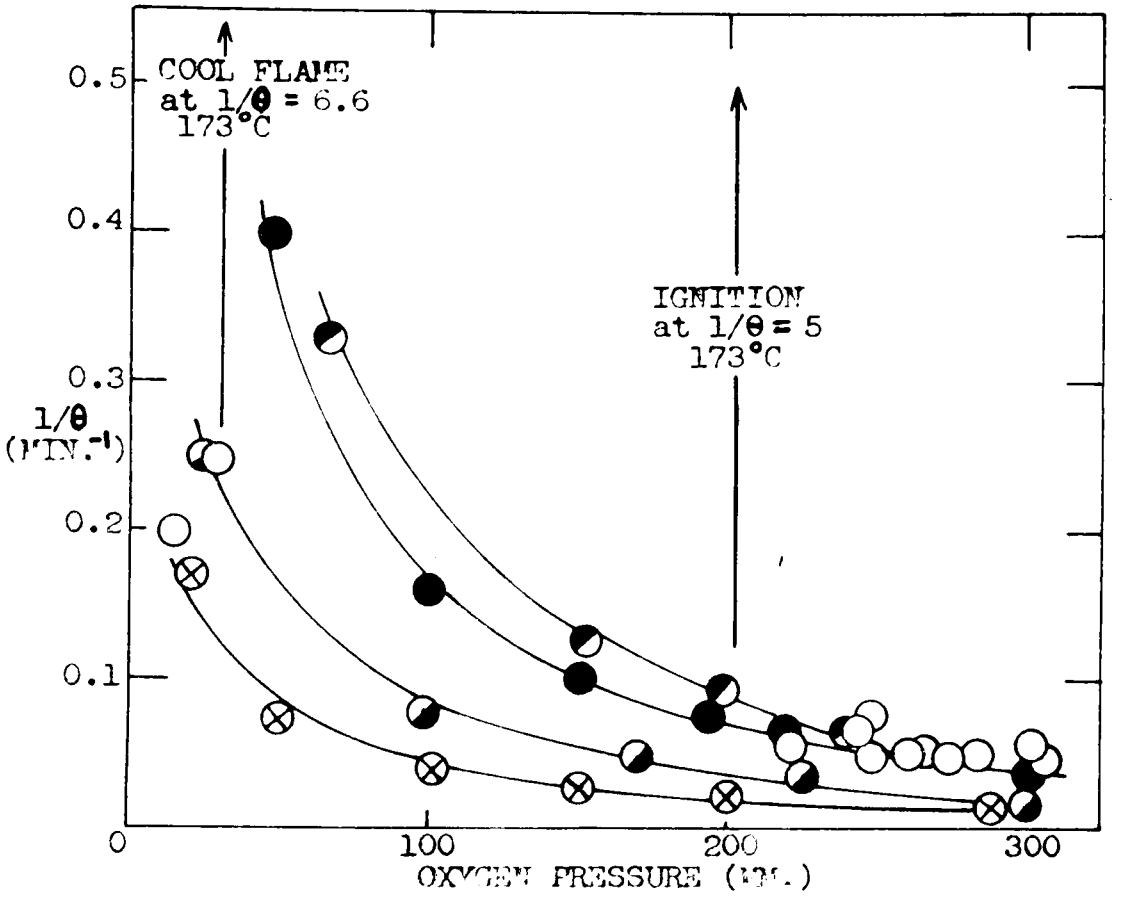
Dimethyl ether pressure 150 mm.

Temperature

229°C
233°C
235°C

FIGURE 29

The Variation of the
Induction Period with the Initial Oxygen Pressure

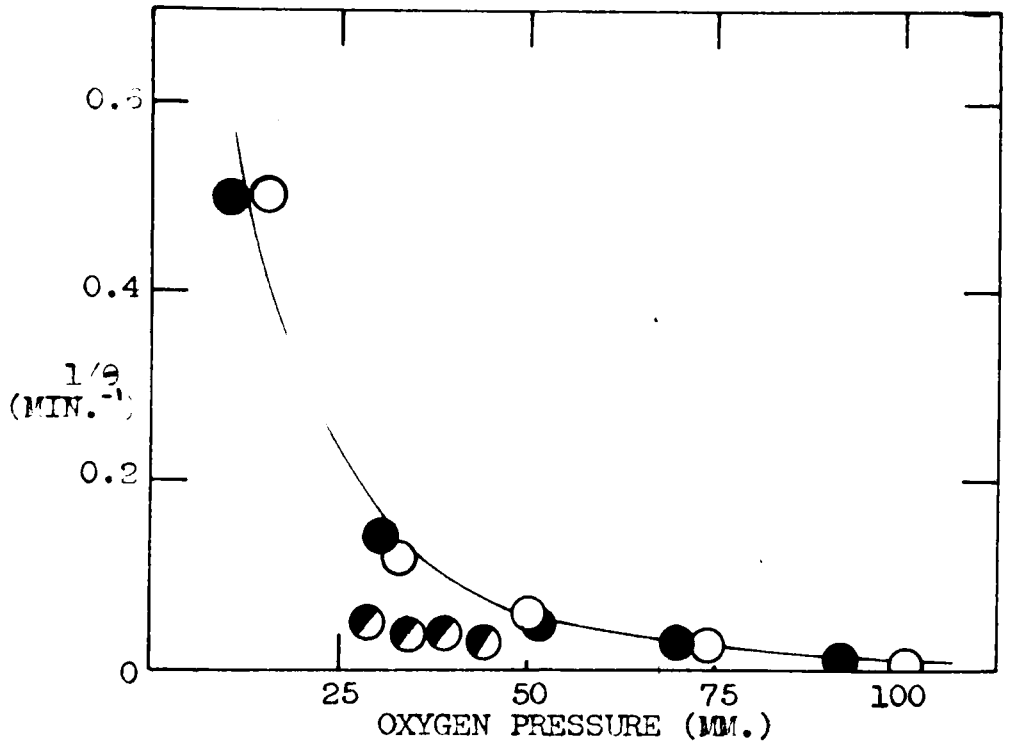


Diethyl ether pressure 150 mm.

Temperature
157°C ⊗
162°C ◪
167°C ●
168°C ◪
173°C ○

FIGURE 30

The Variation of the Induction Period With Initial Oxygen Pressure



Ether pressure 50 mm.

Di-normal-propyl ether (171°C) ●
Methyl ethyl ether (190°C) ◐
Methyl n-propyl ether (194°C) ○

results at low oxygen pressures, and there is the possibility that if the measurements could be extended to higher pressures the dependence would pass through a minimum and thereafter increase.

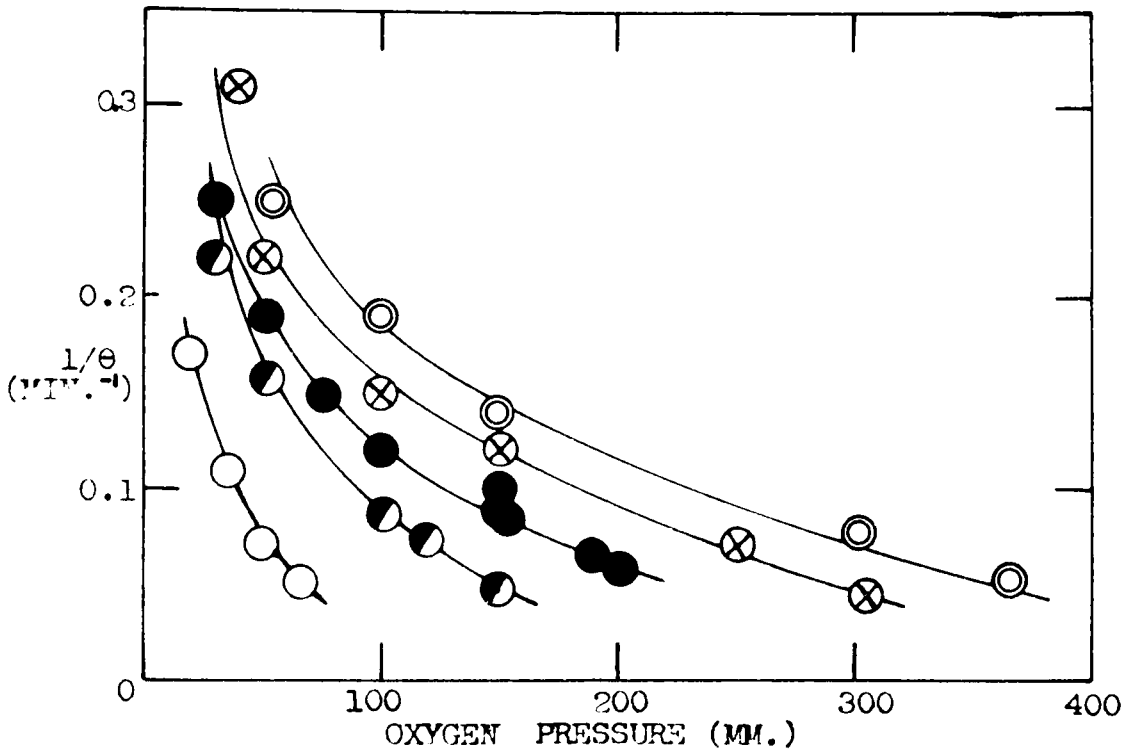
Figures 28 and 29 show that the behaviour is the same throughout the portion of the low temperature region in which measurements could be made. An interesting feature of Figure 29 is the large discontinuity at 173°C. on passing from slow reaction conditions to cool flames or ignitions. With normal-pentane, normal-hexane (15) and butanone (16) the relation is perfectly continuous between the two zones, as has been pointed out in the Introduction. At pressures below the cool flame limit and above the ignition limit in Figure 29 it was very difficult to reproduce the induction period, probably because under these conditions minor factors affect the delicate poise between the two types of reaction.

Since ethers show an unusual dependence of the rate on oxygen concentration compared to other compounds additional experiments were made with diethyl and dimethyl ethers. The results, presented in Figures 31 and 32 indicate that oxygen exerts the same influence on the induction period over a wide range of initial ether concentrations.

The influence of oxygen on the oxidation of normal-pentane is compared with Cullis' observations in Figure 33. It is clear that the general relationship is unaltered.

FIGURE 31

The Variation of the
Induction Period with the Initial Oxygen Pressure



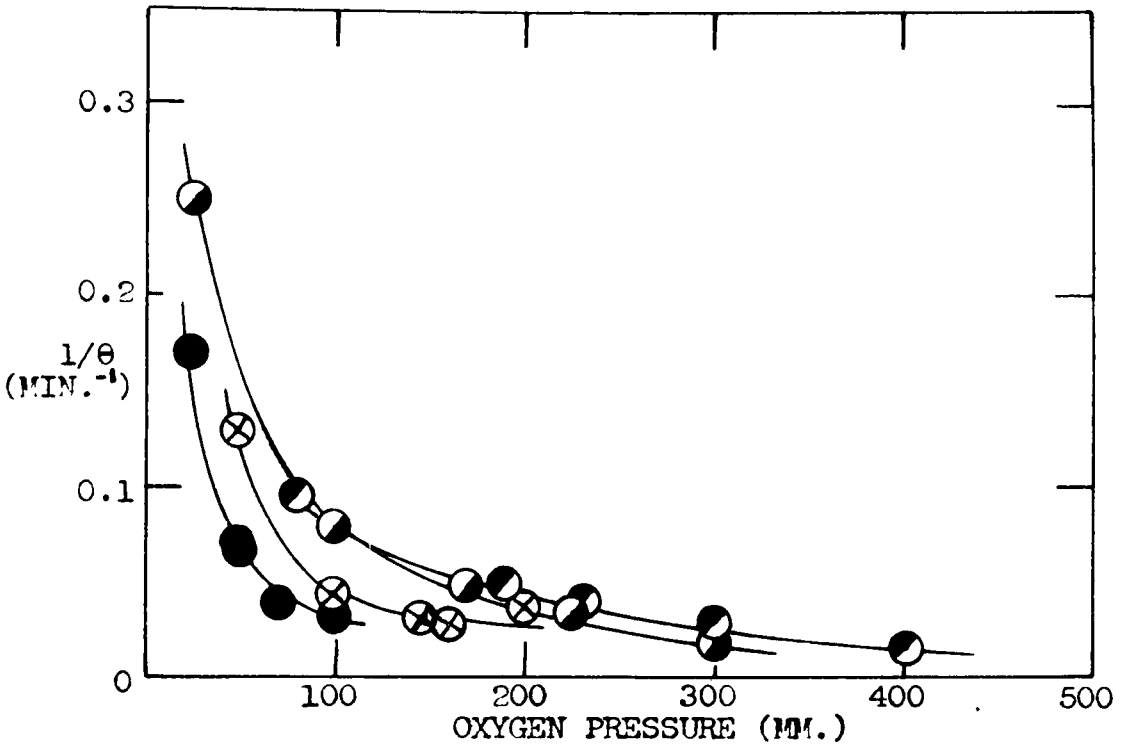
Temperature 233°C

Dimethyl ether pressure

50 mm. ○
100 mm. ◐
150 mm. ●
200 mm. ⊗
250 mm. ◎

FIGURE 32

The Variation of the
Induction Period with the Initial Oxygen Pressure

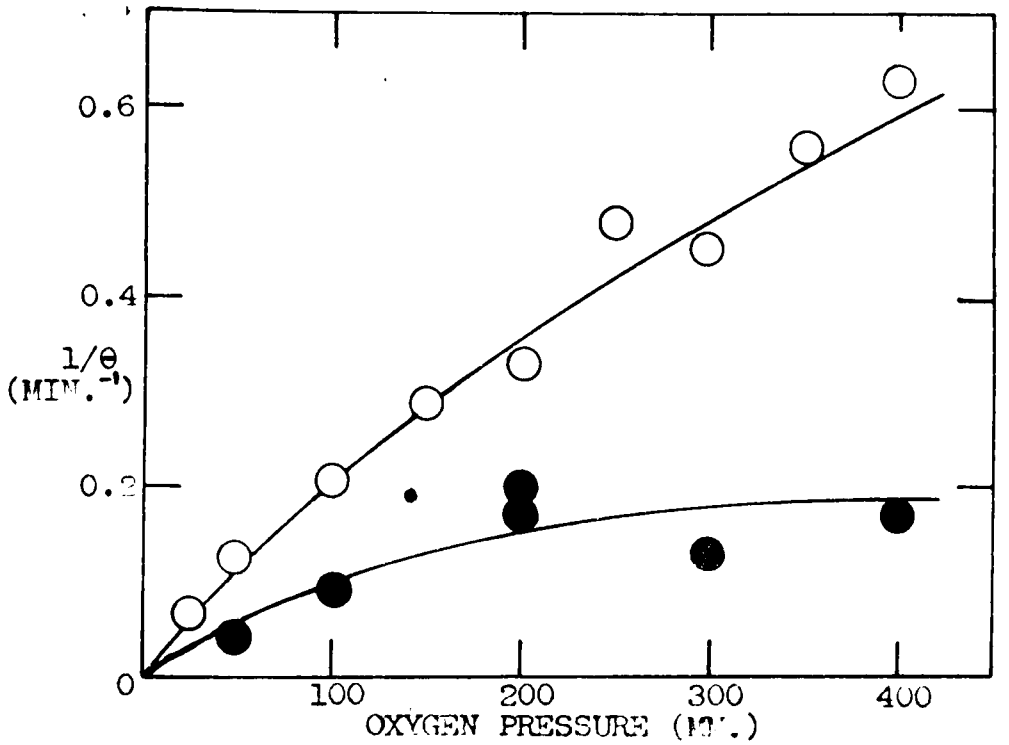


Temperature 162°C

Diethyl ether pressure
50 mm.
100 mm.
150 mm.
200 mm.

FIGURE 33

The Variation of the Induction Period with the Initial Oxygen Pressure



n-Pentane pressure 50 mm.

Results from reference (1) (227°C) ○

Comparison results (254°C) - - - - - ●

The Influence of Ether Pressure.

The induction period was found to decrease with increasing initial ether pressure, the oxygen pressure being constant. These results, plotted in Figures 34-36, are in accord with the observations of similar experiments made with other organic compounds.

More detailed comparison of the results in the figures and in Table III shows that although the dependence on ether concentration is linear at low reactant ratios it decreases at higher ratios. It was impossible to make measurements at lower ratios for reasons already discussed, but extrapolation of the data for dimethyl ether at 150 mm. pressure in Figure 34, and for other ethers in Figure 36 indicates that the curves would have upward curvature if the measurements could be extended in this direction. In so far as this is true, ethers and other compounds are identical.

