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A T H E S I S

entitled

KINETIC STUDIES OF THE GASEOUS
OXIDATION OF OLEFINS

submitted by

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A B S T R A C T.

An investigation of the slow combustion of 2-methyl-but-2-ene and of some ^{14}C -labelled 2-methyl-but-2-enes is described. This work was designed to elucidate the mechanism of formation of the oxidation products and in particular the mode of initial oxygen attack.

In the Introduction conflicting theories concerning the mode of attack of olefins by oxygen are critically reviewed. The advantages of the use of isotopic tracers in studies of hydrocarbon combustion are discussed.

Kinetic and analytical studies of the slow combustion of 2-methyl-but-2-ene at ca. 250°C show that an initial pressure decrease, which represents the formation of peroxidic intermediates, is followed by an autocatalytic pressure increase during which the main processes are breakdown and further oxidation of the primary reaction products. Acetone and acetaldehyde are the principal early non-peroxidic products and these are formed initially in equivalent quantities and in closely parallel fashion. Methyl isopropyl ketone is produced in somewhat smaller amounts and methyl alcohol, which appears comparatively late in the reaction, probably arises from the oxidation of acetaldehyde. The results suggest that the predominant mode of attack of the olefin is the addition of oxygen to the double bond followed by decomposition of the resulting cyclic peroxide to acetone and acetaldehyde, although some hydroperoxylation leading to methyl isopropyl ketone probably also occurs.

$[2-^{14}\text{C}]$ and $[4-^{14}\text{C}]$ 2-methyl-but-2-enes were synthesised, subjected to radioassay and oxidised under similar conditions.

Measurement of the specific molar activities of derivatives and degradation products of the carbonyl compounds and alcohols formed enabled the fate during combustion of specific carbon atoms to be traced. These studies provided further evidence for the modes of formation of major products postulated from kinetic and analytical data, and suggested that the minor products (propionaldehyde, methyl ethyl ketone, isopropyl alcohol and t-butyl alcohol) were formed by rearrangement reactions from the same peroxy species as the major products.

PART 1.

I N T R O D U C T I O N .

INITIAL OXYGEN ATTACK IN THE COMBUSTION OF
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INITIAL OXYGEN ATTACK IN THE COMBUSTION OF OLEFINS.1A. Introduction.

Organic compounds can be oxidised by a wide variety of reagents, many of which are highly specific in their action. This is particularly true of oxidation in the liquid-phase where, by choice of suitable oxidants and conditions, certain parts of an organic molecule may be oxidised while others remain unaffected. From the nature of the products formed in such cases the position and mode of attack are usually obvious.

In contrast to liquid-phase oxidation, the gaseous reaction of organic compounds with molecular oxygen does not, in general, lead to products the origin of which is unambiguous. The detailed mechanism whereby complex organic fuel molecules are degraded to final products is still a matter for conjecture. The reason for this uncertainty lies in the fact that gaseous oxidation involves complex chain cycles which, while theoretically capable of resolution into a number of simple steps, are, nevertheless, very difficult to study directly. In recent years direct methods such as mass spectroscopy^{1,2}, and flash photolysis³, have made substantial contributions to our knowledge of the free radical intermediates involved in combustion processes, but even methods such as these do not always yield unambiguous information, and most of the reaction schemes that have been put forward have, of necessity, been based on indirect evidence. Much emphasis has been placed on analytical data in deriving such schemes, but the primary steps involved in the formation of a given reaction product are not always clear. Furthermore, if such data are used to calculate the relative frequencies of two or more modes of attack, or of attack at two or more different points, the results will always tend to be weighted in favour of those schemes which lead to reaction products resistant to decomposition or further oxidation.

1B. Theories concerning the point and mode of attack of olefins by molecular oxygen.

In the gas-phase oxidation of paraffins the fundamental steps are well established, and have been classified by Tipper⁴. The initial chemical step is almost invariably the abstraction of a hydrogen atom, to leave a reactive alkyl radical, followed by attachment of molecular oxygen, and reaction of the $RO_2^{\cdot}$ radical so formed with a further fuel molecule to give a hydroperoxide $ROOH$ as the first molecular product and another alkyl radical $R^{\cdot}$ which continues the chain.

Olefinic hydrocarbons may react with molecular oxygen to give hydroperoxides, the chain cycle again being initiated by hydrogen abstraction. Olefins are also, however, susceptible to additive attack, a mode of reaction not available to paraffins. The combustion of olefins may therefore involve either, or both, of two initiation mechanisms.

- I) Abstraction of a hydrogen atom.
- II) Addition of molecular oxygen at the C=C double bond.

I) Hydrogen abstraction as the initiation step.

The close similarity between autoxidation of olefins in the liquid state and their low-temperature gas phase combustion has been frequently stressed,^{e.g. 5,6,7,8} and under both conditions a considerable body of evidence points to the conclusion that peroxides are the first molecular products and that the point of oxygen attack is determined by the condition of minimal energy expenditure and is as a rule at the weakest C-H linkage. The allylic position is thus favoured and in particular the hydrogen of an α -CH₂ group.

Liquid-phase oxidation: work in support of theory I.

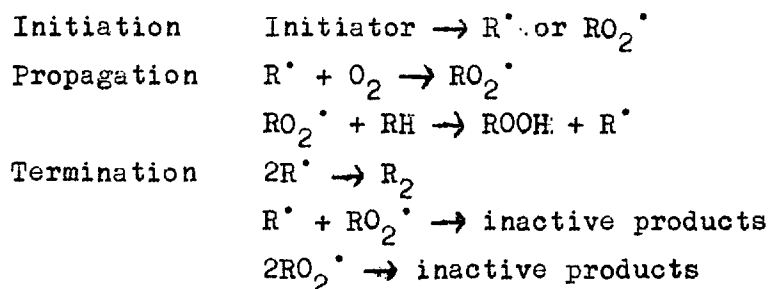
Criegee, Pilz, and Flygare (1939)⁹ prepared a peroxide from cyclohexene by oxidation under the influence of ultra-violet light and found that it still contained one double bond per molecule

(4)

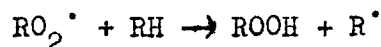
and was reduced by sodium amalgam to cyclohexen-3-ol. They therefore concluded that the compound was an α -hydroperoxide. Farmer and Sundralingam (1942)¹⁰ confirmed these conclusions and showed that the primary autoxidation products of 1-methyl and 1,2-dimethyl cyclohexenes were also α -hydroperoxides. Farmer and Sutton (1942)¹¹ extended this work to the polyisoprenes dihydrofarnesene, dihydromyrcene and squalene, concluding that the primary reaction was again production of hydroperoxide by attack of an α -methylene group and that any loss of unsaturation was due to secondary autoxidative changes such as the thermally promoted reaction of hydroperoxide with olefin at the double bond to give alcohol and epoxide, chain scissions at the double bond giving carbonyl compounds, subsidiary scissions of C-C single bonds, and polymerisation reactions.¹² Bolland (1949)¹³, in a review, showed that the general rate equation

$$\text{Rate} = R_i^{\frac{1}{2}} k [RH] [O_2] \frac{1}{k' [RH] + [O_2]}$$

was applicable to olefin oxidation, where R_i is the initial rate of formation of chain carriers. The kinetic characteristics of this equation were accounted for by the chain mechanism:



The influence of olefin structure on the products of oxidation was shown to be largely due to its effect on the rate constant and activation energy of the reaction



(eg. Bateman and Gee¹⁴). In this way, for example, the effect of the introduction of methyl substituents at the double bond and in the α positions on α -methylenic activity was readily explained. In particular, the values of rate constants and activation energies obtained illustrate the following interesting effects.

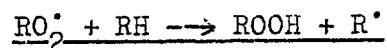
- a) Increase of methyl substitution at the double bond increases α -methylenic activity (Table 1.1 egs. (i)-(iii))
- b) In unsymmetrical methyl-substituted olefins, the α -CH₂ further from the methyl substituent is activated, that nearer being very slightly inactivated. (Table 1.1 egs. (iv), (v))
- c) The degree of substitution of the α grouping itself influences its reactivity. The strength of $\alpha\beta$ C-H bonds is in the order primary > secondary > tertiary. (Table 1.1, egs. (v), (vi), (vii)) The point of attack of α -substituted olefins is determined by such bond strengths. (cf. the work of Cullis, Hardy and Turner on paraffins^{15,16})

Less work has been done on the propagation step $R^\cdot + O_2 \rightarrow RO_2^\cdot$, but such radical additions are less sensitive to the structure of R than are exchange reactions such as $RO_2^\cdot + RH \rightarrow RO_2H + R^\cdot$.

The results of many other workers (eg. Atherton and Hilditch (1944)¹⁷, Bawn, Pennington and Tipper (1951)¹⁸ and Bateman (1954)¹⁹) are all in agreement with the general theories of olefin autoxidation postulated by Farmer, but it should perhaps be pointed out that the "hydroperoxylation theory" of autoxidation is based on results obtained predominantly from cyclohexenes and rubber models rather than simple acyclic mono-olefins.

