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ABSTRACT

The work described in this thesis falls into three distinct sections. In Part 1, the methods available for the analysis of peroxides are discussed. Particular attention is paid to their application to the analysis of peroxides in combustion products and the reasons are indicated for trying to develop a gas chromatographic method.

Part 2 describes the effects of variables in gas liquid chromatography on the retention times, peak shapes and separabilities of several peroxides which may be formed in the combustion of isopentane. The peroxides studied are (a) Tert-amyl hydroperoxide, (b) 3 methyl but-2-hydroperoxide, (c) 2 methyl but-1-hydroperoxide, (d) 3 methyl but-1-hydroperoxide, (e) di tert-amyl peroxide and (f) hydrogen peroxide. The optimum conditions for separating the tert-alkyl (a), the sec-alkyl (b), the two primary alkyl hydroperoxides (c and d) and the dialkyl peroxide (e) have been established. It was not possible to separate the two primary isomers. Decomposition generally does not occur on columns up to 4 ft. long at temperatures up to 76°C, although there is some danger of decomposition if the inlet pressure is near atmospheric. Hydrogen peroxide appears to decompose under

all the conditions investigated.

Part 3 describes the analysis of the intermediate products of the combustion of isopentane between 337° and 440°C. The most significant result is the absence of any of the simple mono-hydroperoxides studied in Part 2, despite the fact that acid potassium iodide analysis shows the presence of large quantities of alkyl hydroperoxides or peroxides of similar reducibility. Studies of the decomposition of tert-amyl hydroperoxide have been carried out and the results indicate that decomposition takes place well below the combustion temperature of isopentane. From a consideration of the results, a mechanism for the combustion of isopentane is proposed, which excludes the formation of a simple mono-hydroperoxide, but which accounts for the products by postulating reactions of the peroxy radical other than

$$RO_2' + RH \longrightarrow ROOH + R'.$$

PART 1

A REVIEW OF METHODS FOR THE DETECTION AND ESTIMATION OF ORGANIC PEROXIDES

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A. INTRODUCTION.

Several methods are now available for the analysis of peroxides, their development having been mainly concerned with the analysis of combustion, autoxidation and polymerisation products. Although the following review is intended to be quite general, particular attention is paid to the usefulness of each method for the determination of peroxides formed during the combustion of hydrocarbons and related compounds.

An attempt is indeed made to classify each method from the point of view of its possible application to the analysis of combustion products. For this purpose, each method can be placed in one of three broad classifications.

(i) Those only capable of determining total peroxides.

(ii) Those capable of distinguishing different classes of peroxides.

(iii) Those capable of distinguishing individual peroxides.

Clearly, a method, although falling into either category (ii) or (iii), may be limited in its application. For example, paper chromatography has been used to identify a wide range of peroxides, but it can give only a very approximate indication

of the amount of a particular peroxide present. Further, most instrumental methods require calibration with pure peroxides, whose preparation may be difficult.

However, provided that the inherent limitations of a particular method are realised, the above classification can be a useful basis for considering the application of methods to the analysis of peroxides in combustion products.

B. VOLUMETRIC METHODS.

(i) Iodometric Methods.

Iodometric methods depend upon the oxidation of the iodide ion, thus,

$$ROOR' + 2I^- \longrightarrow RO^- + R'O^- + I_2$$

the iodine liberated being titrated against thiosulphate solution. R and R' can represent a number of groups, e.g. hydrogen, alkyl, aryl, acyl, aroyl and hydroxyalkyl. The particular groups attached to the O-O linkage determine the ease with which a peroxide can be reduced by iodide ions. Since different types of peroxides exhibit widely different reactivities, several iodometric methods have been developed for their analysis, none of which is generally applicable.

Iodometric methods are subject to three important sources of error, (a) oxidation of iodide by atmospheric and absorbed oxygen, (b) incomplete reaction and (c) loss of iodine through side reactions, particularly addition to double bonds.

Factors which influence the usefulness of a particular method are the nature of the solvent, the presence or absence of oxygen, catalysts, the source of the iodide ion, sample size, reaction time and temperature.

(a) Errors due to atmospheric and absorbed oxygen.

If the peroxides to be analyzed are easily reduced, the presence of oxygen has a negligible effect on their determination. However, with less reactive peroxides, when long reaction times are necessary, air must be rigorously excluded. The commonest methods for removing air are bubbling gaseous nitrogen or carbon dioxide through the reaction mixture, and the addition of liquid nitrogen or solid carbon dioxide.

(b) Errors due to incomplete reaction.

The principal factors influencing the completeness of reaction are the nature of the solvent, catalysts, the source of the iodide ion, reaction time and reaction temperature.

It is desirable that the solvent should give a homogeneous reaction mixture and not react with iodide or any of the species present. Kokatnur and Jelling(1) tried several solvents, and found isopropyl alcohol to be the most suitable. It required no blank determination, reaction between iodine and sodium thiosulphate was instantaneous and the analysis was independent of the quantities of isopropyl alcohol and other reagents used. Ethyl alcohol and acetic acid were satisfactory to a lesser extent. Acetone proved to be unsatisfactory, giving low and inconsistent results, particularly with acyl peroxides. Presumably this is due to

a reaction between acetone and iodine. Nozaki (2) found that acetic anhydride was a good solvent. It readily dissolves both peroxides and potassium iodide, and does not react with iodine.

Isopropyl alcohol and acetic acid are considered to be the best solvents for most analyses. In general, however, alcohols have the disadvantage of requiring high temperatures for quantitative reaction.

The addition of certain catalysts considerably increases the rates of some iodometric reactions. Silbert and Swern (3) showed that 0.002% ferric chloride hexahydrate in glacial acetic acid reduces reaction times considerably. Hock and Kropf (4) used cuprous chloride; with acetic acid as solvent and a mixture of hydrogen iodide and potassium iodide as sources of iodide ion, two drops of a molar solution of catalyst gave a near theoretical determination of aromatic peroxides in hydrocarbons after 30 min.

When the peroxides to be analysed are reduced only with difficulty, it is necessary to replace potassium iodide by the much more reactive hydriodic acid. Vaughan et al (5) have developed an extremely stringent method, capable of reducing the most stable dialkyl peroxides. They used concentrated hydriodic acid in acetic acid, under anaerobic

conditions,at 60°C for 45 min. Some aldehydes, sulphur containing compounds and unsaturated compounds interfere with this method.

Lea (6) has made studies of the effect of time and temperature on the determination of peroxides in fats and oils. As a result of a thorough investigation of all variables, both hot and cold iodometric methods were developed. In both methods the solvent is a 3:2 acetic acid: chloroform mixture, potassium iodide is the source of iodide ions and anaerobic conditions are used. The hot method is carried out at the boiling point of the solvent (60°C), and the reaction is complete within 2 min. In the cold method, room temperature is used and the reaction takes 1 hr. Excellent agreement was obtained between the two methods.

(c) Errors due to side reactions.

The occurrence of side reactions in some iodometric analyses has been shown by the decrease in peroxide concentration with increased sample size. The most likely interfering reaction is the addition of iodine to double bonds, and attempts have been made to minimise this effect.

Dastur and Lea (7) tried to eliminate the error by determining both iodine formed and residual iodine. Their work and that of Panyutin and Gindin (8) showed that addition

to double bonds only occurred under certain conditions. Wagner et al (9) state that the use of trivalent iodide ions in solution removes the possibility of addition to double bonds. Nozalic (2) added several olefinic compounds to reaction mixtures, but found that of these, only cyclohexene interfered with the method used.

Iodometry is by far the most common volumetric method for the analysis of peroxides in combustion products. As long ago as 1904, Clover and Houghton (10) developed a method for distinguishing between peroxyacids, hydrogen peroxide and organic peroxides. Peroxyacids liberate iodine from an acidic aqueous potassium iodide solution at $0^{\circ}C$. Under these conditions, hydrogen peroxide is said to react slowly, and organic peroxides not at all. At $5^{\circ}C$, hydrogen peroxide reacts quantitatively with potassium iodide in the presence of two drops of a saturated solution of ammonium molybdate. Organic peroxides are quantitatively reduced only if heated at $40^{\circ}C$ for 1 hr., so that, by a careful adjustment of temperature and catalytic conditions, the amounts of each type of peroxide in the combustion products can be estimated. The method cannot be applied to dialkyl peroxides.

(ii) Stannous Ion Reduction.

This method was first used in 1894 by Von Pechman and Vanino (11). Phthalyl peroxide was reduced with stannous chloride and the excess was back titrated with iodine. An accuracy of 3% was obtained. Hock and Schrader (12) further developed the method, using a temperature of 95°C and back titrating the unused stannous chloride with ferric chloride. Later , Koch and Pohl (13) showed that this method gave an absolute accuracy of only 85 to 95% with tetralin hydroperoxide while Schildwachter (14) obtained similar results for several other peroxides.

The most accurate stannous reduction method is that devised by Barnard and Hargrave (15). The reduction of various peroxides (e.g. tert-butyl hydroperoxide, cumene hydroperoxide, tetralin hydroperoxide, hydrogen peroxide, benzoyl peroxide and cyclohexane hydroperoxide) was carried out in an inert atmosphere, using acetic acid as solvent, and reaction was found to be complete within 30 min. at room temperature. Acyl peroxides require a temperature of 80°C for reduction within 30 min. Di tert-butyl peroxide is not reduced by the stannous ion, either at room temperature or at 80°C. The unused stannous ion is determined by reaction with a ferric solution, containing ammonium chloride, which catalyses the

Sn^{++} - Fe^{+++} reaction. The Fe^{++} formed is titrated with standard potassium dichromate to complete the procedure.

When it is essential to use a non-acidic solvent, tert-butyl alcohol or benzene may be used instead of acetic acid. Determinations carried out in tert-butyl alcohol give results which are about 2% too low. This error is probably due to the formation of a non-reducible dialkyl peroxide, thus,

$$(CH_3)_3COH + ROOH \longrightarrow (CH_3)_3COOR + H_2O$$

Application of the Barnard and Hargrave method is limited by interference from substances which are either reduced by stannous chloride or oxidised by potassium dichromate. Aldehydes are reduced by stannous chloride at room temperature, and when present in amounts up to twice the molarity of the peroxide sample, give rise to errors of 1 to 2%. Thioethers and primary alcohols are oxidised by potassium dichromate. Thioethers can be removed by shaking the solution with carbon tetrachloride. Under these conditions, no error is detected from thioethers present in less than 8 M excess, compared with the peroxide. When primary alcohols are present in concentrations greater than equimolar in relation to that of the peroxide, they give rise to serious errors. Barnard and Hargrave found no interference from

ketones, secondary and tertiary alcohols, carboxylic acids, olefins, thioethers, sulphoxides and sulphones.

Egerton et al (16) performed the reduction in alkaline solution. The peroxides studied were isopropyl hydroperoxide and tert-butyl hydroperoxide. Before the addition of stannous chloride, the peroxides were converted by sodium hydroxide to their sodium salts. This method is much quicker than that of Barnard and Hargrave, the reation being complete in 3 min.

The application of stannous ion reduction methods to the analysis of peroxides in combustion products is limited by the effect of interfering substances. In several cases, particularly when the peroxide yield is small, the concentration of interfering products will seriously affect the results.

(iii) Ferrous Ion Reduction.

The determination of peroxides by oxidation of ferrous to ferric thiocyanate, followed by titration of the ferric ion formed with titanous sulphate or of unused ferrous ion with potassium dichromate, is more sensitive than iodometric methods, but inherently less accurate. For this reason, the method is only useful where relative peroxide values are required.

Yule and Wilson (17) used a ferrous-titanous method to estimate peroxides in gasoline, but found that when applied to pure peroxides, of the type found in autoxidised materials, the results were extremely inaccurate. Lea (18), using a similar method, showed that much lower results are obtained in the absence of air than in its presence. The effect of oxygen on the ferrous-titanous method has been investigated by Wagner, Smith and Peters (19). The results were compared of passing carbon dioxide and oxygen respectively through the reaction mixture for 2 min. before the peroxide sample was added. There was found to be considerable discrepancy between the two sets of results. For example, analysis of tetralin peroxide, using oxygen as the purging gas, gave a peroxide value 900% higher than that using carbon dioxide. Values obtained in air were usually between those obtained in oxygen and carbon dioxide.

The effect of oxygen concentration was at first thought to be due to oxidation of ferrous ion by atmospheric and dissolved oxygen, However, Kolthoff and Medalia (20) have shown that there is an opposing effect caused by an acid-catalysed decomposition of the peroxide, induced by the ferric ion. If oxidation of the ferrous ion is to be stoichiometric, a peroxide molecule must react with a ferrous

ion by single electron transfer,

$$ROOH + Fe^{++} \longrightarrow RO' + OH' + Fe^{+++} \qquad \text{(i)}$$

and the free radical RO' must react further with another Fe^{++} ion to produce another Fe^{+++} ion.

$$RO' + Fe^{++} + H^{+} \longrightarrow ROH + Fe^{+++} \qquad \text{(ii)}$$

However, the RO' radical can undergo various other reactions, which will compete with stage (ii). In the absence of oxygen, reactions of the type

$$RO' + R_1H \longrightarrow ROH + R_1'$$

may occur, giving low analytical results. If oxygen is present, the new organic radical, R^1', might add on a molecule of oxygen to give an organic peroxy radical,

$$R^1' + O_2 \longrightarrow R^1OO'.$$

This radical might then react with a ferrous ion,

$$R^1OO' + Fe^{++} + H^{+} \longrightarrow R^1OOH + Fe^{+++},$$

and the occurrence of this reaction would lead to high results for peroxides.

Kolthoff and Medalia (20) have reviewed the ferrous oxidation methods for the analysis of peroxides and compared the results with those obtained by iodometric methods. From their conclusions and the above discussion, it is clear that the ferrous oxidation methods are too unreliable for accurate analysis of peroxides in combustion products.

(iv) Arsenious Oxide Reduction.

The reduction of peroxides by arsenious oxide is an accurate analytical method. The method was developed by Siggia (21), who analysed benzoyl peroxide in various solvents. Although the method involves titration of excess arsenious oxide with iodine, no interference has been found in samples containing unsaturated compounds. The arsenious oxide takes up the iodine instantly.

The presence of large quantities of organic solvent makes the end point somewhat indefinite, and the excess solvent must therefore be boiled off before titration. The solvents used were methyl alcohol, acetone, benzene, styrene, isobutyl vinyl ether and methyl methacrylate. All gave excellent results.

Little is known concerning the possibility of using arsenious oxide for the analysis of peroxides in combustion products. Studies of its suitability and specificity for different classes of peroxides would be of value.

(v) Ceric Ammonium Sulphate Reduction.

Ceric ammonium sulphate will selectively oxidise hydrogenperoxide in the presence of other peroxides, with the exception of certain hydroperoxides. Greenspan and

MacKellar (22) used this reaction to analyse hydrogen peroxide-peroxyacid mixtures, the peroxyacid being determined by an iodometric method. Neither the initial Ce^{4+} nor the Ce^{3+} formed react with the peroxyacid. The method is therefore more reliable than that using permanganate as the oxidising agent, since Mn^{2+} reacts with the peroxyacids.

The application of this method to the analysis of hydrogen peroxide in combustion products is severely limited, since the Ce^{4+} ion also oxidises some organic hydroperoxides, thus,

$$2\ Ce^{4+} + SO_4^{2-} + ROOH \longrightarrow 2\ Ce^{3+} + RHSO_4 + O_2.$$

(vi) Other Volumetric Methods.

Titanous chloride has been used as a reducing agent by Hock and Schrader (12). Analyses of tetralin peroxide gave values up to 5% too low, this being attributed to side reactions.

Mitchell and Smith (23) have used a method which involves reduction of the peroxide by hydrogen, esterification of the alcohol formed and finally determination of the water produced in esterification by Karl Fischer reagent. They successfully used the method to estimate diethyl peroxide, di tert-butyl peroxide and tert-butyl hydroperoxide. Several

organic compounds will interfere.

Sulphite and bisulphite ions have been used as reducing agents for certain hydroperoxides by Ashby (24) and O'Neill (25).

A method which does not involve the reactivity of the O-O bond is potentiometric titration. Everett and Minkoff (26) titrated peroxyacids in water as weak acids potentiometrically with 0.1 N sodium hydroxide. Hydroperoxides act as very weak acids, and can be titrated in strongly basic solvents, such as ethylene diamine.

C. COLORIMETRIC METHODS.

(i) Ferrous Ion Reduction.

The colorimetric determination of peroxides by the ferrous reduction method can be performed by measurement of either the ferric ion produced or the excess ferrous ion remaining.

Ferric ions are determined by a thiocyanate reagent, which has a particularly high sensitivity in solvents of low dielectric constant, and has the added advantage of being satisfactory in strong acid solution.

Kolthoff and Medalia (20) used amixture of 96% acetone and 4% water to dissolve the sample. Air was removed by boiling and a 0.1 M solution of ferrous perchlorate in 2 M perchloric acid was added as the reducing agent. After the reaction mixture had been boiled for a further 5 min. and allowed to cool, a 14% solution of ammonium thiocyanate in acetone was added. The colour was allowed to develop for 5 min. and the absorbance was measured at 460 millimicrons. The samples studied were cumene hydroperoxide, methyl oleate hydroperoxide, autoxidised fatty acids and oxidised cottonseed oil. The results, compared with iodometric analyses, are very low, except for cumene hydroperoxide.

The disadvantages in the use of ferrous thiocyanate as a colour reagent are that the colour depends on the concentration of both thiocyanate and acid. In addition, the red colour of the ferric thiocyanate complex is unstable, requiring colorimetric readings to be taken without delay.

In determinations of the hydroperoxide content of natural rubbers and synthetic fibres, Laitinen and Nelson (27) used o-phenanthroline as a colour reagent for unchanged ferrous ion. The peroxide was allowed to react with ferrous ion in benzene + methyl alcohol solution for 15 min. o-Phenanthroline was added, followed by dilution with benzene, and the absorbance was measured at 508 millimicrons. The procedure will detect 10-20 p.p.m. active oxygen, and the reproducibility is about 20%.

The disadvantages of the ferrous ion-peroxide reaction are outlined in the preceding section on volumetric methods, and this reaction is clearly unsuitable for the accurate analysis of peroxides.

(ii) Iodometric Method.

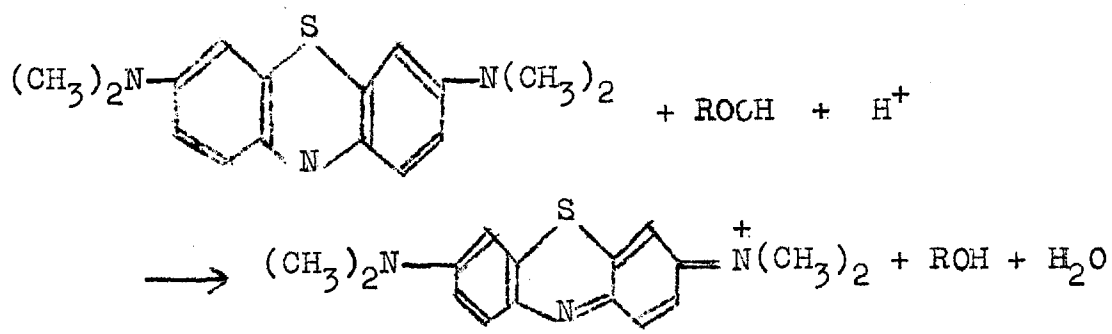
Following the observation by Siddigi (28) that the variation of the colour intensity of iodine solutions formed by the oxidation of iodides obeys Beers law, Heaton and

Uri (29) showed that the colorimetric method could be used for samples containing from 0.02 to 5 micromole of peroxide to a maximum concentration of 5×10^{-4} M, above which Beer's law is not followed. In an acetic acid + chloroform solution, iodine showed continuous and increasing absorption in the range 500-350 millimicrons. Absorption appears to be due to the I_3^- ion.

This method may find application in the analysis of traces of peroxides in combustion products.

(iii) Reduction of Leuco Base of Methylene Blue.

Sorge and Uerberreiter (30) used the following method, based on the oxidation of the leuco base of methylene blue to methylene blue itself.



The rate of the reaction varies with the type of peroxide. Fluorenone, 1,1' dihydroxy-dicyclohexyl, 1 hydroxy 1' hydro peroxy-dicyclohexyl and 1,1' bis hydroperoxy-dicyclohexyl peroxides reach constant absorbance within 3 min., whereas

tert-butyl hydroperoxide and lauroyl and benzoyl peroxides react much more slowly. Di tert-butyl peroxide does not appear to react at all. The peroxide content of polystyrene and polymethyl methacrylate was quantitatively determined. The reaction was carried out in a solution of trichloroacetic acid in benzene (between 1.5 and 5 g/litre) and the absorbance of the blue solution was measured at 643 millimicrons. The absorptions of the reaction mixtures studied suggest that an unknown peroxide can be determined to an accuracy within 5%. In the case of fluorenone peroxide, as little as 0.03 micrograms of active oxygen can be determined in concentrations of fractional p.p.m.

This reaction may be useful for analysing peroxides in combustion products. However, since it is best carried out in benzene solution, it would be satisfactory only for peroxides which are readily soluble in this solvent. In addition, interference could occur through oxidation of the leuco base by other combustion products.

Several other colorimetric methods have been used for peroxide determinations. These are listed by Martin (31), who states that they may be applicable to specific systems.

D. SPECTROSCOPIC METHODS.

(i) Infrared Spectroscopy.

Investigations of the infrared spectroscopy of organic peroxides have been mainly concerned with trying to establish the position of a band which is characteristic of the O-O linkage. The most common method of attack has involved comparison of the spectra of particular peroxides with those of the corresponding alcohols, in the hope of finding one or more extra bands which could be attributed to the peroxide group.

There is considerable evidence for the O-O stretching frequency being in the region of 11.4 microns, but the use of this for the identification of peroxides is limited, firstly by the dependence of the exact position of the absorption band on the structure of the rest of the molecule, and secondly by the fact that bands in this region can sometimes be derived from other sources.

Shreve, Heether, Knight and Swern (32) studied the spectra of four pure hydroperoxides and their parent compounds, viz. tert-butyl hydroperoxide and tert-butyl alcohol, cyclohexene hydroperoxide and cyclohexene, tetralin hydroperoxide and tetralin and cumene hydroperoxide and cumene.

Since the spectra of the tert-butyl compounds are less complex than those of the others, a detailed comparison of these two was made. Several common bands were found and these were attributed to O-H and C-H stretching, deformation vibrations of the CH_3 groups and vibrations of the tert-butyl group. Bands at 9.8 and 13.4 microns were of uncertain origin, but occur in both the hydroperoxide and alcohol spectra. The most marked variation was the disappearance of a strong band at 11 microns and the appearance of two new bands, a weak one at 11.3 microns and a strong one at 11.8 microns.

Cyclohexene, cumene and tetralin hydroperoxides also have absorption bands near 12 microns, which are absent in their parent compounds.

Di tert-butyl peroxide also shows a strong band in this region. However, in the case of benzoyl peroxide, a band at 11.7 microns was of very low intensity, while another at 10.0 microns was very strong. If this strong band is due to stretching of the peroxide linkage, the vibration frequency of O-O is influenced by the nature of the attached groups.

Minkoff (33) obtained the infrared spectra of over thirty organic peroxides, including alkyl hydroperoxides, dialkyl and diacyl peroxides, peroxyesters and hydroxyalkyl peroxides. He concluded that most peroxides have absorption

bands in the region 11.0 to 12.0 microns and that if the skew configuration is retained, one of these is due to the O-O stretching vibration. It is not possible to assign a particular band to a particular type of peroxide, so that this region cannot be used to identify the type of peroxide or to determine whether it contains a primary, secondary or tertiary alkyl group.

Williams and Mosher (34) investigated the infrared spectra of nine primary and eight secondary hydroperoxides and their corresponding alcohols. All the saturated alkyl hydroperoxides absorbed in the 11.4 to 11.8 microns region. Several alcohols were also found to give bands in this region, which seriously weakens its usefulness for characterising peroxides. However, hydroperoxides and alcohols can be easily distinguished by their characteristic absorption curves.

Williams and Mosher suggest that frequencies other than the 11.0 to 12.0 microns region might be useful for detecting peroxides in specific cases. For example, between 6.72 and 6.98 microns, a singlet is obtained from alcohols and secondary hydroperoxides and a triplet from primary hydroperoxides. This triplet is probably derived from interactions between the hydrogen of the alpha methylene group and the unsymmetrical hydroperoxy radical, and may

therefore be used as evidence for the presence of a primary hydroperoxide. However, absorption in this region is weak, and, in addition, the triplet becomes less well defined as the homologous series is ascended, until with n decyl hydrperoxide, two of the peaks are just inflections on the main absorption band. In addition, all the peroxides and alcohols except cyclopentyl hydroperoxide and cyclopentanol showed strong absorption near 7.2 microns, due to the wagging and rocking of the CH_3 group, but only secondary hydroperoxides have a weaker band at 7.4 to 7.5 microns. Williams and Mosher found that all the primary and secondary peroxides studied showed absorption in the region 12.0 to 12.5 microns, and observed an interesting phenomenon in this region. Normal alkyl hydroperoxides containing an even number of carbon atoms show two maxima, at 12.1 and 12.4 microns, while those containing an odd number of carbon atoms show only one, at 12.3 microns. None of the corresponding alcohols except n octyl alcohol, gave interfering bands in this region.