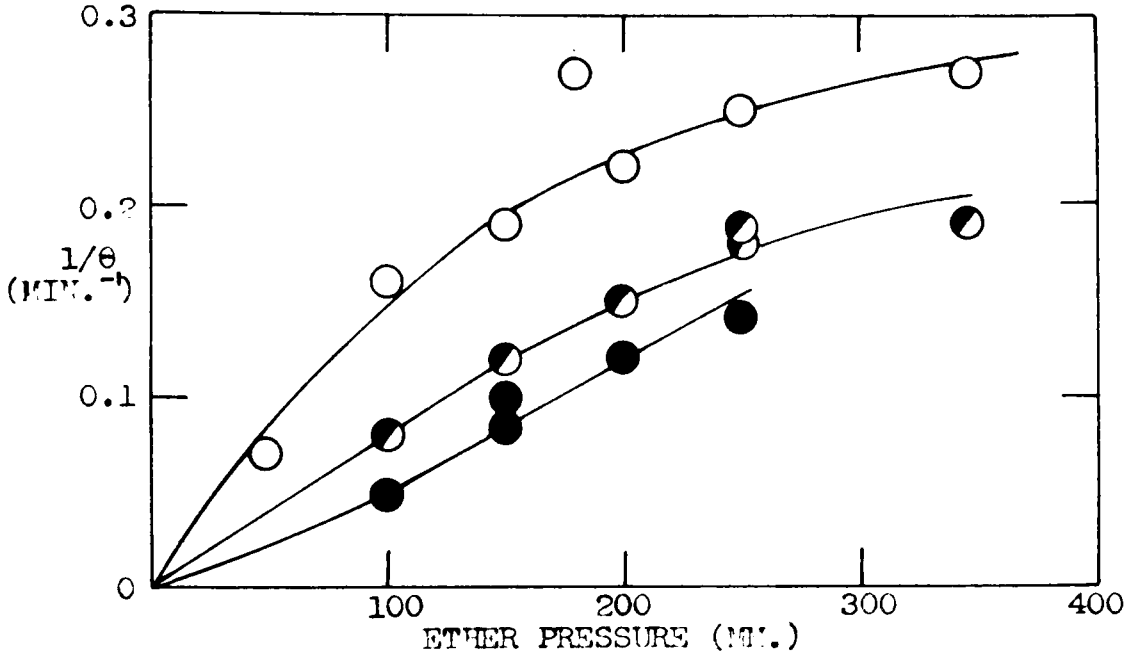
The curves for normal-pentane (Figure 37) again show general agreement.

The Influence of Added Inert Gas.

The results presented in Table IV show conclusively that additions of nitrogen are without effect on the kinetics of the oxidation of ether.

FIGURE 34

The Variation of the Induction Period with Initial Pressure of Dimethyl Ether.



Temperature 233°C

Oxygen pressure

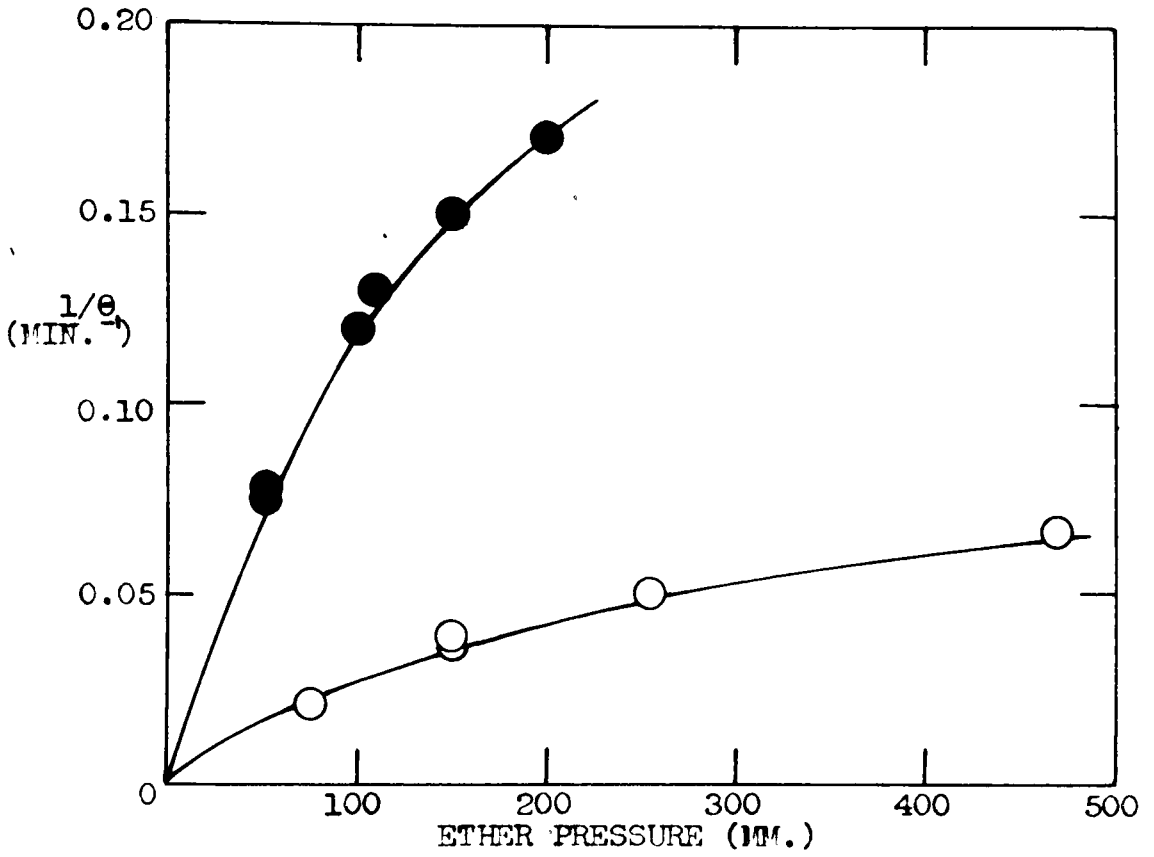
50 mm. ○

100 mm. ◐

150 mm. ●

FIGURE 35

The Variation of the Induction Period with the Initial Pressure of Diethyl Ether.

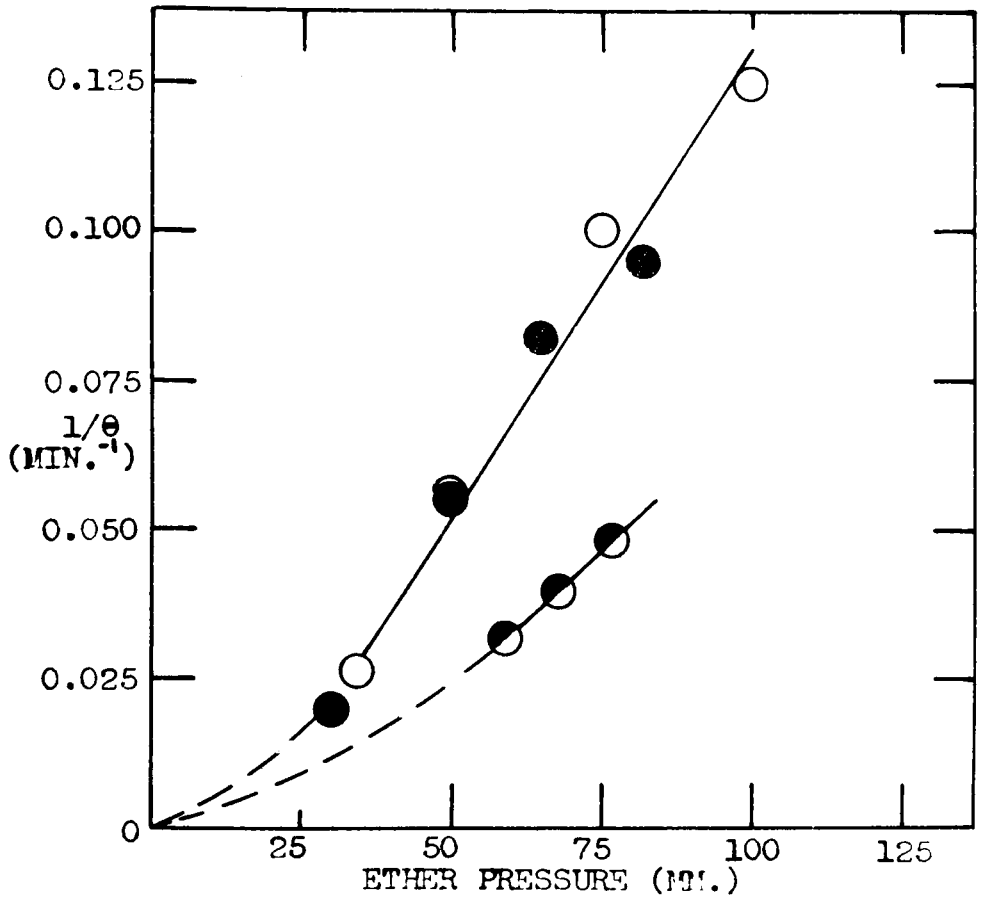


Temperature 157°C

Oxygen pressure
50 mm. - - ●
100 mm. - - ○

FIGURE 36

The Variation of the Induction Period with Initial Ether Pressure.

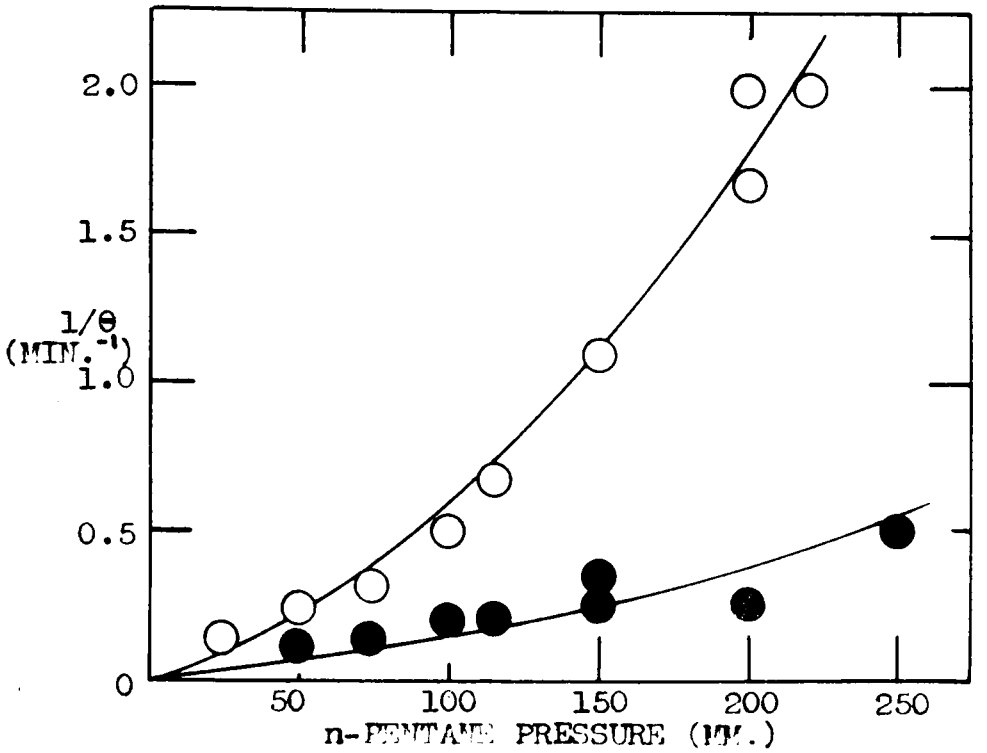


Oxygen pressure 50 mm.

Di-normal-propyl ether (171°C) ●
Methyl ethyl ether (190°C) ◐
Methyl n-propyl ether (194°C) ○

FIGURE 37

The Variation of the Induction Period with Initial Pressure of n-Pentane.



Oxygen pressure 100 mm.

Results from reference (1) (227°C) - - ○
Comparison results (254°C) - - - - - ●

Factors Influencing the Rate of the Initial Pressure Decrease

During the induction period a pressure decrease is observed with ethers just as with normal-octane and the higher hydrocarbons (1). Since the rate of this pressure decrease may shed some light on the primary stages of the reaction, the effect of variations of the initial pressure of reactants on the maximum rate of pressure decrease, $\rho^-_{max.}$, was observed.

The accuracy of the observations is not high because the pressure decrease is sometimes small and its maximum rate is not maintained for long.

The Influence of Oxygen Pressure

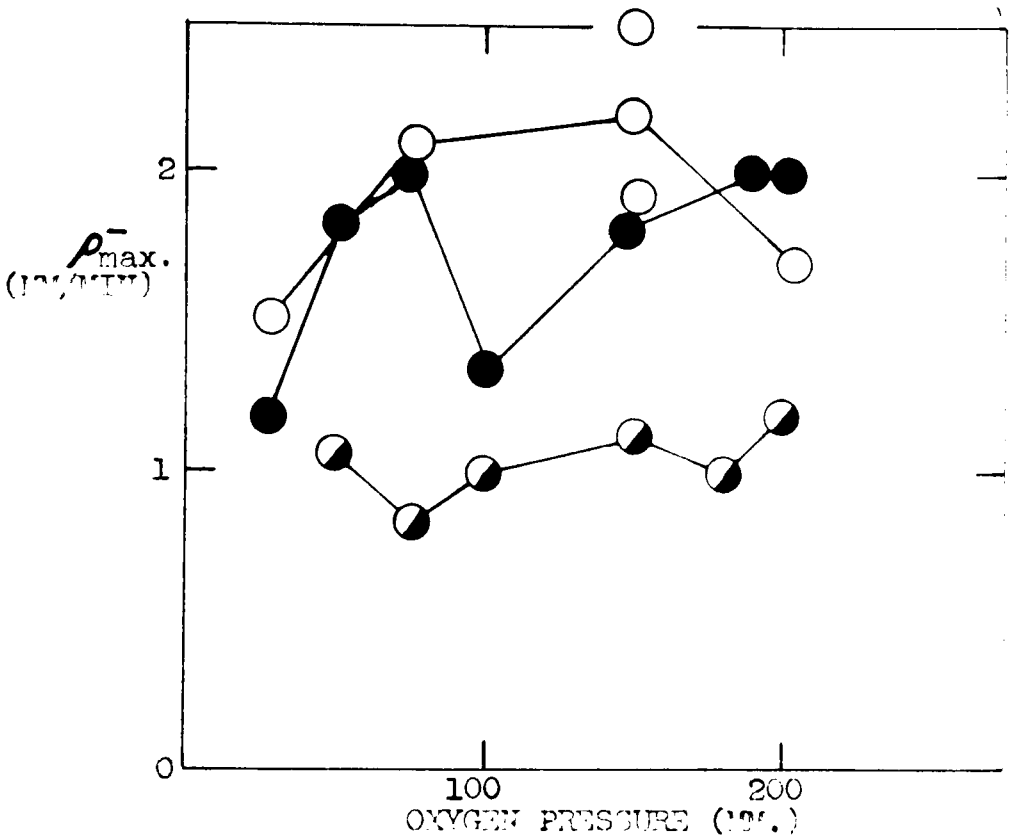
It appears from Figures 38 to 42 that the maximum rate of pressure decrease is indifferent to variations in the initial oxygen pressure. No particular significane is attached to the lines in the figures; they were put in merely as an aid to the visualization of the influence of oxygen under the various reaction conditions.

The Influence of Ether Pressure

The maximum rate of pressure decrease increases with increasing ether pressure in the range of concentrations that can be studied and the "apparent order" of the reaction is less than unity (Figures 43-45).

Figure 38

The Variation of the Rate of Initial Pressure Decrease with the Initial Oxygen Pressure.

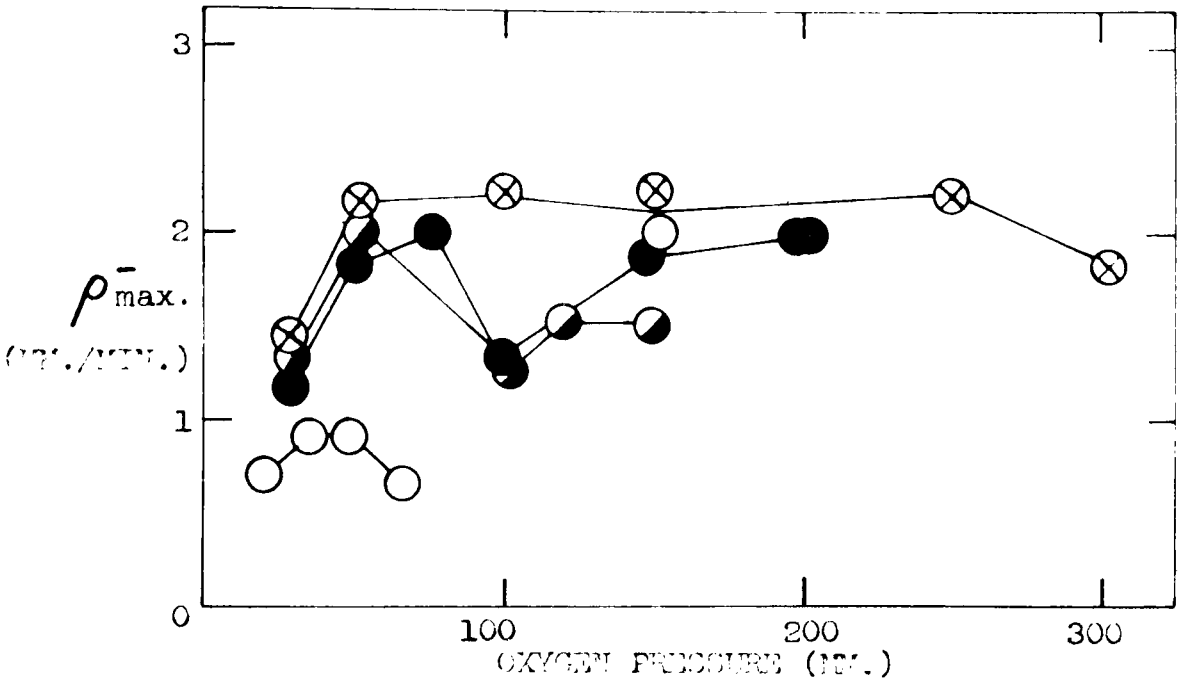


Dimethyl ether pressure 150 mm.