TABLE 1.1.

THE INFLUENCE OF METHYL SUBSTITUTION IN THE RATE
CONSTANT AND ACTIVATION ENERGY OF THE REACTION

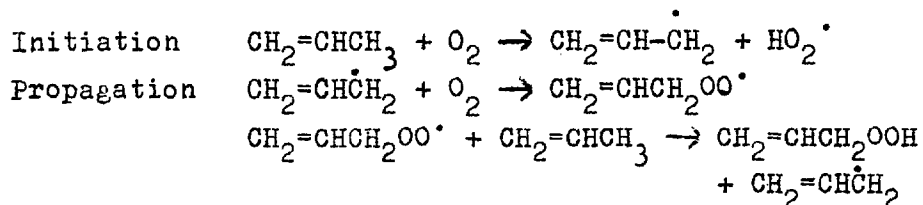


Structure	k_3 mole ⁻¹ litre sec ⁻¹	E_3 Kcal/mole	$D_{\text{C-H}}$ Kcal/mole
(i) $\text{RCH}_2\text{CH}=\text{CH}_2$	1.35	11.6	85.0
(ii) $\text{RCH}_2\text{CH}=\text{CHCH}_3$	4.2	10.0	80.9
(iii) $\text{RCH}_2\text{CH}=\text{C}(\text{CH}_3)_2$	20	7.9	75.5
(iv) $\begin{array}{c} \text{(b)} \quad \text{(a)} \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \\ \quad \quad \quad \\ \quad \quad \quad \text{(c)}\text{CH}_3 \end{array}$	$\begin{array}{l} \text{(a)} \ 12.6 \\ \text{(b)} \ 5.0 \\ \text{(c)} \ 1.72 \end{array}$	$\begin{array}{l} 8.5 \\ 9.7 \\ 11.2 \end{array}$	$\begin{array}{l} 77.1 \\ 80.2 \\ 84.0 \end{array}$
(v) $\text{-CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$	5.0	9.7	80.2
(vi) $\begin{array}{c} \text{RCH}=\text{CH}-\text{CH}- \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}_3 \end{array}$	16.2	8.1	76.1
(vii) $\text{RCH}=\text{CH}-\text{CH}_3$	1.72	11.2	84.0

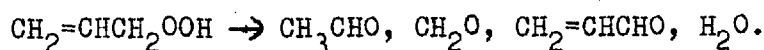
* Position of attack.

Gaseous oxidation: work in support of theory I.

Mulcahy and Ridge (1953)²⁰ studied the oxidation of propylene and considered that the fundamental mechanism involved α -H abstraction as initiation.



followed by degenerate chain-branching:



If these reactions were the only ones taking place, it might be expected that the induction period would be terminated when the hydroperoxide concentration reached some critical value. Batten and Ridge (1955)²¹ proved experimentally, however, that this was not so.

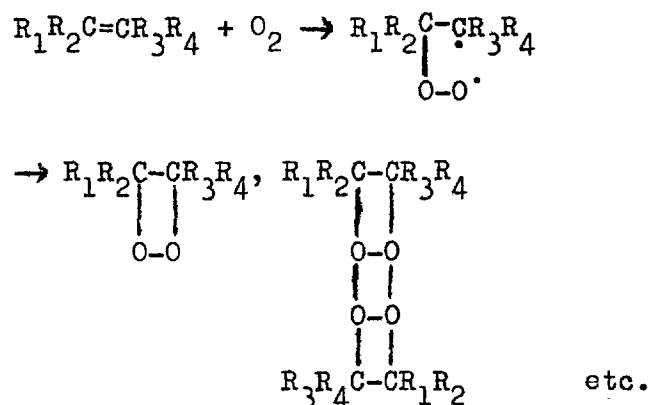
Mullen and Skirrow (1958)²² showed that the pressure-time curves of the gas-phase oxidation of propylene between 340° and 400° are sigmoid, being similar to those obtained during the slow combustion of paraffins. These workers agreed with the initiation and propagation steps proposed by Mulcahy and Ridge, but postulated that acetaldehyde, not hydroperoxide, was the agent responsible for chain-branching.

Blundell and Skirrow (1958)²³ studied the gas-phase oxidation of butene-2; their results give no unambiguous indication of the initiation reaction, but are compatible with initiation by hydrogen abstraction. These workers found no crotonaldehyde in the reaction products, so that the hydroperoxide $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{OOH}$ is presumably not formed

and the radical $\text{CH}_3\text{CH}=\text{CH}-\dot{\text{C}}\text{H}_2$ which would be produced by α -hydrogen abstraction must isomerise completely to $\text{CH}_3-\dot{\text{C}}\text{H}-\text{CH}=\text{CH}_2$ before reacting with oxygen. The results of Skirrow (1958)²⁴ using hexene-1 as fuel also support such a mechanism.

II) Addition of molecular oxygen as the initiation step.

The possibility of direct attack of oxygen at the double bond of an olefin has long been considered as an initiation mechanism. The reaction may be represented

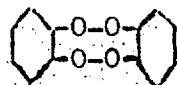


Any attempt to study such a reaction, however, will normally be masked by initiation by hydrogen abstraction occurring simultaneously, making the effects of these two modes of initiation difficult to separate. Much of the evidence in favour of the occurrence of initiation by oxygen addition must needs therefore be 'negative', depending on deviations from the results expected if a hydrogen abstraction mechanism alone were operative.

Liquid-phase oxidation: work in support of theory II.

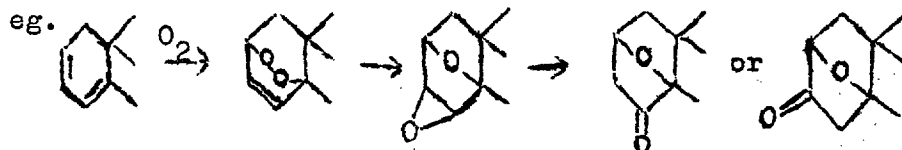
Cyclic peroxides of the type $\text{R}_2\underset{\text{O}-\text{O}}{\underset{|}{\text{C}}}-\text{CR}_2$ were first postulated

by Engler (1897)²⁵. Staudinger (1925)²⁶ suggested an addition mechanism for the autoxidation of 1,1-diphenyl ethylene, the cyclic peroxide breaking down to give formaldehyde and benzophenone. Stephens (1928 and 1933)^{27,28} studied the autoxidation of cyclohexene, finding a dimeric material of peroxidic properties which may have been

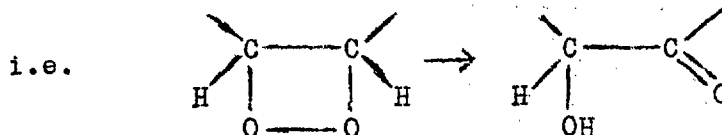


although this is doubtful^{9,10}.

The formation of cyclic peroxides by the transannular addition of oxygen across conjugated double bonds is well established, eg. for terpinene, 2,4-cholestadiene, ergosterol, dehydroergosterol, rubrene, naphthacene, pentacene and anthracene (Ref. 29, see also 30, 31, 32.) Frequently ketonic products are formed from such cyclic peroxides,

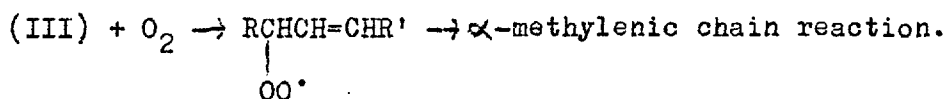
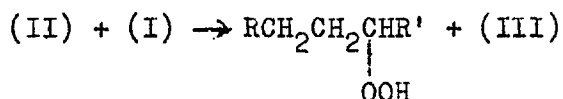
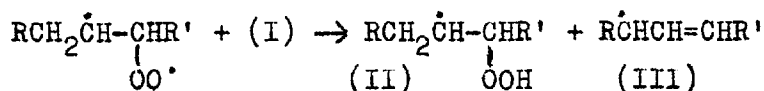
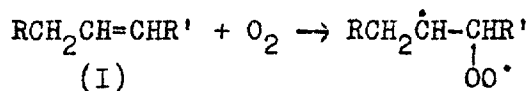


and Morrell (1940)³³ suggests that certain of the ketonic products found in the autoxidation of drying oil acids and glycerides are formed in a similar way.



Farmer¹² also considers that cyclic peroxides may be formed by the direct addition of oxygen to olefins with no α -methylene group, and may be responsible for chain scission to carbonyl compounds.