Philpotts and Thain (35) studied the effect of molecular weight on the absorption bands in the region of 11.4 microns, by recording the infrared spectra of three series of compounds, ROH, ROR, and ROOH, where R = tert-butyl, R = tert-amyl and R = cumyl. The three hydroperoxides

absorbed at 845 (11.83), 840 (11.90) and 835 cm^{-1} (11.98 microns), the peroxides at 875 (11.43), 869 (11.51) and 858 $cm.^{-1}$ (11.66 microns) and the alcohols at 915 (10.93), 882 (11.34) and 863 cm^{-1} (11.59 microns). Thus the alcohol frequency changes more rapidly than the peroxide frequency with increasing size of the group R. In the case of the tert-butyl and tert-amyl compounds, the frequencies are sufficiently different to identify the constituents of a mixture of hydroperoxide, peroxide and alcohol. But for the cumyl compounds, the alcohol and peroxide bands are too close together. This suggests that the frequency of the absorption bands is influenced more by the RO group than by the O-O stretching vibration, and would explain why tert-alkyl hydroperoxides and di tert-alkyl peroxides absorb more strongly than primary hydroperoxides and peroxides.

The infrared spectra of peroxyacids have been studied by Giguere and Olmos (36), Minkoff (33) and Stephens, Hanst and Doerr (37). Giguère and Olmos found that peroxyformic and peroxyacetic acids absorbed at 11.7 microns. Stephens et al and Minkoff obtained similar spectra for peroxyacetic acid. However, Minkoff's spectra of peroxypropionic and peroxy-butyric acids differ from those of Giguère and Olmos and of Stephens et al. Minkoff has indicated that his samples were

impure, the chief impurities being aliphatic acids, and this would explain the discrepancy.

Stephens et al concluded from the spectra of peroxypropionic and peroxybutyric acids that the chief bands which could be attributed to the peroxyacid structure were at 3.05, 6.9 and 8.5 microns. The band at 3.05 microns is considered to be the most useful for analysis and is thought to arise from the OO-H stretching vibration.

Skeletal vibrations in some types of peroxides have been recorded by Minkoff (33) and may prove useful for analysis. Percarbamates have a strong band at 8.22 microns and peroxy-esters at 8.04 microns. Monohydroxydialkyl and dihydroxy-dialkyl peroxides which contain the group, $CH_3—\underset{OH}{CH}-O—O—$ have bands at 8.93 and 10.9 microns, while the others show absorption in the region 8.7 to 9.5 microns.

The available evidence suggests that it is not possible to assign absorption bands to the O-O stretching frequency for different types of peroxide. The complexity of the spectra suggest that it would be impossible to detect either types of peroxide or specific peroxides in combustion products. A possible line of attack would be to separate the peroxidic material from the other products and to compare the whole infrared spectrum of this with the whole spectra of pure

peroxides. This method is called "fingerprinting" and requires a considerable amount of tedious work. Apart from this, it is likely that the complexity of the spectra would make it impossible to find enough points of similarity between the spectrum of an individual peroxide and the spectrum of the combustion products to provide conclusive evidence that the peroxide is present.

(ii) Ultraviolet Spectroscopy.

Ultraviolet spectroscopy has not found very much application in the determination of peroxides. Egerton, Harris and Young (38) and Everett and Minkoff (39) have shown that peroxides exhibit absorption peaks below 3,000 Å. Egerton et al investigated the pressure limits at which absorption could be detected, thereby finding the order of absorption intensities for the peroxides studied. These were found to absorb in the following order:-

$$H_2O_2 > CH_3OOH > C_2H_5OOH > C_3H_7OOH$$
$$C_2H_5OOH > C_2H_5OOC_2H_5 > C_3H_7OOC_3H_7$$

The limit of the photographed spectrum, or the "cut off", for methyl hydroperoxide occurred at 1.8 cm.Hg and had a value of about 2150 Å. With increasing pressure, the cut off moved towards the visible, e.g. 2300 Å at 2.8 cm. Hg. Ethyl

hydroperoxide required a pressure of 2.0 cm. Hg to give a cut off at 2150 Å. The other peroxides listed above showed similar but less intense absorption.

The hydroxyalkyl peroxides investigated were dihydroxy-dimethyl peroxide and dihydroxy-dimethylperoxide. The former gave a "cut off" extending to 2600 Å at 1.5 cm. Hg and the latter a "cut off" extending to 2350 Å at 1.2 cm. Hg.

Three monohydroxy-dialkyl peroxides were studied, viz. (a) monohydroxymethyl ethyl peroxide, whose vapour gave a general absorption extending to 2500 Å at 2 cm. Hg; (b) monohydroxydiethyl peroxide, whose vapour gave a similar absorption, except that at low pressures a very weak band appears in the region 2700 to 2500 Å in addition to the"cut off" at 2200 to 2300 Å; (c) Monohydroxydipropyl peroxide, which gave absorption in the region 2500 to 2000 Å only.

All the hydroxyperoxides studied absorb more strongly than the alkyl peroxides, but less strongly than hydrogen peroxide. The limit of detection of hydrogen peroxide in the liquid phase was 0.007%, which gave a "cut off" at 2100 Å. The absorptions of hydrogen peroxide in aqueous solution and in the vapour phase do not differ appreciably.

Ultraviolet spectroscopy does not appear to have any advantage over less complex methods for the analysis of organic peroxides in combustion products.

E. POLAROGRAPHIC METHODS.

The polarographic method for the determination of peroxides is based on the reduction of the O-O linkage by 2 electron reactions, e.g.,

$$ROOR' + 2H^{+} + 2e \longrightarrow ROH + R'OH$$

$$R-\overset{O}{\overset{\|}{C}}-OOR' + 2H + 2e \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + ROH$$

and is of more or less general application, since di tert-butyl peroxide is the only peroxide known to be non-reducible over the normal polarographic potential region.

A peroxide is detected, under a specific set of conditions, by its half wave potential, and may be quantitatively determined from the value of its limiting diffusion current.

Dobrinskaya and Neiman (40) have shown that half wave potentials vary only slightly with the acidity of the electrolyte solution. In general, aqueous solutions are preferred, on account of their high conductivity. The most commonly used electrolytes in aqueous solution are potassium and lithium chlorides, sulphuric acid, the acetic acid-sodium acetate buffer and the potassium dihydrogen phosphate-borax buffer.

To make quantitative determinations, it is necessary to calibrate for each particular peroxide, i.e. to determine its diffusion current constant, I. This is given by the equation,

$$I = \frac{i_d}{cm^{2/3}t^{1/6}}$$

where i_d = diffusion current, c = peroxide concentration (mmole/litre), t = mercury drop time (sec.) and m = mass of mercury flowing per sec. (mg.). I can therefore be determined from polarograms obtained at known concentrations. Analysis for a specific peroxide can then be made under the calibration conditions, the diffusion current being in every case studied directly proportional to the concentration.

Martin (31) has summarised the half wave potentials and diffusion current constants for a wide range of peroxides, in various electrolytic media.

Bruschweiler and Minkoff (41) have studied the polarographic behaviour of hydrogen peroxide, methyl, ethyl and tert-butyl hydroperoxides, diethyl peroxide and peroxyformic, peroxyacetic and peroxypropionic acids. The supporting electrolyte was 0.1 M lithium sulphate. Lithium hydroxide or 0.1 M sulphuric acid was added, according to whether an alkaline or an acid medium was required. Satisfactory waves can be obtained from hydrogen peroxide in neutral, alkaline or

acid solutions. In neutral and acid solutions a drawn out, cathodic wave is obtained, with a half wave potential of -0.88 volts. In alkaline solutions, the half wave potential shifts to more negative values, being -1.02 volts at a pH of 11.3 and -1.21 at a pH of 11.9. In alkaline solution an anodic wave is produced,in addition to the cathodic step. This is due to electrochemical oxidation of hydrogen peroxide to molecular oxygen. When the alkali concentration is greater than 1.4 N, the anodic and cathodic diffusion currents are equal in magnitude. The alkyl hydroperoxides studied gave shallow, cathodic waves, the half wave potential becoming more positive with larger alkyl groups. Diethyl peroxide also yielded satisfactory chromatograms, the half wave potential being unaffected by pH. The peroxyacids can be determined in acid solution and give half wave potentials of about 0.20 volts. Peroxypropionic acid is reduced at a slightly more positive potential than the corresponding peroxyacetic and peroxyformic compounds.

The analysis of a mixture of low molecular weight alkyl hydroperoxides is limited because their half wave potentials lie too close together. Adjacent members in a homologous series certainly cannot be separated. However, since the limiting diffusion currents of constituents in a mixture are

additive, it is possible to analyse for total alkyl hydroperoxides and hydrogen peroxide when they occur together. Hydrogen peroxide can be determined direcly from the anodic step, and total peroxides by subtracting the diffusion current of this anodic step from the total diffusion current, measured from the cathodic step. To determine peroxyacids, another polarogram must be obtained in acid solution.

Skoog and Lauwzecha (42) have made a systematic study of the polarographic behaviour of alkyl hydroperoxides from C_4 to C_9, using aqueous solutions of ethyl alcohol as solvent and a number of supporting electrolytes, which include 0.1 N potassium hydroxide, a phosphate buffer, an acetate buffer and various concentrations of sulphuric acid. The most satisfactory results were obtained from the sulphuric acid solutions. The phosphate and acetate buffers also yielded good results, but potassium hydroxide gave extremely "drawn out" waves, which considerably reduce the accuracy of the results. The half wave potentials become slightly less negative with increasing pH.

The concentration of ethyl alcohol is important, the higher the concentration the less well defined and more drawn out are the waves. This is particularly marked for the lower peroxides. Butyl peroxides only gave well defined waves at

alcohol concentrations below 10% and amyl peroxides below 20%. As the alcohol content is increased, the half wave potentials become more negative and the diffusion currents are smaller. Increasing molecular weight causes the half wave potentials to become more negative. In addition, there is a slight negative shift on going from normal to secondary and tertiary isomers. The half wave potentials of isomers and adjacent members of a homologous series lie too close together to allow determination of individual peroxides in a mixture.

Willits et al (43) used a non aqueous electrolytic solution, originally employed by Lewis and Quackenbush (44). This consisted of 0.3 M lithium chloride in equal volumes of methyl alcohol and benzene. Several high molecular weight peroxides were studied, including tert-butyl, tetralin, cumene and cyclohexene hydroperoxides, and benzoyl and succinic peroxyacids. The hydroperoxide half wave potentials, -0.61 to -0.91 volts, differed considerably from the peroxide half wave potentials, 0.00 to -0.19 volts, so that these classes of compounds were readily distinguished.

The determination of peroxides in the presence of aldehydes has been studied by Bruschweiler and Minkoff (41) and Stern and Polak (45). The former found that hydrogen peroxide and formaldehyde react reversibly to form hydroxyalkyl

peroxides.

$$HOOH + HCHO \rightleftharpoons HCH(OH)OOH$$
$$\rightleftharpoons HCH(OH)OO(OH)HCH$$

Four waves were obtained from an aqueous solution of hydrogen peroxide and formaldehyde, which had been allowed to stand for 24 hr. at room temperature. Decinormal solutions of hydrogen peroxide and acetaldehyde and of methyl and ethyl hydroperoxides with formaldehyde and acetaldehyde showed no change in polarographic behaviour from the pure peroxide after standing for 24 hr. at room temperature. This is surprising, since the formation of addition compounds between hydrogen peroxide and acetaldehyde has been noted by Knox and Norrish (46).

Stern and Pollak measured the reduction potentials in aqueous lithium chloride of some organic peroxides in the presence of lower aldehydes. Values obtained were: -0.25 to -0.3 volts for methyl and ethyl hydroperoxides, -0.40 volts for dihydroxymethyl peroxide, -0.60 volts for diethyl peroxide and -0.80 volts for hydrogen peroxide. When the peroxide concentration was about 0.0001%, the error in its determination in the presence of aldehydes was less than 8%. Since aldehydes have reduction potentials less than -1.4 volts, the method can be used to analyse peroxides in the presence of aldehydes.

The polarographic method has been applied to the study of peroxidic polymers. Barnes et al (47) obtained polarograms of peroxides, isolated from reactions of styrene and methyl methacrylate with oxygen. The electrolytic solution was a 0.05 M solution of tetramethyl ammonium bromide in a mixture of 58% benzene, 37% ethyl alcohol and 5% water. Bovey and Kolthoff (48) studied polystyrene peroxide, formed in the emulsion polymerisation of styrene. The electrolyte was ammonium acetate in the same benzene + ethyl alcohol + water solvent. The waves obtained at concentrations of 0.00075 and 0.00155 M, calculated per $\overset{C_6H_5}{\underset{}{-CHCH_2}}\overset{}{\underset{}{OO}}$ unit, resemble those obtained by Stern and Polak for diethyl peroxide, with the exception that the polymer shows a large drop in diffusion current just before the start of the principal reduction wave. Diethyl peroxide does not show this drop in diffusion current. It appears that the polymer peroxide is adsorbed on the surface of the mercury, but as the potential becomes more negative than -1.5 volts, desorption occurs, causing the diffusion current to drop.

The application of polarography to the analysis of peroxides in combuation products is limited by (a) lack of specificity for particular peroxides and (b) lack of

knowledge about the polarographic behaviour of the complicated mixtures obtained from the combustion of hydrocarbons. Studies of the polarograms, obtained under various conditions from hydrocarbon combustion products, might nevertheless yield valuable results. The evidence at present indeed suggests that this could be the best method for distinguishing types of peroxide and determining the amount of each type present.

F. CHROMATOGRAPHIC METHODS.

(i) Paper Chromatography.

In recent years, paper chromatography has been used by several workers for separating mixtures of peroxides and is now the most useful method for the qualitative analysis of such mixtures. The work has generally been concerned with investigating the use of various stationary phases, mobile phases and detectors.

Abraham, Davies, Llewellyn and Thain (49) were able to measure satisfactorily the retention values for 1,2,3,4 tetrahydro 1 naphthyl hydroperoxide (0.74), 2 phenyl 2 butyl hydroperoxide (0.84) and hydrogen peroxide (0.58), using paper treated with ethylene glycol and chloroform, and with glycol as solvent. However, it was found that a silicone treated paper permits a wider choice of solvents. This was prepared by soaking Whatman No4 paper in a 5% solution of silicone fluid (MS 1107, Hopkins and Williams Ltd.) in cyclohexane and baking at 110°C for 1hr. 10 mg. of a 1% peroxide solution were placed on the base line and the paper was allowed to equilibrate for 1 hr., with the vapour from the lower layer of a mixture of water (6 vol.), ethyl alcohol (10 vol.) and chloroform (10 vol.). The chromatogram was run

by the ascending method, using the upper layer of the solvent mixture. The spots were developed with a fresh ferrous thiocyanate reagent, which will detect , by a blood red colour, less than 15 micrograms of a hydroperoxide, peroxyester or diacyl peroxide. It is less sensitive for 9 xanthenyl peroxides and fails for triphenyl methyl peroxide and other dialkyl peroxides.

Cartlidge and Tipper (50) have developed techniques for identifying peroxides in a mixture, which are essentially modifications of the methods of Davies et al and of Bruschweiler, Minkoff and Salooja (51), who carried out chromatograms on untreated Whatman No 1 paper, using diethyl ether and isopropyl alcohol as solvents. Cartlidge and Tipper used Whatman No 3 paper and followed Minkoff's procedure of clamping it between two glass plates to prevent the evaporation of volatile components. The paper was either (a) untreated, (b) treated with a 5 or 20 vol.% solution of silicone oil in petroleum ether (b.p.=80-100°C) or (c) treated with a 5 or 20 vol.% solution of ethylene glycol in acetone. After treatment, the paper was dried in a stream of air. It was necessary to cover the glass plates with silicone solution before use, as otherwise the plates were solvent repellent, and gave poor chromatograms.

The mobile phases used were :-

with untreated paper - (i).water:diethyl ether:n butyl alcohol (1:10:10 by vol.), (ii) diethyl ether;

with 5% silicone solution - (i) water:ethyl alcohol: chloroform (20:17:2 by vol.);

with 20% silicone solution - (i) 80 vol.% of methyl alcohol in water;

with 5% ethylene glycol solution - (i) 10 vol.% n butyl alcohol in petroleum ether (b.p. = 80-100°C);

with 20% ethylene glycol solution- (i) 50 vol.% chloroform in petroleum ether (b.p. = 80-100°C), (ii) 5 vol. % diethyl ethyl in petroleum ether (b.p. = 80-100°C).

Detectors used were (i) a solution of ferrous thiocyanate, (ii) a solution of p phenylene diamine and acetaldehyde in aqueous acetic acid, (iii) a dilute solution of o-toluidine and a small amount of ferrous ammonium sulphate in aqueous acetic acid, and (iv) a 10 vol.% solution of hydrogen iodide in glacial acetic acid.

The untreated paper was useful for the detection of hydrogen peroxide, which gave R_F values of 0.50 with the water-diethyl ether-n butyl alcohol solvent, and 0.14 with diethyl ether as solvent. Hydroxyperoxides had R_F values of 0.95 to 0.98 and hydroperoxides moved at the solvent front

(R_F=1.00). The ethylene glycol proved to be the more versatile. Usually, at least one of the three systems used gave a satisfactory R_F value for each peroxide studied. Non polar peroxides, such as dialkyl peroxides, are best detected by the silicone treated paper, while hydroperoxides can be detected by chromatographic separation of their xanthydrol derivatives on a paper treated with 20% silicone solution, using 80% methyl alcohol as solvent.

Cartlidge and Tipper (52) have applied their methods to the detection of peroxides formed during the slow combustion of n heptane, propane, n butane, 2,2,3 trimethyl butane (triptane) and cyclohexane.

Another successful procedure was used by Rieche and Schulz (53). Using partially acetylated Schleicher and Schull 2043 b filter paper, with a solution of ethyl acetate:dioxane :water (2:4.5:4.6 vol.), several peroxyacids were separated. Milas et al (54) developed paper chromatographic methods for the separation and identification of organic peroxides formed during the reaction of aliphatic ketones with hydrogen peroxide. Three solvents were used. These were (i) dimethyl formamide:decalin, (ii) methyl formamide:decalin and (iii) n butyl alcohol:ethyl alcohol:water (45:5:50 vol.%). The detecting agents were (a) p-aminodimethylaniline

hydrochloride, (b) glacial acetic acid:saturated aqueous potassium iodide:starch solution (30:20:50 vol.%) and (c) 56% hydriodic acid:glacial acetic acid (10:90 vol.%). The peroxides, in hexane or methyl alcohol, were applied by means of a microburette on Whatman No1 paper. The sensitivity of the spots depended on the solvent and detector used. The smallest quantity of dibenzoyl peroxide detected by solvents (i) and (ii) using detectors (a) or (b) was about 0.2 micrograms, and using detector (c) about 2 micrograms. With solvent (ii) and detector (c), 1 microgram was detected. The most useful results were obtained when solvent (i) was used with detectors (a) or (b). Solvent (i) gave a better separation than the other two.

Clearly, paper chromatography provides an easy, sensitive method for the identification of specific peroxides in a mixture, provided of course, that the pure peroxides are readily available for calibration purposes. Cartlidge and Tipper have shown that the method can be used to identify organic peroxides in combustion products, and the only serious drawback is that it is not quantitative.

(ii) Gas Liquid Chromatography.

The development of gas liquid chromatography has brought

about a revolution in the analysis of intermediate combustion products. Volatile aldehydes, ketones, alcohols, acids, paraffins, olefins and epoxides can now be detected and analysed rapidly and easily. It is then perhaps surprising that little work has been done on the gas chromatography of peroxides.

Abraham, Davies, Llewellyn and Thain (49) found that some stable, relatively volatile hydroperoxides could readily be identified and estimated by gas chromatography. A 185 x 0.7 cm. column was used, packed with 20 mesh purified celite (Johns-Manville 545), coated with 30% dinonyl phthalate. The carrier gas was nitrogen and the flow rate was 23 ml./min. Liquid samples of about 0.1 ml. were introduced by a micro-syringe through a serum cap and the eluate was detected by means of a katharometer, connected to an automatic, recording potentiometer. The peroxides separated in this way were di tert-butyl peroxide, tert-butyl tert-amyl peroxide and tert-butyl and tert-amyl hydroperoxides.

Abraham and Davies (55) later used a similar method for the analysis of isobutyl and n butyl hydroperoxides.

Dykstra and Mosher (56) used a 100 x 0.6 cm. column, packed with 50 mesh firebrick, impregnated with GFSF 81 silicone oil, to analyse distillation fractions obtained in

the preparation of allyl hydroperoxide. Helium was used as carrier gas at a flow rate of 205 ml./min. and the column temperature was 38°C. Under these conditions, the retention time of allyl hydroperoxide was 7.3 min.

It is clear that if gas chromatography could be applied to the analysis of peroxides in combustion products, it would overcome one of the major problems in this field. The work of Davies et al suggests that further investigations might yield useful results. In particular invstigations of the chromatographic behaviour of the more unstable, lower molecular weight peroxides and of the less volatile, higher molecular weight peroxides would be of great value.

G. SUMMARY.

Table 1 is a list of methods which have been applied to the analysis of peroxides in combustion products and of those, which from a consideration of the preceding discussion, may find application in this field. Depending on the particular analytical problem involved, it is normally possible, by using a single method, or a combination of methods, to analyse quantitatively the various types of peroxide present. However, it would be desirable to have a method available, which is capable of giving a quantitative determination of specific peroxides in a mixture and in the presence of other organic species. Clearly, if a gas chromatographic method were to be developed, it would fulfil this objective.

The objections to the use of gas chromatography for the analysis of organic peroxides have been based on their thermal instability and on the fact that,with a few exceptions, these compounds are of low volatility. However, since Mosher and Williams (57) have shown that several primary and secondary alkyl hydroperoxides do not decompose below about 90°C, it is possible that no decomposition will occur on gas chromatography columns, provided that they are not operated above this temperature. As regards the second objection, it is true that

TABLE 1.

Methods which have been applied to the analysis of peroxides in combustion products.

Method.	Specificity.	Quantitivity.	Remarks.
Iodometry	Total peroxides	Quantitative	The colorimetric method should be used for traces.
Iodometry	Classes of peroxide	Semi-quantitative	
Paper Chromatography	Specific peroxides	Qualitative	

Methods which may find application.

Arsenious oxide redn.	Total peroxides	Quantitative	
Infrared spectroscopy	Uncertain	Uncertain	Whatever the specificity, a characteristic peak must be established for quantitat--ive analysis.
Polarography	Classes of peroxide	Quantitative	
Gas liquid chromatography	Specific peroxides	Quantitative	

organic peroxides generally have very high boiling points, but this should not preclude the possibility of their having sufficient vapour pressures to enable the minute quantities used in gas chromatography to be carried on to the column in a stream of carrier gas.

It was therefore decided to investigate the behaviour of some organic peroxides on gas chromatography columns, with a view to developing a method which could be applied to the analysis of combustion products. In order conveniently to associate the work with a particular combustion problem, a suitable hydrocarbon had to be selected for study. Isopentane was chosen because it is the simplest hydrocarbon whose molecule has four possible points of attack; thus this compound could yield as initial products one tertiary, one secondary and two primary mono-hydroperoxides. The object of the work described in Part 2 is to find conditions under which the four mono-hydroperoxides derived from isopentane as well as di tert-amyl peroxide and hydrogen peroxide (which are also possible combustion products) could be analysed by gas chromatography. The object of the work described in Part 3 is to gain information about the mechanism of the combustion of isopentane by the analysis of the peroxidic and other combustion products, using mainly gas chromatographic

procedures and applying the developments and information derived from Part 2.

PART 2.

THE BEHAVIOUR OF PEROXIDES ON GAS CHROMATOGRAPHIC COLUMNS

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A. PREPARATION OF PEROXIDES.

(i) A Survey of Available Methods.

The most common method of preparing primary, secondary and tertiary alkyl hydroperoxides and di tert-alkyl peroxides is by alkylation of hydrogen peroxide in alkaline solution. The most common alkylating agent for the preparation of the lower molecular weight peroxides is the corresponding hydrogen sulphate, which can be obtained by reaction of the appropriate alcohol with 70% w/w sulphuric acid. Milas and Surgenor (58) used this method for the preparation of tert-butyl hydroperoxide and di tert-butyl peroxide, an equivalent amount of 30% w/v hydrogen peroxide being added to the hydrogen sulphate. The resulting mixture contained 50-70% tert-butyl hydroperoxide and 30-50% di tert-butyl peroxide. There are two alternative methods of separation, viz., careful fractional distillation through an efficient column or extraction of the hydroperoxide by a strong alkaline solution, followed by acidification to regenerate it. Further measures for synthesis of the dialkyl peroxide involve performing the same reaction with the optimum alkyl hydrogen sulphate:hydrogen peroxide ratio or the use of the reaction of tert-butyl hydrogen sulphate with tert-butyl hydroperoxide.