Temperature
229°C
233°C
235°C

FIGURE 39

The Variation of the Rate of Initial Pressure Decrease with Initial Oxygen Pressure.

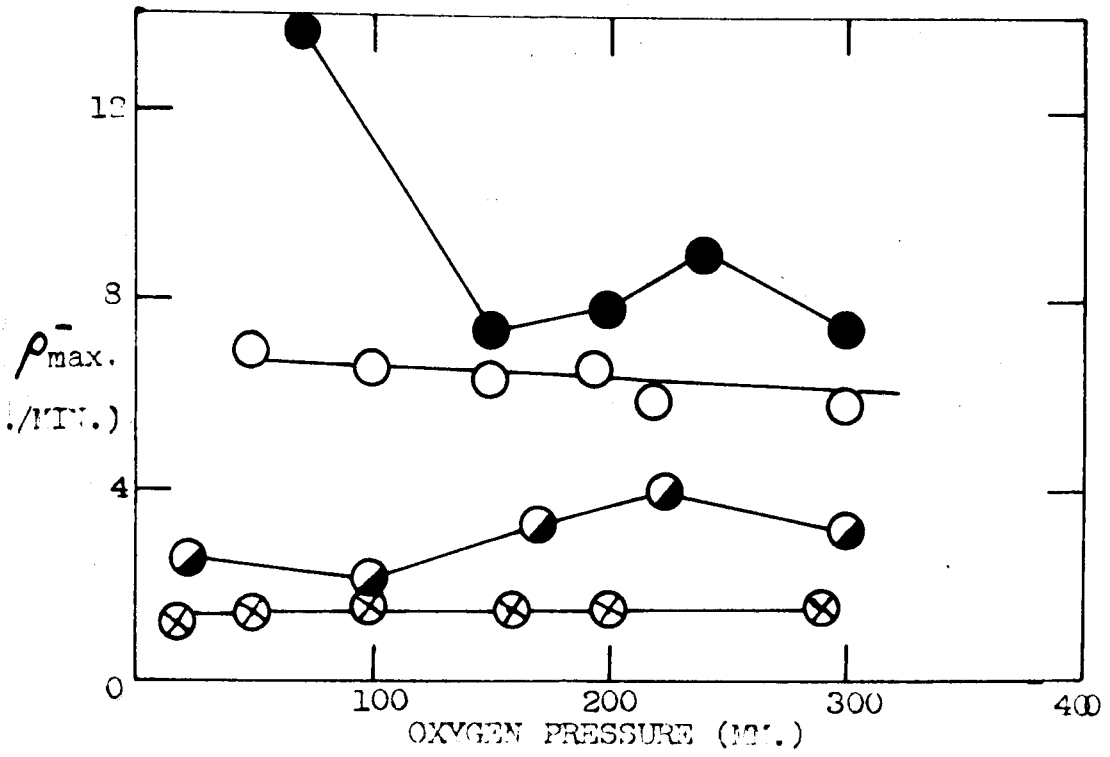


Temperature 233°C

Dimethyl ether pressure
50 mm.
100 mm.
150 mm.
200 mm.

FIGURE 40

The Variation of the Rate of Initial Pressure Decrease with Initial Oxygen Pressure.

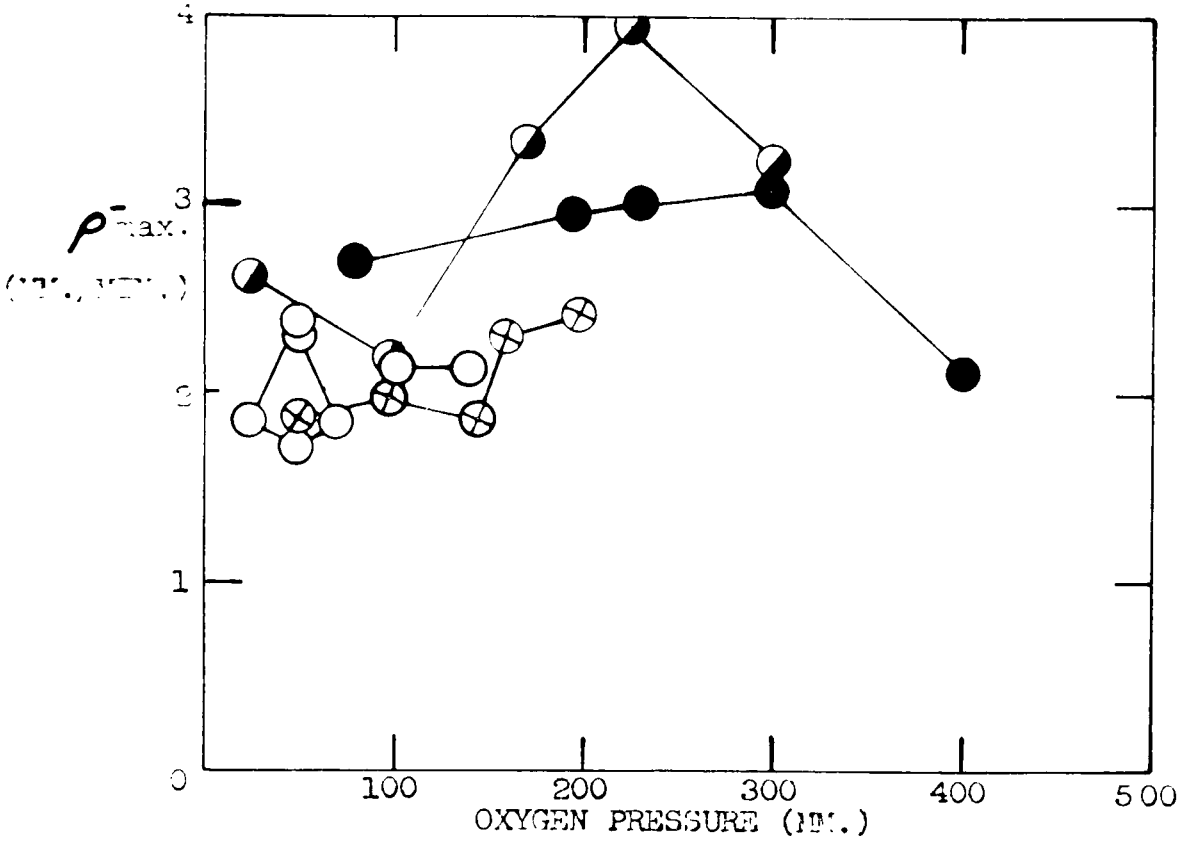


Diethyl ether pressure 150 mm.

Temperature
168°C
167°C
162°C
157°C

FIGURE 41

The Variation of the Rate of Initial Pressure Decrease with Initial Oxygen Pressure.



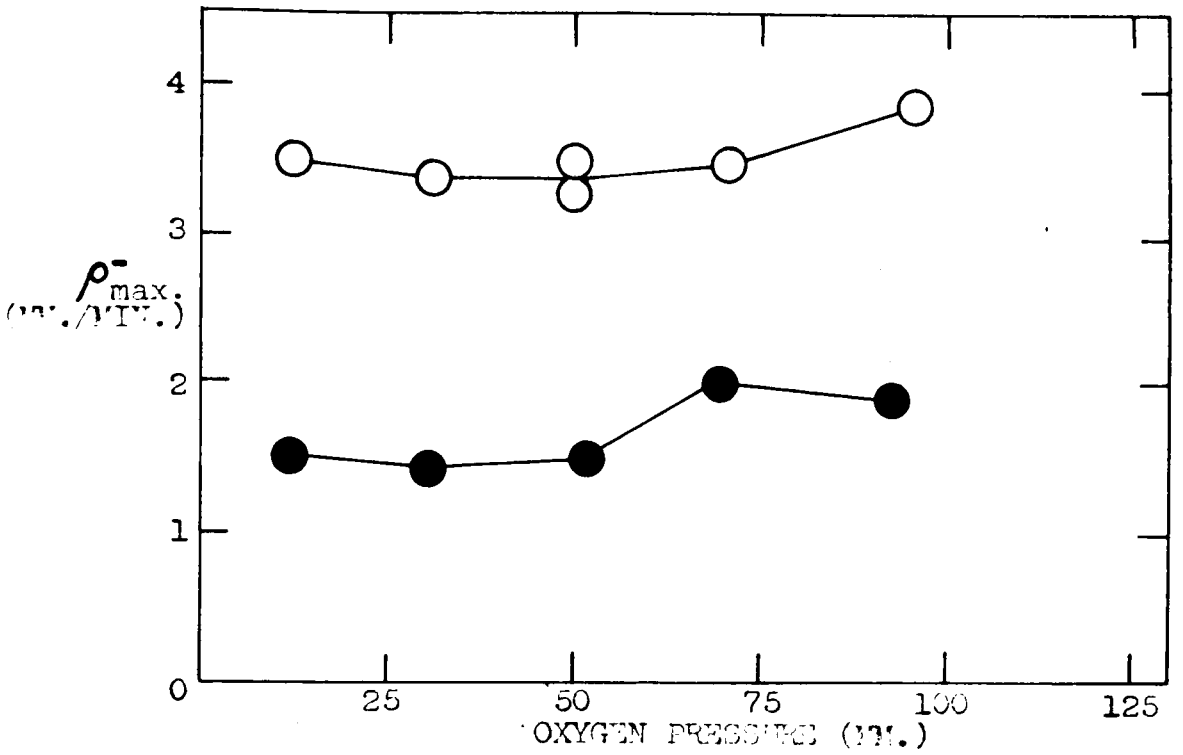
Temperature 162°C

Diethyl ether pressure

200 mm.
150 mm.
100 mm.
50 mm.

FIGURE 42

The Variation of the Rate of Initial Pressure Decrease with Initial Oxygen Pressure.

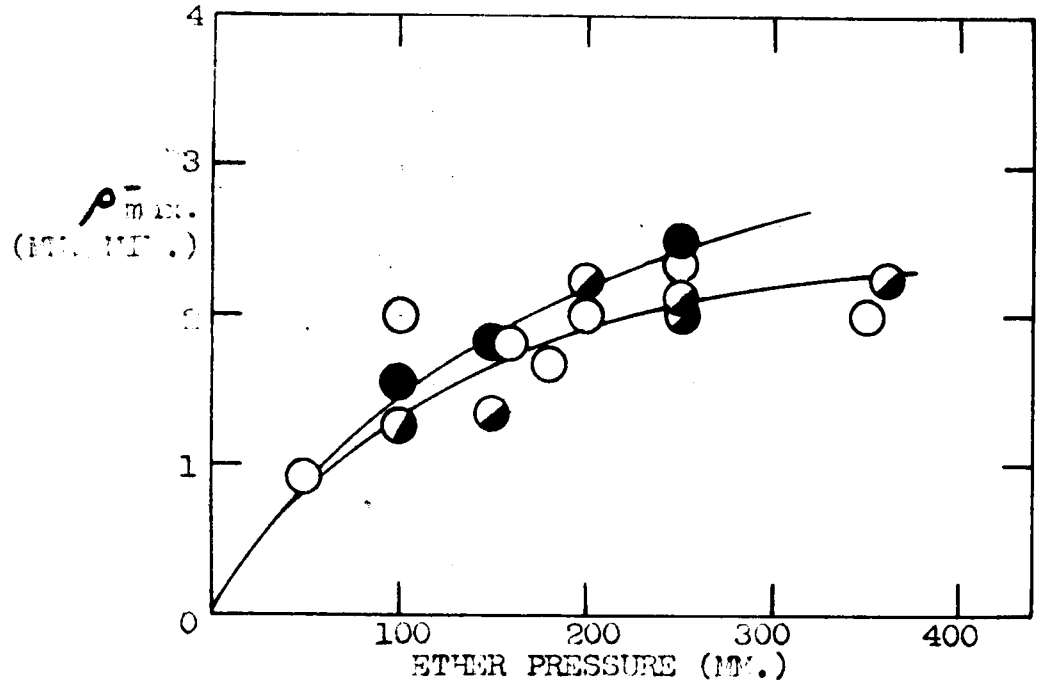


Diethyl ether (50 mm. 171°C) - - - - - - - ○

Di-normal-Propyl ether (50 mm. 171°C) - - ●

FIGURE 43

The Variation of the Rate of Initial Pressure Decrease with Initial Pressure of Dimethyl Ether.

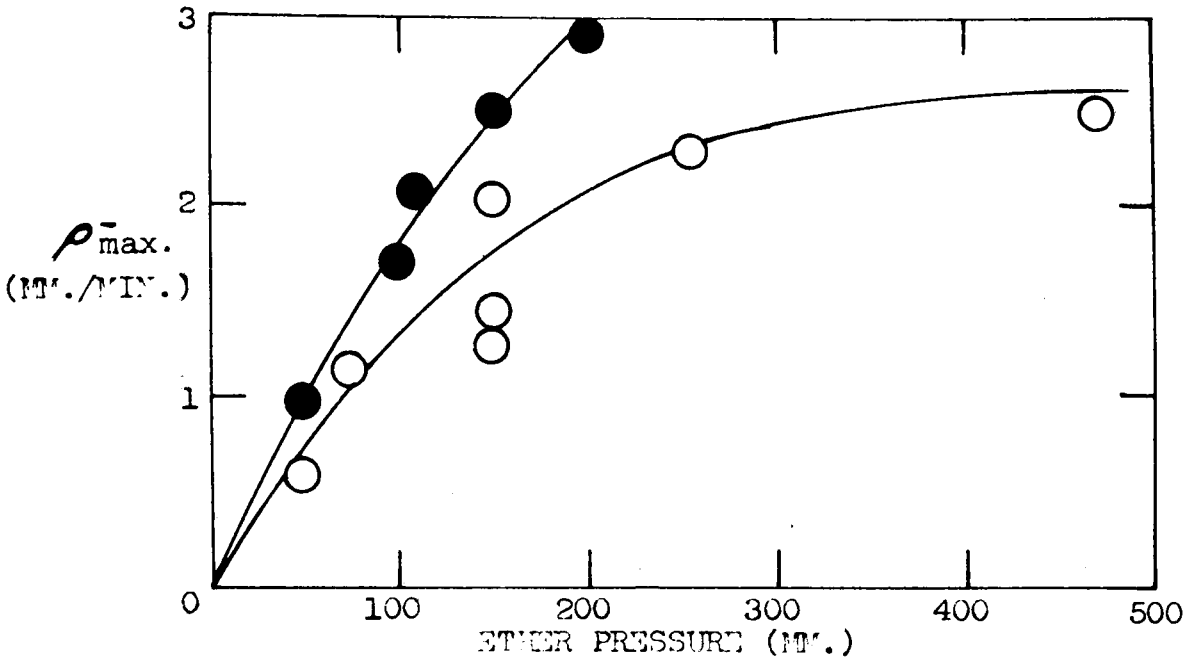


Temperature 233°C

Oxygen pressure
50 mm.
100 mm.
150 mm.

FIGURE 44

The Variation of the Rate of Initial Pressure Decrease with Initial Pressure of Diethyl Ether.