Bolam, Sim et al. (1942)^{34,35} postulated the formation of ketol in methyl linoleate oxidation from cyclic peroxide, and criticised Farmer's suggestion that ROOH is responsible for chain scissions¹². They state that such scissions occur so easily that some much more effective oxidising agent (such as oxygen) must be responsible. Atherton, Gunstone and Hilditch (1944-5)^{17,36}, considered that the primary autoxidation product of methyl oleate was hydroperoxide at 20°C, but cyclic peroxide at 120°C. Paquot (1945)³⁷ suggested that the autoxidation of olefins may lead to two kinds of peroxidic compound simultaneously, both H-abstraction and O₂-addition initiations being operative. It is pointed out by Farmer (1946)³² that if oxygen were to begin its attack at the double bond by addition, and thereafter continue substitutive attack, the energy required would be considerably reduced. There is then, he considers, perhaps good justification for postulating universal initiation for autoxidative attack by addition at C=C and for formulating the α-methylenic reaction by the scheme:

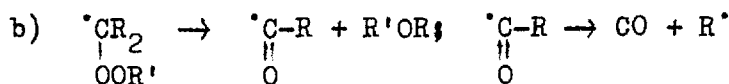
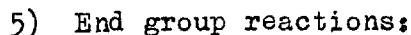
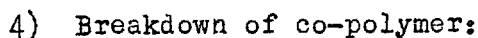


As thus envisaged the extent of actual addition at C=C would be insignificant but sufficient to start chains. It may be mentioned that both Mukherjee³⁸ and Blundell and Skirrow²³ have made similar suggestions, the latter with reference to gaseous oxidation reactions.

Several workers have studied hydroperoxide yields in autoxidation reactions, and frequently found that even in the early stages of reaction, where secondary autoxidation is relatively unimportant, a significant proportion of the peroxides formed was not hydroperoxide. Thus, for example, Swern et. al.³⁹ found 28% of the peroxides formed during the autoxidation of methyl oleate were not hydroperoxide (by comparison of chemical and polarographic analyses).

The peroxide concentrates were reduced and the reduction products were found to contain an α -glycol whose concentration was, in some cases, equivalent to (total peroxide - hydroperoxide). The other peroxide present was therefore considered to be cyclic. Furthermore, Hargrave and Morris (1956)⁴⁰ autoxidised more than twenty olefins and showed that the yields of hydroperoxide varied between 42 and 100%. These yields decreased as hydrogen abstraction became less facile; particularly striking was the reduction caused by methyl substitution at the double bond, especially anomalously low yields of ROOH being produced from olefins with trisubstituted double bonds. The authors suggested fast molecular scission to ketones and alcohols. Such scission could well involve cyclic peroxides. It may be mentioned here that epoxides, not hydroperoxides, are found to be the major products in the autoxidation of 2,2,4,tri-methyl-pentene-1,⁴¹ mesityl oxide, trichloroethylene^{42,43,44}, tetrachloroethylene^{45,46,47}, and (in general) olefins of the general formula $RR'C=CH_2$ ⁴⁸.

i.e. 1) Formation of some peroxy radicals, $R'O_2^{\cdot}$ (by hydrogen abstraction followed by addition of oxygen to the radical $R'^{\cdot}$).

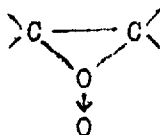


The final products formed would be very similar to those which would result from molecular addition of oxygen to the olefin and breakdown of the resulting cyclic peroxide. Much of the liquid-phase work supporting initiation by oxygen addition may thus be capable of alternative explanation. However, it is difficult to see how large co-polymers could be formed in gas-phase reaction at sub-atmospheric pressures, so that the above co-polymerisation mechanism cannot effectively explain

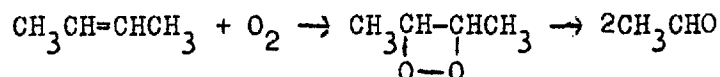
the gas-phase results supporting the 'oxygen addition' mechanism.

Gas-phase oxidation: work in support of theory II.

Lenher (1932)^{49,50} postulated that oxygen could activate the double bond of ethylene or propylene and thus react to give a compound of the form



Lucas, Prater and Morris (1935)⁵¹ oxidised butene-2, and failed to find methyl ethyl ketone among the products. They therefore rejected a hydroperoxylation mechanism and accounted for acetaldehyde, the major product, via a cyclic peroxide



Dobrinskaya and Neiman (1947)⁵² also postulated this mechanism for butene-2 oxidation, considering it to occur concurrently with the more usual hydroperoxylation mechanism. These workers, in contrast to Blundell and Skirrow²³, found some crotonaldehyde among the reaction products.

Szabo (1957)⁵³ has compared the iodine-catalysed oxidations of ethane and ethylene. In the case of ethane it is found that the concentration of iodine present affects the initiation reaction but not the chain branching, the rate equation being

$$\frac{d\Delta p}{dt} = \underset{\text{initiation}}{n_0 \nu (1 + c[I_2])} + \underset{\text{branching}}{\phi \Delta p}$$

With ethylene however, the equation is

$$\frac{d\Delta p}{dt} = \underset{\text{initiation}}{n_o v} + \underset{\text{branching}}{(\phi + a[I_2]) \Delta p}$$

i.e. the iodine affects the branching, not the initiation. Thus the initiation mechanisms of ethane and ethylene oxidation are unlikely to be similar, and the latter does not, therefore, involve abstraction of hydrogen. Initiation of ethylene oxidation by oxygen addition is plausible, as the addition of iodine as a catalyst would not affect the rate of this process. It is thought that iodine accelerates branching by reacting reversibly with some free radicals, thus preventing their recombination.

The present work.

Considerable controversy has taken place concerning the mode and point of oxidative attack of olefins by molecular oxygen, and there is much support for each of the two initiation mechanisms mentioned above. The influence of olefin structure is such that 'hydrogen abstraction' appears to take place to a major extent when an α -methylene group is present. Hydrogen abstraction from tertiary centres is also known to be particularly easy.

This thesis describes a detailed investigation of the slow combustion of 2-methyl-but-2-ene. With this compound there is no ambiguity as to cis- and trans- isomers. Furthermore, the molecule contains no α -methylene group, having only α -methyl groups which are relatively stable to oxidative attack. Thus there might be a reasonably even competition between the two different modes of initial attack, and the products derived from one mode should not completely swamp the products derived from the other.

1C. Use of the technique of isotopic labelling.

The mechanistic evidence obtained by conventional analysis of combustion products is somewhat indirect, mainly because the simple structures of some of these compounds do not allow unequivocal deductions to be made about their mode of formation. The great advantage in using isotopically labelled fuels is that, however simple or complicated the structure of the combustion products, the origin of any hydrogen and carbon they contain can be traced with certainty. Tracer techniques are thus potentially very powerful, but as yet have been little used in the field of hydrocarbon combustion.

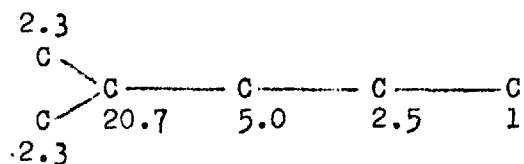
The isotopes which have been commonly employed to 'label' organic fuel molecules are deuterium, tritium, carbon-13 and carbon-14 (^{14}C). Carbon-14 has been used most widely; it has the great advantage of being radioactive, emitting soft β -rays, so that its detection and estimation in reactant and reaction products is relatively straightforward, conventional methods of radioassay being applicable and the attendant radiation hazards being small. Some examples of the use of ^{14}C as a 'label' in hydrocarbon oxidation reactions are given below.

I) Paraffin oxidation.

The oxidation of methane was studied by Moshkina, Galanina and Nalbandyan⁵⁴ who used ^{14}C to determine the relative rates of formation of formaldehyde and methyl alcohol during the reaction, and showed that these two products were formed by parallel routes. Neiman, Lukovnikov and their co-workers have studied the oxidation of ^{14}C -labelled hydrocarbons including propane^{55,56}, butane^{56,57} and pentane⁵⁶, investigating in particular the extent of

formation of formaldehyde, acetaldehyde and oxides of carbon from the various skeletal positions of these hydrocarbons. The object of their work on propane was to test the truth of a radical isomerisation mechanism previously put forward by Semenov⁵⁸, with which their results accorded well. The results of their studies of the oxidation of $[1-^{14}\text{C}]$ n-pentane and $[3-^{14}\text{C}]$ n-pentane showed that the acetaldehyde produced was unlikely to contain the central carbon atom of n-pentane and that oxides of carbon were more likely to be derived from the central rather than the terminal position in this molecule.

Cullis, Hardy and Turner^{15,16} labelled in turn each of the skeletal positions of 2-methyl-pentane with ^{14}C and subjected to radioassay the oxides of carbon and the ketones produced during the slow combustion of these labelled compounds with a deficit of oxygen. They showed that carbon monoxide was derived principally from the 3- and 4- positions and that ketones arose almost exclusively as a result of oxygen attack at the tertiary centre. From these results it was possible to deduce the relative probabilities of oxygen attack at the different skeletal positions in 2-methyl-pentane. The figures for combustion at 242°C are shown below:



It was concluded that while attack is most frequent at the tertiary centre in 2-methyl-pentane, the intermediate so formed does not lead to efficient chain-branching. Secondary centres are considered to be the most effective points of attack. Attack at end-groups is comparatively unimportant.