However, the use of the alkyl hydrogen sulphate as alkylating agent fails for primary and secondary peroxides higher than butyl, and also indeed for some of the lower ones. Thus, for example, Medvedev (59) could not prepare n-propyl hydroperoxide in this way. Harris and Egerton (60) obtained a yield of only 1.3% of the same peroxide, and Lindstrom (61) was unable to prepare sec-butyl hydroperoxide. Lindstrom improved the yields by replacing most of the water, used as solvent, by methyl alcohol, which brings the alkyl hydrogen sulphate, hydrogen peroxide and alkali into solution in the same phase.

A method which has a more extensive application is that of Mosher and Williams (57). By use of the corresponding methane sulphonates as alkylating agents, yields of between 40 and 65% of primary peroxides and of between 10 and 50% of secondary peroxides were obtained for compounds containing carbon chains from C_4 to C_{10}.

Some hydroperoxides may be prepared by controlled oxidation of the appropriate hydrocarbon by molecular oxygen. Since attack occurs preferentially at allyl, substituted benzyl and tertiary carbon atoms, the method is only useful for preparing peroxides of these types.

Walling and Buckler (62) have prepared many aliphatic

hydroperoxides by the slow addition of Grignard reagents to oxygen-saturated diethyl ether. It is generally agreed that the oxidation proceeds by two consecutive stages,

$$RMgX + O_2 \longrightarrow ROOMgX \qquad \text{(i)}$$

$$ROOMgX + RMgX \longrightarrow 2ROMgX \qquad \text{(ii)}$$

In order to order to obtain a high yield of peroxide, it is essential that reaction (i) should be rapid compared with reaction (ii), and this implies that the O_2:ROOMgX ratio should be maintained at as high a value as possible. Walling and Buckler accomplished this by very slow addition of solutions of Grignard reagents to oxygen-saturated ether at very low temperatures. Subsequent hydrolysis of the salt of the hydroperoxide gave yields of up to 90% of hydroperoxide, the yields increasing in the order tertiary > secondary > primary.

Another method that gives high yields of peroxides is autoxidation of alkyl borons by passage of oxygen gas through a very dilute ethereal solution. Abraham and Davies (55) suggested that the reaction mechanism is as follows,

$$\begin{array}{ccccc} R_3B & \xrightarrow{O_2} & R_3BOOR & \xrightarrow{O_2} & RB(OOR)_2 \quad \text{(I)} \\ & & \downarrow O_2,\ RB\lessdot & & \downarrow RB\lessdot \\ & & R_2BOR & \xrightarrow[RB\lessdot]{O_2} & RB(OR)OOR \quad \text{(II)} \\ & & & & \downarrow RB\lessdot \\ & & & & RB(OR)_2 \quad \text{(III)} \end{array}$$

the extent to which (I), (II) or (III) are formed depending

on the prcise experimental conditions. In certain circumstances, compound (II) was the main autoxidation product and the peroxide was obtained by hydrolysis of this compound.

From a consideration of the above methods, it would appear that the simplest route available for the preparation of tert-amyl hydroperoxide and di tert-amyl peroxide is by alkylation of hydrogen peroxide by the alkyl hydrogen sulphate. The method of Mosher and Williams was however preferred for the preparation of 2 methyl but-1- and 3 methyl but-1-hydroperoxides, since it has been employed in the synthesis of many alkyl hydroperoxides, and, in addition, does not require the strictly moisture-free conditions which have to be maintained in the autoxidation of Grignard reagents and alkyl borons. The synthesis of 3 methyl but-2-hydroperoxide presents more difficulty, and both the method of Mosher and Williams and autoxidation of the Grignard reagent were used in attempts to prepare it.

The preparation of the individual peroxides used in the present work will now be described.

(ii) Synthetic Procedures.

(a) Tert-amyl hydroperoxide

Tert-amyl hydrogen sulphate was first prepared by adding with stirring over 1 hr. 17.6 g. (0.2 mole) of tert-amyl alcohol to 19 ml. (0.2 mole) of ice cold 70% w/w sulphuric acid. With this mixture at 0°C, 25.2 ml. (0.2 mole) of 27% w/v hydrogen peroxide were added with stirring over a period of 2 hr. The reaction mixture was allowed to stand overnight at 5°C. An upper, organic layer separated out. This was separated, neutralised with a suspension of magnesium carbonate and washed with water.

Tert-amyl hydroperoxide was extracted from the crude product at 5°C with 20 ml. of 30% w/v potassium hydroxide. The alkaline extract was acidified with 70% w/w sulphuric acid and the neutral solution was extracted with six 50 ml. portions of diethyl ether. The ethereal solution was dried over anhydrous sodium sulphate for 6 hr. and the ether was evaporated off under reduced pressure. The residue was distilled, giving a yield of 6.2 g. (29.8% with respect to the alcohol). The hydroperoxide boiled at 42°C/ 4.5 mm. and had a refractive index, $n_D^{20} = 1.4161$.

Elemental analyses showed the presence of 57.72% C and 11.92% H, compared with theoretical values of 57.69 and 11.54%

(b) Di tert-amyl peroxide.

The sulphate was prepared by adding with stirring over 1 hr. 44g. (0.5 mole) of tert-amyl alcohol to 23.8 ml. (0.25 mole) of 70% w/w sulphuric acid, the temperature being kept below 5°C. At the same temperature, 31.5 ml. (0.25 mole) of 27% w/v hydrogen peroxide and 38 ml. of concentrated sulphuric acid were added over a period of 4 hr. with stirring.

Two layers formed. The upper, organic layer was washed with water, dried over anhydrous sodium sulphate and distilled through a 3 ft. Vigreux column. The weight of the peroxide fraction, boiling at 40-42°C / 10 mm. was 5.1 g. (11.7% with respect to the alcohol), and the refractive index was $n_D^{19} = 1.4106$.

Element analyses showed 73.17% C and 12.86% H, compared with the theoretical values of 68.98% and and 12.65% respectively, which suggests a purity of about 95%.

(c) 2 Methyl but-1-hydroperoxide and 3 methyl but-1-hydroperoxide.

The alkyl methane sulphonates were prepared by the method of Sekera and Marvel (63), in which the alcohol reacts with methane sulphonyl chloride in the presence of pyridine.

$$CH_3SO_2Cl + HOR + C_5H_5N \longrightarrow CH_3SO_3R + C_5H_5N.HCl$$

The alcohols were obtained from Eastman Kodak Chemicals Ltd, and their boiling points were as follows:-

2 methyl 1 butanol, b.p. = 127 - 128.5°C

3 methyl 1 butanol, b.p. = 131 - 132°C.

31.6 ml. (0.4 mole) of freshly distilled, dried pyridine were added with stirring over 3 hr. to a mixture of 22.9 g. (0.2 mole) of methane sulphonyl chloride and 17.6 g. (0.2 mole) of the alcohol in a flask surrounded by ice cold water. When all the pyridine had been added, the stirring was continued for a further 30 min.

The reaction mixture was then poured into 125 ml. of ice cold 10% w/v hydrochloric acid and the resulting solution was extracted with 75 ml. of ether. The ethereal solution was washed with two 20 ml. portions of water and then with a 30 ml. portion of saturated sodium bicarbonate solution. It was dried over anhydrous potassium carbonate, and then heated on a steam bath to remove ether.

The methane sulphonates were then distilled under reduced pressure, yielding 22.7 g. (68.2%) of 2 methyl but-1-methane sulphonate and 24.8 g. (74.5%) of 3 methyl but-1-methane sulphonate. The two methane sulphonates had the following boiling points and refractive indices:-

2 methyl but-1-methane sulphonate: b.p. = 84°C/1 .5mm.

n_D^{16} = 1.4316

3 methyl but-1-methane sulphonate: b.p. = 86°C/1.8 mm.
74°C/1.1 mm.

n_D^{16} = 1.4295

The following procedure was then used for preparing the hydroperoxides from the methane sulphonates.

16.6 g. (0.1 mole) of the methane sulphonate were dissolved in 100 ml. of methyl alcohol and 9 ml. of water, and the mixture was cooled in an ice bath. 50 ml. (0.4 mole) of 27% w/v hydrogen peroxidewere slowly added, followed by 12 ml. of 50% w/v potassium hydroxide. The mixture was left to stand for 20 hr. in a water bath at room temperature. The reaction mixture was then cooled in an ice bath and 30 ml. of 50% w/v potassium hydroxide were slowly added. Unchanged methane sulphonate, alcohol and dialkyl peroxide were removed by extraction with 50 ml. of benzene. The solution was cooled in ice and neutralised with concentrated hydrochloric acid, and the resulting mixture was extracted with four 50 ml. portions of ether. In order to ensure that all the hydrogen peroxide had been removed, the ether solution was extracted with 40 ml. of 25% w/v potassium hydroxide. The alkaline solution was cooled in ice and neutralised with concentrated hydrochloric acid. An iodometric analysis of this neutralised solution indicated that the yield of peroxide was between 12 and 15%.

This compares somewhat unfavorably with the yields of between 40 and 60% claimed by Mosher and Williams for other n alkyl hydroperoxides. The neutralised solution was extracted with four 50 ml. portions of ether. The hydroperoxide solution was dried over anhydrous sodium sulphate and the ether was then evapporated off under reduced pressure. The residue was distilled under reduced pressure to give the hydroperoxide.

The yields, boiling points and refractive indices of the two hydroperoxides were as follows:-

2 methyl but-1-hydroperoxide: Yield = 0.95 g. (9.2%).
b.p. = 35 - 37°C/ 1 mm.
n_D^{20} = 1.4121

3 methyl but-1-hydroperoxide: Yield = 1.01 g. (9.7%)
b.p. = 38 - 40°C/1 mm.
n_D^{20} = 1.4112

Element analyses showed that the 2 methyl but-1-hydroperoxide sample contained 57.8% C and 11.63% H, while the 3 methyl but-1-hydroperoxide contained 58.84% C and 11.88% H. The theoretical values are 57.69% C and 11.54% H.

Early attempts to prepare these hydroperoxides used benzene as the extracting solvent, which was employed for this purpose by Mosher and Williams. It was found by iodometric analysis that the hydroperoxides were almost completely

insoluble in this solvent. Although ether cannot be considered to be by any means a good solvent, its use did enable well over half of the hydroperoxide to be extracted from the aqueous solution.

Several attempts were made to prepare the peroxides in better yield, but the values already quoted were not improved upon.

(d) 3 methyl but-2-hydroperoxide.

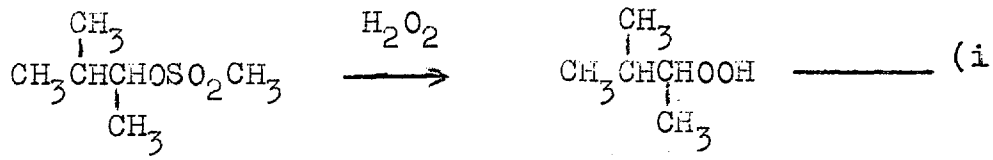
Attempts to prepare this peroxide from its methane sulphonate failed.

The methane sulphonate was prepared by the procedure used for the primary compounds, with slight modifications, which were necessary because of the greater instability of secondary alkyl methane sulphonates. The solvent in the ether extract was evaporated off under reduced pressure and the residue was distilled at the lowest possible pressure in three batches to prevent overheating. On one occasion, decomposition did occur, and this was accompanied by a darkening of the residue and vigorous bubbling, with the rapid evolution of white fumes.

The boiling point and refractive index of the methane sulphonate were, b.p. = 66°C/0.5 mm. n_D^{20} = 1.4299.

The procedure used to prepare the primary hydroperoxides was employed in attempts to make the secondary hydroperoxide. The second ether extract had a peroxide content which would be equivalent to a yield of only 0.5%. It is likely that this is due to residual hydrogen peroxide, since no residue remained when the ether had been evaporated off.

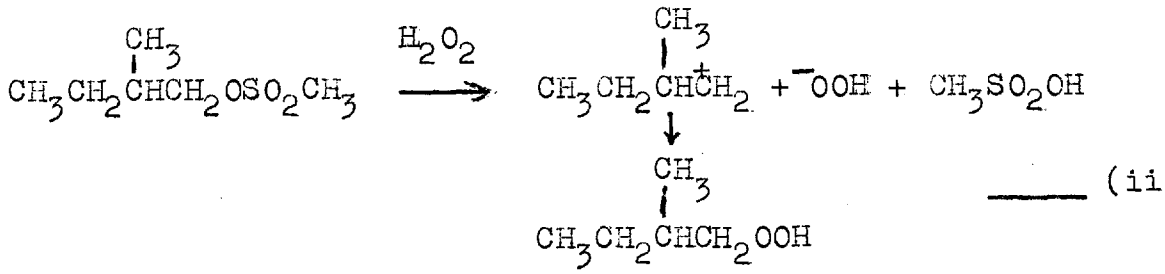
Since Mosher and Williams have successfully prepared several secondary alkyl hydroperoxides, it seems likely that there is something peculiar to th structure of 3 methyl but-2-methane sulphonate which prevents the reaction



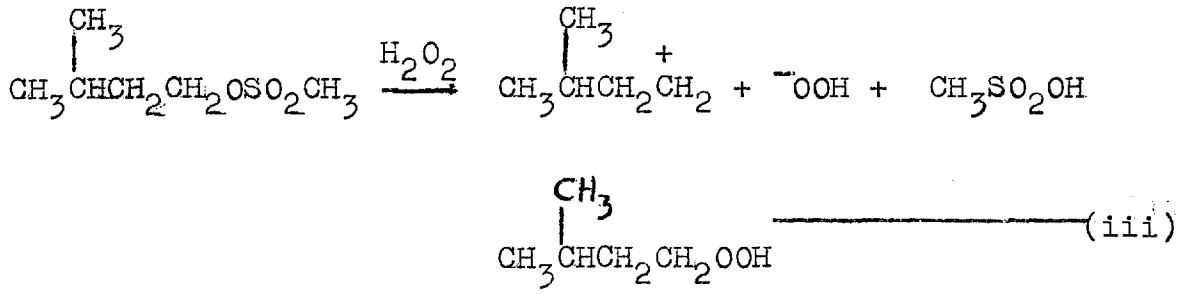
(i)

from taking place.

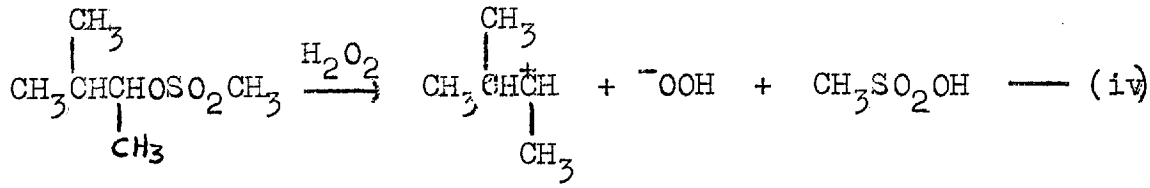
In order to provide an explanation, it is postulated that peroxide formation proceeds via a carbonium ion. For 2 methyl but-1- and 3 methyl but-1- hydroperoxides the mechanisms would thus be as follows,



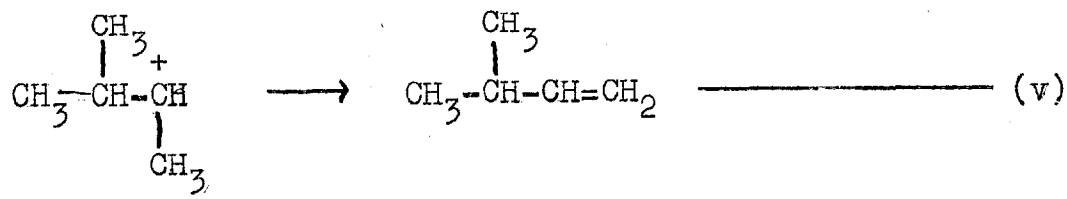
(ii)



An intermediate carbonium ion would be formed in a similar way in the case of the 3 methyl but-2- compound,



The most important structural difference between the carbonium ion formed in (iv) and those formed in (ii) and (iii) is that the former has a methyl group bonded directly to the positively charged carbon atom, whereas the latter ions have sec-butyl and isobutyl groups respectively in this position. The electron feeding methyl radical will support the electron withdrawing by the positively charged centre, and, as a result, the hydrogens on the β carbon atoms will be markedly acidic. There is therefore a strong chance that one of these hydrogen atoms will be abstracted to form an olefin, thus,



This olefin will probably be in equilibrium with its non-terminal isomer,



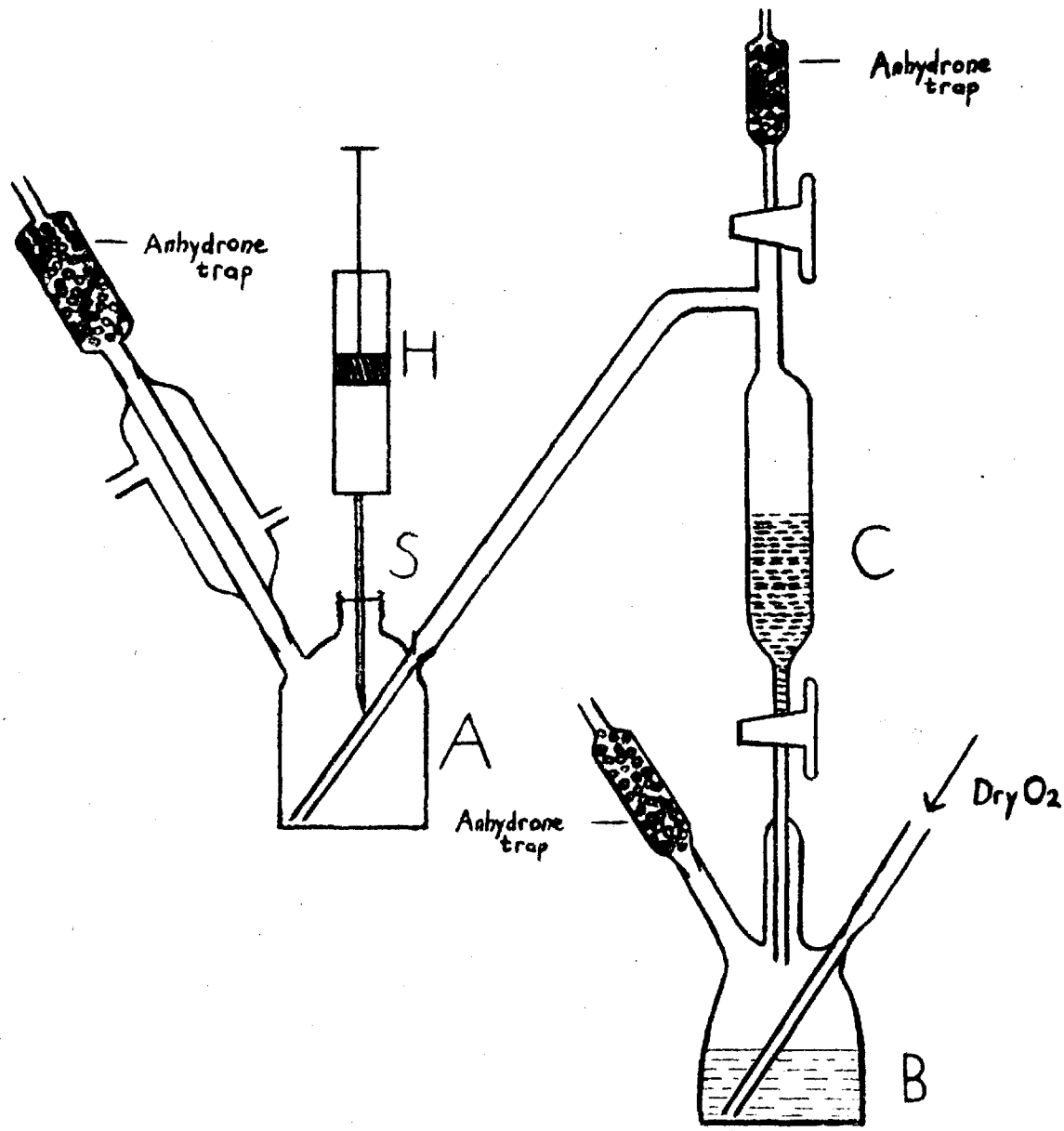
The lesser electron feeding effect of the sec- butyl and isobutyl groups means that the hydrogen atoms in the carbonium ions formed in reactions (ii) and (iii) will not be as acidic as those in the carbonium ion formed in reaction (iv).The conditions are therefore more favorable for the formation of 2 methyl but-1- and 3 methyl but-1- hydroperoxides than for the formation of 3 methyl but-2-hydroperoxide.

Following the failure to prepare 3 methyl but-2-hydroperoxide from the methane sulphonate, a further attempt was made, using autoxidation of the appropriate Grignard reagent. The following procedure was employed.

The Grignard reagent was prepared in reaction vessel A (Fig 1) and the autoxidation was carried out in vessel B. 10 ml. of ether, dried over freshly extruded sodium, 0.9 g. of magnesium, which had been oven dried overnight, and a crystal of iodine were placed in A, which was fitted with a condenser. 20 ml. of ether were placed in B and the whole system was flushed out with nitrogen. A small amount of dry 3 methyl

FIG. 1

APPARATUS FOR AUTOXIDATION OF GRIGNARD REAGENT



but-2-bromide was added to A by means of the syringe, H, through the serum cap, S, and the mixture was stirred by means of a magnetic stirrer. After the reaction had started, the rest of the bromide was added at such a rate that the reaction proceeded steadily. When all the bromide (5 g.) had been added, and the bubbling ceased, ether was added to dilute the reagent to about 0.5 N and the contents of A were forced under nitrogen pressure into the dropping chamber, C, Meanwhile, a flow of dry oxygen, sufficient to agitate the ether, had started to pass through B, and B had been surrounded by a cardice-acetone bath (-80°C). After the gas had been flowing for 5 min., the addition of the Grignard reagent was started. The reagent was added over 90 min., the oxygen flow being maintained throughout. After this time, B contained an appreciable amount of white precipitate. The solution was allowed to reach room temperature and was then poured on to a few pieces of ice. The solution was made faintly acidic with 6 N HCl and extracted with six 50 ml. portions of ether. Analysis of a measured volume of the ether layer showed that the peroxide yield was 9%. The ether was evaporated off under reduced pressure, leaving 0.8 ml. of residue. Gas liquid chromatographic separation of this residue on a 2 ft. long 10% dinonyl phthalate column gave four major peaks, the last

of which had a retention time between those of the two primary hydroperoxides and the tertiary hydroperoxide (see section D). Further evidence for this peak being due to the secondary hydroperoxide was obtained from the fact that as the peak was just reaching completion, the effluent gas from the column released iodine from an acidic potassium iodide trap, placed in the gas stream.

(e) Hydrogen peroxide.

99.6 - 99.7% pure hydrogen peroxide was supplied by Laporte Chemicals Ltd. It was free from inhibitors, the only impurity being water.

B. APPARATUS.

Front and rear views of the apparatus are shown in plates 1 and 2. The apparatus was built in the laboratory on a Kemiframe support, 6 ft. 3 in. high, 2 ft. 6 in. wide and 2 ft. 3 in. deep, and set on four wheels to provide ease of movement.

The flow system, the gas liquid partition column, the method of introduction of samples and the detector will all be described in turn.

(i) The Flow System.

A line drawing of the flow system is shown in Fig. 2. The carrier gas from the cylinder, N, first passes through a pressure controller, V, a needle valve, n_1, a flow meter, F, another needle valve, n_2 and the reference half of a katharometer conductivity cell into the sampling system, I, where it picks up the sample being analysed. The gas then passes through the gas chromatography column, C, the analysing half of the conductivity cell, a third needle valve, n_3, a vacuum pump, P, and hence into the atmosphere. Mercury manometers, M_1 and M_2 are placed on both the inlet and outlet sides of the column.