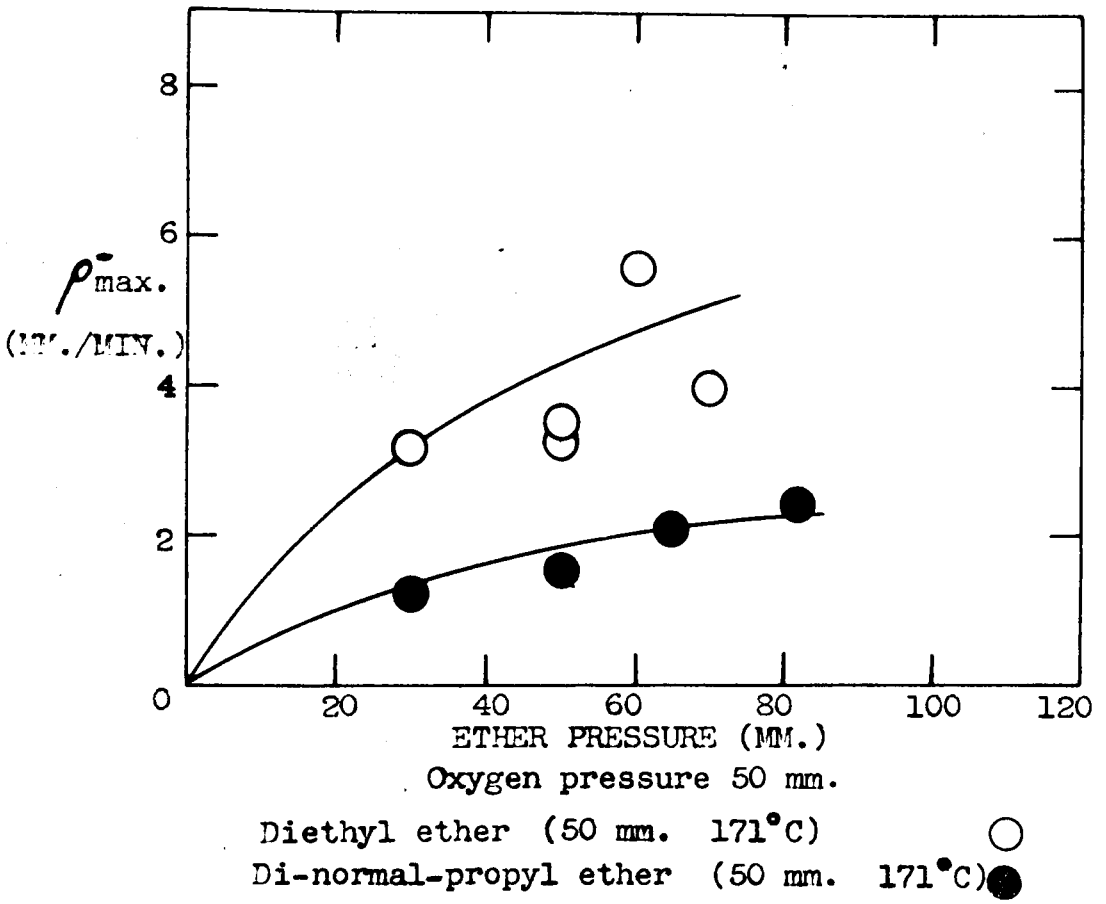


Temperature 157°C

Oxygen pressure
50 mm. - - - - ●
100 mm. - - - - ○

FIGURE 45

The Variation of the Rate of Initial Pressure Decrease with Initial Pressure of Ether .



PEROXIDE FORMATION IN LOW TEMPERATURE REACTIONS

The various conflicting roles assigned in the past to peroxides in slow and cool flame reactions have been described in the Introduction. There is a considerable body of evidence pointing to peroxides as the key intermediates in the slow branching chain mechanism of low temperature oxidation. There is also a sound experimental basis for believing that peroxides are equally important in the cool flame reaction, and the view that cool flames are explosively developing reaction chains of the type involved in the slow reaction has been widely held. Recently, however, Hinshelwood and Bardwell have suggested that peroxides may, in fact, play a dual role, simply decomposing above a critical concentration on the one hand thus giving rise to the cool flame, or on the other hand, dissociating into radicals which contribute to the growth of reaction chains involved in the slow reaction, and they have shown that development of this theme leads to a more satisfactory interpretation of the experimental observations with butanone-oxygen mixtures.

Further information at this juncture in the development of the understanding of the low temperature oxidation phenomena is, of course, very desirable, and since ethers appear to be eminently suitable for this purpose an investigation of peroxide formation during the low temperature oxidation of ethers was undertaken.

The Formation of Peroxides During the Slow Reaction

The results presented in Figures 46-49 show that peroxides form rapidly at first while the pressure decreases, but reach their maximum concentration in the reaction mixture when the maximum rate of pressure increase is attained. In the latter respect ethers are similar to the amines and butanone (4, 16). Since the total peroxides determined by the potassium iodide methods (including the ROOR and ROOH types detected by the ferrous thiocyanate method) reach a maximum coinciding with the maximum rate of pressure increase with normal-hexane and 2-methyl pentane (1,2) it is likely that the ethers also resemble the paraffins.

Each Δp-time curve in the figures is a composite of the experimental curves, and the peroxide content is related to it by the pressure change, rather than the time of sampling, although the reproducibility was such that there was seldom any significant difference between the two.

Additional results obtained during the first few seconds of the reaction will be given in a later section where peroxide formation in the slow reaction and cool flame zones will be compared.

Peroxide analyses were also made with di-iso-propyl ether which, it will be remembered, gives no appreciable pressure change in the slow reaction region. The results (compared

FIGURE 46

The Variation of Peroxide Concentration during the Oxidation of Dimethyl Ether and the Corresponding Δp-Time Curve.

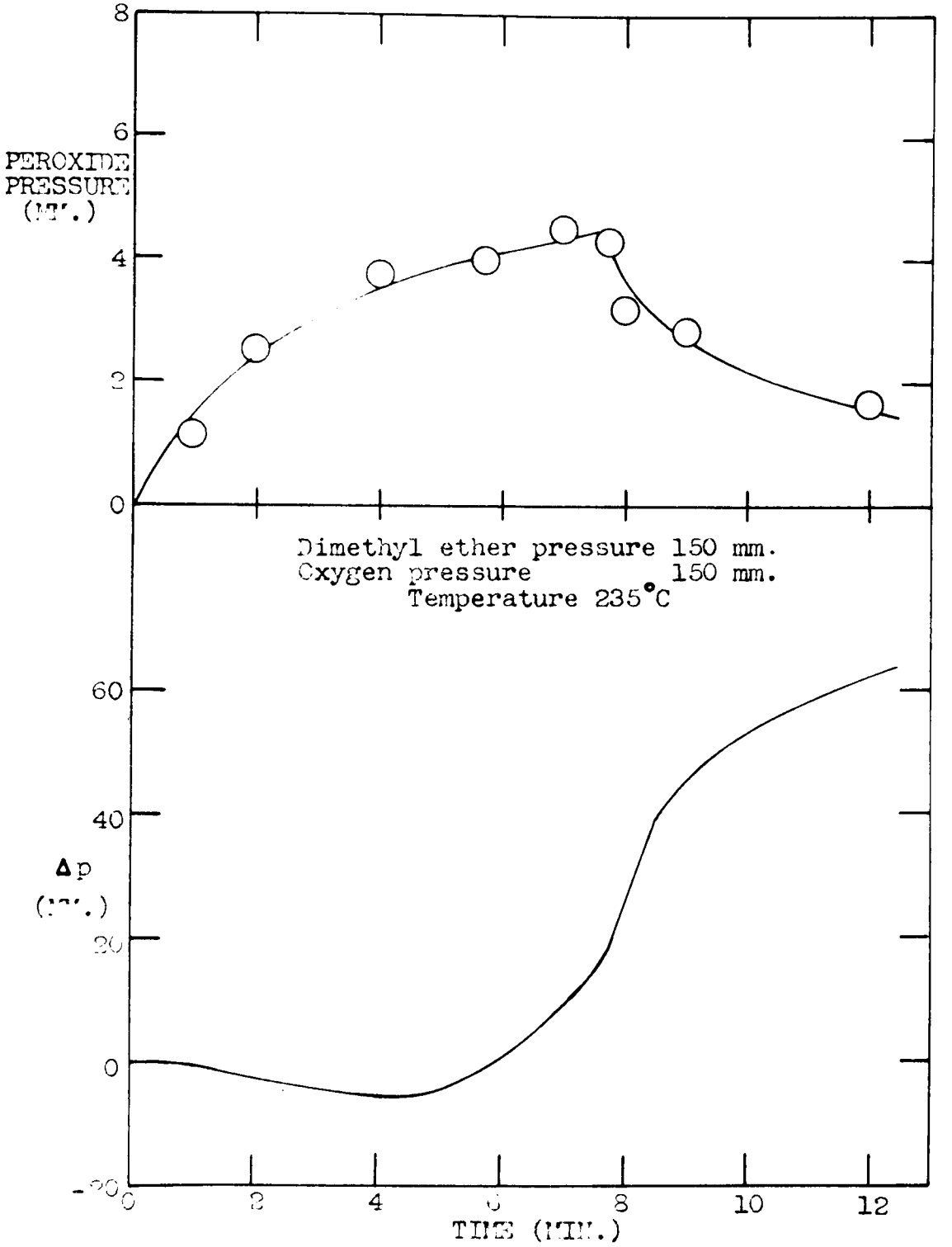


FIGURE 47

The Variation of Peroxide Concentration during the Oxidation of Diethyl ether and the Corresponding ΔP-Time Curve.

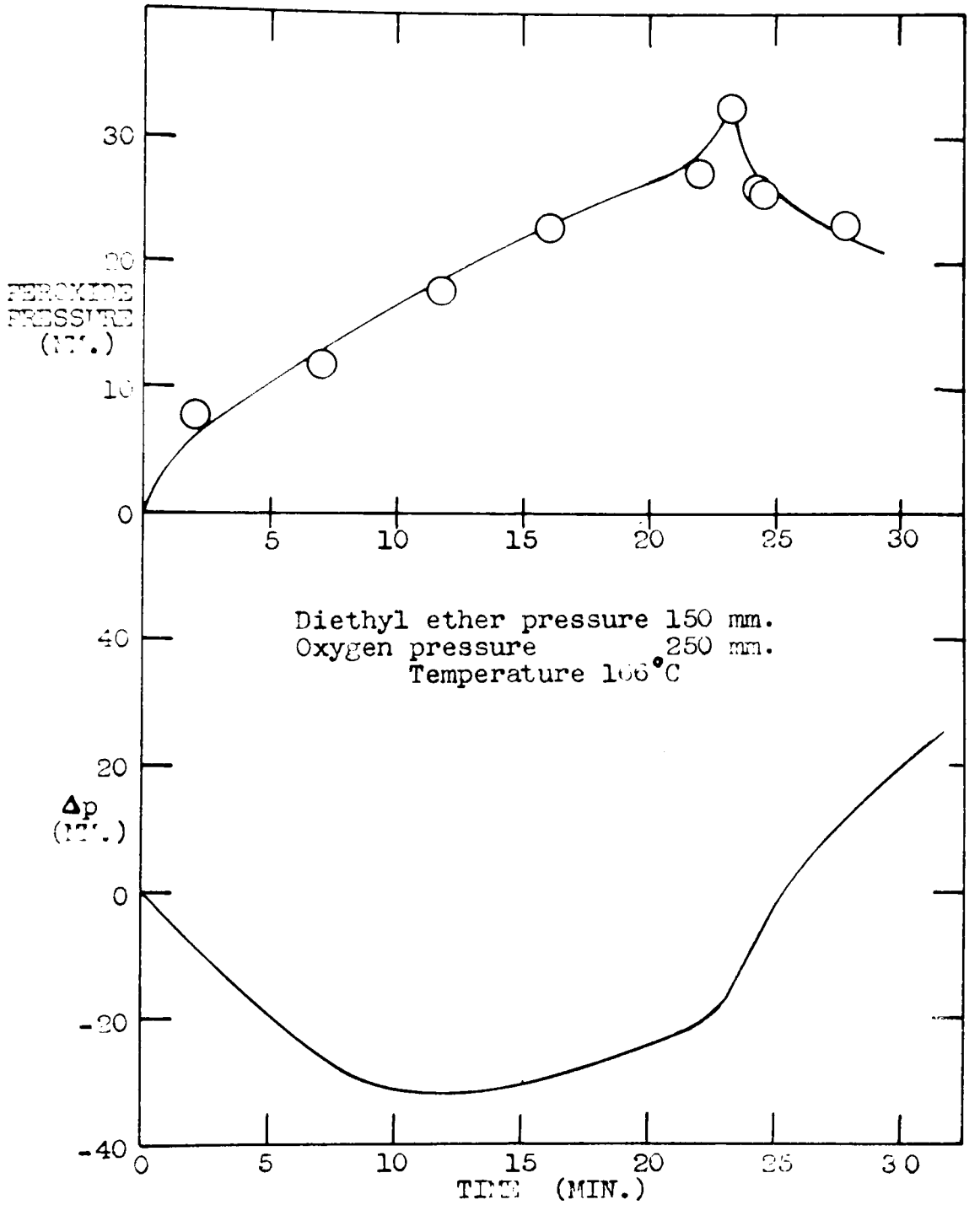


FIGURE 48

The Variation of Peroxide Concentration during the Oxidation of Di-n-Propyl Ether and the Corresponding Δp-Time Curve.

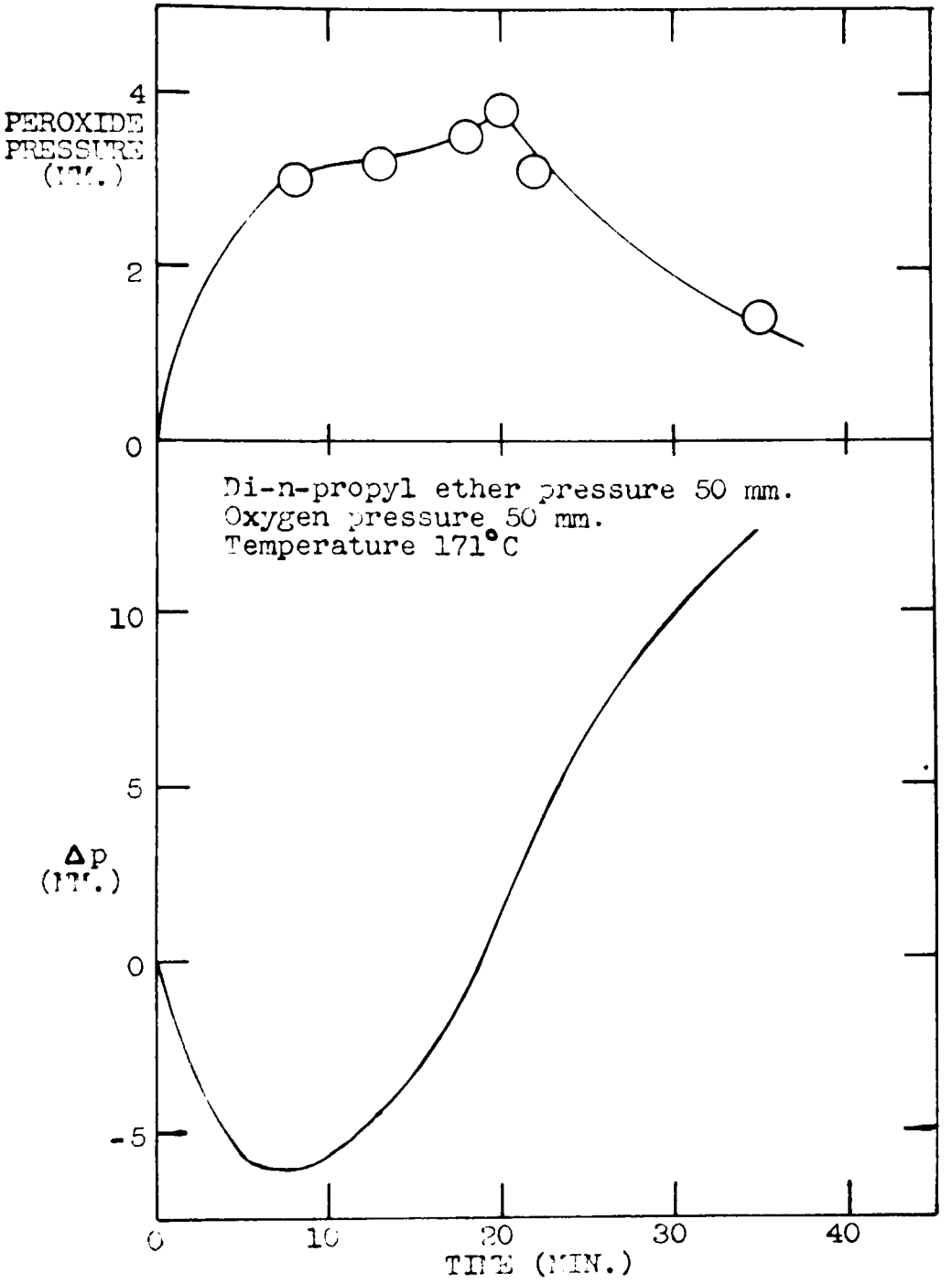
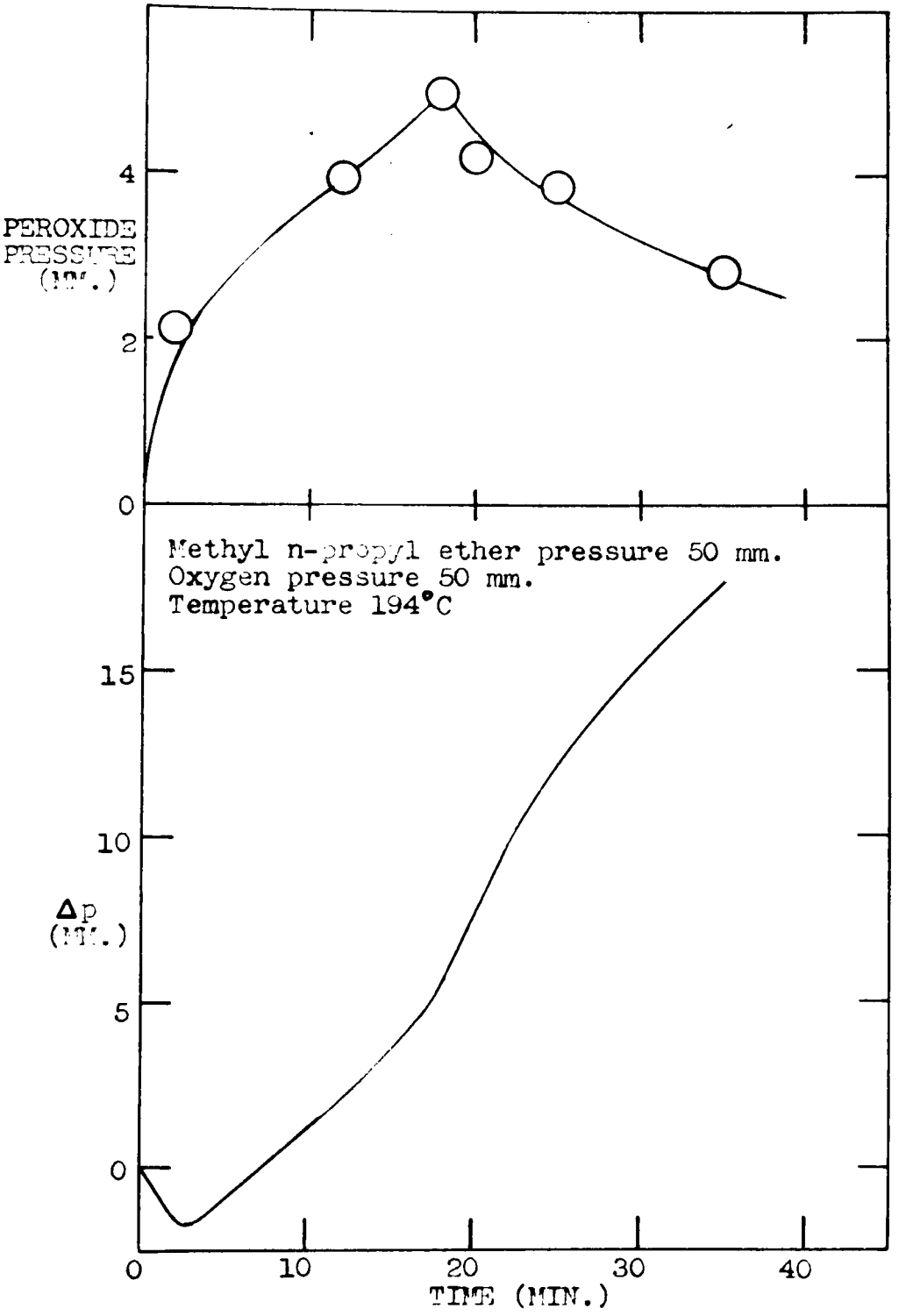