II) Olefin oxidation.

^{14}C -tracer studies of the gas-phase oxidation of olefins have been largely confined to the first two members of the homologous series, ethylene and propylene. The uncatalysed oxidation of $[2-^{14}\text{C}]$ propene was studied by Lukovnikov and Neiman⁵⁹. The $[2-^{14}\text{C}]$ propene was oxidised using an equimolar amount of atmospheric oxygen, the kinetic path of the reaction being followed by observing the resulting change in the total pressure. Analysis of the oxidation products was carried out both at the beginning and at the end of the period of rapid reaction, and a stepwise scheme was proposed to represent the progress of the oxidation. The synthesis of ^{14}C -labelled propylene, its oxidation, and the chromatographic separation and radioassay of the reaction products were later reviewed by Lukovnikov⁶⁰.

This application of isotopic tracer techniques to the study of propylene oxidation was extended by Neiman, Lukovnikov et al.⁶¹. Propylene was oxidised in the presence of $[^{14}\text{C}]$ carbon monoxide and $[1-^{14}\text{C}]$ acetaldehyde and the specific activities of carbon monoxide and carbon dioxide were measured as functions of time. It was shown that only 3-4% of the carbon dioxide formed was derived from carbon monoxide and that 50% of the carbon dioxide and 30% of the carbon monoxide were formed from the carbonyl group of the acetaldehyde.

Margolis and his coworkers have studied the catalysed oxidation of simple ^{14}C -labelled olefins (particularly ethylene) over various catalysts. Margolis and Roginskii⁶² investigated the selectivity of silver and vanadium pentoxide as catalysts for ethylene oxidation. They introduced carbon-14 into the original ethylene and added unlabelled intermediate products of oxidation such as ethylene oxide and acetaldehyde. They also studied the variation in yields and specific activities of ethylene oxide

and carbon dioxide as the silver-catalysed oxidation of the labelled olefin proceeded. The specific activity of the carbon dioxide was found to be several times greater than that of ethylene oxide. Thus the carbon dioxide cannot be formed entirely from ethylene oxide in the manner suggested by Todes and Andrianova⁶³. Kinetic data, however, show that the ethylene oxide concentration passes through a maximum after ca. 20 minutes reaction, at which stage the rate of formation of carbon dioxide passes through a maximum. It is therefore very probable that some of the carbon dioxide formed is produced via ethylene oxide. Thus on the basis of the results obtained it is possible to suppose that the formation of carbon dioxide proceeds simultaneously and independently both through ethylene oxide and through other intermediate products (possibly peroxides). The results thus support the theories of Twigg⁶⁴. The relative importance of these two routes is influenced by macroscopic factors and also by a change in the activity of the catalyst. On selective poisoning of the silver catalyst by addition of an excess of ethylene oxide, the formation of the latter is suppressed, the alternative route to carbon dioxide being favoured.

Margolis and Roginskii further investigated, using a ¹⁴C-tracer technique, the role of ethylene oxide in ethylene oxidation⁶⁵ and attempted to account for its absence in the products of metal oxide-catalysed oxidation. They showed that ethylene oxide intensifies the formation of carbon monoxide but retards complete oxidation to carbon dioxide over such catalysts. Furthermore, ethylene oxide affects the kinetics of acetaldehyde oxidation and breakdown over vanadium pentoxide. These workers also studied the role of aldehydes in ethylene oxidation⁶⁶. Mixtures of ethylene and acetaldehyde were oxidised catalytically, each constituent in turn being labelled

with carbon-14. The presence of the aldehyde increased the rate of formation of carbon dioxide by a factor of 1.7 and rendered the rates of formation of carbon oxides independent of the ethylene concentration. The oxidation of ethylene and propylene over metal oxides (vanadium pentoxide, vanadium tetroxide and magnesium chromite) was further studied by Margolis and Plyshevskaya⁶⁷ who used oxygen-18 as a 'label' and showed that the formation of aldehydes proceeds largely at the expense of the oxygen content of the catalyst.

The mechanism of the oxidation of simple ^{14}C -labelled olefins using metals and semiconductors as catalysts was further investigated by Margolis and Roginskii⁶⁸. Complete oxidation to carbon dioxide and water, selective oxidation of a part of the hydrocarbon not involving the double bond, and selective addition of oxygen to the double bond were studied, and the results of oxygen-18 and carbon-14 labelling methods suggested that neither ethylene oxide nor acetaldehyde was the principal intermediate product under these conditions. A reaction scheme involving the ions O_2^- , O^- , and the ionised oxygenated compounds RO_2^- , RO^- was proposed for such catalytic processes.

Gal and his coworkers used $[1-^{14}\text{C}]$ styrene to study
 a) the oxidation of styrene in solution⁶⁹, and
 b) the inhibition by styrene of n-hexane combustion⁷⁰.

The carbon-14 was found in the combustion products of n-hexane, indicating that the inhibitor decomposed in the course of the reaction.

The present work.

Kinetic and analytical studies of the slow combustion of 2-methyl-but-2-ene are described in Part 2 and discussed in Part 3 of this thesis. From these results, it was possible

to make a number of deductions concerning the mechanism of certain of the steps involved in the reaction. In order to test the correctness of some of the suggestions put forward, 2-methyl-but-2-ene was labelled with carbon-14 in the 2- and 4-positions in turn, and the resulting labelled olefins were oxidised under conditions similar to those used in the kinetic studies. The fate during the reaction of the carbon atoms in these two positions could thus be traced. The results of this study are presented in Part 4 and discussed in Part 5.

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KINETIC AND ANALYTICAL STUDIES: EXPERIMENTAL METHODS
AND RESULTS.

2A. SYNTHESIS OF 2-METHYL-BUT-2-ENE.

I Dehydration of tertiary amyl alcohol.

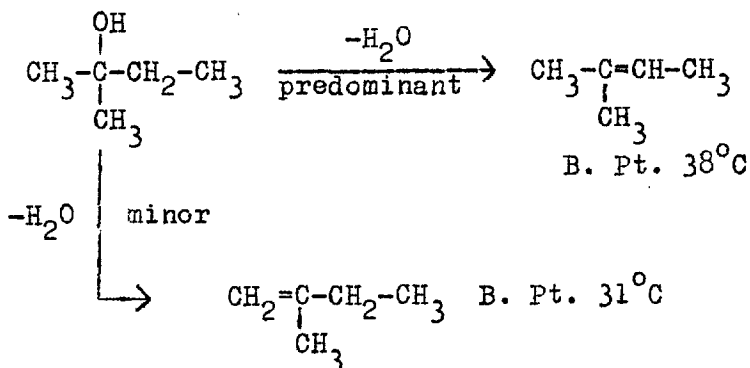
The preparation of 2-methyl-but-2-ene by dehydration of t-amyl alcohol has been studied by many workers (eg. references 71,72,73,74). A variety of dehydrating agents, including hydrogen iodide, hydrogen bromide and aniline hydrochloride, and iodine and sulphuric acid, has been used. In the present work, it is desirable to use the mildest dehydrating agent which will produce the olefin in good yield, in order to minimise the danger of molecular rearrangements which would decrease the radioactive purity of the ^{14}C -labelled olefins to be synthesised (Part 4 Section A). In this connection the use of potassium hydrogen sulphate (fused, ground and dried) and of iodine was investigated, but these agents produced olefin in low yields (< 40% theoretical). It was therefore considered necessary to use a somewhat stronger dehydrating agent, and sulphuric acid (33% by volume) was therefore employed (compare reference 74). Tertiary amyl alcohol was dried with sodium sulphate (a more vigorous drying agent such as calcium oxide or magnesium perchlorate may effect some dehydration) and fractionally distilled using a ten-inch fractionating column. The fraction boiling between 101°C and 103°C was collected, and impurities were determined by three methods:

- (i) Refractive index measurements gave $n_{\text{D}}^{25} = 1.4024$;
Cf. literature, $n_{\text{D}}^{25} = 1.4025$.
- (ii) Microanalytical determination of carbon and hydrogen gave C, 68.07%; H, 13.58%; $\text{C}_5\text{H}_{12}\text{O}$ requires C, 68.13%;

H, 13.72%.

- (iii) Gas-liquid chromatographic analysis, using polyethylene glycol Mol. Wt. 400 as the stationary phase (the apparatus and method are described fully in Section B) showed that no impurities, except possibly $< \frac{1}{2}\%$ water, were present.

35ml of the t-amyl alcohol, thus purified, was treated with 120ml of 33% by volume sulphuric acid. On gentle heating, a product with a boiling range of 35-41°C distilled. This crude product was refractionated with 20ml of 33% v/v sulphuric acid, then again alone, producing an olefin with a boiling range of 37-40°C. Gas-liquid chromatographic analysis (using polyethylene glycol as the stationary phase) showed that t-amyl alcohol was absent, but that a small quantity (ca. 3%) of one impurity was present. This impurity was probably an isomer of 2-methyl-but-2-ene as it was not well separated from this olefin on the column used. The isomer most likely to be present is 2-methyl-but-1-ene, produced by



II Separation of 2-methyl-but-1-ene and 2-methyl-but-2-ene.