PLATE 1

GAS CHROMATOGRAPHY APPARATUS
(Front view)

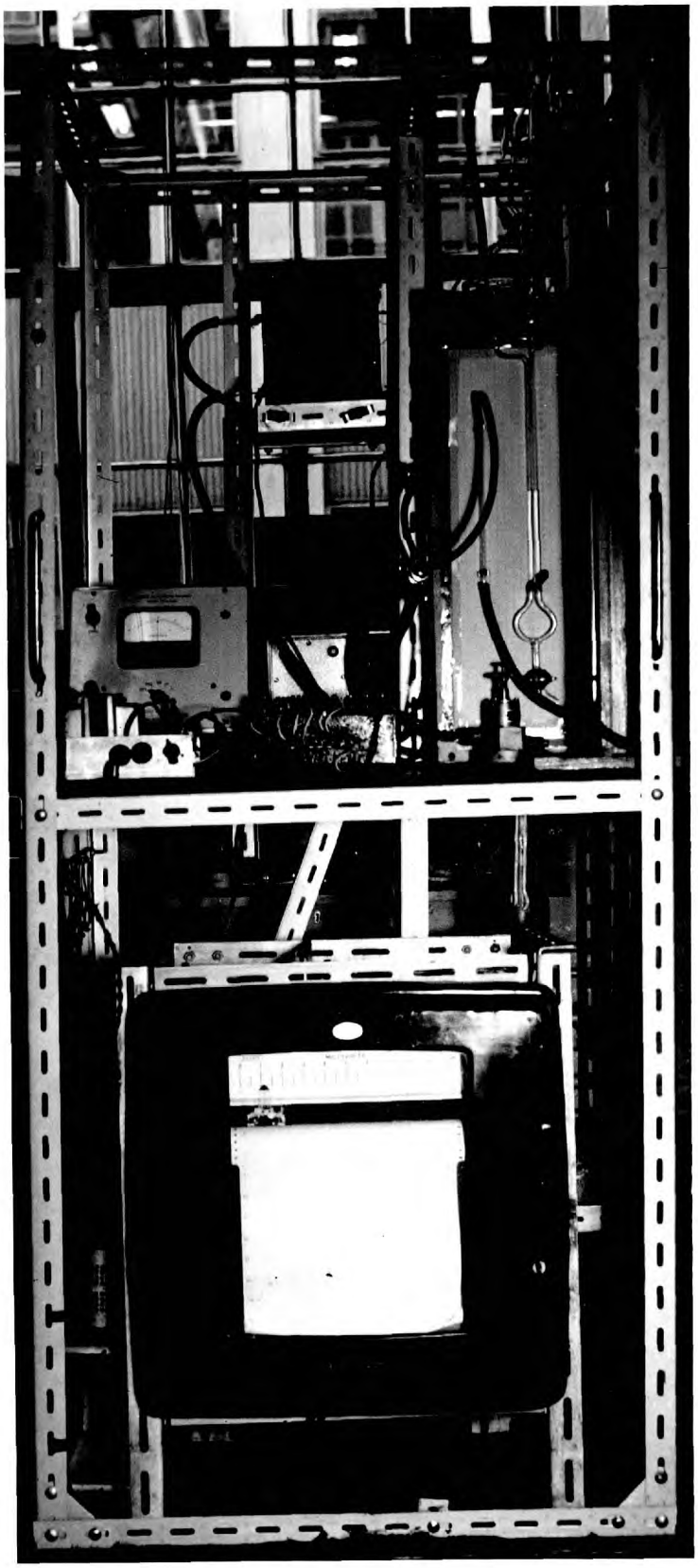


PLATE 2

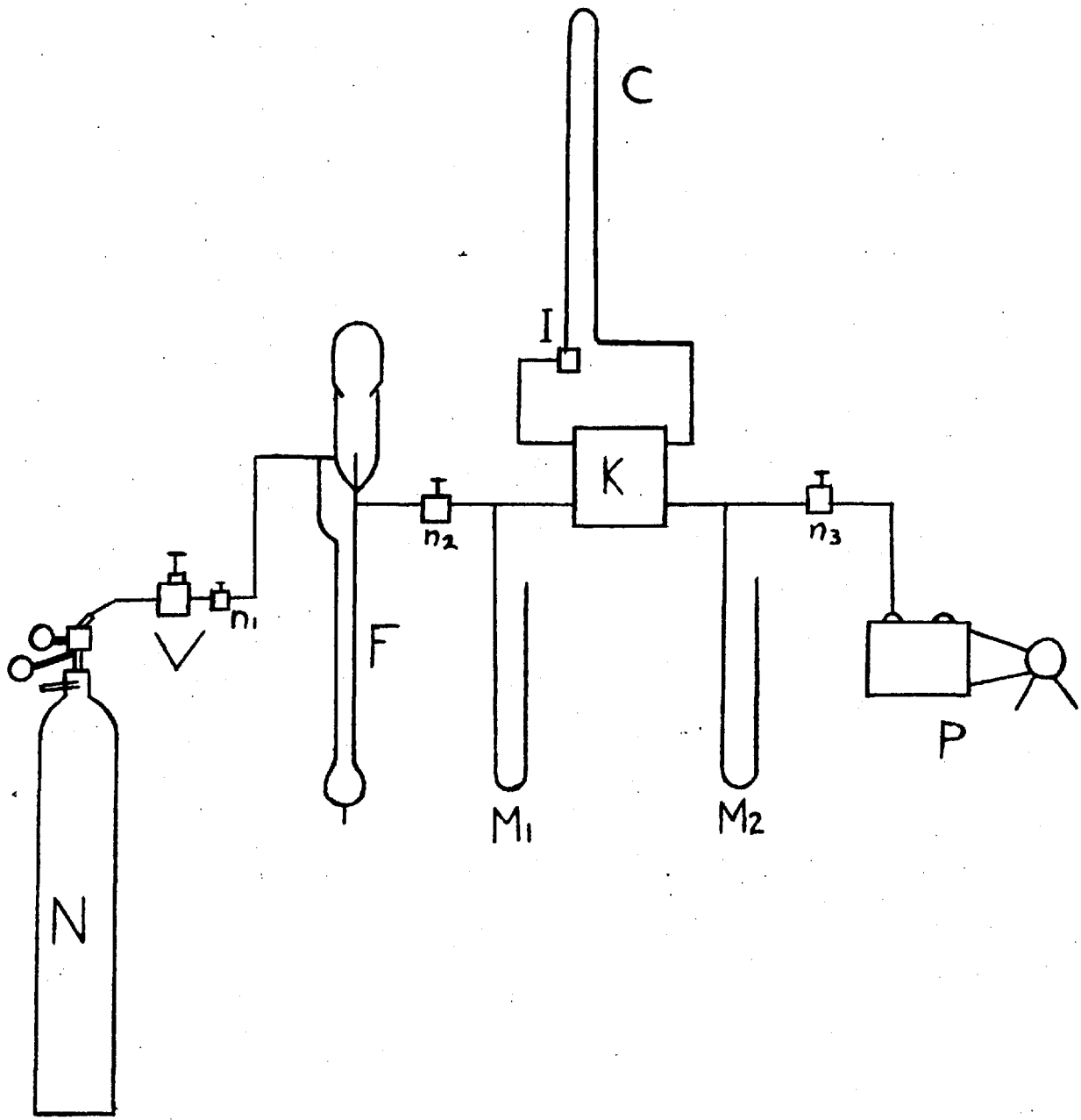
GAS CHROMATOGRAPHY APPARATUS

(Back view)



FIG. 2

GAS CHROMATOGRAPHY FLOW SYSTEM



Oxygen free nitrogen was used as carrier gas, since it is said to give a slightly better separation than do the other frequently used gases, hydrogen and helium, which tend to enhance axial diffusion in the column. However, it should be recorded that some preliminary experiments were performed to compare the efficiences of separation of tert-butyl hydroperoxide, di tert-butyl peroxide and methyl ethyl ketone peroxide, on a diglycerol column, using hydrogen and nitrogen as carrier gases. Little difference was found, using the two gases at their optimum flow rates. However, nitrogen was preferred in this work, since the explosion hazard makes it undesirable to pump hydrogen into the atmosphere.

The nitrogen flow rate was kept constant by a vapour pressure controller (V.P.C.1., W. Edwards & Co Ltd.), whose outlet gas pressure is independent of the cylinder working pressure. When the pressure controller was left out of the flow line, it was impossible to keep a straight base-line on the recorder, except at low sensitivities.

The flow rate was measured by a capillary flow meter, which had been calibrated against a bubble meter, for flow rates between 10 and 35 ml. nitrogen per min. at 15°C and 760 mm. Hg.

(ii) The Partition Columns.

Materials: Solid support - Embacel (May and Baker; 60-100 mesh, acid washed).

Stationary phases- (a) Silicone fluid (MS550, Hopkins and Williams); (b) Dinonyl phthalate (May and Baker, Embaphase brand, Mol. wt. = 418.6); (c) Polyethylene glycol (British Drug House, Mol wt. = 400).

The partition columns used were pyrex glass U tubes, of 0.5 cm. internal diameter, fitted with B7 sockets at each end. The column packing was prepared and the column was filled by the following method.

The solid support was weighed out into a 100 ml. beaker. An amount of liquid phase to give the required percentage by weight was weighed into another beaker and dissolved in 30 ml. of acetone. This solution of the stationary phase was then added to the Embacel with vigorous stirring. The mixture was heated at 70°C over a heating mantle and stirred electrically. When nearly all the acetone had evaporated, the mixture was placed in an oven at 100°C and left overnight.

The mixture was allowed to cool and was then packed into the column through a glass funnel. In order to ensure uniform packing, the column was held against the rotating shaft of an

electric motor. When the column was full and the level of the packing ceased to alter with vibration, the column was removed and its two ends were lightly plugged with glass wool.

The column was mounted in a vertical pyrex glass tube, which was surrounded by a vapour jacket to keep a constant temperature.

(iii) Introduction of the Sample.

When the pressure at the column inlet is atmospheric or above, the simplest way to introduce a sample on to a gas chromatography column is by means of a mirosyringe through a serum bottle cap, and as will be seen in Part 3, Section C(ii), this method was used in the analysis of the non-peroxidic products of the combustion of isopentane, However, when the inlet pressure is below atmospheric, as in most of the present experiments, an alternative method must be employed, since,with the syringe technique, more than the required amount of sample tends to be sucked on to the column. Experiments showed that the syringe method failed to give reproducible chromatograms when the inlet pressure was below 700 mm. Hg.

The method employed in this work consisted in crushing a thin walled glass tube containing the sample. This has a

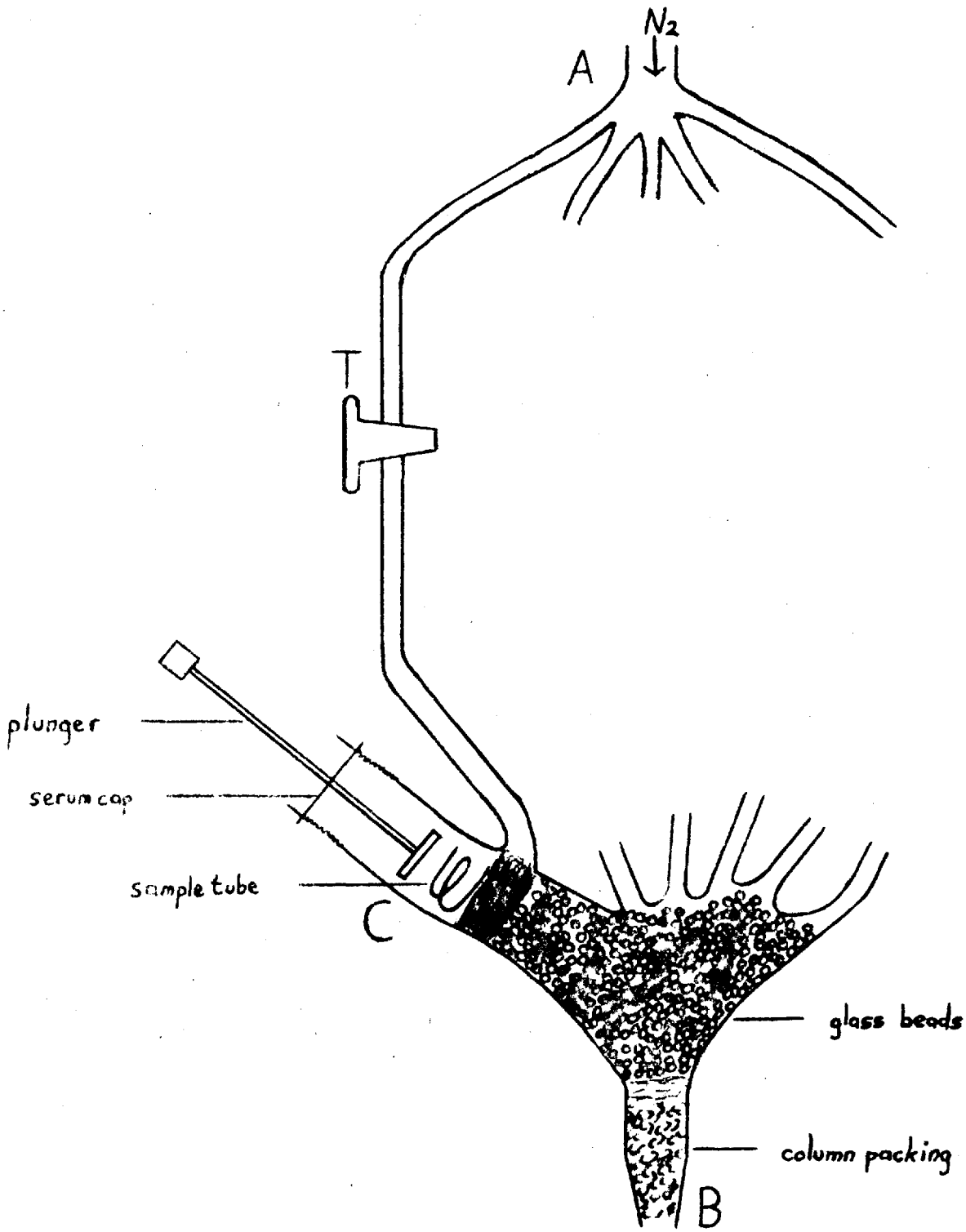
disadvantage in that, after each chromatogram has been obtained, the carrier gas flow must be stopped before the next sample can be introduced, and since it takes up to an hour for the flow rate to reach a constant value again, much time is wasted. To overcome this, a glass inlet system was devised, which allows up to five samples to be put through the column without interfering with the nitrogen flow. The apparatus is shown diagrammatically in Fig, 3.

Nitrogen enters at A, and can be directed, by opening the appropriate tap, T, into any one of five lines, each of which leads to a crushing chamber, C, containing the sample tube. At any given moment, the tube may be crushed, whereupon the sample vapour is carried on to the column, to which the apparatus is connected by a B7 ground glass cone, B. When the analysis has been completed, the nitrogen flow is simply directed through the chamber containing the next sample to be analysed.

The necessity of having five inlets at the top of the column means that there is a considerable amount of dead space, which reduces column efficiency. This volume was however reduced as far as possible by filling the space with small glass beads, of 1 mm. diameter. One crushing chamber is shown in Fig 2, which indicates the method used to break the

FIG. 3

APPARATUS FOR INTRODUCING SAMPLE



sample tubes. The latter are placed on glass wool, which is tightly packed above the glass beads. A serum bottle cap is placed over the open end of the crushing chamber. Through the serum cap is pierced a plunger, which consists of a hypodermic needle (1.5 in. long), attached to a glass disc of about 0.4 cm. diameter. The plunger was made by first piercing a serum cap with a needle as far as it would go, and then plunging the needle into a molten glass disc, which had previously been cut out of a sheet of molten glass with a sharp cork borer. Care was taken to ensure that the needle capillary was completely sealed.

The sample tubes are thin walled glass spirals, made by drawing out 0.4-0.5 cm. diameter glass tubing, while twice quickly turning it round a 0.5 cm. metal rod. As the diagram shows, the spiral is crushed simply by pushing down the plunger.

The part of the apparatus between the crushing chambers and the column was heated electrically, the temperature being controlled by a Variac transformer.

(iv) <u>The Detector</u>.

The most important qualities of a detector are a quick, linear response and high sensitivity and applicability to a

wide range of organic compounds. The thermal conductivity detector satisfies all these requirements.

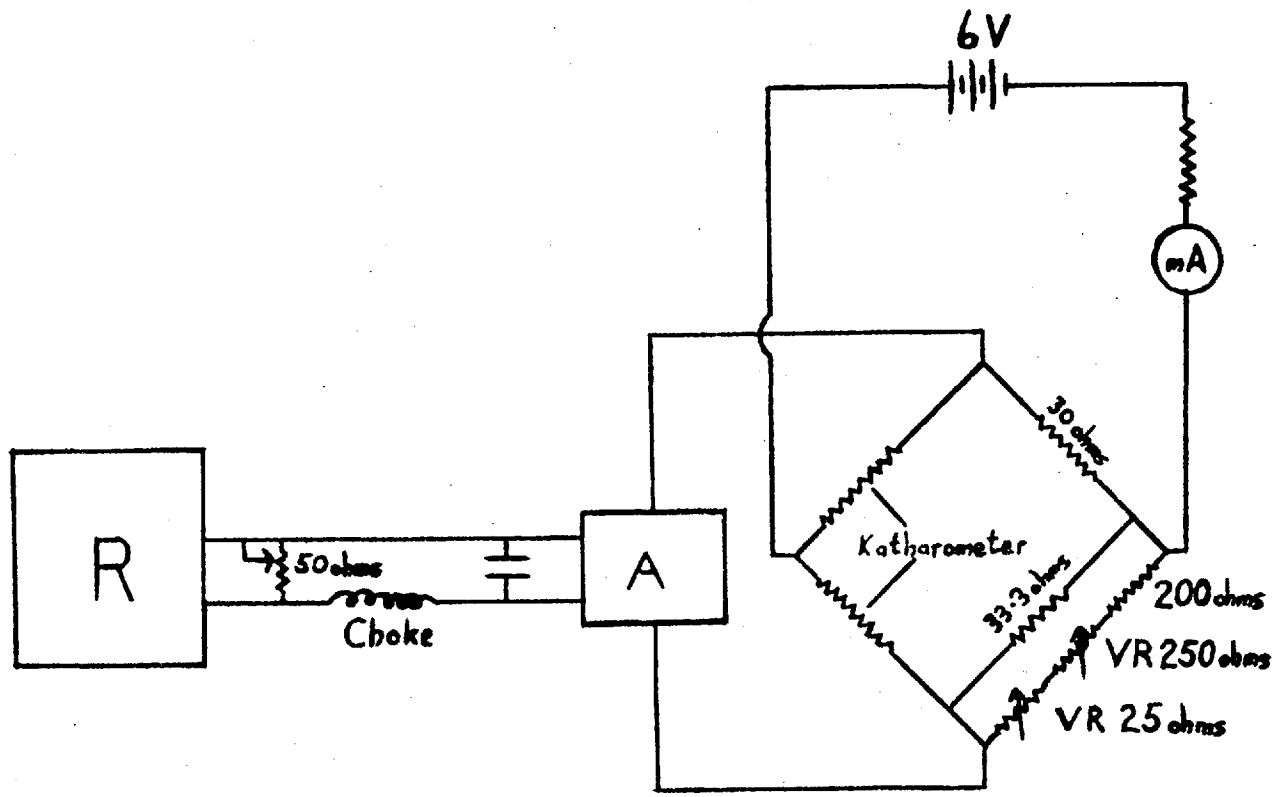
The detector used in this work was a Pye, aluminium body katharometer. This consists of an aluminium block, through which are drilled two holes of about 1 cm. diameter. Passing through each hole is a 0.001 in. platinum wire of about 25 ohm resistance. One compartment acts as the reference half of the cell, through which pure nitrogen flows before entering the gas chromatography column. The gas leaving the column passes through the second chamber, or analysing half of the cell, and its composition determines the rate of loss of heat from the platinum wire and hence its electrical resistance. Thus, by using the platinum wire as two arms of a Wheatstone bridge, variations in the thermal conductivity, and therefore in the composition of the gas, may be determined. To prevent condensation, the katharometer block was heated by non-inductively wound nichrome wire, the temperature being controlled by a Variac transformer. The whole was enclosed in a uralite box, the space between the katharometer and the box being filled with asbestos wool. The outlet from the column was connected to the analysing half of the cell by a short length of Staybrite stainless steel capillary, which was heated to the same temperature as that of the katharometer

block.

The electronic detecting circuit is shown in Fig. 4, and is somewhat similar to that used in previous work in this laboratory (64). A 6 volt battery supplies the bridge current, which is measured by a milliameter and can be altered by a 50 ohm variable resistance. The off balance current is fed into a Pye microvoltmeter amplifier, which is capable of giving an output of 10, 100 or 1000 times the input. Since the amplifier output may be unstable, a smoothing system, consisting of a high frequency choke and a condenser, was placed in the circuit. The output then passes through a 50 ohm potentiometric resistance, and 20 ohm of this are used to develop a voltage, which is applied to an Elliot 10 mv. potentiometric recorder, R, the chart speed of which is 8 in. per hr.

FIG.4

GAS CHROMATOGRAPHY DETECTOR CIRCUIT



C. EXPERIMENTAL PROCEDURE.

The experimental procedure was designed firstly to establish whether or not each of the peroxides studied could be passed through gas chromatography columns without decomposition, and secondly, having established this, to investigate the effect of several variables on the retention times and shapes of the peaks, with a view to finding the best conditions for analysis.

Information as to whether the peroxides were passing through the column unchanged was obtained (a) by noting if the chromatogram had more than one major peak and (b) passing the gas leaving the analysing half of the katharometer through a trap containing an acidic solution of potassium iodide, titrating the iodine released with standard sodium thiosulphate and comparing the value obtained with that found by adding the same amount of peroxide directly to a similar solution of potassium iodide.

The method of introducing the sample into the spiral sample tube was as follows. A drop of the peroxide was spotted on to a clean watch glass. One end of the weighed spiral tube was dipped into the drop, causing the peroxide to enter the tube by capillary action. The tube was then inverted to allow

the thread of peroxide to run into the tube away from the open ends. The ends were sealed with a very small gas-oxygen flame, care being taken to keep the flame well away from the sample. The tube was reweighed to give the weight of sample. It was shown by several weighings that the sealing method had no effect on the weight of the tube. The amount of sample introduced in these experiments was normally 2 to 5 mg., but the method can be conveniently used for up to 20 mg.

The following variables were studied:-

(a) Column temperature. 56°C (boiling acetone), 76°C (boiling carbon tetrachloride) and 100°C (steam).

(b) Column pressure. Inlet pressures between 30 and 76 cm. Hg with the outlet pressure equal to two fifths of the inlet pressure.

(c) Column length. 1, 2 and 4 ft.

(d) Percentage liquid phase. 5, 10, 20 and 30% by weight.

(e) Nature of the liquid phase. Silicone fluid, dinonyl phthalate and polyethylene glycol.

The following conditions were kept constant throughout the investigations.

Bridge current = 120 ma.

Katharometer block temperature = 70°C.

Temperature of crushing chamber = 80°C (If a sample was

left in the crushing chamber overnight at this temperature, the chromatogram was unchanged, indicating that decomposition in the chamber was negligible).

Sensitivity = X 10, as shown on the microvoltmeter dial.

The optimum conditions under which chromatograms may be obtained are best dealt with while considering the results and conclusions, and this will be done in the next section.

D. RESULTS AND DISCUSSION.

(i) Effect of Column Temperature.

At each of the three temperatures, 56°, 76° and 100°C, chromatograms were obtained for tert-amyl hydroperoxide under conditions which should be most conducive to allow the peroxide to pass through the column. The precise conditions employed were:-

1 ft. long 5% silicone column, flow rate = 27 ml./min.; inlet pressure = 43 cm. Hg; outlet pressure = 16.6 cm. Hg. Inaddition, an acid potassium iodide trap was placed at the exit from the katharometer.

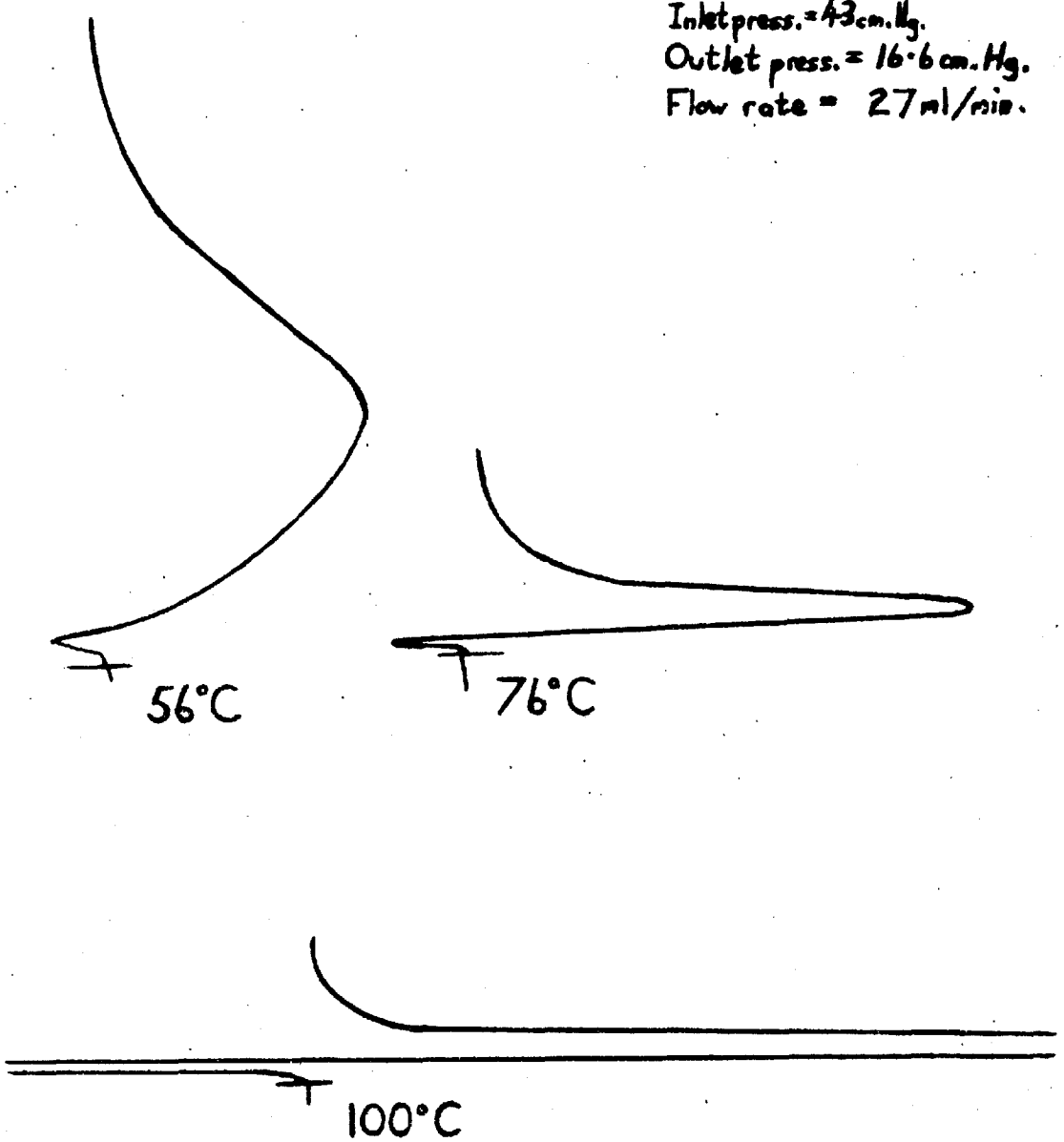
The chromatograms obtained are shown in Fig. 5. At 56°C the peroxide peak is very broad and drawn out, while at 76°C it is quite sharp. At 100°C a large negative peak was obtained, followed by a very large positive peak. Peroxide was detected in the eluent gases at 56°C and 76°C but not at 100°C.