FIGURE 49

The Variation of Peroxide Concentration during the Oxidation of Methyl n-Propyl Ether and the Corresponding Δp-Time Curve.



with diethyl ether under exactly the same conditions, Figure 50) show that there is no significant peroxide formation at this temperature, and that the absence of pressure change is, in fact, indicative of no appreciable reaction.

Peroxide Variation During Cool Flames

Cool flames were produced in equimolar mixtures of various ethers and oxygen by increasing the temperature so that the lower boundry between the slow reaction and the cool flames zones was crossed (Figure 10), and the results of peroxide analysis before and after the cool flames are shown in Figures 51-53.

In all cases the peroxide concentration increases until the appearance of the cool flame, and thereafter slowly falls to zero. Di-iso-propyl ether is similar to the other ethers as far as the peroxide behaviour is concerned. The cool flame appears to consume enough of the reactants to prevent further reaction, and therefore the peroxide which has survived the cool flame undergoes slow thermal decomposition. (The pressure pulse prevents an accurate determination of the sharing factor when a cool flame occurs during sampling so the maximum and minimum peroxide pressure corresponding to the widest fluctuations during the pulse are indicated for such experiments in the figures).

These results are in strong contrast to the observations

FIGURE 50

The Variation of Peroxide Concentration during the Oxidation of Di-i-Propyl Ether and the Corresponding Δp-Time Curve.

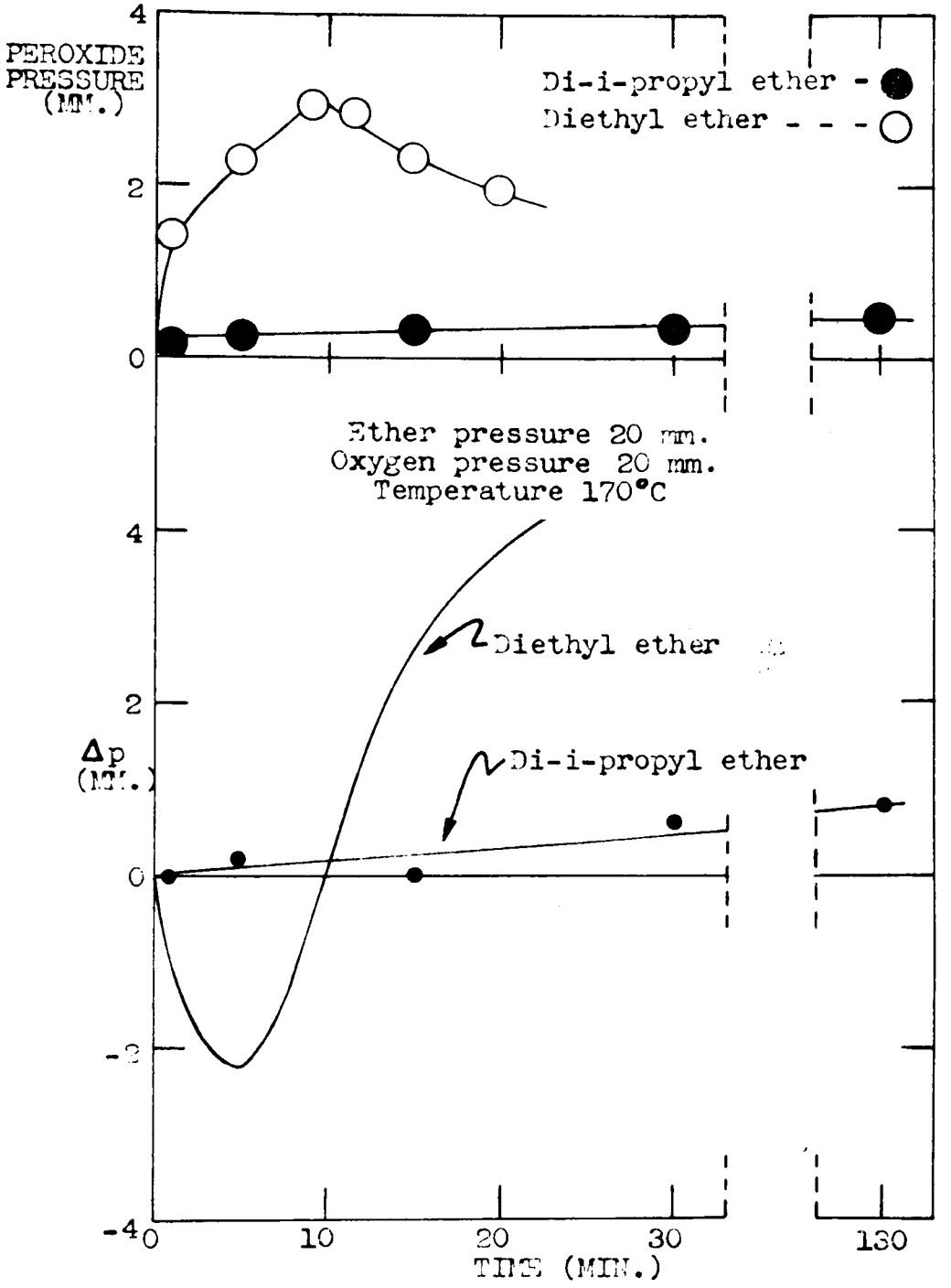
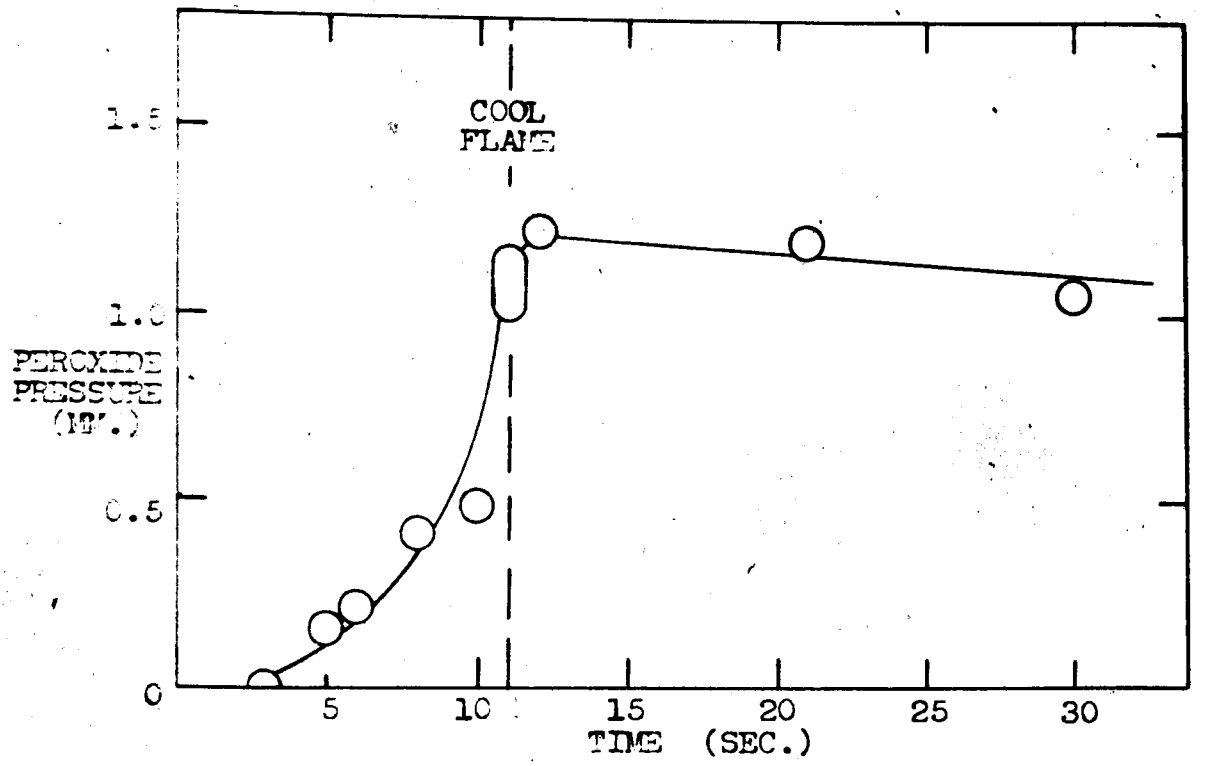


FIGURE 51

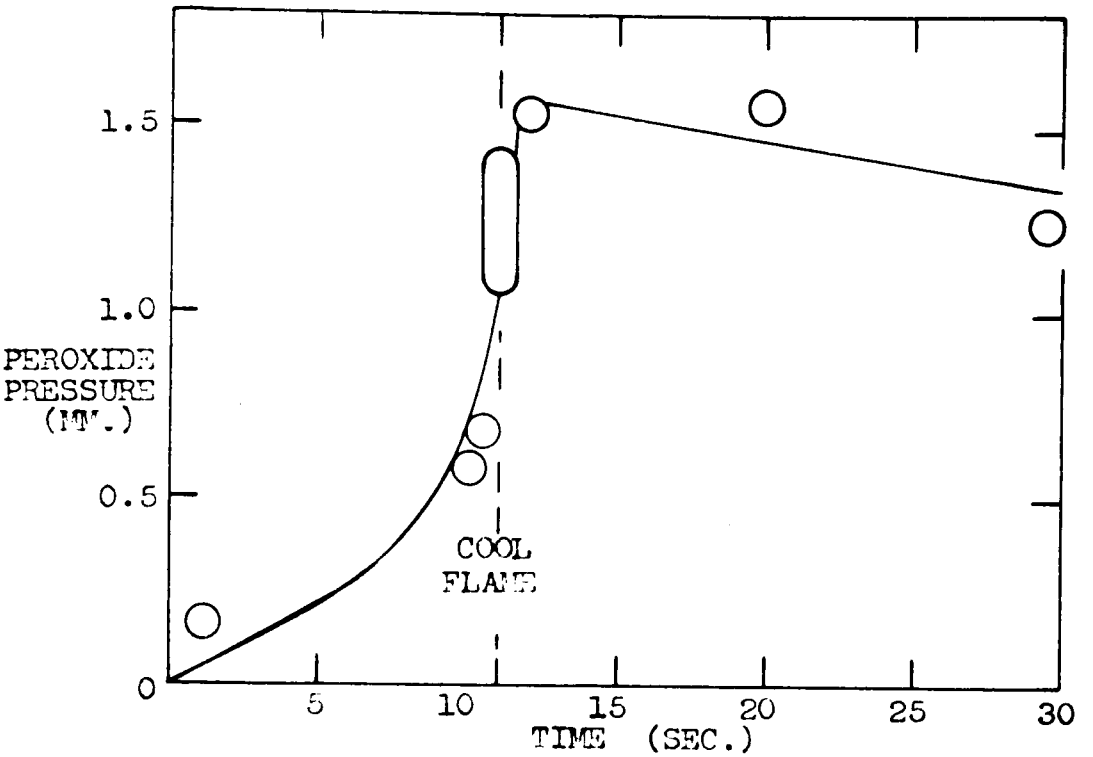
The Variation of Peroxide Concentration during the Cool Flame Reaction with Diethyl Ether.



Ether pressure 30 mm.
Oxygen pressure 30 mm.
Temperature 172°C

FIGURE 52

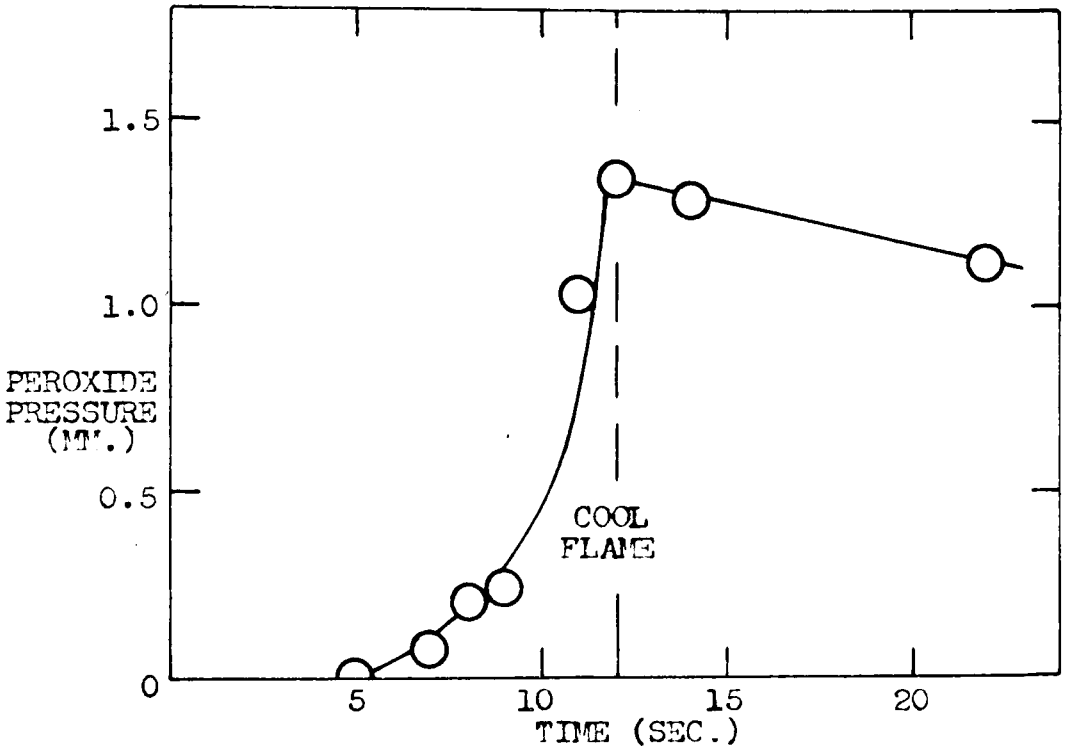
The Variation of Peroxide Concentration during the Cool Flame Reaction with Methyl n-Propyl Ether.



Ether pressure 50 mm.
Oxygen pressure 50 mm.
Temperature 198°C

FIGURE 53

The Variation of Peroxide Concentration during the Cool Flame Reaction with Di-i-Propyl Ether.