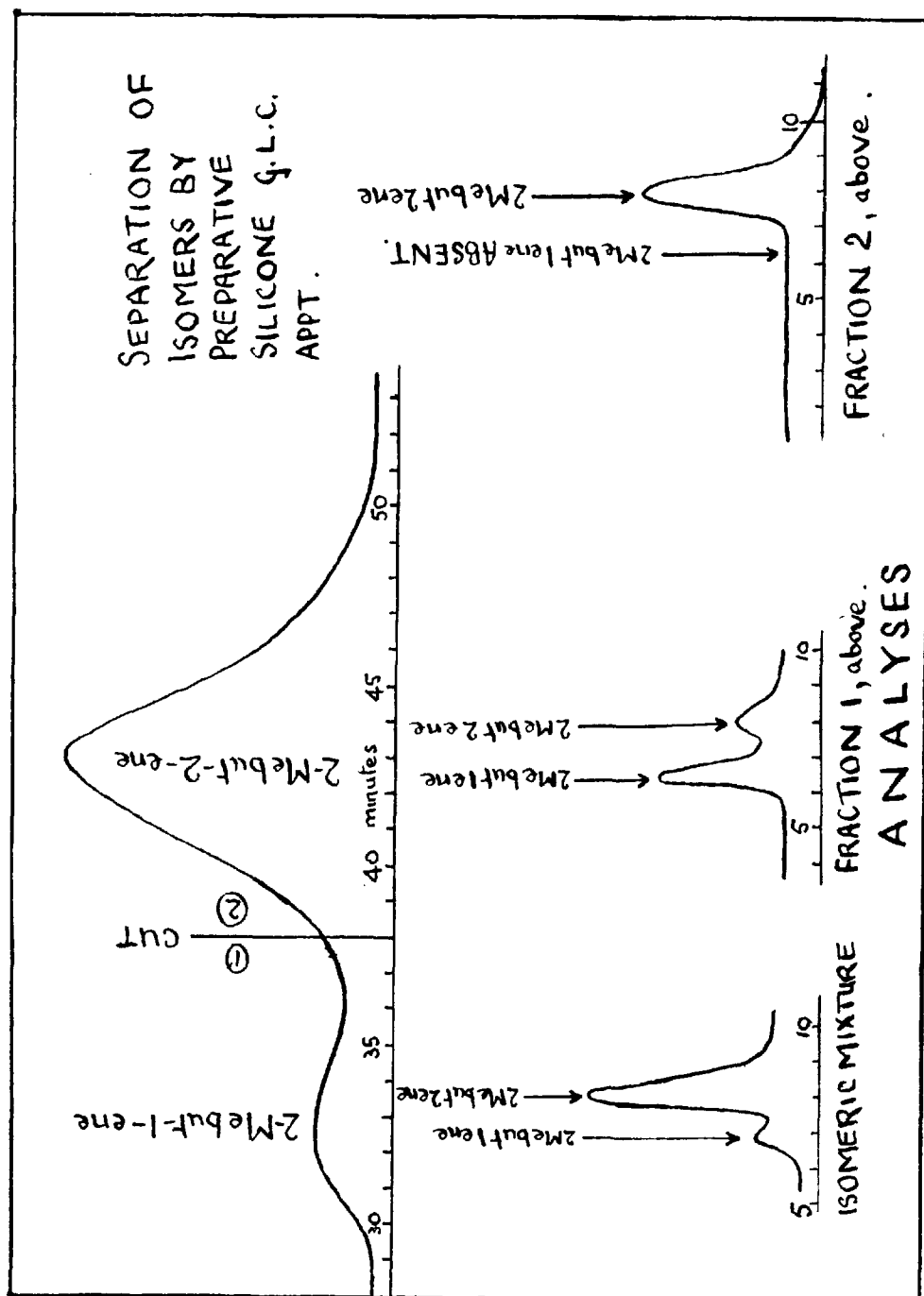
Attempted separation of these isomers by efficient fractional distillation was unsuccessful. As no improvement in purity was achieved by this method, the isomers probably form a

constant boiling mixture.

It was found that the isomers were quite well separated by a gas-liquid chromatographic analytical column with dinonyl phthalate as the stationary phase. A preparative scale gas-liquid chromatographic column was therefore constructed (length 3 metres, diameter 1.6 cm, stationary phase 8% by weight dinonyl phthalate on 40-60 mesh sodium chloride as solid support). Nitrogen was used as carrier gas. A 'dielectric constant change' detector⁷⁵, which was more highly sensitive towards the impurity, 2-methyl-but-1-ene, than towards the major constituent, 2-methyl-but-2-ene, was employed. Some separation was achieved with this apparatus, but the overlap of the two olefin peaks obtained necessitated rejection of at least 25% of the 2-methyl-but-2-ene for collection of a pure sample to be possible.

An analytical g.-l. c. column with 5% by weight of silicone grease on celite 545 as stationary phase was found to separate the isomers well. A preparative scale column (length 5.1 metres, diameter 1.6 cm, containing sodium chloride impregnated with 5% by weight of silicone grease) was therefore built, and used in conjunction with the above carrier gas (inlet pressure 100 mmHg) and detector, the detection of eluents being automatically recorded. The design of this apparatus enabled samples as large as 3 ml. to be used. Good separation of 2-methyl-but-1-ene and 2-methyl-but-2-ene was achieved using this column. Samples of various eluent fractions were analysed using the above 'silicone' analytical column, and it was shown that 2-methyl-but-2-ene could be obtained free from 2-methyl-but-1-ene by rejection of only ca. 5% of the 2-methyl-but-2-ene. A typical chromatogram from the preparative column, together with analytical chromatograms of the fractions taken therefrom, is shown

FIG. 2.1. SEPARATION OF 2-METHYL-BUT-2-ENE AND 2-METHYL-BUT-1-ENE.



in fig. 2.1.

A microanalytical determination of the carbon and hydrogen content of a sample of the 2-methyl-but-2-ene thus prepared showed C, 85.58%; H, 14.33%; C_5H_{10} requires C, 85.63%; H, 14.37%. Refractive index measurements gave $n_D^{15} = 1.3906$, cf. literature, $n_D^{15} = 1.3908$.

III Storage of 2-methyl-but-2-ene.

The deterioration of 2-methyl-but-2-ene on storage in air has been studied by Bawn, Pennington and Tipper¹⁸ who report that, between 20°C and 50°C, the oxidation of samples exposed to air is very slow, less than 0.5% peroxide being detected after one year. The 2-methyl-but-2-ene used in the present studies was stored under air in a closed glass vessel at 0°C, and was generally used within six months after its preparation.

2B. GASEOUS OXIDATION OF 2-METHYL-BUT-2-ENE.I Apparatus.(a) The vacuum system.