From these findings it is concluded that the most favorable temperatures of the three is 76°C. The effect of other variables was therefore studied with the column at this temperature.

FIG. 5

VARIATION OF tA_mOOH PEAK WITH TEMPERATURE

5% silicone column on Embacel
Length = 1ft.
Inlet press. = 43 cm. Hg.
Outlet press. = 16·6 cm. Hg.
Flow rate = 27 ml/min.



(ii) Effect of Column Pressure.

When the inlet and outlet pressures are varied, the volumetric gas rate changes and, in consequence, so does the retention time. The variation of retention time is expressed by the equation,

$$\frac{t_g}{t'_g} = \frac{V'_t}{V_t} \cdot \frac{(p_i/p_o)^3 - 1}{(p_i/p_o)^2 - 1} \cdot \frac{(p'_i/p'_o)^2 - 1}{(p'_i/p'_o)^3 - 1}$$

where t_g and t'_g are initial and final retention times,

V_t and V'_t are initial and final volumetric flow rates,

p_i and p'_i are initial and final inlet pressures

and p_o and p'_o are initial and final outlet pressures.

A proof of this equation is given by Keulemans (65).

Thus, if the retention time is measured under certain pressure conditions, it is possible to calculate what it should be under another set of pressure conditions.

Fig. 6 compares the calculated retention times with those obtained experimentally for tert-amyl hydroperoxide and 3 methyl but-1-hydroperoxide on a 1 ft. long, silicone column at 76°C, the retention times at inlet pressure = 36 cm. Hg. being taken as standard (t_g).

It is seen that the retention time is always longer than expected, the effect being much more noticeable for 3 methyl but-1-hydroperoxide than for tert-amyl hydroperoxide.

FIG. 6

VARIATION OF RETENTION TIMES WITH COLUMN PRESSURE

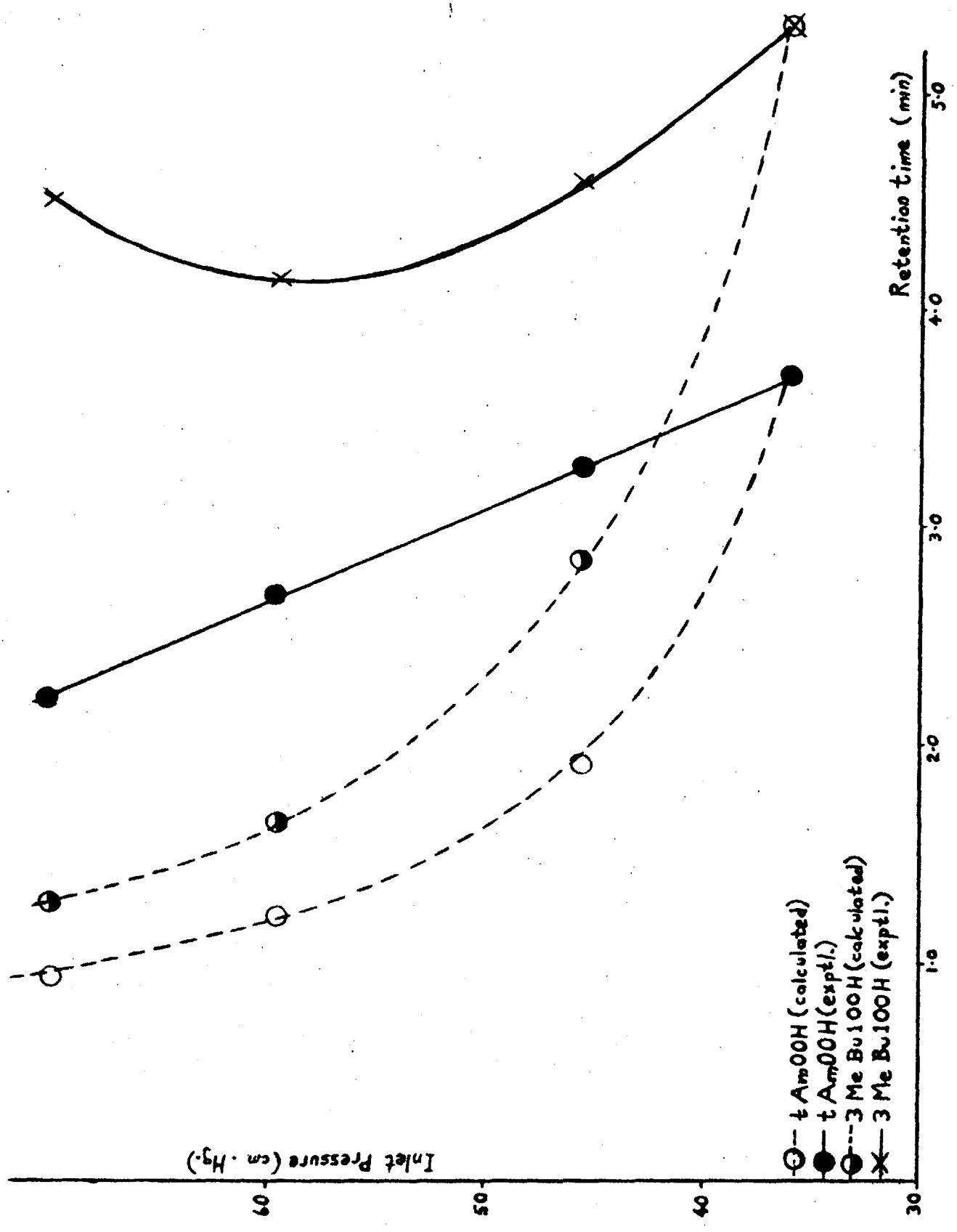
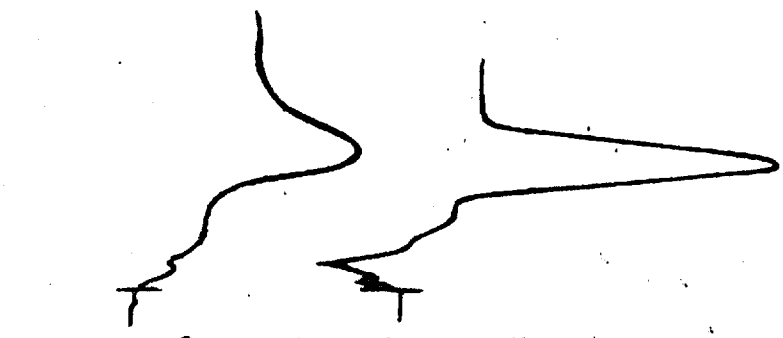


FIG. 7

VARIATION OF 3METHYL BUT-1-HYDROPEROXIDE PEAK WITH COLUMN PRESSURE

20% silicone on Embacel
temp. = 76°C
length = 1ft.



Inlet Press. = 36·0 cm Hg. 46·2 cm Hg.



Inlet Press. = 59·5 cm Hg. 70·3 cm Hg.

An investigation of the 3 methyl but-1-hydroperoxide peaks (Fig. 7), shows broadening at low and high inlet pressures with comparatively sharp peaks at intermediate inlet pressures, whereas an increasing skarpening of peaks could be expected in going from low to high pressures, since the flow rate is increasing.

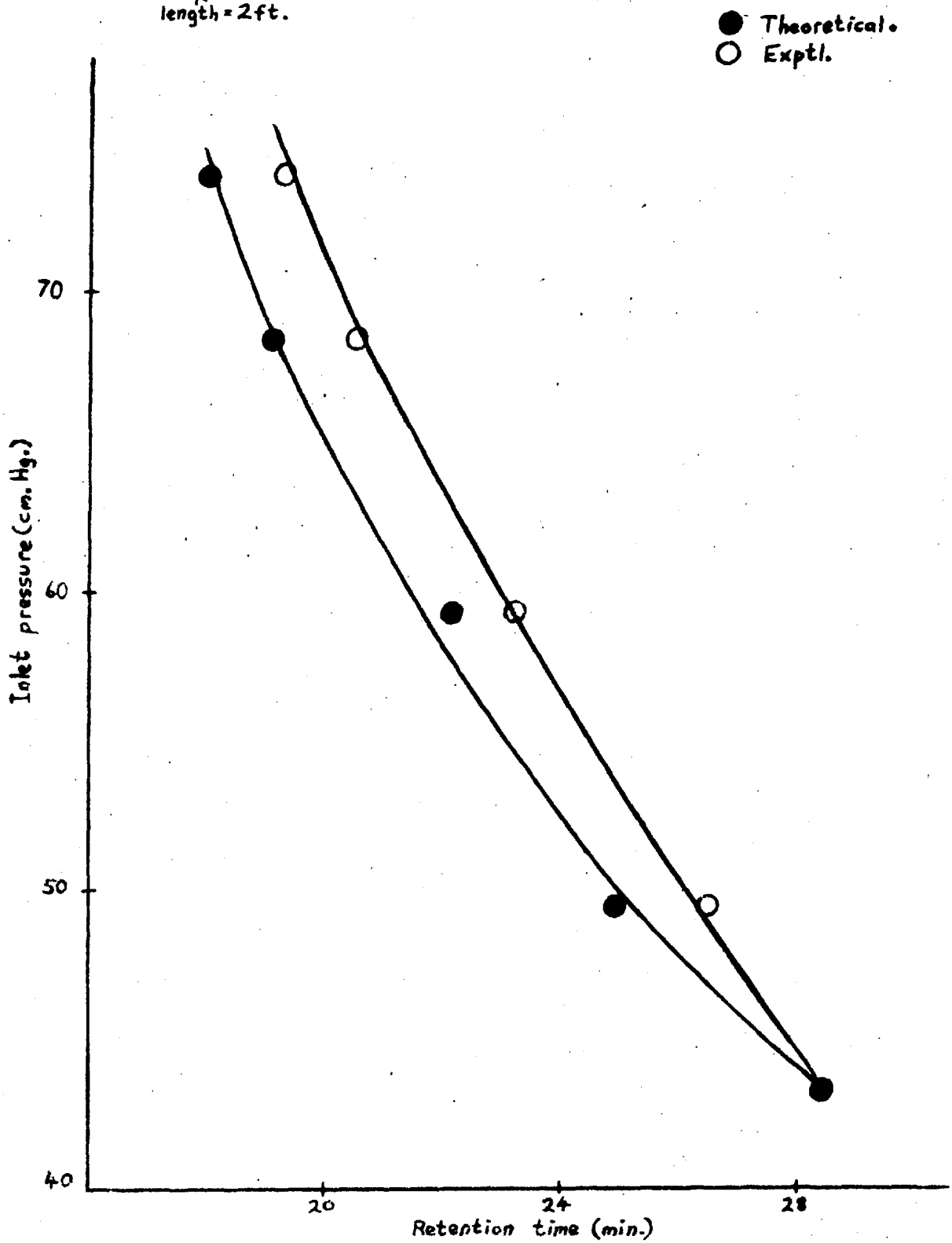
An explanation of this is that at high inlet pressures the peroxide is slow in evaporating on to the column, thus giving a brosdening of the peak and a longer retention time than expected. Further evidence for this was found from an investigation of the pieces of sample tube after the chromatogram had been obtained. Tiny droplets of peroxide adhered to the pieces, showing that all the sample had not gone on to the column, at inlet pressures near atmospheric, and suggesting a sluggishness in evaporation under these pressure conditions.

A further investigation of this effect was made on a 2 ft. long dinonyl phthalate column at 76°C , under which conditions the retention times were longer. As seen in Fig 8 the effect was not so marked, but again the retention times found were longer than expected. In addition, an investigation of the sample tube pieces again revealed that all the sample had not gone on to the column at inlet pressures near

FIG 8

VARIATION OF 2 METHYL BUT-1-HYDROPEROXIDE RETENTION TIME WITH COLUMN PRESSURE

10% dinonyl phthalate on Embacel
temp. = 76°C
length = 2ft.



atmospheric.

It is concluded from these studies that the optimum pressure range for gas chromatographic separation of the peroxides is between 45 and 55 cm. Hg.

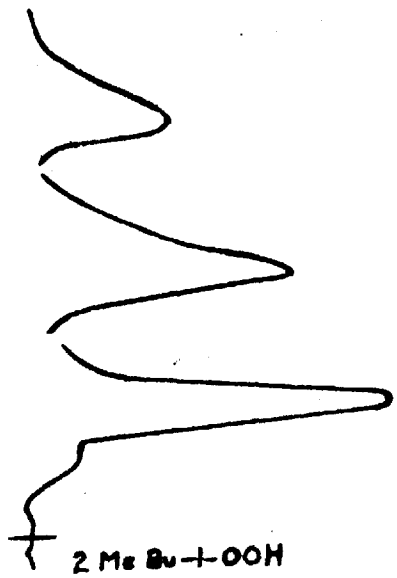
(iii) Effect of Column Length.

The effect of column length on the retention times and peak shapes of the peroxide was investigated on 20% silicone columns at 76°C, with an inlet pressure of 47 cm. and an outlet pressure of 18.3 cm. Hg., the flow rate being between 18 and 22 ml./ min. The variation in retention time and peak shape is shown in Fig. 9. As expected, the column efficiency increased with increasing column length. This is shown in Fig. 10, where the theoretical plates, calculated from the tert-amyl hydroperoxide and 2 methyl but-1-hydroperoxide peaks, are plotted against column length. Theoretical plates were calculated as $(4\ \frac{d}{w})^2$, where d is the distance of the peak apex from the point of injection and w is the peak base width. Although the efficiency of separation increases with column length, so does the broadening of the peaks. A compromise length must be employed which will give both good separation and a peak shape which allows easy measurement of the area. Column lengths between 3 and 4 ft. are suitable when using a

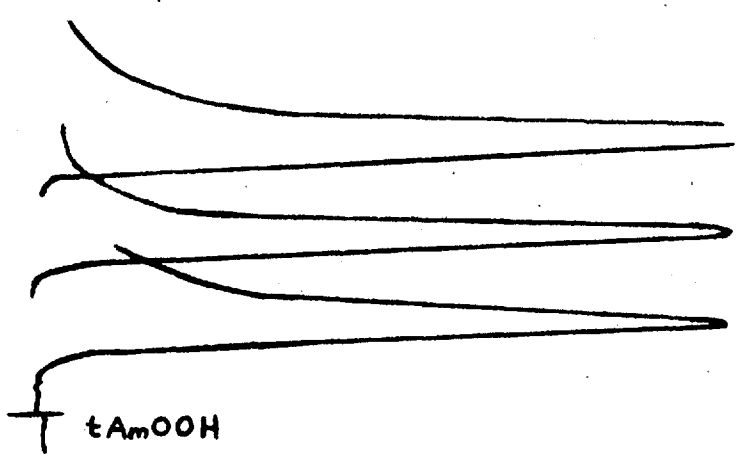
FIG. 9

VARIATION OF PEROXIDE PEAKS WITH COLUMN LENGTH

2% silicone on Embacel
Temp = 76°C
Inlet press. = 47cm. Outlet press. = 18·3cm. Hg.
Flow rate = 22 ml/min.



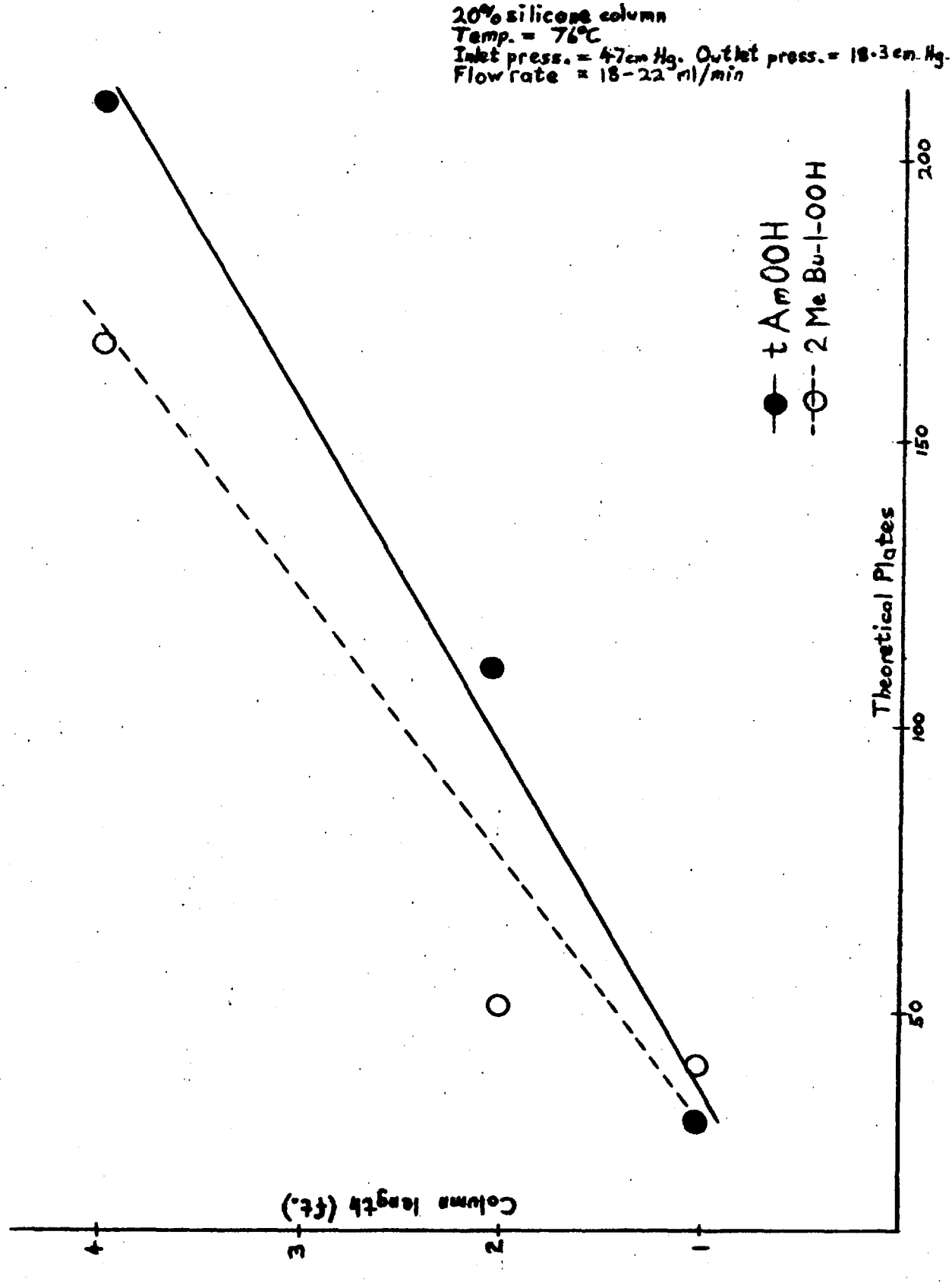
Length. (ft.)	Retention time. (min.)
4	17·1
2	10·2
1	4·6



Length. (ft.)	Retention time. (min.)
4	10·5
2	6·2
1	3·3

FIG. 10

EFFECT OF COLUMN LENGTH ON COLUMN EFFICIENCY



20% silicone packing.

(iv) Effect of Percentage Liquid Phase.

The effect of variation of the percentage of liquid phase (silicone) was studied for 2 ft. columns at 76°C, with an inlet pressure of 47.3 cm. Hg. and an outlet pressure of 18.5 cm. Hg. and a flow rate of 21.3 ml./ min.

Fig. 11 shows the variation in retention time and peak shape for 3 methyl but-1- and tert-amyl hydroperoxides with percentage liquid phase. As with column length, the column efficiency increases, and so does the peak broadening. The peak broadening for 3 methyl but-1-hydroperoxide on the 30% silicone column is particularly marked, and again a compromise percentage liquid phase must be used. The 20% column seems the most likely to yield satisfactory analytical results.

(v) Effect of Nature of Liquid Phase.

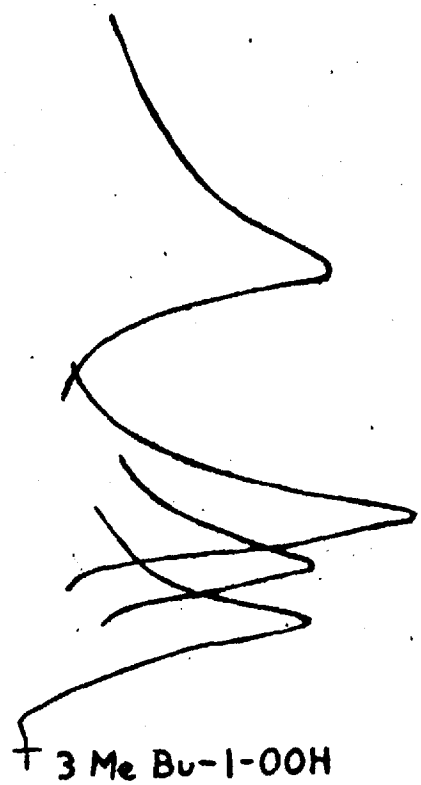
The retention times and shapes of the peroxide peaks on 10% polyethylene glycol, silicone and dinonyl phthalate columns at 76°C, with the inlet and outlet pressures at 47.5 and 19.1 cm. Hg. respectively, and the flow rate at 21.2 ml./ min. , are shown in Figs, 12a and 12b. As is clearly shown, the order of retentivity is

dinonyl phthalate $>$ silicone $>$ polyethylene glycol.