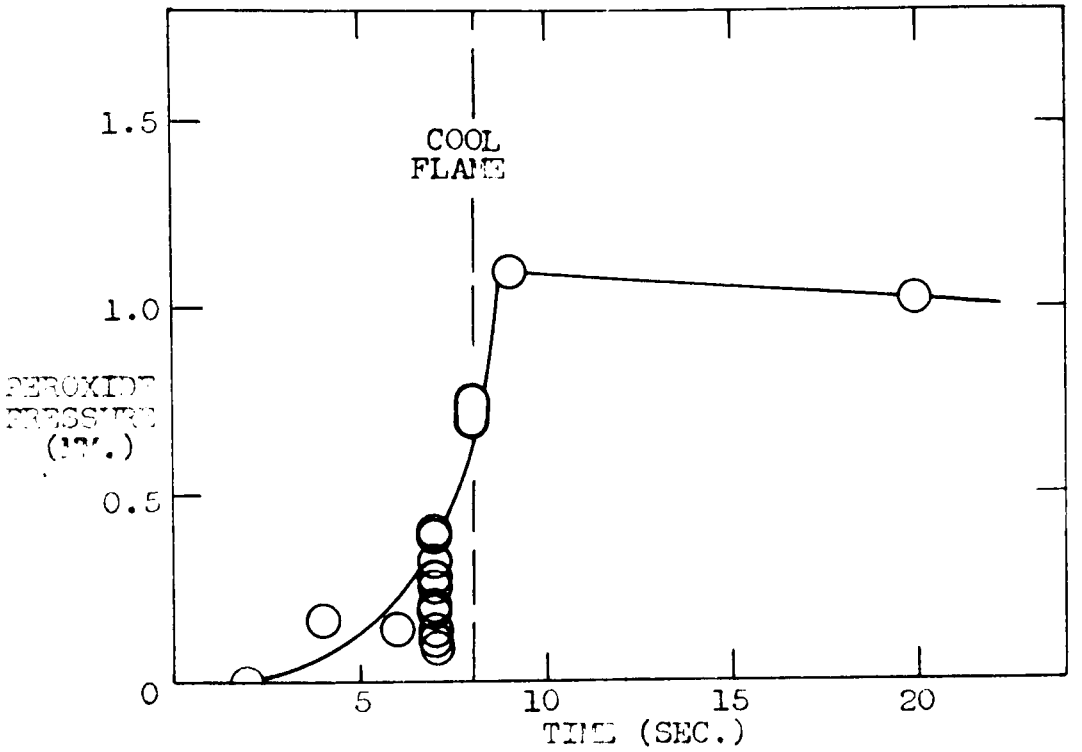
Ether pressure 50 mm.
Oxygen pressure 50 mm.
Temperature 161°C

with butanone where the peroxides disappear almost completely during the cool flame.

Since the peroxide pressure with the ethers is increasing very rapidly in the few seconds before the cool flame appears, there was a possibility that it reached a much higher value than had been detected in the experiments. It was important to determine whether this happened because if a high peroxide pressure were established momentarily before the cool flame but fell to lower values shown in Figures 51-53 afterwards, then the peroxide variations would, after all, be the same with ethers and butanone. Further very careful experiments were therefore made with a reaction mixture of 30 mm. of diethyl ether and 30 mm. of oxygen. Since the cool flame does not appear at exactly the same time in every run, but varies by a second or two, there is a chance that if a large number of samples are taken at the earliest time of cool flame appearance one will be obtained just at the moment when the cool flame is due to appear, and this sample might show a high peroxide content. In all, 15 experiments were made and sampled at this time. Two gave cool flames during sampling and the remainder, shown in Figure 54 together with some analyses before and after the cool flame, indicate that it is unlikely that a high peroxide pressure ever exists even at the last instant before the cool flame passes.

FIGURE 54

The Variation of Peroxide Concentration during the Cool Flame Reaction with Diethyl Ether.



Ether pressure 30 mm.
Oxygen pressure 30 mm.
Temperature 174°C

Comparison of the Formation of Peroxides in the Slow Reaction and Cool Flame Zones.

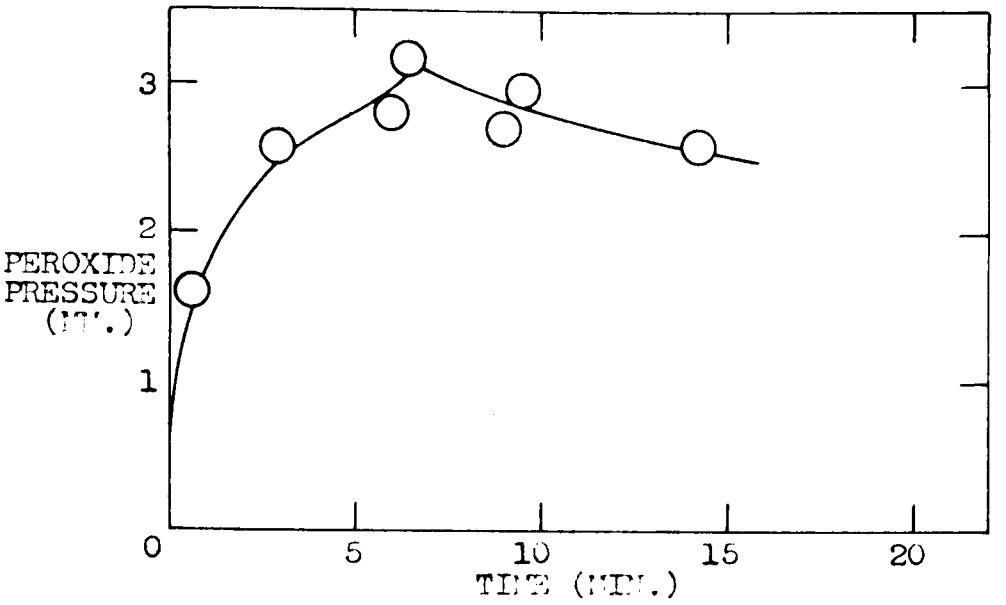
A comparison of the peroxide formation above and below the cool flame temperature boundary was made with a standard reaction mixture. The results obtained are shown in Figures 51, 54 and 55. Peroxide formation during the slow reaction at 170°C. is shown in Figure 55; the details of the early stages appear in the lower half of the figure. An increase in temperature produces a cool flame in this mixture and the results of analysis at 172° and 174°C. are given in Figures 51 and 54. The formation of peroxide in the two cases can then be compared in Figure 56 where the pertinent data from the previous figures are collected.

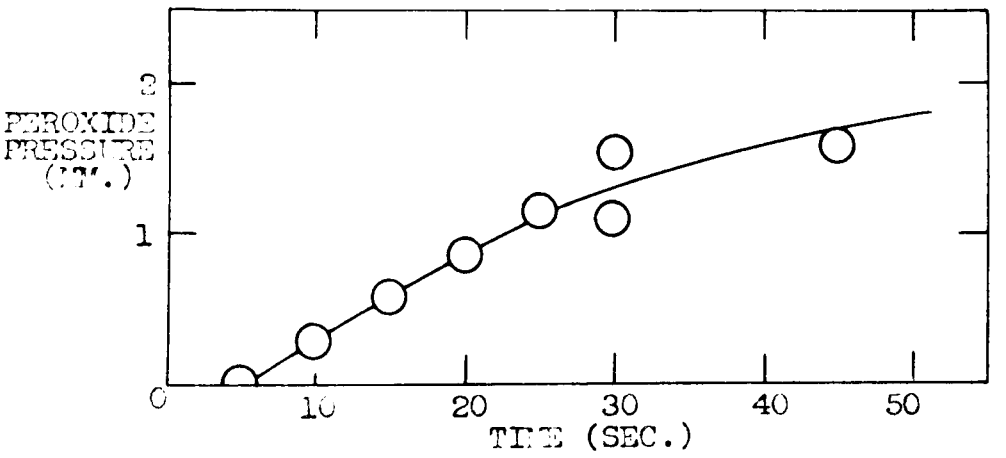
Figure 17 suggests that a similar comparison can be made at one temperature with different ether-rich mixtures, and the results of a slow reaction with 150 mm. of diethyl ether and 30 mm. of oxygen (Figure 57) are compared with results of a cool flame reaction with 150 mm. of ether and 50 mm. of oxygen (Figure 58) in Figure 59.

It would appear from Figure 59 that the cool flame does not form in a mixture of 150 mm. of ether and 30 mm. of oxygen because there is an inadequate initial concentration of the latter reactant. However, Figure 56 indicates that at 170°C. the concentration of peroxides can be greatly in excess

FIGURE 55

The Variation of Peroxide Concentration during the Slow Reaction with Diethyl Ether.

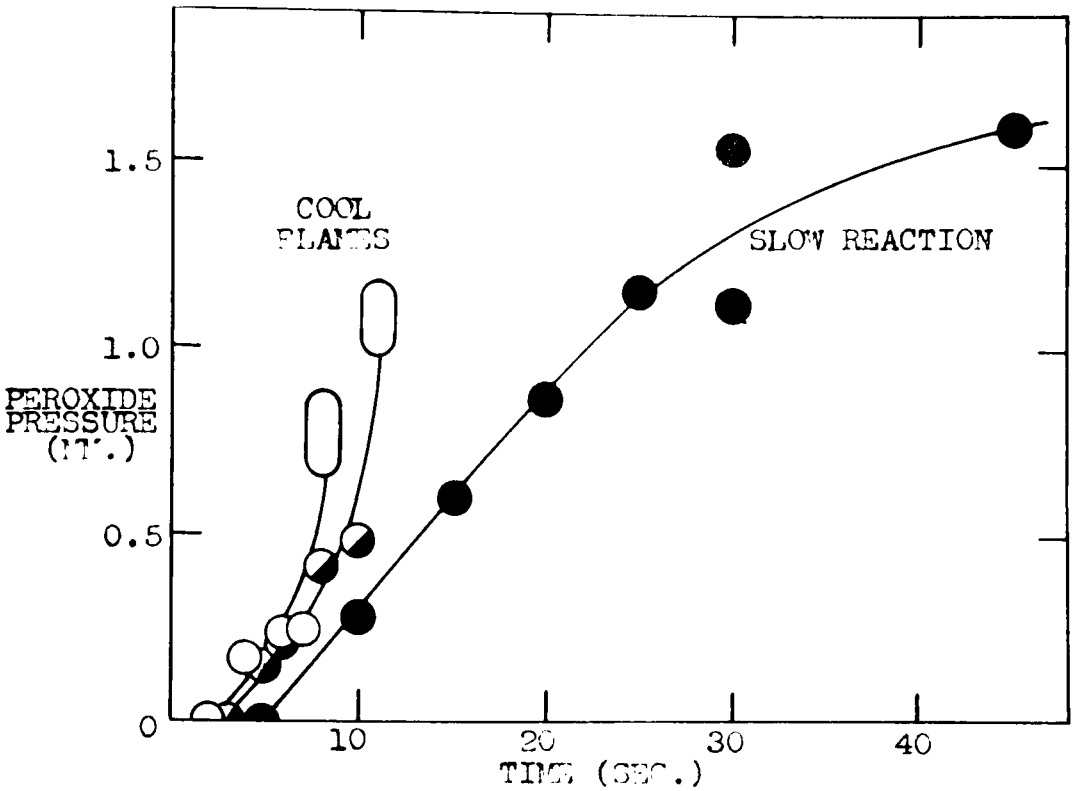




Ether pressure 30 mm.
Oxygen Pressure 30 mm.
Temperature 170°C

FIGURE 56

Comparison of Peroxide Formation in
Cool Flame and Slow Reactions with Diethyl Ether.

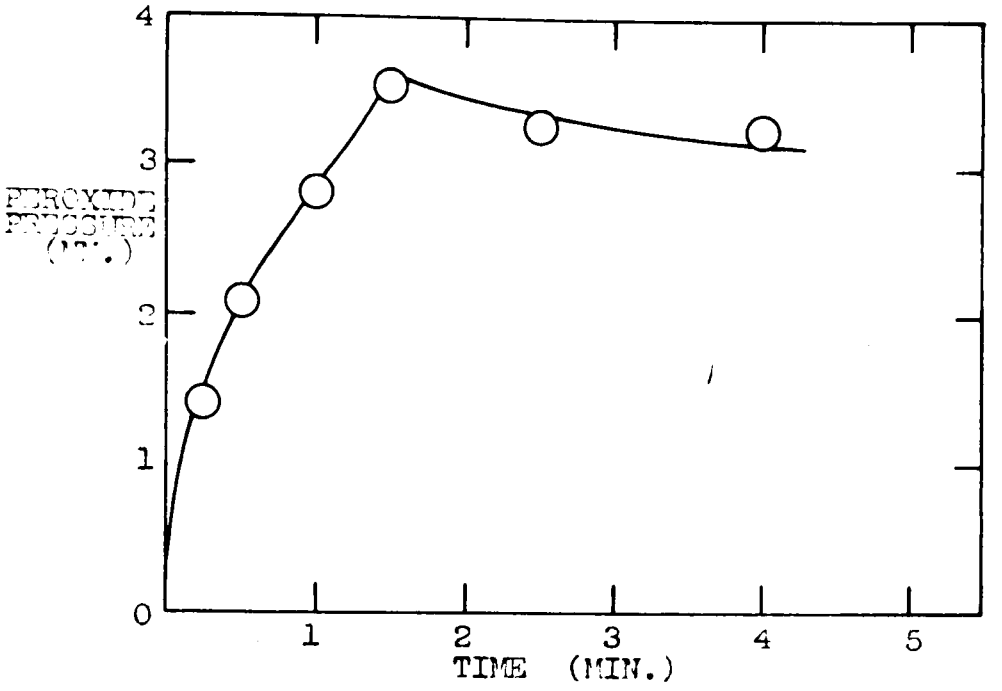


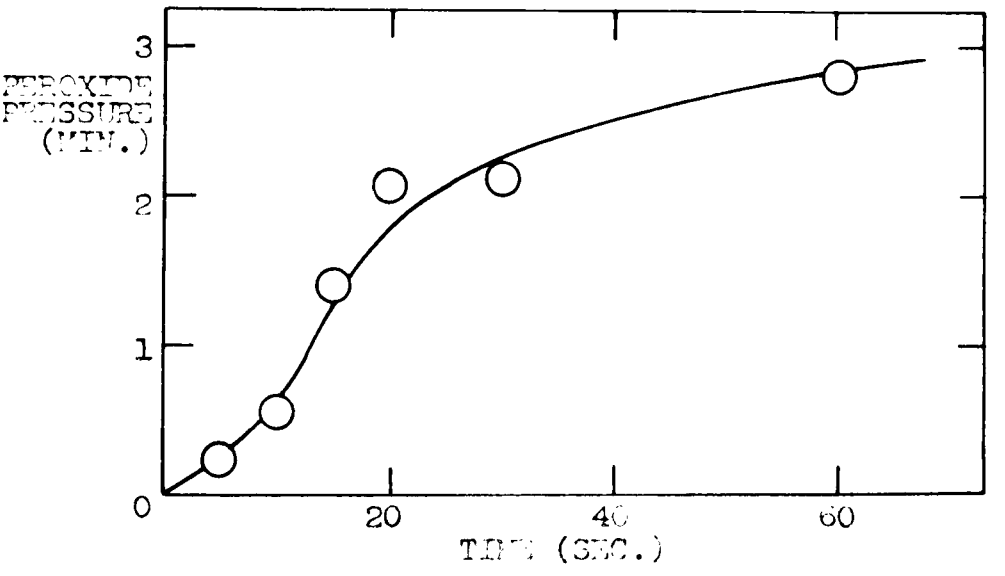
Ether pressure 30 mm.
Oxygen pressure 30 mm.

Temperature
174° C
172° C
170° C

FIGURE 57

The Variation of Peroxide Concentration during the Slow Reaction with Diethyl Ether.