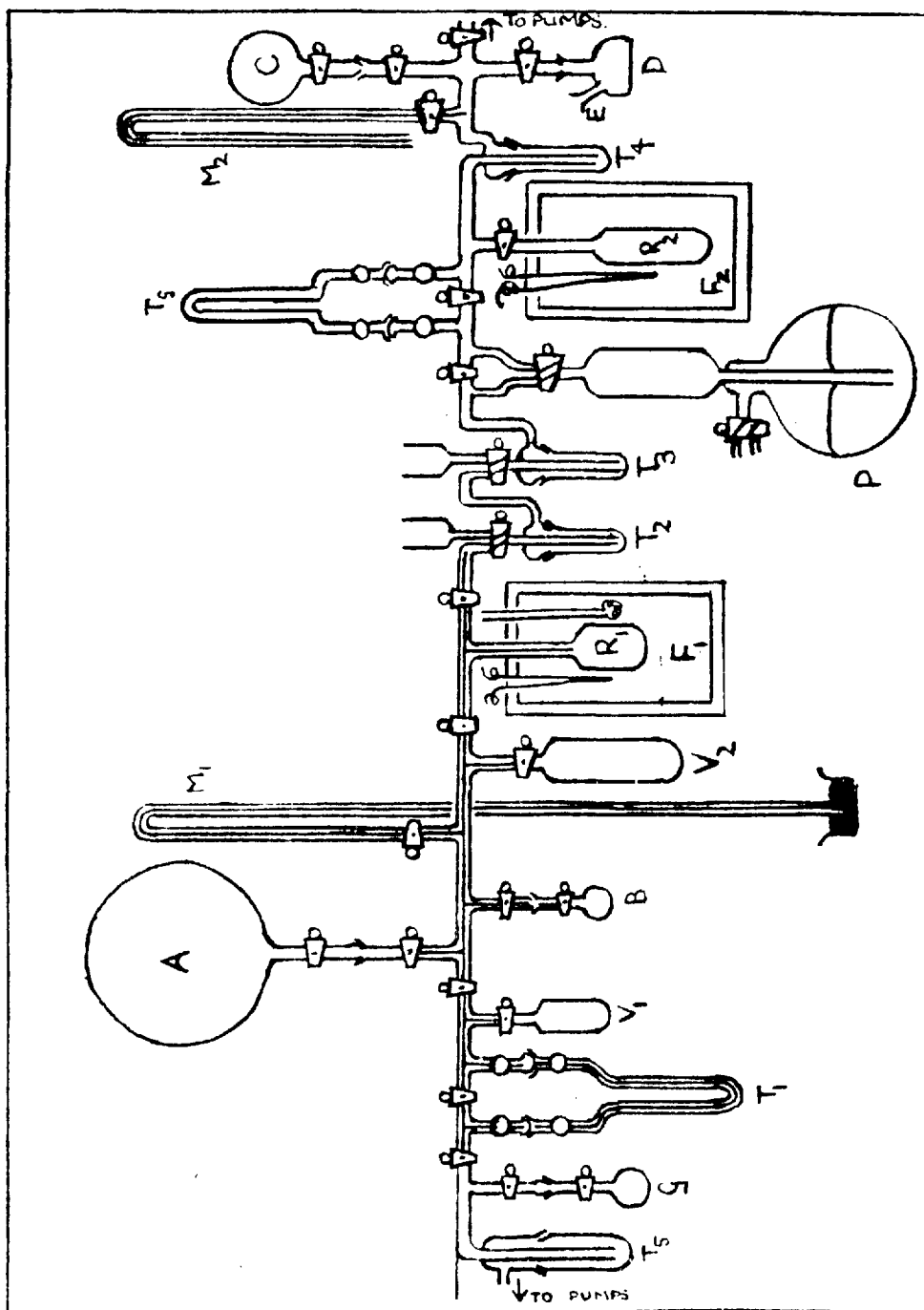
The vacuum system used for the gaseous oxidation studies is represented in diagrammatic form in fig. 2.2. The two cylindrical pyrex reaction vessels R_1 and R_2 were 9 cm. long and 6 cm. in diameter and 11 cm. long and 1.5 cm. in diameter respectively. Before being sealed to the vacuum line, each vessel was cleaned with hydrofluoric acid and with hot nitric acid; vessel R_2 was packed with 'wire form' cupric oxide. From time to time, reaction vessel R_1 was replaced. With each new vessel, reproducible kinetic measurements were obtained only after some thirty combustions had been carried out. Reagents were admitted to, and stored in, the system as follows.

- i) Oxygen from the cylinder was admitted to the system at G (fig. 2.2) and the gas was allowed to escape through B to the atmosphere. After a few minutes the gas stream was redirected to fill the evacuated admission section and finally Globe A. All taps were opened slowly in order to prevent the pressure at B falling below atmospheric.
- ii) Carbon dioxide was admitted through inlet D, and frozen into trap T_4 , which was cooled in liquid oxygen. D was then closed, and the carbon dioxide was allowed to evaporate through the manometer M_2 , the globe C being filled from the middle fraction.
- iii) Liquids were introduced into the apparatus at B or G. 2-methyl-but-2-ene, prepared and purified as in section A, was introduced in a 10 ml. flask

Key to Fig. 2.2.

A	Oxygen storage globe.
B	2-methyl-but-2-ene storage vessel.
C	Carbon dioxide storage globe.
D	Flask containing potassium hydroxide/ ethylene glycol solution.
F ₁ ,F ₂	Electric furnaces.
G	Liquids storage vessel.
M ₁ ,M ₂	Mercury manometers.
P	Topler pump.
R ₁	Reaction vessel.
R ₂	Reaction vessel packed with copper oxide.
T ₁ ,T _G	Detachable U-traps.
T ₂ ,T ₃ ,T ₄	Cold traps.
T ₅	Waste trap.
V ₁	Sharing vessel.
V ₂	Pre-mixing vessel.

FIG. 2.2. APPARATUS FOR STUDYING THE GASEOUS OXIDATION
OF 2-METHYL-BUT-2-ENE.



at B, and cooled in liquid nitrogen. The air above the liquid was pumped away, and the olefin itself was outgassed three times by successive freezing and pumping, leaving pure 2-methyl-but-2-ene in B. For the purpose of calibrating the gas-liquid chromatographic apparatus, it was necessary to collect known quantities of pure samples of likely reaction products in the U-tube T_1 . Each of such oxygenated compounds ('Analar' grade, redistilled) was introduced at B or G, the admission and purification procedure being similar to that described above.

(b) Vacuum lubricants.

In those parts of the apparatus having contact with organic vapours, all taps and ground glass joints were lubricated with high-vacuum silicone grease. In order to prevent condensation of combustion products, and to minimise absorption of these and the initial olefin by the lubricant, these parts of the apparatus were heated electrically by means of nichrome wire (17.1 ohms/yard). In addition to the backing pump, a single-stage diffusion pump was employed to facilitate rapid removal of any organic material which was so absorbed.

(c) The furnaces.

Two silica furnace tubes, F_1 and F_2 (fig. 2.2), were employed. The dimensions of these were 34 cm. long x 14 cm. diameter (F_1) and 28 cm. long x 5 cm. diameter (F_2). Each was wound with nichrome resistance wire (4.2 ohms/yard), lagged with asbestos wool and supported in an outer Sendanyo casing. In order to achieve a reasonably uniform temperature distribution along the whole length of the furnace

tubes, the spacing of the windings was arranged to compensate for the greater heat losses from the ends of the tube.

(d) Temperature measurement and control.

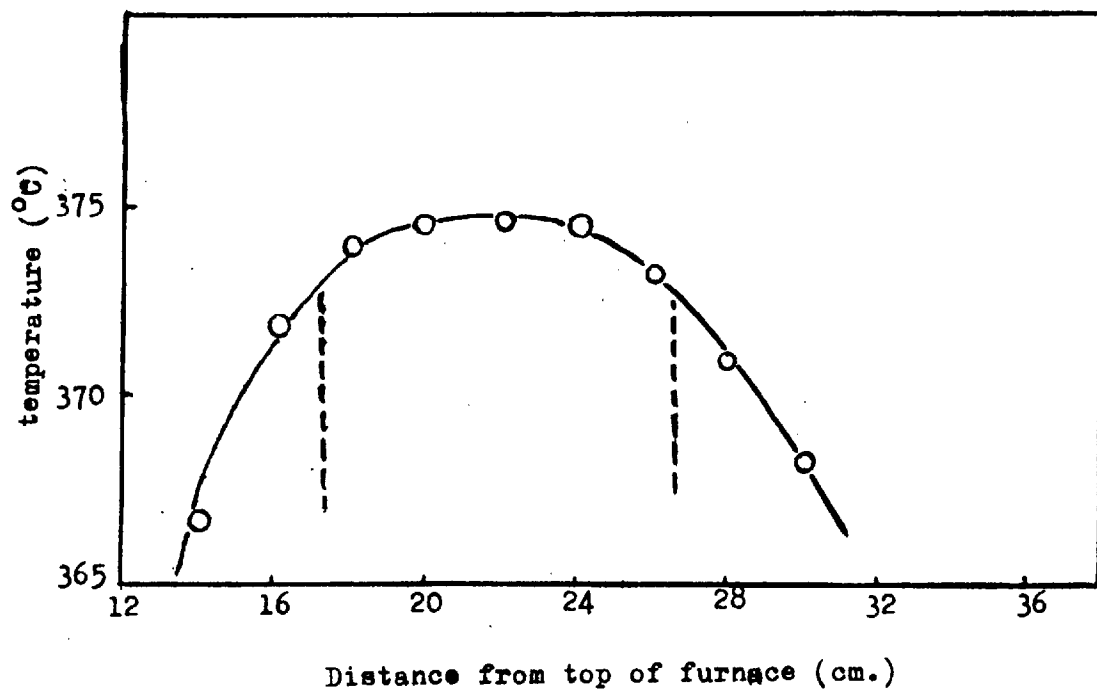
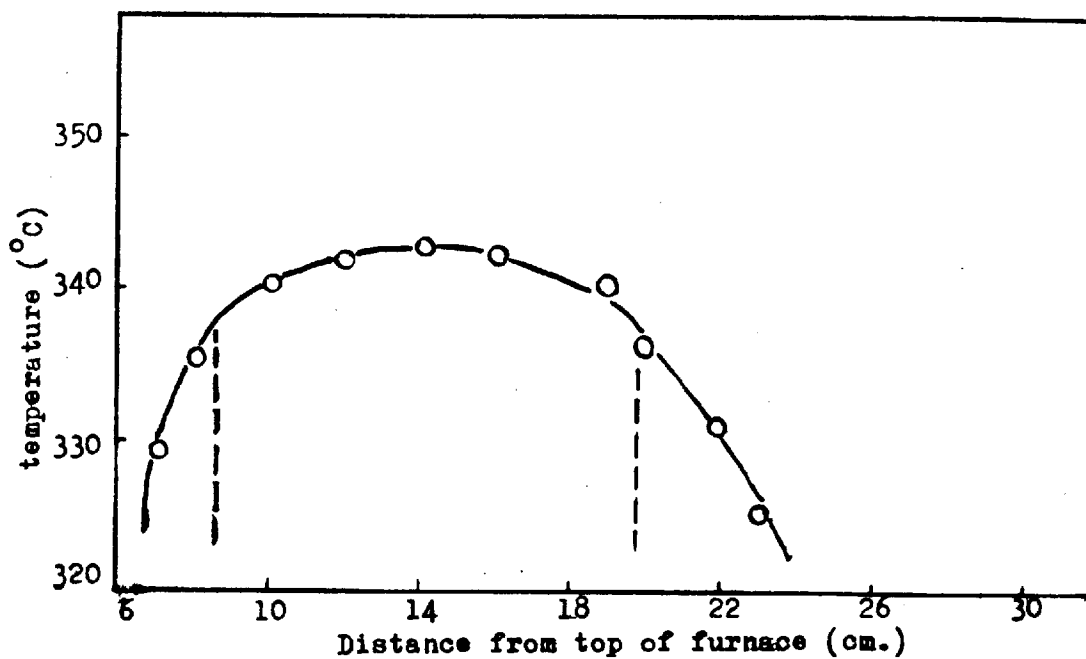
(i) Temperature measurement.