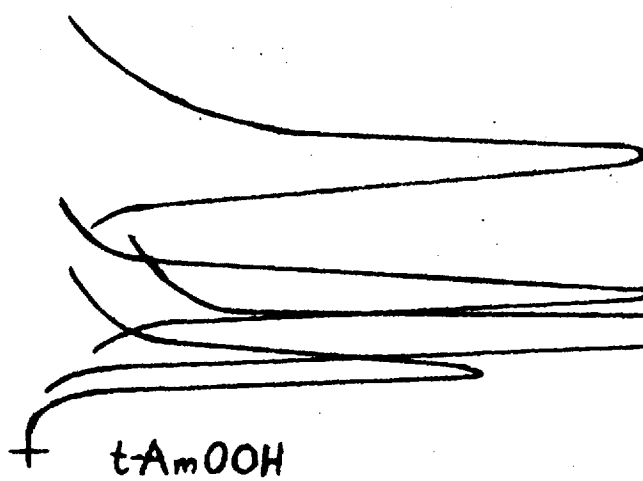
FIG. 11

VARIATION OF PEROXIDE PEAKS WITH PERCENTAGE SILICONE

Length = 2ft.
Temp. = 76°C
Inlet press. = 47·3cm. Hg. Outlet Press. = 21·3 cm. Hg.
Flow rate = 21·3 ml/min



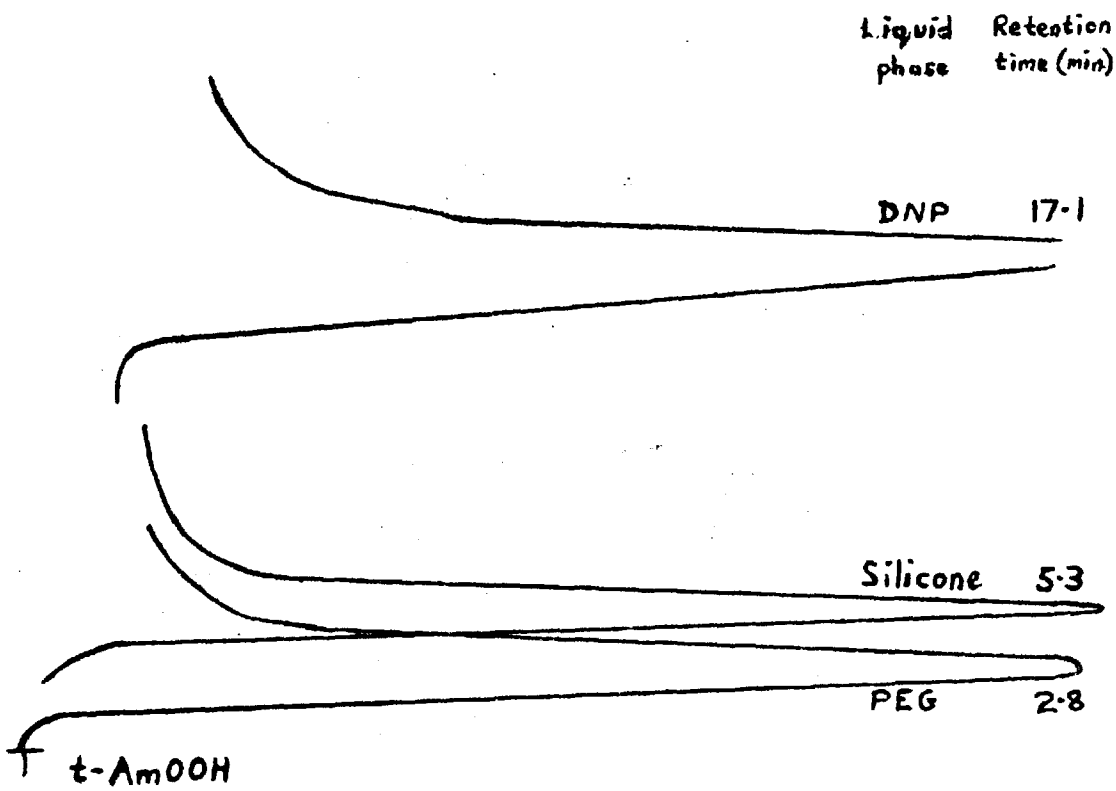
Percentage silicone	Retention time (min)
30	19·0
20	9·5
10	7·4
5	5·2



Percentage silicone	Retention time (min)
30	12·7
20	6·5
10	5·3
5	3·8

FIG. 12(a)
EFFECT OF NATURE OF LIQUID PHASE

10% liquid phase on Embacel
Temp = 76°C. Length = 2ft.
Inlet press = 47.5 cm. Hg. Outlet press. = 19.1 cm Hg.
Flow rate = 21.2 ml/min



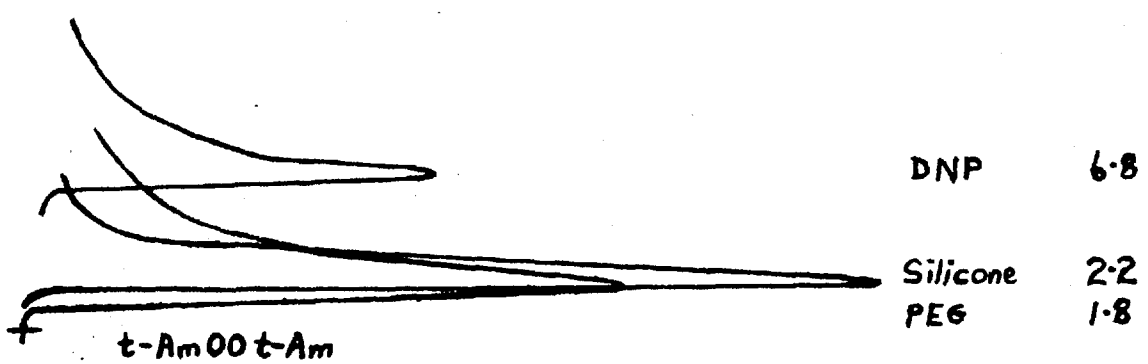
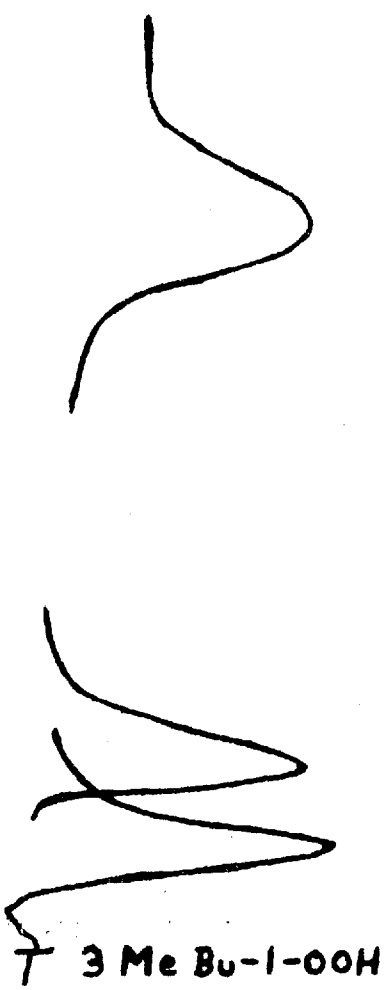


FIG. 12(b)
EFFECT OF NATURE OF LIQUID PHASE

Liquid phase	Retention time (min.)
DNP	28·4
Silicone	7·4
PEG	4·0



In addition, the column efficiencies are in the same order, the respective theoretical plates being approximately 180, 60 and 16.

Polyethylene glycol was investigated using 20% and 30% liquid phase. Only a slight improvement was obtained, the retention times increasing little, while the peak broadening became very marked. Polyethylene glycol was therefore rejected as a convenient liquid phase for the analysis of peroxides.

From the foregoing series of investigations, it is now possible to state the conditions most conducive to the separation of the peroxides investigated.

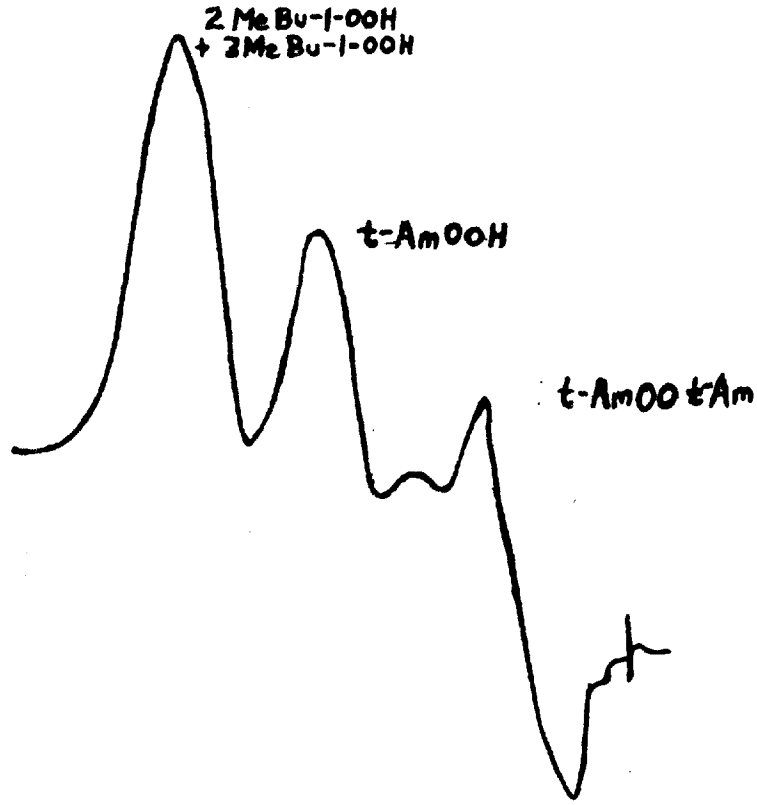
These are:-

I.	Liquid phase	20% silicone
	Column length	3 to 4 ft.
	Column temperature	76°C
	Inlet pressure	45 to 55 cm. Hg.
II.	Liquid phase	10% dinonyl phthalate
	Column length	2 ft.
	Column temperature	76°C
	Inlet pressure	45 to 55 cm. Hg.

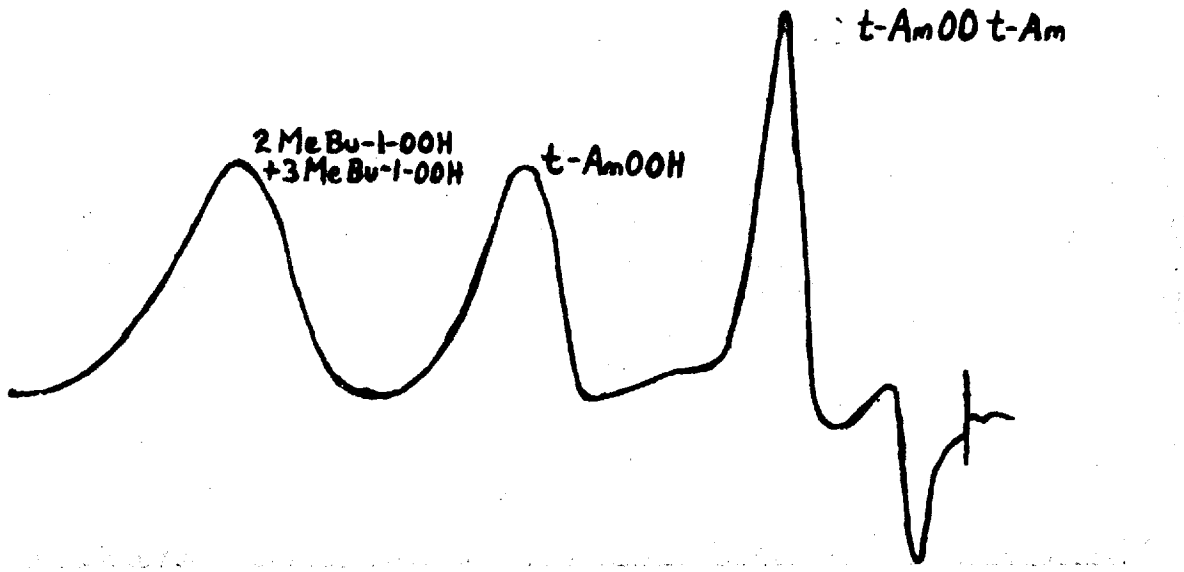
Mixtures of the peroxides were separated chromatographically under these two sets of conditions (Fig.13). It is

FIG.13. SEPARATION OF ORGANIC PEROXIDES

I. 20% SILICONE. Length = 4ft. Temp. = 76°C
Inlet press = 47.5 cm Hg. Outlet press. = 19.4 cm Hg.
Flow rate = 22 ml/min.



II. 10% DINONYL PHTHALATE. Length = 2ft. Temp. = 76°C
Inlet press. = 47.5cm Hg
Outlet press. = 18.8 cm Hg. Flow rate = 224 ml/min



seen that it was not possible to separate the two primary hydroperoxides from each other, but a good separation is obtaine between these two (in one peak), tert-amyl hydroperoxide and di tert-amyl peroxide. The retention time of 3 methyl but-2-hydroperoxide (see page 69) suggests that this too would be separated. The retention times under the conditions stated on Fig. 13 are:-

	I	II
Di tert-amyl peroxide	5.3 min.	6.9 min.
Tert-amyl hydroperoxide	11.5	17.3
3 methyl but-2-hydroperoxide		20.8
2 methyl but-1-hydroperoxide	17.3	28.4
3 methyl but- 1-hydroperoxide	17.3	28.4

(vi) Behaviour of Hydrogen Peroxide.

Hydrogen peroxide was passed through gas chromatographic columns under a wide variety of conditions. In every case, a broad negative peak was obtained, but no peroxide was detected by the acidic potassium iodide trap, even when this was placed immediately adjacent to the exit from the column. It is concluded that the hydrogen peroxide decomposes on the column and that the negative peak is due to water, particularly since water and hydrogen peroxide samples give similar peaks. However, no oxygen peak was obtained, and the only explanation offered for this anomaly is that the decomposition is slow enough for the large negative peak to mask the oxygen peak.

(vii) Decomposition on the Column.

Decomposition occurred on nearly every occasion with the column at 100°C. Decomposition of tert-amyl hydroperoxide also occurred on two occasions on a 4 ft. long silicone column and once on a 2 ft. long silicone column at 76°C, when the inlet pressure was near atmospheric. On these occasions, two positive peaks were obtained and no peroxide was detected in the eluent gas by an acid potassium iodide trap. In successful chromatograms the value determined for the peroxides eluted from the column agreed to within 10 to 20% with that obtained by introducing a similar sample straight into an acidic potassium iodide solution.

Attempts were made to reproduce decomposition on 4 ft. and 2 ft. long columns at a later date. However, no decomposition occurred on these occasions. In summing up, it can therefore be said that generally decomposition does not occur on columns up to 4 ft. long at temperatures up to 76°C, but there is some danger of decomposition if the inlet pressure is near atmospheric.

It is apparent then that under carefully selected conditions, the peroxides studied here can be satisfactorily separated and determined by gas liquid chromatography.

PART 3.

THE SLOW COMBUSTION OF ISOPENTANE

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A. THE PEROXIDE THEORY OF HYDROCARBON COMBUSTION.

There now seems to be no doubt that, under certain conditions, organic peroxides are formed during the slow combustion of hydrocarbons. However, there are still considerable differences of opinion as to the precise part played by such compounds in the mechanism of combustion reactions.

The interaction of hydrocarbons with oxygen is characterised by an induction period, which is followed by an accelerating increase in pressure. Hydrocarbons with three or more carbon atoms usually have a different mechanism of combustion at high temperatures from that at low temperatures (66), each mechanism being considered to proceed through degenerate chain branching reactions. An important aspect of the mechanism is the identity of the intermediate responsible for degenerate chain branching in the low temperature oxidation. Norrish (67, 68) and Knox and Norrish (69) suggested a mechanism which involved aldehydes as the active intermediate. In connection with their studies of the oxidation of propane, they pointed out that the presence of 1% of acetaldehyde will result in the initiation of a chain reaction. Knox and Norrish suggest a linear chain reaction,

involving hydroxyl radicals and aldehydes.

$$RCH_3 + OH' \longrightarrow RCH_2' + H_2O$$

$$RCH_2' + O_2 \longrightarrow RCH_2O_2' \longrightarrow RCHO + OH'$$

$$RCHO + OH' \longrightarrow R' + CO\ H_2O$$

On the basis of earlier work by Mondain-Monval and Quanquin (70), Egerton and Pidgeon (71), Egerton, Smith and Ubbelohde (72) and others, in order to predict the point of oxygen attack and the relative knock ratings of hydrocarbon fuels, a mechanism has been suggested (73) which involves a peroxide as the active intermediate responsible for degenerate chain branching. The initial step is abstraction of a hydrogen atom to give two free radicals,

$$RH + O_2 \longrightarrow R' + HO_2 \qquad \text{(i)}$$

a consideration of bond energies suggesting that the order of ease of attack is tertiary > secondary > primary. The free radicals then act as chain carriers, thus,

$$R' + O_2 \longrightarrow RO_2' \qquad \text{(ii)}$$

$$RO_2' + RH \longrightarrow RO_2H + R' \qquad \text{(iii)}$$

Decomposition of the hydroperoxide can then occur by fission of the O-O bond, followed by splitting of the weakest C-C bond attached to the α carbon atom, which is generally the one attached to the largest alkyl group.

$$RR_1R_2\ COOH \longrightarrow OH' + RR_1R_2\ CO \qquad \text{(iv)}$$

$$RR_1R_2\ CO \longrightarrow R_1R_2\ CO + R' \qquad \text{(v)}$$

The smaller alkyl radical may then associate with oxygen by reactions (ii) and (iii) to form a lower peroxide. Primary and secondary peroxides may also decompose heterogeneously by dehydration, yielding a carbonyl compound, this reaction playing no part in the chain process,

$$RR^1CHOOH \longrightarrow RR^1CO + H_2O.$$

Later, to explain the appearance of two lobes in the cool flame boundary of certain hydrocarbons, Malherbe and Walsh (74) suggested that chain branching occurs through oxidation of the hydroperoxide,

$$ROOH + O_2 \longrightarrow ROO' + HO_2'$$

If the peroxide has two types of C-H bond, oxidation will occur at two slightly different temperature ranges, thus accounting for the two lobes. However, this reaction seems unlikely, since, as Knox (75) has pointed out, it would require an activation energy as low as 25 kcal. mole^{-1} for reaction between a saturated molecule and oxygen.

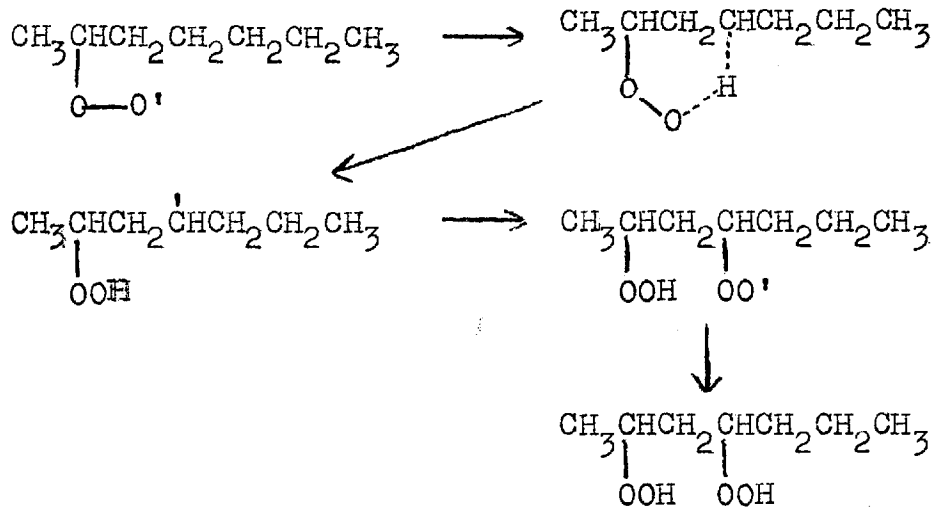
The negative temperature coefficient exhibited by some hydrocarbons when cool flames disappear, can be explained on the peroxide theory by an increasing amount of non-branching decomposition of peroxy radicals before they react with more

hydrocarbon molecules,

$$RCH_2OO' \longrightarrow RCHO + OH'$$

In recent years, more refined techniques have been employed for the detection of peroxides in hydrocarbon combustion products, and these have shown that the course of oxidation cannot be represented entirely by simple schemes. Batten and Ridge (76) identified tert-butyl hydroperoxide as a product of the combustion of isobutane That it was not, however, the active intermediate was shown by destruction of the peroxide a few minutes after the end of the induction period, removal and storage of the reaction mixture and then replacement of the reaction mixture in the reaction vessel. The reaction continued as though the interruption had not occurred.

Cartlidge and Tipper (52) have identified a wide range of organic peroxides in the combustion products of five hydrocarbons. Of particular interest is the formation of large amounts of peroxide-aldehyde addition products in the products of all the combustions and of dihydroperoxides in the combustion products of n-heptane. Cartlidge and Tipper suggest that dihydroperoxyheptane is formed by internal abstraction of hydrogen rather than by further attack on the mono-hydroperoxide.



This type of process has been suggested by Thomas and Crandall (77) to account for the production of β dicarbonyl compounds during the combustion of various hydrocarbons.

Although the simple theory of low temperature combustion of hydrocarbons explains many of the experimental observations, it is clear that the peroxidic intermediates are more complicated than was at first thought. More information about the precise nature of these peroxides would be of great value.

B. FUEL AND APPARATUS.

(i) Fuel.

The isopentane fuel was supplied by the British Petroleum Company and was at least 99.0% pure. It had a boiling point of 29 to 29.6°C and a refractive index of $n_D^{24} = 1.3505$, compared with the literature value $n_D^{25} = 1.35067$. (78)

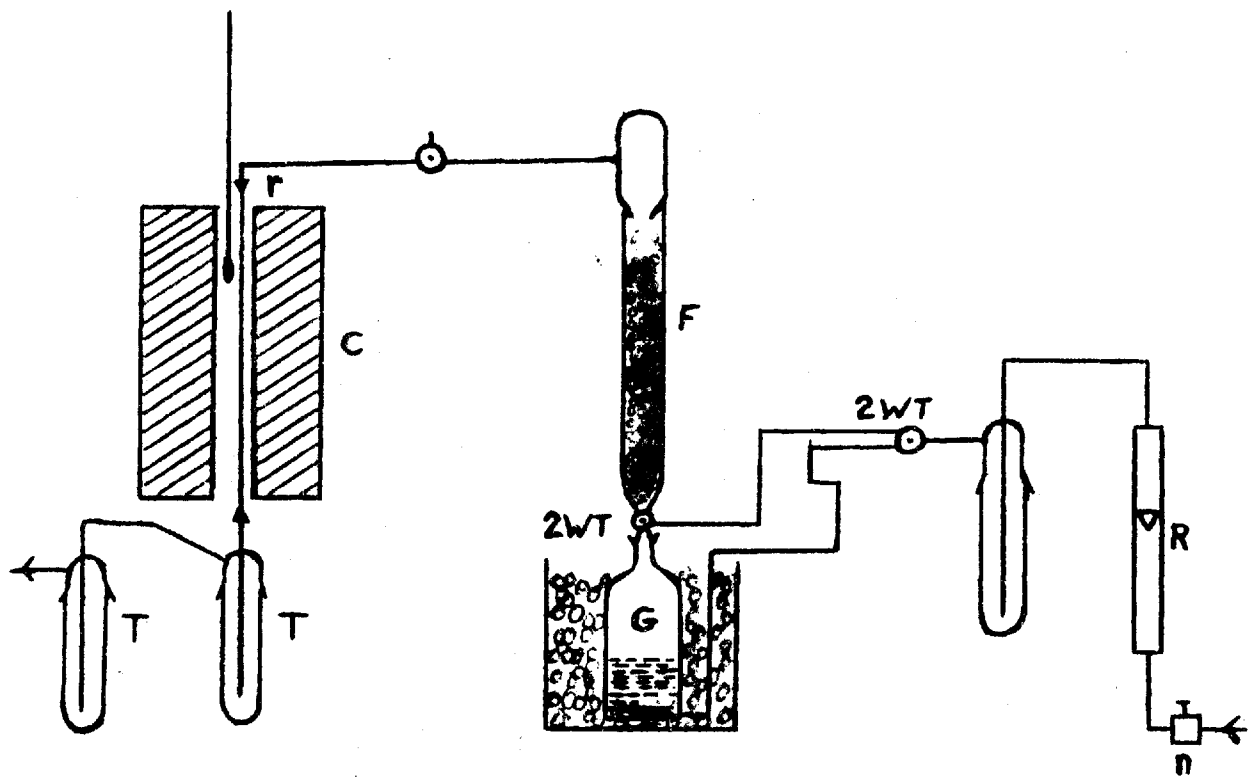
(ii) Apparatus.

The apparatus used for studies of the combustion of isopentane was a flow system and is shown diagramatically in Fig. 14.

Oxygen, the flow of which was regulated by a needle valve, n, was passed from a cylinder through a rotameter, R, calibrated to measure oxygen flow rates from 20 to 200 ml./min. at 20°C. It was then passed through a cold trap at -78°C, to remove impurities, into a gas washbottle, G, containing isopentane. In order to keep the liquid fuel at a constant temperature, the gas washbottle was surrounded by a freezing mixture, which was either melting ice or an ice-salt eutectic (-22°C). The isopentane should thus be picked up to give a mixture with an oxygen:fuel ratio equal to the ratio of the oxygen pressure to the saturated vapour pressure of the

FIG 14

THE COMBUSTION APPARATUS



hydrocarbon at the particular temperature employed. Saturated vapour pressures were obtained from a graph, drawn from literature data (78). The gas washbottle may be by-passed by means of the two way taps, 2WT.

The reaction mixture was then passed through a flame trap, F, consisting of a glass tube, 30 cm. long and 2.5 cm. in diameter, three quarters filled with fused silica packing (30 to 100 mesh). From the flame trap, the mixture passed into a pyrex glass reaction tube, r, 31 cm. long and 8 mm. in internal diameter. The reaction tube, which had been pretreated with 10% hydrofluoric acid, was placed in an electric furnace, C, the temperature of which was controlled to within $\pm$ 0.5°C by an electronic regulator. The furnace temperature was measured by a pressurised mercury thermometer, calibrated from 200 to 500°C. The reaction products leaving the apparatus passed through two cold traps at -78°C , T, the first being placed as near as possible to the end of the furnace.

Since other workers in this laboratory have found that alcohols and esters are not taken up to their saturated vapour pressures, experiments were performed to determine to what extent the composition of the oxygen + fuel mixtures used in these studies deviate from the theoretical composition

The mixture obtained by bubbling oxygen through isopentane at $-22^{\circ}C$ was passed for 30 min. through the cold traps, with the furnace switched off. A measured amount of n-butyl ether was added to the isopentane collected and the mixture was analysed by gas chromatography. A comparison of the resultant isopentane:n-butyl ether ratio with that obtained from an expected synthetic mixture showed that the percentage of isopentane was within 2% of the theoretical value.

C. EXPERIMENTAL PROCEDURE.

(i) The Combustion Procedure.

It is generally found in the study of gas reactions that reproducible results are only obtained if a standard procedure is employed for each run. Therefore, the following procedure was adopted throughout the combustion studies.