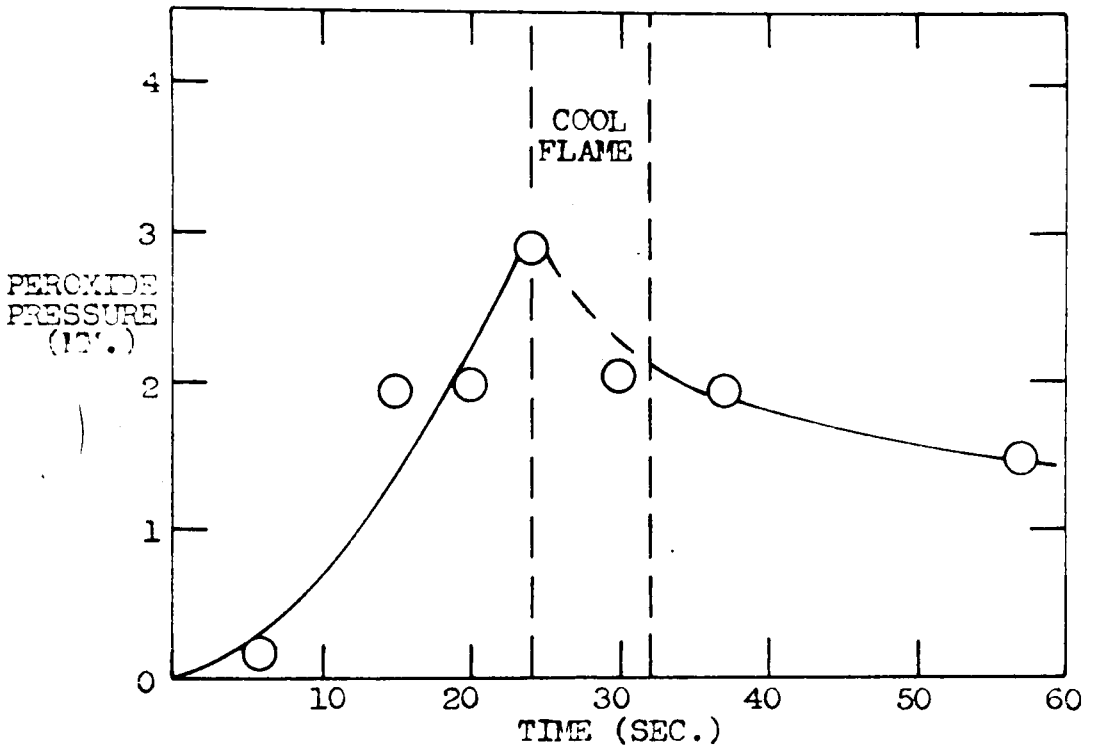




Ether Pressure 150 mm.
Oxygen Pressure 30 mm.
Temperature 174°C

FIGURE 58

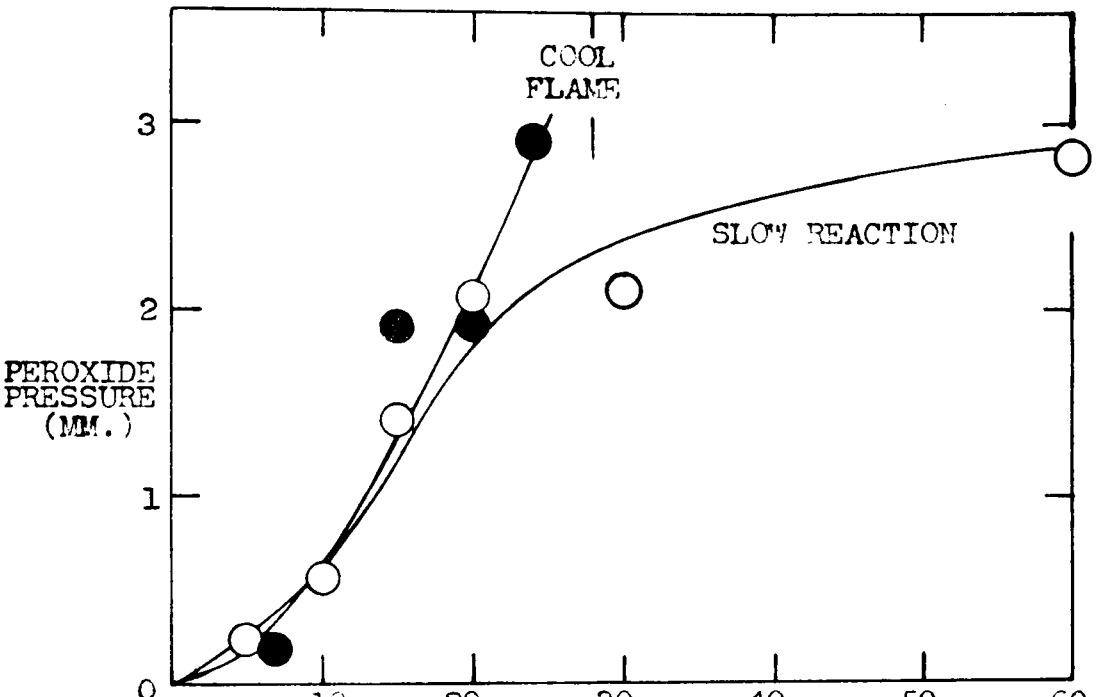
The Variation of Peroxide Concentration during the Cool Flame Reaction with Diethyl Ether.



Ether pressure 150 mm.
Oxygen pressure 50 mm.
Temperature 174°C

FIGURE 59

Comparison of Peroxide Formation in
Cool Flame and Slow Reactions with Diethyl Ether.



Ether pressure 150 mm.
Temperature 174°C

Oxygen pressure
30 mm. ○
50 mm. ●

of that, which at a slightly higher temperature, gives a cool flame.

If peroxide decomposition is in some way responsible for cool flame formation an interpretation of this observation might be that the decomposition reaction has a high energy of activation. That this cannot be, however, is demonstrated by a further experiment in which a reaction mixture initially at 170°C. was heated to 172°C. 3 minutes after the reaction had started and to 198°C. 5½ minutes later without the appearance of a cool flame, even though the peroxide pressure was determined to be 2.9 mm. at this point.

It is also possible that cool flame formation depends on reaction with oxygen as suggested by equation (17) in the Introduction, and that no cool flame appears at 170°C. because the oxygen has been completely consumed. This is unlikely for two reasons, first, the reaction continues after the initial rapid formation of peroxide and secondly, addition of both ether and oxygen to a mixture at 170°C. 30 seconds after the reaction has started does not produce a cool flame.

Since peroxides as a whole survive the cool flame and, indeed, exist at temperatures and pressures far higher than those at which cool flames occur, it would appear that with diethyl ether they do not have an important role in the formation of cool flames. Since, moreover, the kinetic

behaviour of the other ethers is similar to that of diethyl ether the same is likely to be true of them as well.

It is possible that a particular peroxide, different from the bulk of material determined by the ferrous thiocyanate method, is responsible for the cool flame. If the amount of this compound were relatively small, variations in its concentration during the cool flame reaction would pass undetected. Alternatively, the compound responsible for cool flame formation may not be determined by the thiocyanate method at all. Previous work suggests that the extremely unstable peroxides formed in the auto-oxidation of liquid diethyl ether might be responsible. Such compounds, in contrast to the ROOR and ROOH types, liberate iodine from neutral potassium iodide solution (68, 83). But analyses for this type of peroxide in a diethyl ether reaction mixture were not conclusive because a substance which liberates iodine slowly appeared after the cool flame and masked the effect of the compounds which liberated iodine immediately. In some experiments a solution of potassium iodide buffered at a pH of 7.0 with citric acid and di-sodium phosphate was used to maintain a neutral medium in spite of acids produced during the oxidation, but the results were unaltered.

Unfortunately, so little is known about the chemistry of peroxides, particularly those related to the ethers, that a decision on the matter is not at the moment possible.

The Influence of Surface

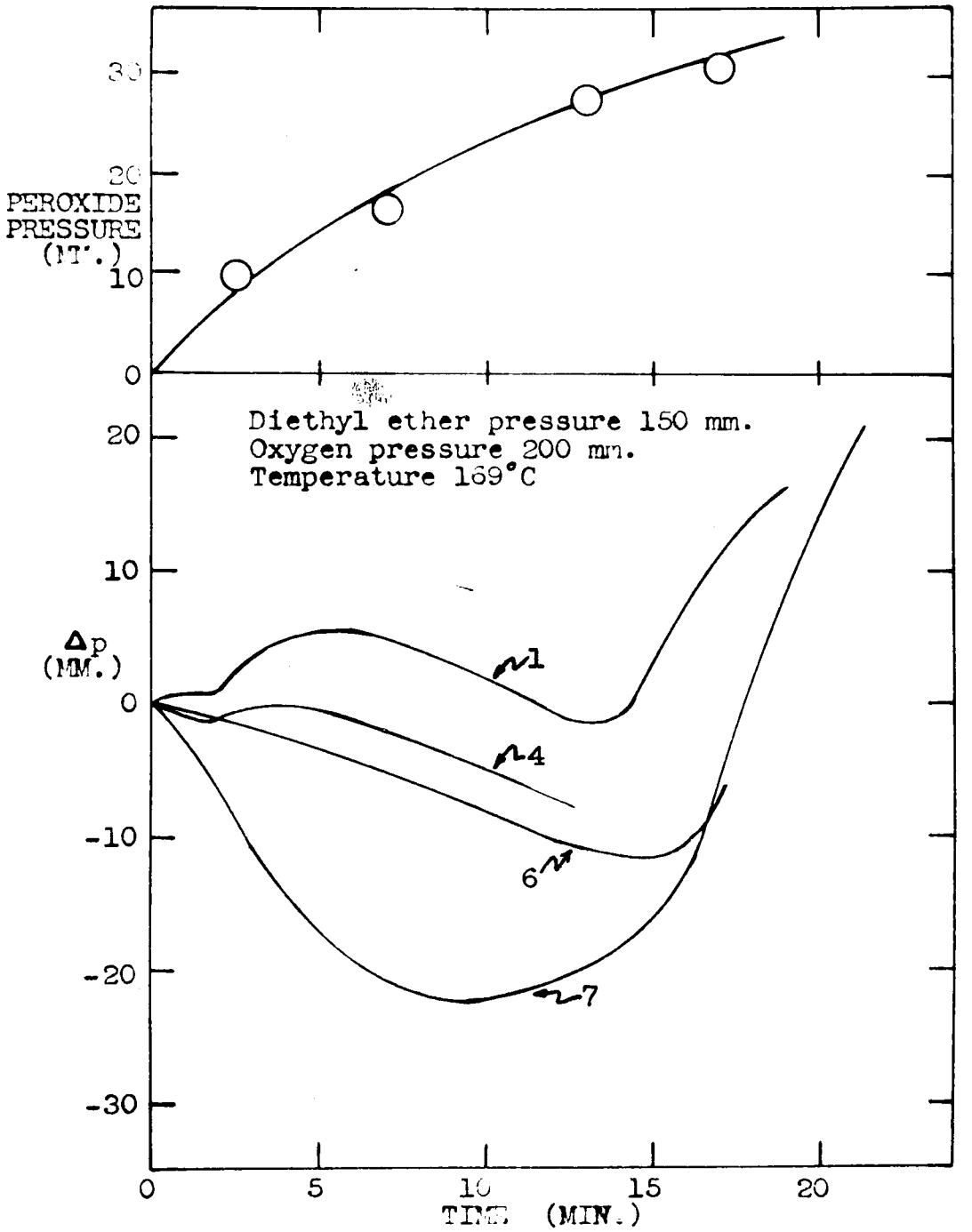
Although no specific experiments were made to determine what influence the surface-volume ratio or the nature of the surface had on the reaction, it was soon obvious that minor deviations from the normal experimental technique changed the surface characteristics and had a marked effect. It was found, for example, that if air was admitted to the hot reaction vessel the Δp-time curves of subsequent reactions were no longer normal but showed the deviations illustrated by curves 1,4 and 6 in Figure 60. Some of the reactions in the figure are not complete because the experiments were stopped for peroxide analysis, but it is clear that the normal pressure decrease does not take place. It is remarkable, however, that the peroxide pressure is about normal even though the pressure change is not. Usually the maximum rate was reduced and occasionally the induction period was altered.

If a number of experiments were made in the reaction vessel when its surface was in this condition it was often observed that the Δp-time curves tended to become normal and such a change appears in Figure 60; simultaneously the maximum rate approaches a steady value and remains unaltered by further reactions (Table V). In this condition the surface was considered to be "normal".

Later it was found that thorough cleaning produced normal

FIGURE 60

The Influence of Surface on the Δp-Time and Peroxide-Time Curves with Diethyl Ether.



surface conditions immediately, and this was usually more expedient because it often took a large number of reactions to completely restore normal conditions.

TABLE V

Restoration of Normal
Surface Conditions by Successive Reactions

Diethyl ether pressure 150 mm.
Oxygen pressure 250 mm.
Temperature 166°C.

Experiment number.	Maximum rate (mm/min.)	Reciprocal induction period (min.)
1	3.5	0.05
3	4.6	0.04
12	7.7	0.04
14	7.8	0.04
16	7.9	0.04
19	8.0	0.05
20	8.0	0.05

Cleaning was invariably necessary after an explosion with oxygen-rich mixtures because soot was deposited and the reactions thereafter were slow and un-reproducible.

The cleaning procedure found to be most satisfactory and used during the latter part of the investigation was as follows. If soot was present it was oxidised by heating in air. The vessel was then washed with water and 50 ml. of 15% hydrofluoric acid was shaken in it for two minutes at room temperature. It was washed eight times with hot distilled water and rinsed three times with reagent-grade ethanol.

Finally, it was dried and attached to the apparatus.

Unless one of these occurrences spoils the surface it stays in its normal condition and the results are reproducible as shown previously in Figures 13 and 26. These experiments were made in three groups in a total of about 600 experiments using one or other of each of the ethers studied and involving cool flames and ignitions as well as slow reactions.

Summary of Results

Previous results on the maximum rate of oxidation of normal-pentane and on the corresponding induction period having been generally confirmed in the present apparatus, the study of ether oxidation was undertaken.

Dimethyl, methyl ethyl, methyl normal-propyl, diethyl, and di-normal propyl ethers exhibit slow reactions, cool flames and ignitions in the low temperature region. With di-iso-propyl ether, however, slow reactions and ignitions were not observed at all over a wide range where cool flames or negligible reaction occurred.

Dimethyl, methyl ethyl, methyl normal-propyl, diethyl, and di-normal-propyl ethers resemble the straight and branched chain paraffins, amines and ketones in the following kinetic aspects of the low-temperature, slow reaction:

(a) The maximum rate increases with the initial ether pressure.

(b) Increase in initial oxygen pressure first increases the maximum rate then produces inhibition.

(c) Increase in the initial ether pressure decreases the length of the induction period.

(d) Increase in the initial oxygen pressure increase the length of the induction period; in this respect the ethers resemble butanone at low oxygen pressures.

(e) Inert gas additions have no influence on the reaction.

(f) The reaction is sensitive to the condition of the surface of the reaction vessel.

(g) An initial pressure decrease is observed during a reaction, in this respect ethers resemble normal-octane and higher paraffins which oxidize at about the same rate.

(h) The maximum concentration of the ROOR (and ROOH) type of peroxide coincides with the maximum rate of pressure increase, as is observed with ethylamine and butanone, and with hexane and 2-methyl pentane (where the concentration of total peroxides coincides with the maximum rate).

In the following features the oxidation of the ethers differs from that of some of the other compounds:

(a) The temperature coefficient of the maximum rate is normal in the low temperature region.

(b) The plot of the reciprocal induction period against the initial oxygen pressure and the plot of the logarithm of the reciprocal of the induction period against the reciprocal of the absolute temperature seems to show a discontinuity between the slow reaction and cool flame regions: with butanone, normal-pentane and normal-hexane there is continuity.

(c) The ROOR (and ROOH) types of peroxide survive the passage of the cool flame of diethyl ether and are stable at

temperatures above the cool flame temperature.

(d) Large amount of peroxide are formed in the initial stages of ether oxidation.

The relative ease of oxidation of the ethers and normal-pentane is as follows:

TABLE VI

Relative Rates of Oxidation of Ethers and Pentane

Compound	Relative Rate				
Pentane	1				
Dimethyl ether	25	1			
Methyl n-propyl ether	175	7	1		
Methyl ethyl ether	175	7	1.1	1	
Di-n-propyl ether	1300	50	7	7	1
Diethyl ether	2500	100	14	14	2

Di-iso-propyl ether: slower than diethyl ether at 170°C.

As far as it is possible to make a comparison, the relative ease of cool flame formation, judging from the lowest temperature at which equimolar mixtures of ethers and oxygen give cool flames, agrees with an estimate of the relative ease of cool flame initiation made by Spence and Townend (14), and based on the minimum cool flame ignition pressure for equimolar ether-oxygen mixtures at constant

temperature. For comparison the values have been tabulated below:

Compound	Minimum Cool Flame Temperature (°C.)	Minimum Cool Flame Pressure (mm.)
Di-iso-propyl ether	158	
Diethyl ether	174	80
Di-n-propyl ether	180	
Methyl ethyl ether	193	110
Methyl n-propyl ether	197	190
Dimethyl ether	240	310

DISCUSSION

It is clear from the comparative survey in the last section that in certain general aspects the slow oxidation of ethers is kinetically similar to the low-temperature, slow oxidation of the other organic compounds previously investigated. The influence of initial reactant concentrations exemplifies this fact, and, what is equally important, peroxides of the ROOR (and to some extent ROOH) type known to be key intermediates in the branching chain mechanism of oxidation of the paraffins, amines and ketones are also intermediates in the slow oxidation of ethers. The important role which these peroxides play has been described in detail in the Introduction, but for convenience it will be re-stated here. The peroxides are assumed to be responsible for a "degenerate" branching chain in a series of the following type.