The temperature of each furnace was measured by means of a spot-welded chromel/alumel thermocouple connected to a potentiometer capable of reading to 0.005 mV (equivalent to 0.23°C in the range used). The leads from the hot junction were individually sheathed in thin pyrex tubing and these tubes were contained in a wider pyrex tube, sealed at the junction end, which was supported in the furnace so that its tip was close to the reaction vessel and mid-way along its length. The cold junction had its leads similarly enclosed in a glass tube which was immersed in melting ice. Both these thermocouples were calibrated periodically against a given platinum/rhodium thermocouple over the temperature range 100-400°C.

The distribution of temperature over the length of each furnace, and hence the most suitable position for each reaction vessel, was determined in the following way. With the furnace temperature steady at about 350°C, the hot junction of the thermocouple was moved in 1 cm. stages along the axis of the furnace tube. At each stage the junction was kept stationary until a constant e.m.f. was obtained. A graph was then constructed of temperature against the depth of the hot junction in the furnace (figs. 2.3 and 2.4). Each reaction vessel was then placed so that the temperature difference between its ends was a minimum.

(ii) Temperature control.

The power supplied to the furnace windings was controlled by a platinum resistance thermometer, situated in the furnace close to the centre of the reaction vessel and

Fig. 2.3. Furnace F₁Fig. 2.4 Furnace F₂

Key to Fig. 2.5.

The Roberts Controller.

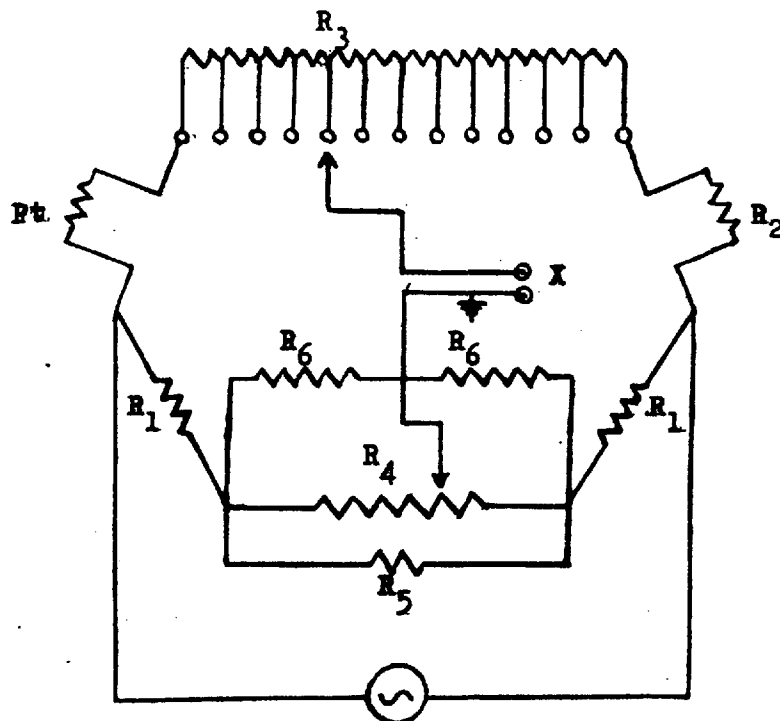
Pt	Platinum resistance (11 ohms at 25°C)
R ₁	21 ohms
R ₂	24 ohms
R ₃	12 x 1 ohm
R ₄	10 ohms
R ₅	1.6 ohms
R ₆	1000 ohms
X	Connected to a phase-sensitive circuit controlling the output to the Sunvic switch.

The Furnace Circuit.

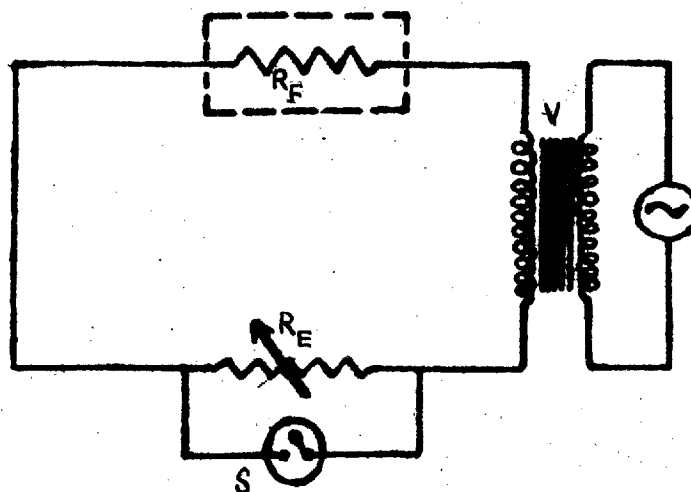
R _F	Resistance of furnace (ca. 70 ohms at 300°C)
R _E	External resistance (0-50 ohms)
S	Sunvic high vacuum switch
V	Variac transformer

FIG. 2.5. THE FURNACE TEMPERATURE CONTROL.

The Roberts Controller.



The Furnace Circuit.



connected to one arm of the Wheatstone bridge circuit⁷⁶ shown in fig. 2.5. The output from the bridge was fed into a Sunvic relay across which was connected an external variable resistance R_E . The temperature of the furnace was set as follows;

- 1) The coarse and fine adjustments (R_3 , R_4 respectively) on the controller were set at maximum.
- 2) The current flowing through the furnace was adjusted so as to produce a temperature about 10°C higher than desired.
- 3) R_3 and R_4 were then adjusted until the relay opened and the current fell to an extent dependent on the value of R_E (which was usually maintained at about 10% of the furnace resistance at that temperature).
- 4) When the temperature had fallen to the desired value, the fine adjustment R_4 was increased until the relay just closed restoring the current to its previous value.

(e) Analytical gas-liquid chromatographic apparatus.

(i) General description.

The gas-liquid chromatographic apparatus used was a commercial model manufactured by the 'Shandon' Scientific Co. Ltd., and incorporating the hydrogen flame detector originally devised by Scott⁷⁷.

The carrier gas was hydrogen containing 25% nitrogen in order to reduce the amount of longitudinal diffusion of the vapour in the gas stream. This was introduced through a special reducing valve to the capillary flow meter and thence to the column (fig. 2.6.). The copper column was attached to both gas inlet pipe and combustion chamber by standard petrol pipe connections. Both the column and the combustion chamber were immersed in the vapour jacket. The gas passed