When the furnace temperature had settled at the required value, the freezing mixture was poured into a Dewar flask, surrounding the isopentane container. With the two way taps arranged to by-pass the isopentane, the oxygen was turned on and its flow rate was adjusted. 10 min. were allowed for the isopentane temperature to reach a steady value before the two way taps were turned so that oxygen bubbled through the isopentane. The condensable products were collected for 30 min., after which time the isopentane supply was cut off, allowing only oxygen to pass through the reaction tube. Immediately after this, the traps were removed. The flow of oxygen was maintained for 10 min. after the end of the reaction. The apparatus was then swept out with nitrogen for a further 5 min. The reason for these precautions is that an explosion can occur if the reaction mixture remains in the furnace.

No oxidation of the liquid isopentane in the gas wash bottle was detected by an acidic solution of potassium iodide after a month. Nevertheless, as a precaution, it was changed every two weeks.

Analyses were carried out when the traps had reached room temperature. Usually, all the condensable products had collected in the first trap. The products consisted of two layers, which were analysed for peroxidic and non-peroxidic species by the methods descibed in the next three sections.

(ii) Analysis of Non-Peroxidic Combustion Products.

Over the last few years, gas chromatography has been widely applied to the qualitative and quantitative analysis of intermediate and final combustion products and this method was employed in this work. Two columns were used; a 6 ft. long column, containing 20% silicone on Embacel and a 12 ft. long column, containing 20% polyethylene glycol on Embacel.

Each column was calibrated for many possible combustion products, the following conditions being maintained during the calibrations.

Silicone column:

Column temperature	=	76°C.
Inlet pressure	=	86.7 cm. Hg.
Outlet pressure	=	39.8 cm. Hg.
Flow rate	=	16 ml./ min.
Bridge current	=	120 ma.
Katharometer block temperature	=	75°C.
Sensitivity	=	x 10.

Polyethylene glycol column:

Column temperature	=	56°C
Inlet pressure	=	89.3 cm. Hg.
Outlet pressure	=	58.7 cm. Hg.
Flow rate	=	17.5 ml./ min.

Bridge current	120 ma.
Katharometer block temperature	75°C
Sensitivity	= x10

For compounds with retention times below about 10 min., it was found that peak heights were proportional to the amounts placed on the column, and these therefore were used for quantitative determinations. For compounds with retention times above 10 min. the measurement of peak areas was used. The characteristic retention times were recorded for all the compounds studied. It is convenient to express retention times in relation to a common standard, since these are independent of the flow rate employed. In this case, retention times are expressed relative to that of acetone. The values obtained are recorded for the silicone column in Table 2 and for the polethylene column in Table 3.

On completion of a combustion run, the analysis of non-peroxidic products was carried out as follows.

On reaching about 10°C, the volumes of the upper and lower layers were measured by sucking them into a 1 ml. pipette by means of a rubber teat. A sample (usually 5 microlitres) of each layer was then examined by gas chromatography, and, from the recorded chromatograms, the qualitative and quantitative

TABLE 2.

Retention Times of Possible Combustion Products.

6 ft. 20% silicone column.

Compound.	Retention time (relative to acetone as unity)
Formaldehyde	- 1.3 approx. (very spread out peak)
Acetaldehyde	0.58
Isobutyraldehyde	1.42
Isovaleraldehyde	2.86
Acetone	(1.00)
Methyl ethyl ketone	1.88
Methyl isopropyl ketone	2.90
Methyl alcohol	0.47
Ethyl alcohol	0.91
Isopropyl alcohol	0.89
Isobutyl alcohol	2.17
n-Propyl alcohol	1.36
n-Butyl alcohol	2.97
Tert-amyl alcohol	2.30
3 Methyl 2 butyl alcohol	3.28
3 Methyl 1 butyl alcohol	5.08
2 Methyl 1 butyl alcohol	5.00
Formic acid	- 1.12
Acetic acid	- 2.61
Propionic acid	- 8.25
Isopentane	0.61
2 Methyl but-2-ene	0.83
Isobutene epoxide	1.19
Trans but-2-ene epoxide	1.31

Compound.	Retention time
2,3 Epoxy 2 methyl but-2-ene	2.70
Methyl ethyl ketone peroxide	2.20
Water	- 1.20 approx. (very spread out peak)

TABLE 3.

12 ft. 20% Polyethylene glycol column

Compound.	Retention time (relative to acetone as unity)
Acetaldehyde	0.57
Isobutyraldehyde	0.77
Isovaleraldehyde	1.30
Acetone	(1.00)
Methyl ethyl ketone	1.42
Methyl isopropyl ketone	1.61
Methyl alcohol	2.00
Ethyl alcohol	2.26
Isopropyl alcohol	1.77
Tert-butyl alcohol	1.55
Tert-amyl alcohol	2.73
3 Methyl 2 butyl alcohol	3.99
2 Methyl but-2-ene	0.25
2,3 Epoxy 2 methyl but-2-ene	1.23
Methyl ethyl ketone peroxide	1.42
Isopentane	0.27

results were deduced.

(ii) Analysis of Classes of Peroxide.

An iodometric method was used to determine classes of peroxide. 1 ml. of a saturated solution of potassium iodide was added to 10 ml. of water in a conical flask. To this was added 1 ml. of 2 N sulphuric acid, followed by a small piece of cardice to drive out the air. The flask was cooled to $0^{o}C$ and a known volume of the bottom layer was added, followed by 1 ml. of starch solution. The iodine liberated was immediately titrated with 0.025 N sodium thiosulphate to determine peroxyacids. The flask was warmed to $5^{o}C$. A crystal of ammonium molybdate was added and the flask was left at $5^{o}C$ for 5 min. Then the solution was titrated with 0.025 N sodium thiosulphate to determine hydrogen peroxide. Following this, the loosely stoppered flask was heated to $50^{o}C$ on a steam bath. It was then removed and set aside for 30 min. The solution was then titrated with 0.025 N sodium thiosulphate to determine alkyl hydroperoxides and other peroxides with similar reducibilities.

The analysis of the peroxides in the top layer was performed in the same way. However, in no case was any peroxide detected in this solution.

(iv) Analysis of Specific Peroxides.

Attempts to detect the organic peroxides investigated in Part 2, in the combustion products, were made using a 2 ft. long 10% dinonyl phthalate column. A sample (about 10 mg.) of the bottom layer of the combustion products was placed in a spiral crushing tube, using the procedure described on page 81 . The sample was analysed under the conditions stated in Fig. 13. All the volatile combustion products were eluted from the column in under 6 min.

Analyses for specific organic peroxides were made on combustion products from runs at three temperatures; 340°, 375° and 400°C. However, in no case was aperoxide peak obtained.

To increase sensitivity, the products of three combustion runs at 375°C were concentrated by distillation of the volatile components at 5mm. Hg. pressure. Iodometric tests showed that all the peroxide remained in the residue, whose volume was about 10% of the total combustion products. Chromatographic analysis of the concentrated combustion products again revealed no peroxide peak, despite the fact that the highest sensitivity (x 1) was used and a very large sample (20 mg.) was introduced on to the column.

As a final check that no peroxide was going through the

column, an analysis of the concentrated products was performed with an acid potassium iodide trap at the exit from the katharometer. No iodine was liberated, once again indicating that no peroxide was passing through the column.

(v) Decomposition of Tert-Amyl Hydroperoxide.

As a result of the investigations of the combustion of isopentane, it was decided to study the decomposition of tert-amyl hydroperoxide under similar conditions. The aims were to establish the extent to which it decomposed under these conditions and to determine the nature of the products.

The reactions were performed in the combustion apparatus. When the furnace temperature had settled at the required temperature, 1 ml. of tert-amyl hydroperoxide was placed in the gas wash bottle, which was then surrounded with water at 50°C. The oxygen flow was started and the condensable products were collected in a trap cooled to -78°C for 5 hr. During this time the temperature of the gas washbottle was maintained between 47 and 50°C.

In order to establish the composition of the reaction mixture, the procedure was repeated with the furnace turned off. From the volume of tert-amyl hydroperoxide collected in the cold trap after 5 hr. and the oxygen flow rate, it was

calculated that the mixture entering the furnace was in the mole ratio 790oxygen:1 tert-amyl hydroperoxide.

The reaction was carried out at three temperatures; 230, 310 and 370°C.

The products collected in the cold trap were analysed for tert-amyl hydroperoxide by gas chromatography, using a 2 ft. long 10% dinonyl phthalate column under the conditions stated in Fig. 13.

The products of the reaction at 375°C were also analysed for non-peroxidic products on a 12 ft. long 20% polyethylene glycol column, under the same conditions as those used to analyse the non-peroxidic products of the combustion of isopentane.

D. RESULTS.

(i) Preliminary Experiments.

Early combustion experiments were performed with a 3.1 O_2 + 1.0 C_5H_{12} mixture. In attempts to obtain optimum yields of peroxides, the reaction of this mixture was studied at temperatures from 340 to 460°C and at contact times between 5 and 20 sec. However, under no conditions did the total amount of peroxides obtained exceed 0.02 mmole for runs of 30 min. In addition, it was found impossible to stabilise temperature conditions.

The following qualitative observations were made in the reaction of the above mixture .

(a) About 2 min. after the start of the reaction, smoke appeared from the exhaust and this was accompanied by a temperature rise. The temperature increased rapidly, the extent of the rise depending on the conditions. The maximum observed rise was 104°C, in reactions carried out initially at 360°C. The temperature rose to a maximum and then fell again to a value in the region of the starting temperature. It then stayed at a relatively constant value ($\pm$ 3°C). Between each run the apparatus was flushed out with nitrogen.

(b) Periodic flashes occurred in the reaction tube, starting

usually between 6 and 15 min. after the start of the reaction. The frequency of the flashes was about one every two seconds. (c) Large amounts of carbonaceous deposits collected at the exit from the reaction tube.

It is not within the scope of this thesis to discuss these observations further, which are clearly associated with the complex subject of periodic reactions in chemical kinetics. A treatment of this subject, both from purely kinetic and kinetic-thermal approaches, has been made by Frank-Kamenetskii (79).

(ii) Analytical Data.

Large yields of peroxides were obtained from a 6.6 O_2 + 1.0 C_5H_{12} mixture. The effect of temperature on the nature and amounts of condensable products of this reaction was therefore studied in some detail.

Preliminary runs showed that no oxidation occurred below 330°C with a contact time of 9.4 sec. The condensable products were in one layer, and this was shown by gas chromatography to consist entirely of isopentane.

The lowest temperature at which oxidation occurred at a conveniently measurable rate was 337°C and the condensable products were analysed at various temperatures between this

temperature and 440°C. Three attempts were made to study the reaction above 440°C, but each resulted in an explosion soon after the run had started.

The variation in the consumption of isopentane with temperature is shown in Fig. 15. The temperature coefficient is very high up to 340°C, but this is followed by a period of negative temperature coefficient up to 380°C. From this temperature, the consumption of isopentane increases at a steady rate, until, at 420°C, nearly 95% is oxidised.

From Figs 16, 17, 18 and 19, it is seen that the major product in the low temperature region (340 to 370°C) is acetone (Fig. 16). Appreciable yields of acetaldehyde, methyl alcohol and alkyl hydroperoxides (or peroxides of similar reducibility) are obtained. The yield of hydrogen peroxide increases rapidly with temperature in this region, until, at 370°C, it is the major product. 2 methyl but-2-ene and 2,3 epoxy 2 methyl but-2-ene occur to a lesser extent. In the region 370 to 390°C, the yield of acetone decreases rapidly and the major ketonic product becomes methyl ethyl ketone. There are still large amounts of acetaldehyde, methyl alcohol and organic peroxides. Towards the top end of this region, the hydrogen peroxide yield reaches a maximum, while small amounts of 2 methyl but-2-ene and 2, 3, epoxy 2 methyl but-2-ene are