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

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

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

$$ROO\text{-} + RH \longrightarrow \text{Relatively inactive products} \qquad (4)$$

$$ROOR \longrightarrow 2\ RO\text{-} \qquad (5)$$

$$ROOR \longrightarrow \text{Inactive products} \qquad (6)$$

$$R'CH_2O\text{-} \longrightarrow R'\text{-} + HCHO \qquad (7)$$

$$R'\text{-} + RH \longrightarrow R\text{-} + R'H \qquad (8)$$

$$R'\text{-} + O_2 \longrightarrow \text{Less active products} \qquad (9)$$

For butanone, which seems to oxidize by a "degenerate" non-stationary branching chain, modifications have been introduced to give better agreement between the predicted and observed dependence of the rate on the initial reactant concentrations and these are:

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad (10) \text{ in place of } (3)$$

$$ROO\cdot \longrightarrow \text{Less active products} \qquad (11)$$

The way in which this mechanism is able to account for the marked dependence of the rate of oxidation on the structure of the organic reactant has also been discussed in the Introduction and is briefly as follows. The expression for the oxidation rate contains a factor of the form $\phi / [1 - ck_5]$ (or $\phi / [ck_5 - 1]$ if the reaction is non-stationary) and the condition for rapid reaction is that ck_5 should not be far removed from unity. In these circumstances the term $1 / [1 - ck_5]$ changes rapidly with a change in k_5. The oxidation rate therefore gives a magnified and sensitive measure of the influence of R on the stability of the peroxide bond the rupture of which is involved in (5). The expression for the rate contains two factors, the one just mentioned and the other proportional to the rate of initial attack of oxygen on the organic molecule, ϕ. Both may be influenced by the molecular structure of the combustible substance but the former is likely to be the more important because its influence is magnified by the characteristic kinetics of the branching

chain reaction. Therefore, the influence of changes in the structure of R on the strength of the -O-O- link has received special attention.

It has been pointed out that the only substituent which stabilises the organic reactant towards oxidation is the methyl group. This is an electron repelling group with an inductive effect represented by +I. Substituents with the opposite inductive action, such as Cl, NH_2 or C=O, favour oxidation. It has therefore been suggested that electron attracting groups (with a -I effect) weaken the peroxide linkage and electron repulsive groups strengthen it. This conclusion is in agreement with the view expressed by Walsh that the bond between strongly electronegative elements should be strengthened by the attachment of electron repelling groups since these facilitate the expansion of atomic orbitals without the occurrence of nuclear repulsion.

The second factor on which the rate of oxidation depends is ϕ, the rate of the chain-initiation process. Before taking part in the initiation reaction the attacking oxygen must be changed, more or less completely, into the biradical form. In this change electrons must be drawn from the O=O bond, and the very initial stages of the re-distribution may well be helped by the action of a positive centre at the seat of reaction which would tend to attract electrons towards it. If this were so, -I substituents would favour attack by creating

the necessary positive centre, while +I substituents, such as the methyl group, would weaken the attack. Thus it appears that if the influence of substituents can be assessed in terms of the ease of approach of the attacking agent and the initiation of the requisite re-organisation, the effects of substitution on both the chain-branching and the chain-initiation steps are in the same direction and tend to reinforce one another.

Since ethers oxidize more readily than pentane (Table VI) it is concluded, on the basis of these hypotheses, that the -O-O- bond is weaker in the peroxides derived from the ethers. If an ether, R_1O-R, is considered to be a paraffin with an alkoxy substituent, R_1O, it appears that the alkoxy group must exert a -I effect just as the amino or carbonyl groups or the chlorine atom. Thus the inductive action of the R_1O group determined from oxidation measurements agrees with the -I effect of the CH_3O group determined by independent means(38).

A comparison of the relative rates of oxidation of the ethers shows some of the features observed with other molecules. Dimethyl ether, the most primitive member of the ether series, resembles ethane and acetone in being much more stable towards oxidation than the higher members of the series. That it reacts at such a low temperature (240°C.) compared to ethane (450°C.) (8, 92) and acetone (510°C.) (16, 62) is further evidence of the promoting influence of the oxygen atom. The

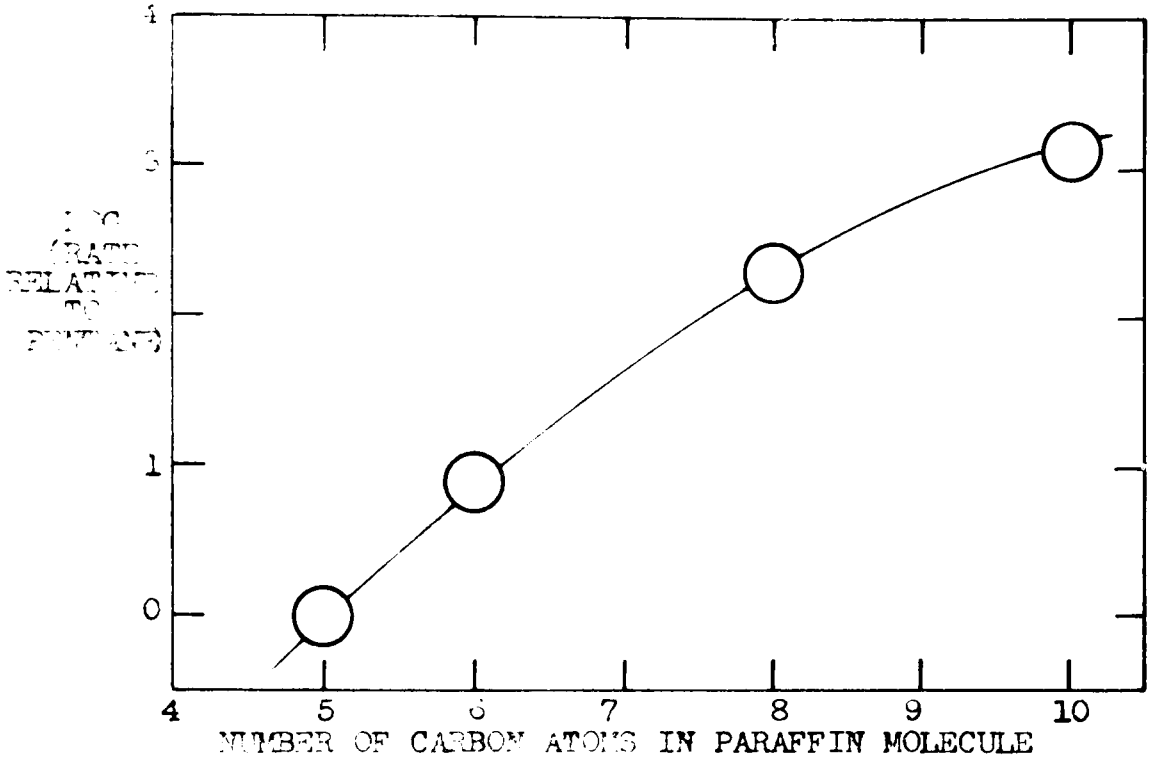
stability of di-iso-propyl ether, in so far as it can be compared in the region of slow reaction, emphasises the +I effect of the methyl group already so evident in oxidation reactions.

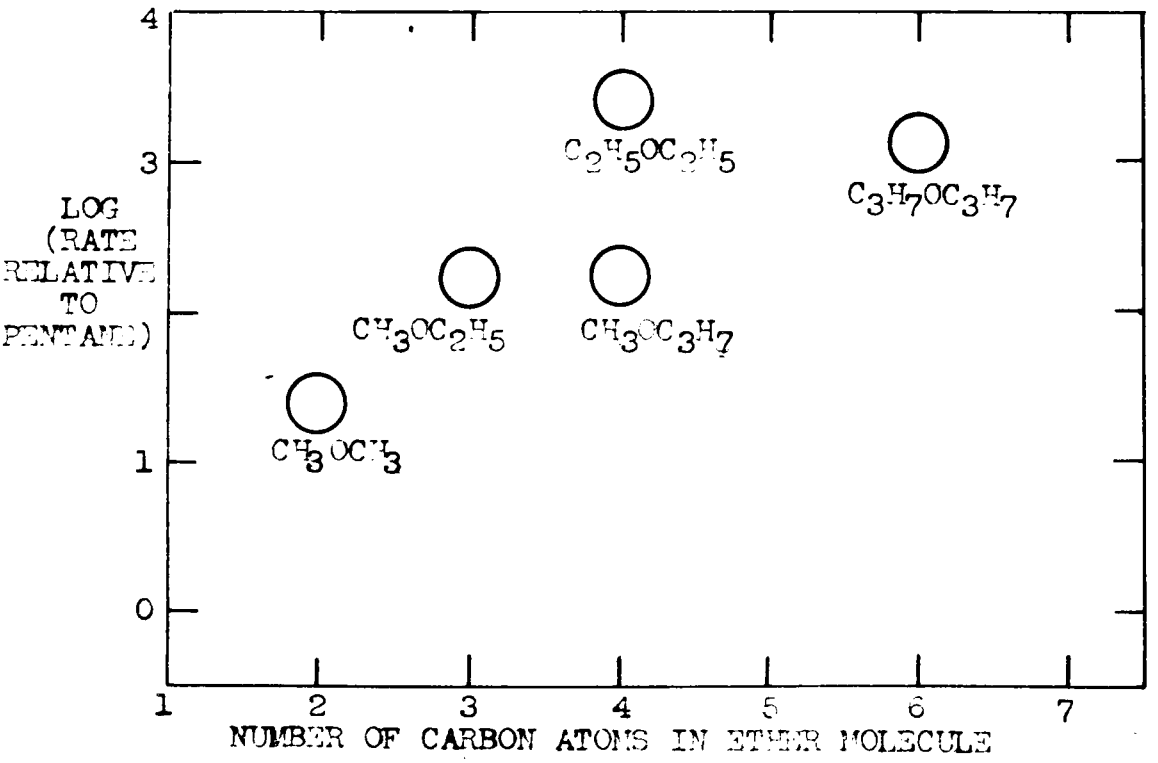
Ethers do not exhibit the progressive and marked increase in the rate of oxidation with increasing length of the normal carbon chain which is observed with the unsubstituted hydrocarbons, chloro-compounds, amines and ketones. The variation of oxidation rate with the length of the carbon chain is clear from the results in Table VI and also from Figure 61 where a plot of the logarithm of the maximum oxidation rate relative to pentane, and the number of carbon atoms in the molecule is shown for the ethers. A similar plot for the normal paraffins, taken from reference (1), is shown for comparison. It appears that the inductive action of the alkoxy group has to some extent saturated the response of the molecule, and the effect of the introduction of -O- is not reinforced by lengthening of the carbon chain. The results with paraffins show a similar tendency towards saturation of the response of the molecule but additional information for the higher paraffins would be necessary to confirm the trend.

It is also interesting to note that except for dimethyl ether, the symmetrical straight-chain ethers oxidize more readily than the unsymmetrical ones. The relative rates

Figure 61

Comparison of the Influence of Structure on the Reactivity of the Paraffins and Ethers.





are:

$CH_3O-\overset{*}{C}H_2CH_3$ 1 $CH_3O-\overset{*}{C}H_2CH_2CH_3$ 1

$CH_3CH_2O-\overset{*}{C}H_2CH_3$ 14 $CH_3CH_2CH_2O-\overset{*}{C}H_2CH_2CH_3$ 7

Further information would be required before speculation would be profitable but comparisons of this sort might prove to be a source of information concerning the effect of alkoxy groups. It is likely that the peroxide group will replace secondary hydrogen on the α carbon atom indicated with an asterisk (37, 69). If this is so, the peroxide bond will be influenced by the methoxy and ethoxy group in methyl ethyl and diethyl ether respectively, and it appears that the ethoxy group has the greater tendency to attract electrons. Similarly, by comparing methyl normal-propyl and di-normal-propyl ethers it is seen that the propoxy group has a greater -I effect than the methoxy group. Apparently the propoxy group is less effective in this respect than the ethoxy.

An important point in the theory of oxidation on which these implications are based is the assumption that reaction (9) leads to termination of the reaction chain and that the R'H molecule produced in (8) does not take an effective part in the reaction. This has been amply justified for paraffins,

amines and ketones by the observation that decrease in carbon chain length diminishes the rate of reaction. However, the rate of oxidation of the ethers does not show this marked dependence on chain length. Nevertheless, the assumption is probably sound for them as well, because an examination of the reactions and the most likely structures of R'- and R'H shows that they are lower molecular weight paraffins and aldehydes (33, 93). The reactions involved with diethyl ether, for example, might be:

$$CH_3\,CH_2\,O\,CH_2\,CH_3 \xrightarrow[(1,2\text{ and }3)]{\text{via}} CH_3\,CH_2\,O\,\underset{\underset{R'}{O}}{\overset{O}{CH}}\,CH_3$$

$$CH_3\,CH_2\,O\,\underset{\underset{R'}{O}}{\overset{O}{CH}}\,CH_3 \xrightarrow{(5)} CH_3\,CH_2\,O^- + \underset{O}{\overset{\|}{CH}}\,CH_3 + R'O^-$$

$$CH_3\,CH_2\,O^- \xrightarrow{(7)} CH_3^- + HCHO$$

R'- would therefore be the methyl radical, and R'H, methane, the most stable of the paraffins.

Unfortunately, little can be said about the role played by acetaldehyde or the higher aldehydes in a reacting ether-oxygen system, but it is known that acetaldehyde has no catalytic effect on the oxidation of normal-hexane at 202°C. nor propaldehyde on the oxidation of normal-pentane at 227°C. (1) and since these temperatures are 32-57°C. higher than

those at which diethyl ether oxidizes it seems likely that aldehydes are equally unreactive in a reacting ether-oxygen mixture.

Although the slow oxidation of ethers resembles that of other compounds, the cool flame reaction is quite different. In contrast to the precipitous decline in the concentration of peroxides of the ROOR (including ROOH) type previously observed after the cool flame in butanone-oxygen mixtures, the concentration of peroxides derived from ethers is practically unaffected by the passage of the cool flame. In fact, peroxides derived from ethers exist at temperatures and pressures considerably higher than those at which cool flames appear. Evidently peroxides of this type do not play the prominent part in the cool flame reaction of ethers that they seem to play in the butanone cool flame. Furthermore, if the definition of the induction period is widened to include the time interval between the admission of the reactants and the appearance of the cool flame as well as the time for the establishment of the maximum rate of slow oxidation, then, in contrast to the behaviour of normal-pentane, normal-hexane and butanone, the ethers seem to show a discontinuity in the relationship between the induction period and the temperature or the initial oxygen pressure in the transition from conditions which give slow reactions to those which give cool flames.

The theories of cool flame formation have been outlined

in the Introduction. Walsh has suggested that cool flames are very rapid, branching-chain reactions of the type responsible for the slow oxidation. According to this hypothesis the plot of the induction period of the slow oxidation against pressure should be continuous with a plot of the induction period for the cool flame against pressure. Since such is not the case with the ethers, this mechanism does not seem to provide a satisfactory explanation of the ether-oxygen cool flame results.

A more rigid test of the theories of cool flame formation cannot be made until further information about ether cool flames, and more particularly, about the substance which is responsible for them, is available. Two general suggestions about the source of cool flames in ether-oxygen reactions have been made in an earlier section. On the one hand, there is a possibility that if the Salnikov mechanism is applicable, the reaction of a particular peroxide, different from the bulk of material determined by the ferrous thiocyanate method of analysis, may give rise to cool flames. If the amount of this compound were relatively small, variations in its concentration during the passage of a cool flame would pass undetected. The inconclusive search for such a substance has already been described. On the other hand, the agent responsible for the cool flame in ether-oxygen mixtures may not respond to the method of analysis at all.

Another possibility is that the cool flame arises from a reaction of peroxide radicals, ROO-, instead of peroxide molecules. It is questionable whether a large enough concentration of ROO- can accumulate in a reacting ether-oxygen system to give a visible cool flame. Unfortunately, even less is known about the ROO- radical than of the ubiquitous HOO- radical, so a decision on the matter is not at the moment possible. Walsh has considered the thermochemical evidence and concludes that in its ground state HOO- may be comparatively inert (39). The chemical evidence for the existence of HOO- has been reviewed by Minkoff and he has also contributed to the theoretical discussion (94). Since the ROO- and HOO- radicals may be similar in structure, the former may be somewhat unreactive and may accumulate in large enough quantities in ether-oxygen mixtures to give a cool flame by the Salnikov mechanism.

The different source of cool flames with the ethers suggests an alternate reason for the complexity of the cool flame diagram of diethyl ether. As mentioned previously the cool flame area in the pressure-temperature explosion diagram appears to be composed of two overlapping peninsulae directed towards the temperature axis. Walsh has suggested that these lobes correspond to reactions involving different points of attack of oxygen on the ROOH molecule in reaction (17) of the

Introduction:

$$ROOH + O_2 \longrightarrow OH- + \text{other products} \qquad (17)$$

Alternatively, it may be that peroxides of the ROOR' (where R' may be H) type are responsible for the lobe at the higher temperature and that an unknown, less stable, compound, shown by the present investigation to be responsible for the cool flame of ethers, is associated with the lower lobe.

In summary it may be said that:

(a) the mechanism of slow oxidation of ethers is fundamentally the same as that observed for straight and branched chain paraffins, amines and ketones,

(b) the alkoxy group, RO, has an inductive effect represented by -I and the effect of the ethoxy and propoxy is greater than that of the methoxy, and

(c) the type of compound which gives rise to cool flames in ether-oxygen mixtures is different to that which is responsible for butanone cool flames.

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