FIG. 15

VARIATION OF ISOPENTANE CONSUMPTION WITH TEMPERATURE

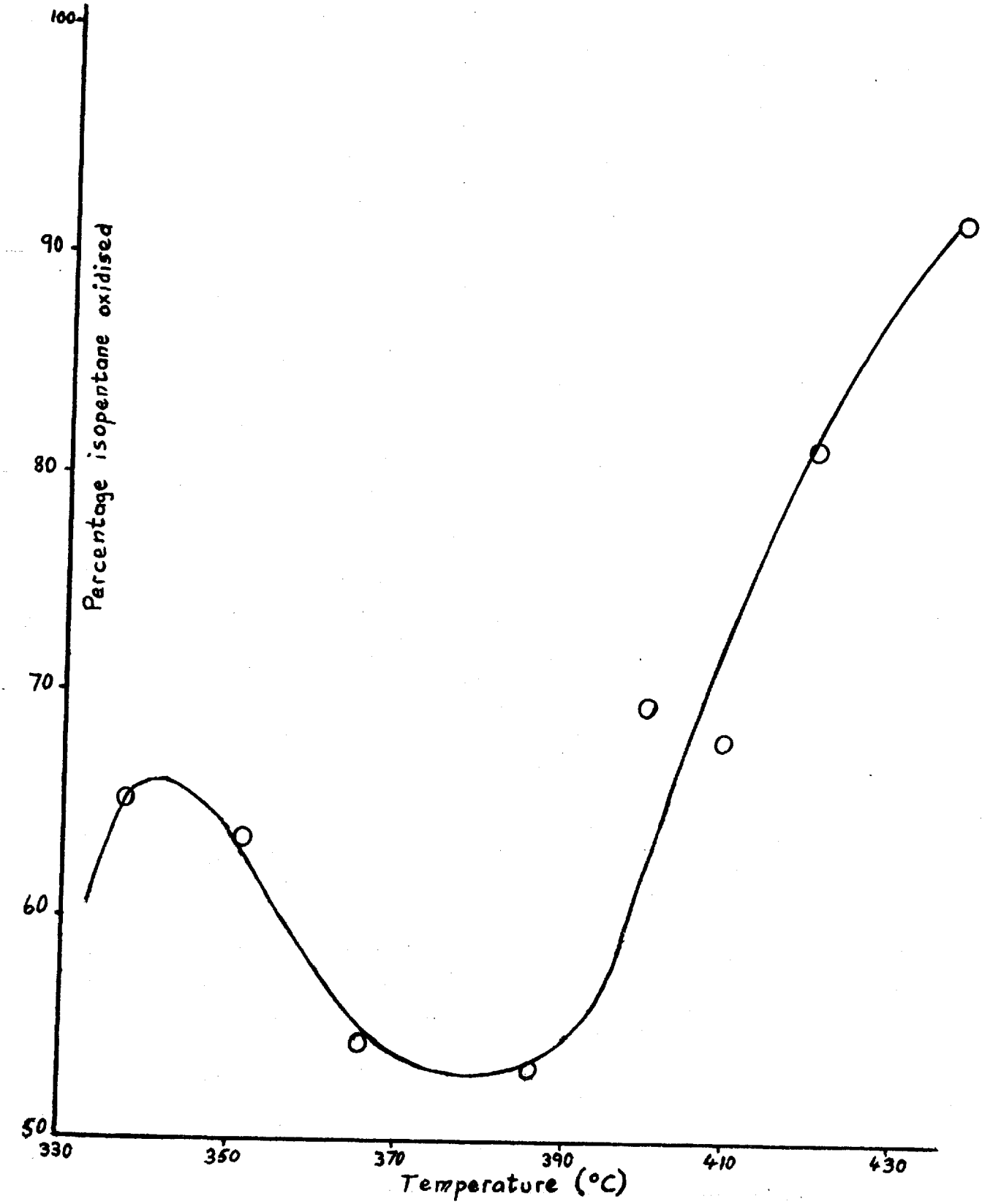


FIG. 16

VARIATION IN YIELDS OF PRODUCTS WITH TEMPERATURE

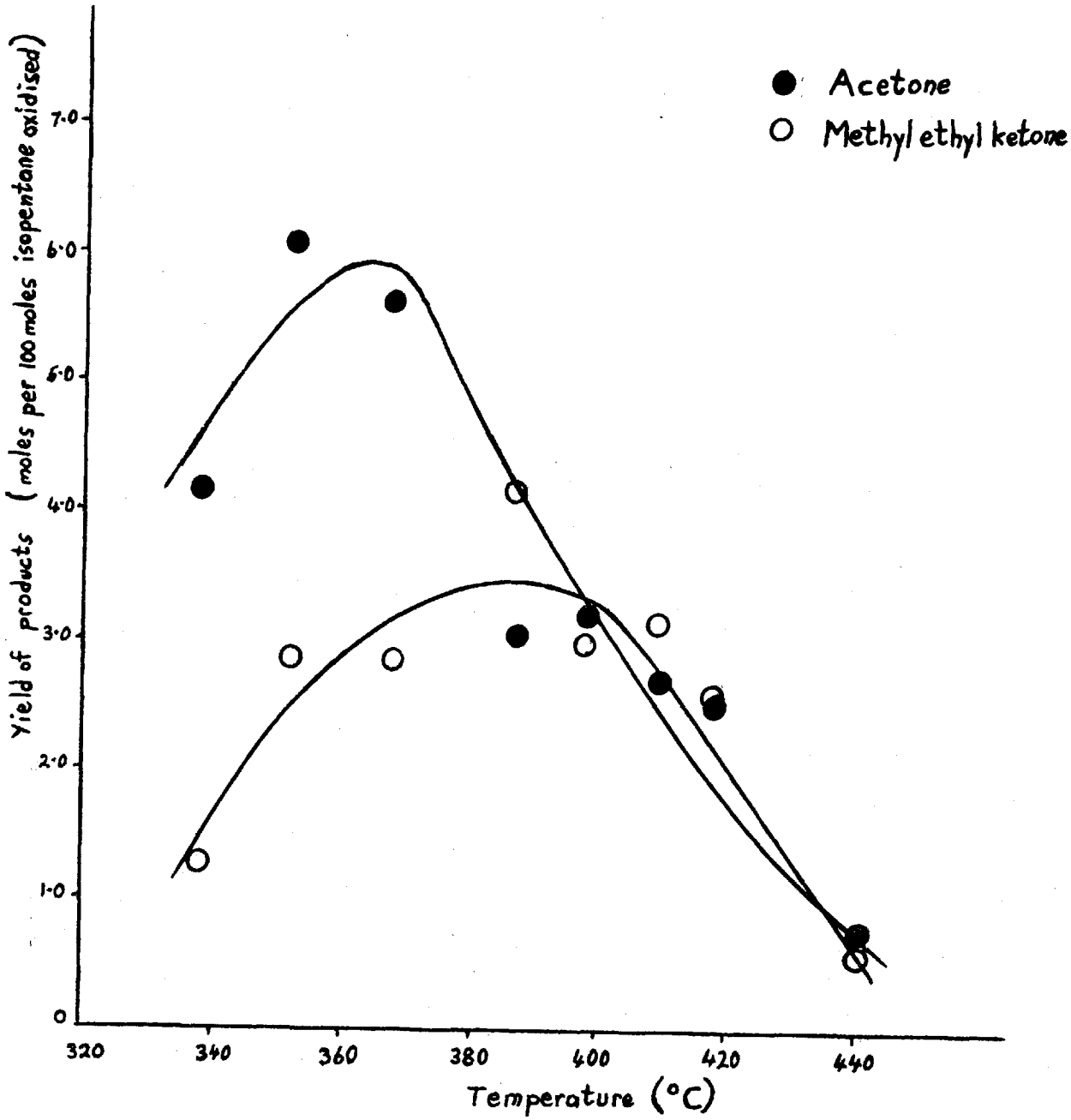


FIG. 17

VARIATION IN YIELDS OF PRODUCTS WITH TEMPERATURE

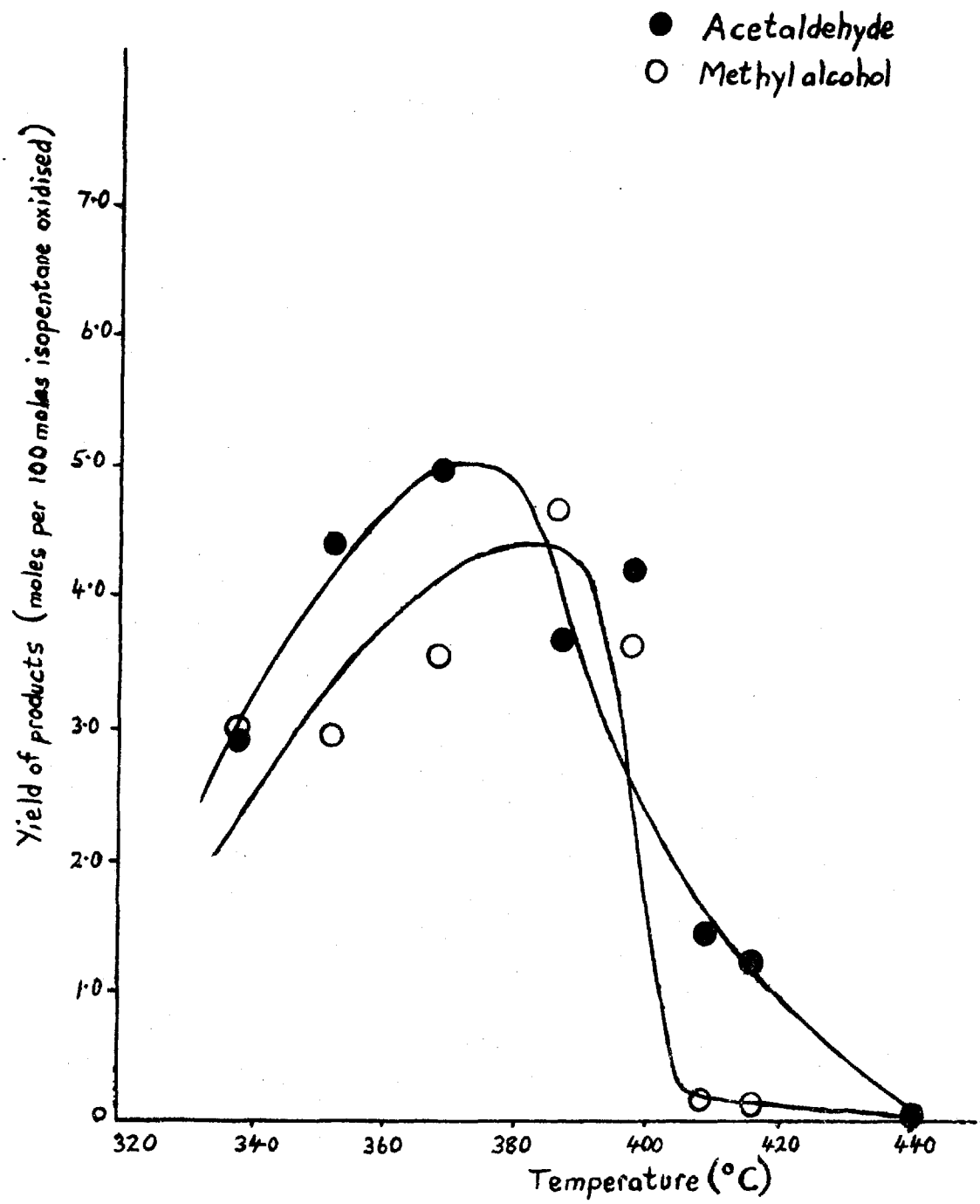


FIG 18

VARIATION IN YIELDS OF PRODUCTS WITH TEMPERATURE

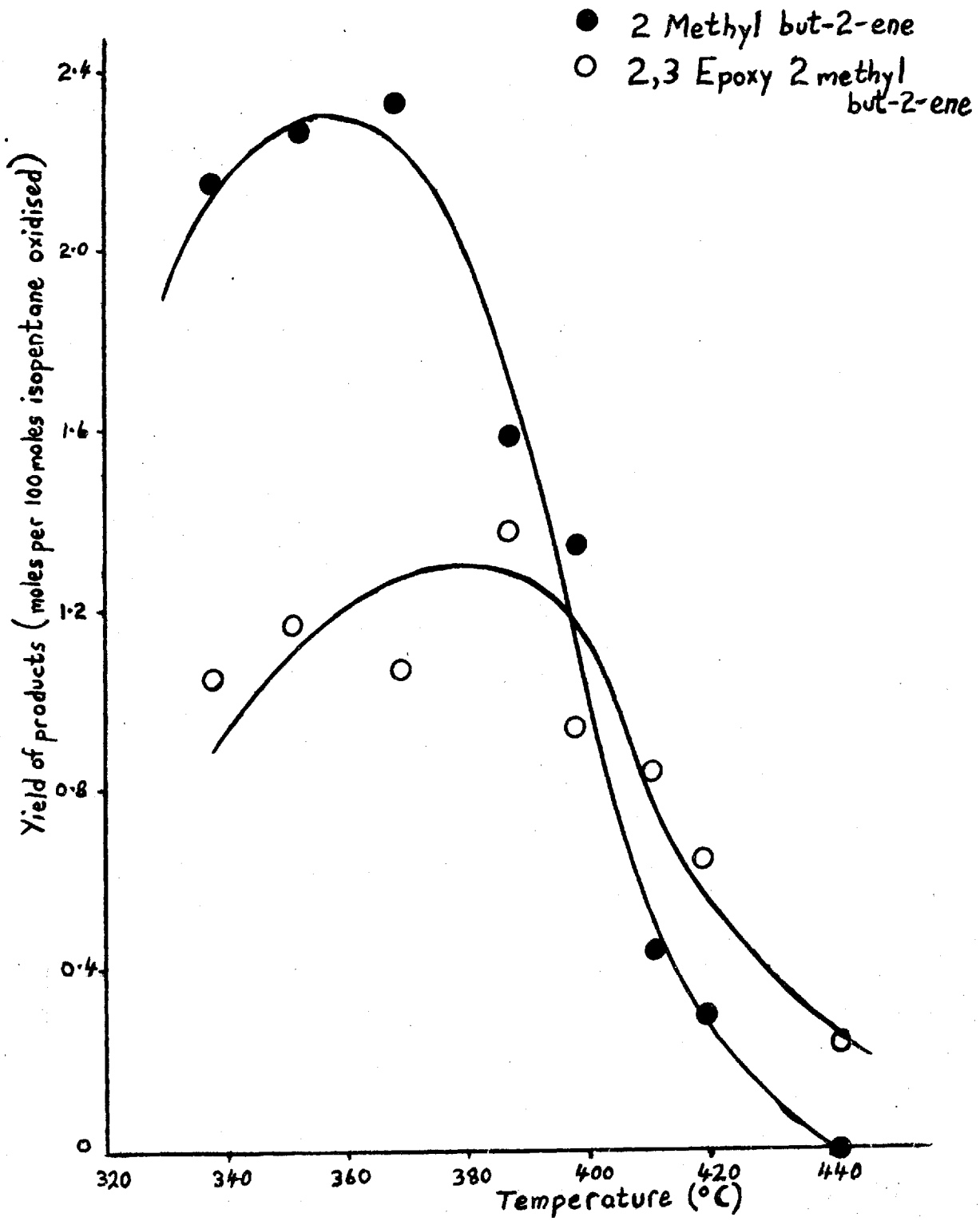
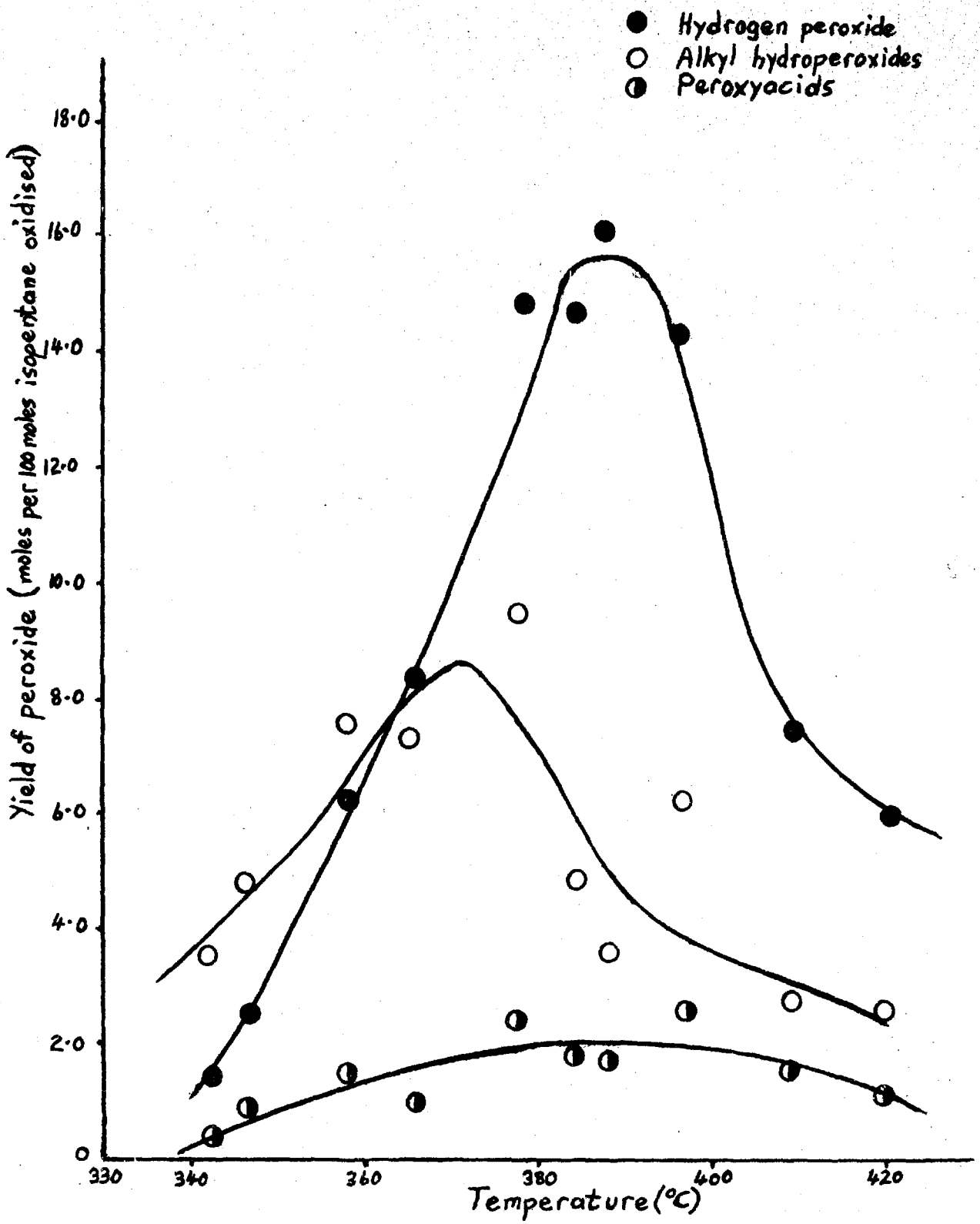


FIG. 19

VARIATION IN YIELDS OF PEROXIDES WITH TEMPERATURE



still obtained. Above 390°C. hydrogen peroxide is easily the predominant product. The yield of methyl alcohol falls to almost zero at 410°C and the yields of acetone and methyl ethyl ketone fall, but remain approximately equal to each other. Throughout the whole range studied, small amounts of peroxyacids were detected in the products.

In addition to the products represented graphically, the other compounds detected were:-

(a) Ethyl alcohol. A trace was obtained at 337°C, while at 410°C the yield was 0.8%.

(b) Isobutyraldehyde. Traces were detected at all temperatures up to 420°C, but the yield was never larger than 0.04%.

(c) Methyl isopropyl ketone. Traces were obtained at 337 and 398°C.

As has already been mentioned, when describing experimental methods, neither tert-amyl, 3 methyl but-2-, 3 methyl but-1- and 2 methyl but-1- hydroperoxides nor di tert-amyl peroxide were detected in the products of the combustion of isopentane.

(iii) Extent of Decomposition of Tert-Amyl Hydroperoxide.

Table 4 indicates the extent to which tert-amyl hydroperoxide decomposes at three different temperatures. It is seen that virtually all the hydroperoxide is decomposed at 375°C, while at 230°C it remains completely unaffected. The value of 9.3% decomposed at 310°C indicates that most of the tert-amyl hydroperoxide decomposes well below the lowest temperature at which combustion of isopentane occurs.

Table 5 is a list of the decomposition products of the reaction at 375°C. Acetone is by far the most abundant product, while the only product which is not a carbonyl compound is tert-amyl alcohol.

TABLE 4.

Extent of Decomposition of Tert-Amyl Hydroperoxide.

Temperature (°C)	% tAmOOH decomposed.
375	99.6
310	9.3
230	0.5

TABLE 5.

Products of Reaction at 375°C.

Product.	Yield (moles per 100 moles tAmOOH decomposed)
Acetaldehyde	2.93
Acetone	12.10
Methyl ethyl ketone	1.48
Tert-amyl alcohol	9.90

E. DISCUSSION.

The absence in the slow combustion products of simple mono-hydroperoxides, which would result from reaction with molecular oxygen at one of the four possible points of attack in the isopentane molecule, does not necessarily mean that such compounds are not formed during the reaction. The results show that tert-amyl hydroperoxide, which is the most likely peroxide to be formed and the most likely to survive, reacts under the experimental conditions used well below the combustion temperature region, and that the products formed from it also occur in the combustion products of isopentane (see Table 5). Nevertheless, it is unlikely that this hydroperoxide is the species responsible for degenerate chain branching, since it is completely decomposed within 10 sec. at 375°C and it is generally agreed that to be an effective degenerate chain branching agent, a species should have a much longer life time than this (80). As a result of these observations, a mechanism will now be proposed, which excludes the formation of hydroperoxides, but which accounts for the occurrence of products in the low temperature region by postulating reactions of the peroxy radical other than the process

$$RO_2' + RH \longrightarrow ROOH + R'.$$

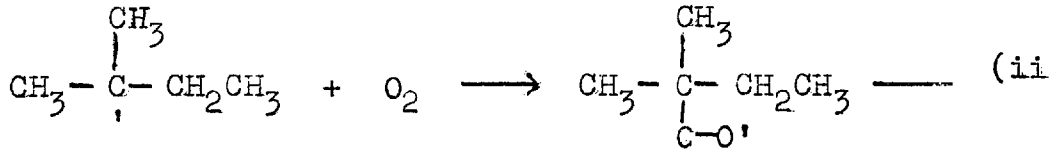
The most likely initiation step is abstraction of the hydrogen atom in the tertiary position by molecular oxygen, to give an alkyl radical and a HO_2' radical,

$$CH_3CHCH_2CH_3 + O_2 \longrightarrow CH_3\overset{\cdot}{C}CH_2CH_3 + HO_2. \quad \text{(i)}$$

The supposition that attack takes place in the tertiary position is based on the results of isotopic tracer studies (81, 82) and of work on competitive oxidation (83, 84), which have shown that, as a rough approximation, the extents of oxidation at the primary, secondary and tertiary positions respectively, in paraffin hydrocarbons are in the ratio 1:3:15. Reaction (i) is of course far more likely to occur than is thermal decomposition, since the slow combustion of isopentane takes place at a much lower temperature than pyrolysis (85, 86), and, in addition, it is well known that traces of oxygen lower considerably the pyrolysis temperatures of several compounds (87, 88).

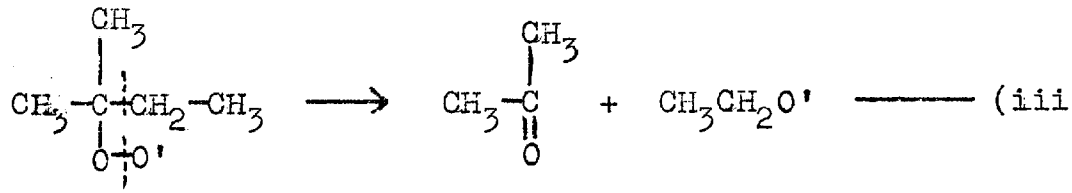
Once the tertiary alkyl radical has been formed, it could theoretically undergo several alternative reactions. Apart from reaction with oxygen, these radicals can either decompose, isomerise or recombine with one another. All the available evidence goes to show that the latter processes

require an appreciable activation energy (89), whereas, addition to oxygen apparently takes place with almost zero activation energy (90, 91, 92). It may therefore be assumed that at low temperatures, reaction (ii) is the predominant fate of the radicals produced in reaction (i)

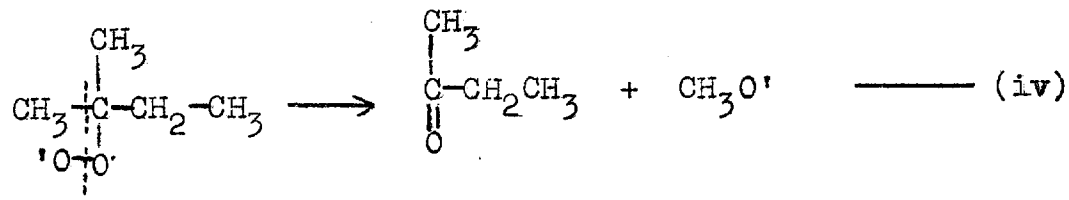


(ii)

The peroxy radicals may then decompose in various ways. The O-O bond is split, and this is accompanied by fission of any of the C-C bonds, e.g.



(iii)



(iv)

Thus, reaction (iii) would give acetone and an ethoxy radical, while reaction (iv) would give methyl ethyl ketone and a methoxy radical. Acetone is the predominant product in the low temperature region (340 to 370°C), so that it is likely

that reaction (iii) occurs preferentially. Above 380°C the yields of acetone and methyl ethyl ketone are nearly equivalent, which suggests that reaction (iv) assumes an importance more or less equal to that of reaction (iii).

The ethoxy radicals formed in reaction (iii) can decompose further to give acetaldehyde (93, 94, 95,96), which is one of the abundant products in the low temperature region.

$$CH_3CH_2O' \longrightarrow CH_3CHO + H' \qquad \text{(v)}$$

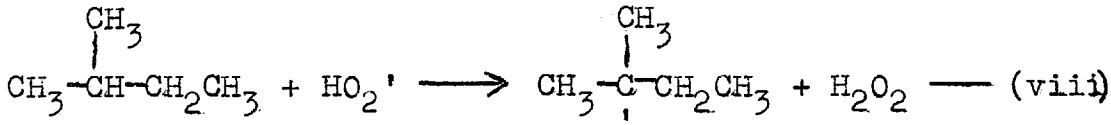
The formation of methyl alcohol can be explained by hydrogen abstraction from a fuel molecule by a methoxy radical (93, 97),

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_3 + CH_3O' \longrightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_2CH_3 + CH_3OH \qquad \text{(vi)}$$

In the high temperature region (above 390°C), hydrogen peroxide becomes the most abundant product. The simultaneous formation of 2 methyl but-2-ene strongly suggests that another reaction between molecular oxygen and the radicals formed in reaction (i) can take place under these conditions, viz,

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_2CH_3 + O_2 \longrightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CHCH_3 + HO_2' \qquad \text{(vii)}$$

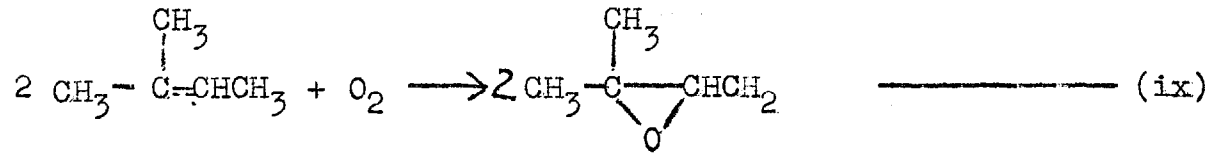
The HO_2 radical will then be stabilised as hydrogen peroxide by abstraction of hydrogen from isopentane.



(viii)

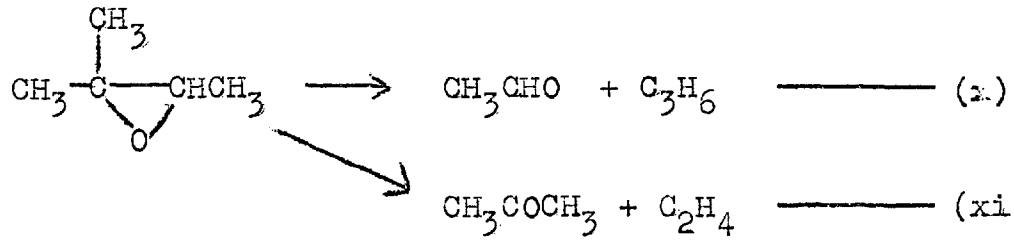
It is noticeable, however, that the yield of 2 methyl but-2-ene decreases quite rapidly in the high temperature region. Since the olefin is oxidised appreciably at temperatures as low as 250°C (98), its concentration in the system is no guide to the extent of its formation. Thus, while at about 350°C the yields of hydrogen peroxide and 2 methyl but-2-ene are approximately equal, although very low, indicating that these compounds are relatively stable under these conditions, the wide diversity in the amounts of the products present at higher temperatures suggests that the olefin is rapidly further oxidised.

One mode of oxidation is evidently to the corresponding epoxide, 2,3 epoxy 2 methyl but-2-ene, which, in fact, is more abundant than the olefin above 400°C.

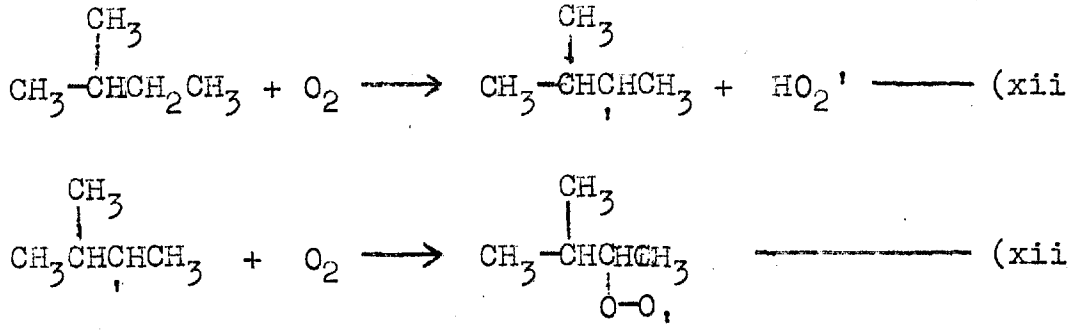


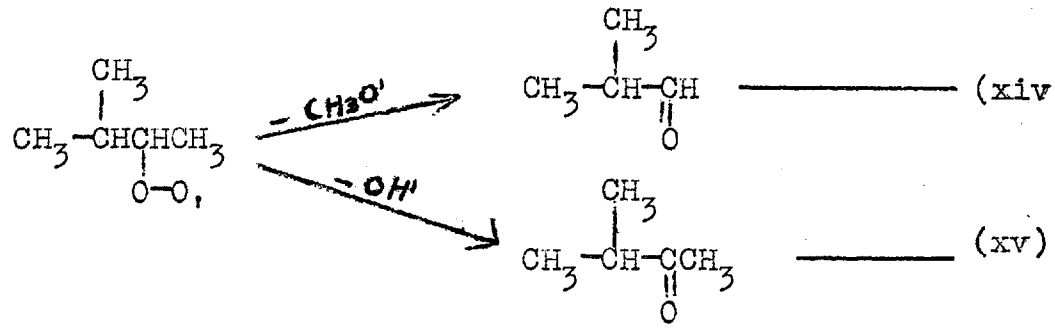
(ix)

The epoxide is subject to decomposition, either to acetone or acetaldehyde, both of which are still present in the products at high temperatures.



Although oxidation of isopentane is believed to occur predominantly at the tertiary carbon atom, some attack probably takes place at other positions, particularly at higher temperatures, when the differences in vulnerability of the various C-H groups become less marked. The formation of small amounts of isobutyraldehyde and methyl isopropyl ketone, are in fact evidence for some attack in the secondary position, viz.,





It remains now to make some comment about the nature of the compounds which liberate iodine from acid potassium iodide at 50°C. Cartlidge and Tipper (52) detected several addition compounds of aldehydes with both hydrogen peroxide and hydroperoxides in the combustion products of certain hydrocarbons and it is probable that similar compounds are formed in the reaction studied here. The mode of formation of these addition compounds would be by reactions of the type,

$$ROOH + R'CHO \longrightarrow ROOCHR'(OH) \qquad \text{(xvi)}$$

Whether or not this kind of species is responsible for degenerate chain branching is a matter for conjecture, since very little is known about either their formation or their decomposition in the gas phase. It would be an extremely useful step, if as a follow up of this work, the organic peroxides present in the combustion products were positively

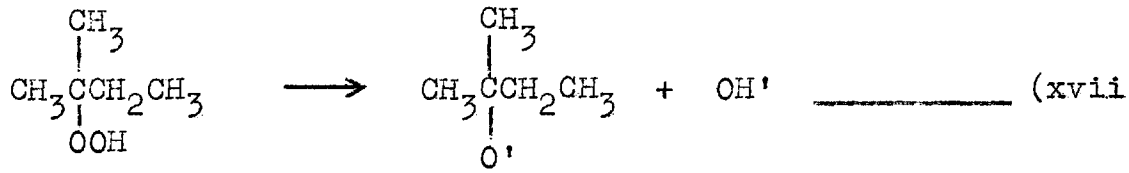
identified, perhaps by further development of the gas chromatographic method devised in the course of this research.

APPENDIX.

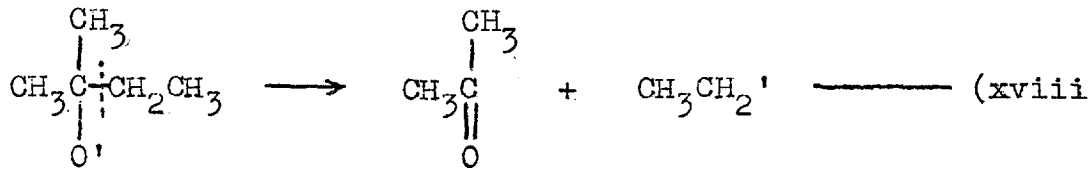
The Decomposition of Tert-Amyl Hydroperoxide.

Although the mechanism which has been proposed for the combustion of isopentane has deliberately excluded the formation of simple mono-hydroperoxides, it is felt that the results obtained from the study of the decomposition of ter-amyl hydroperoxide should not be neglected. Therefore, the mechanistic inferences of the analytical data obtained in these experiments will now be discussed. The thermal decomposition of di tert-amyl hydroperoxide has been studied (99), but no previous work appears to have been reported on the corresponding hydroperoxide.

The formation of acetone as by far the most abundant product of the reaction at 375°C suggests that the initial cleavage of the O-O bond to form the alkoxy radical is followed by a splitting off of the largest alkyl group, which would be expected from a consideration of C-C bond energies.

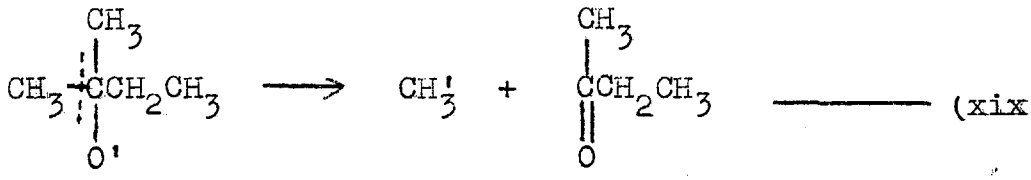


(xvii)



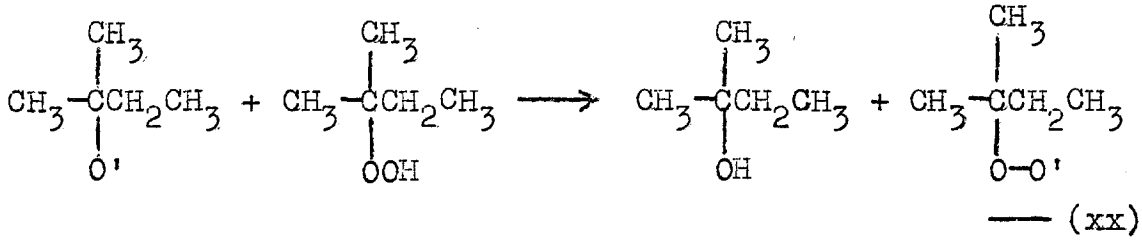
(xviii)

However, it appears that the alternative rupture of the C–CH_3 bond must be occurring to some extent, since there is a small amount of methyl ethyl ketone in the products.



(xix)

The formation of 1% of tert-amyl alcohol can be explained by the reaction,

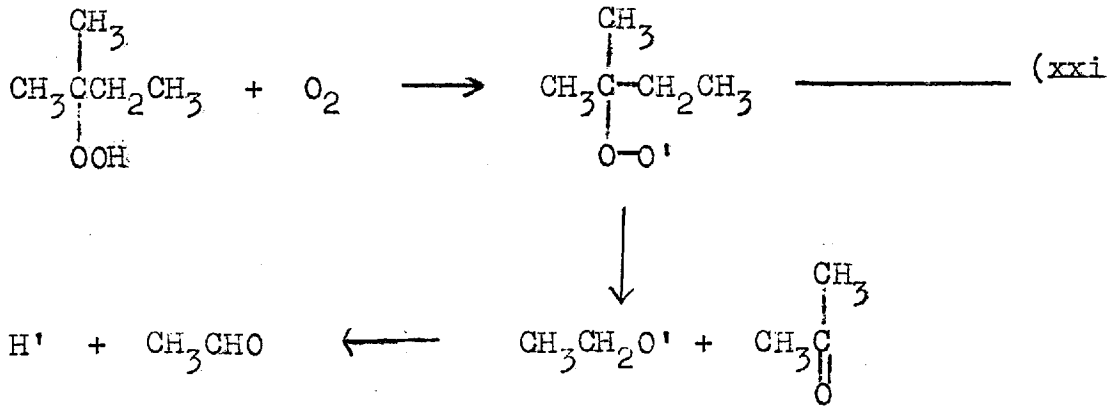


(xx)

although it is surprising that this reaction should occur with such a low concentration of hydroperoxide.

The formation of quite appreciable amounts of acetaldehyde can be accounted for by oxidation of the hydroperoxide, subsequent decomposition of the peroxy radical,

followed by decomposition of the ethoxy radical.



Although a consideration of activation energies suggests that the reaction (xxi) would not proceed in preference to the O-O cleavage of reaction (xvii), it is possible that in the presence of the large excess of oxygen used it would become more prominent than expected.

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