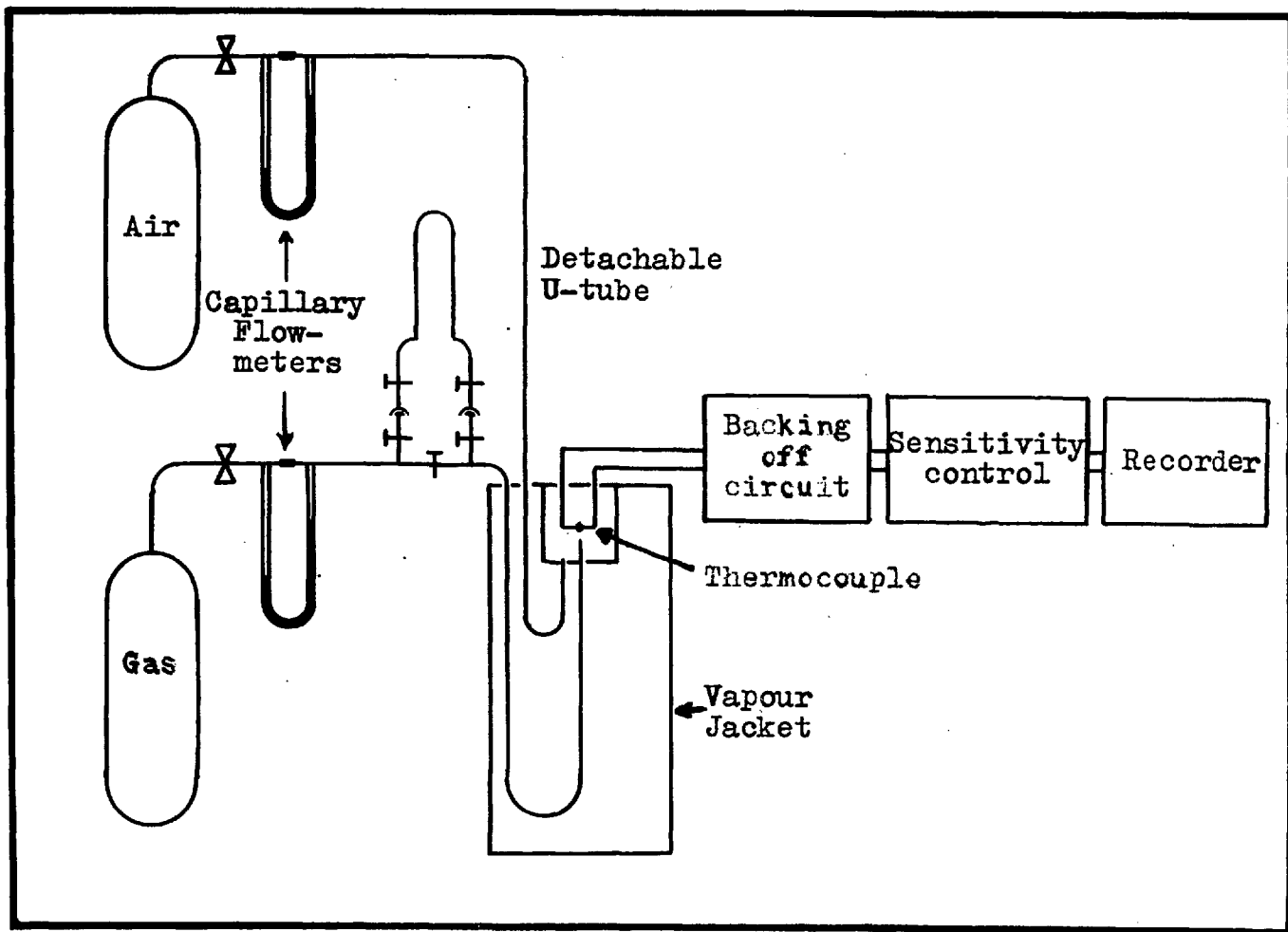
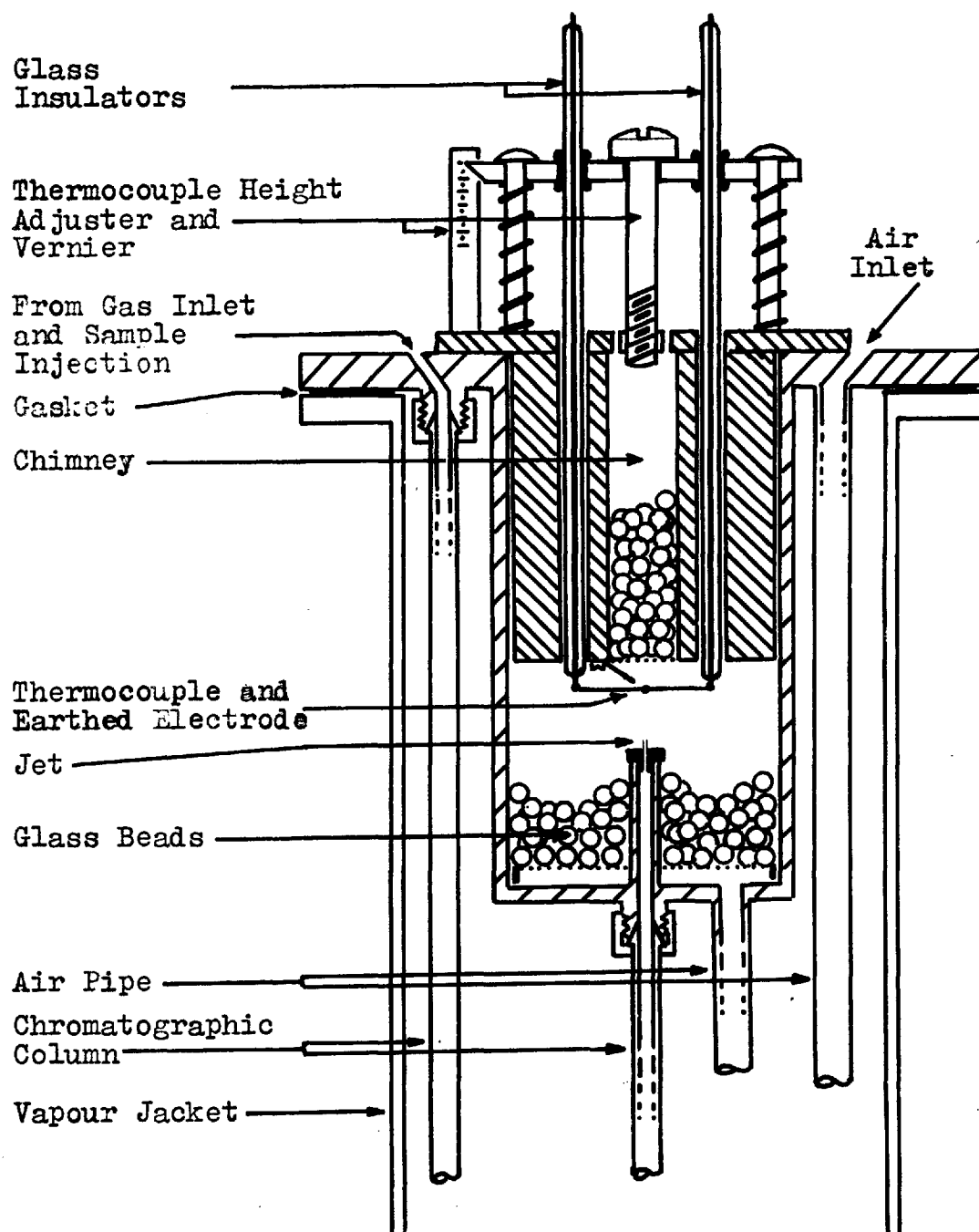


Fig. 2.6, THE GAS-CHROMATOGRAPHY APPARATUS.

Fig. 2.7, THE THERMOCOUPLE DETECTOR.

from the column, through the centre of the combustion chamber base and then through a short length of pipe to the jet. Air was led from a needle valve through another capillary flow meter and a pipe situated in the vapour jacket, and then through another hole in the base of the chamber, being finally allowed to diffuse through porcelain beads to the hydrogen flame at the jet (fig. 2.7.).

The thermocouple was situated a few mm. above the jet (fig. 2.7.) and the gas was ignited by passing a high voltage electrical discharge from the thermocouple to an earthed electrode 1 mm. away. The thermocouple (gold-palladium/platinum-iridium) was supported from two copper wires sheathed in glass insulators. These insulators passed through the thermocouple housing which was a hollow chromium-plated brass cylinder containing, in addition to the two holes for the thermocouple leads, a central chimney filled with porcelain beads and an arrangement for adjusting the height of the thermocouple relative to the jet. The thermocouple housing fitted precisely into the combustion chamber which itself was bolted to the top of the vapour jacket.

The thermocouple leads were connected by a cable covered with an earthed sheath to a simple potentiometer arrangement by which the thermocouple output was balanced and the out of balance voltage fed to another potentiometer capable of reducing this voltage, if necessary, by a factor of 2, 5, 10 or 20. The final output was then fed into a Sunvic High Speed Potentiometric Recorder (full scale deflection = 1.0 mV).

(ii) The sample injection system.

The apparatus as manufactured used micropipettes for the injection of samples. This system was considered unsuitable for the introduction of accurate amounts of volatile substances and was replaced by the capillary glass U-tube (volume ca. 1 ml)

and the by-pass arrangement shown in the photograph (fig. 2.8.), which enabled the gaseous contents of the U-tube (which was heated electrically to ca. 100°C) to be swept rapidly onto the column⁸⁷.

(iii) The column.

(a) The fixed phase.

Polyalcohols, such as diglycerol⁷⁸, polyethylene glycol^{79,80,81} and polypropylene glycol^{79,80} have been found useful for separating a wide range of hydrocarbons and, especially, oxygenated organic compounds. In the present studies, a single column containing B.D.H. polyethylene glycol (Molecular weight 400) has been found to give satisfactory separation of a wide variety of condensable combustion products and to yield quantitative analytical data⁹⁰.

(b) The supporting material.

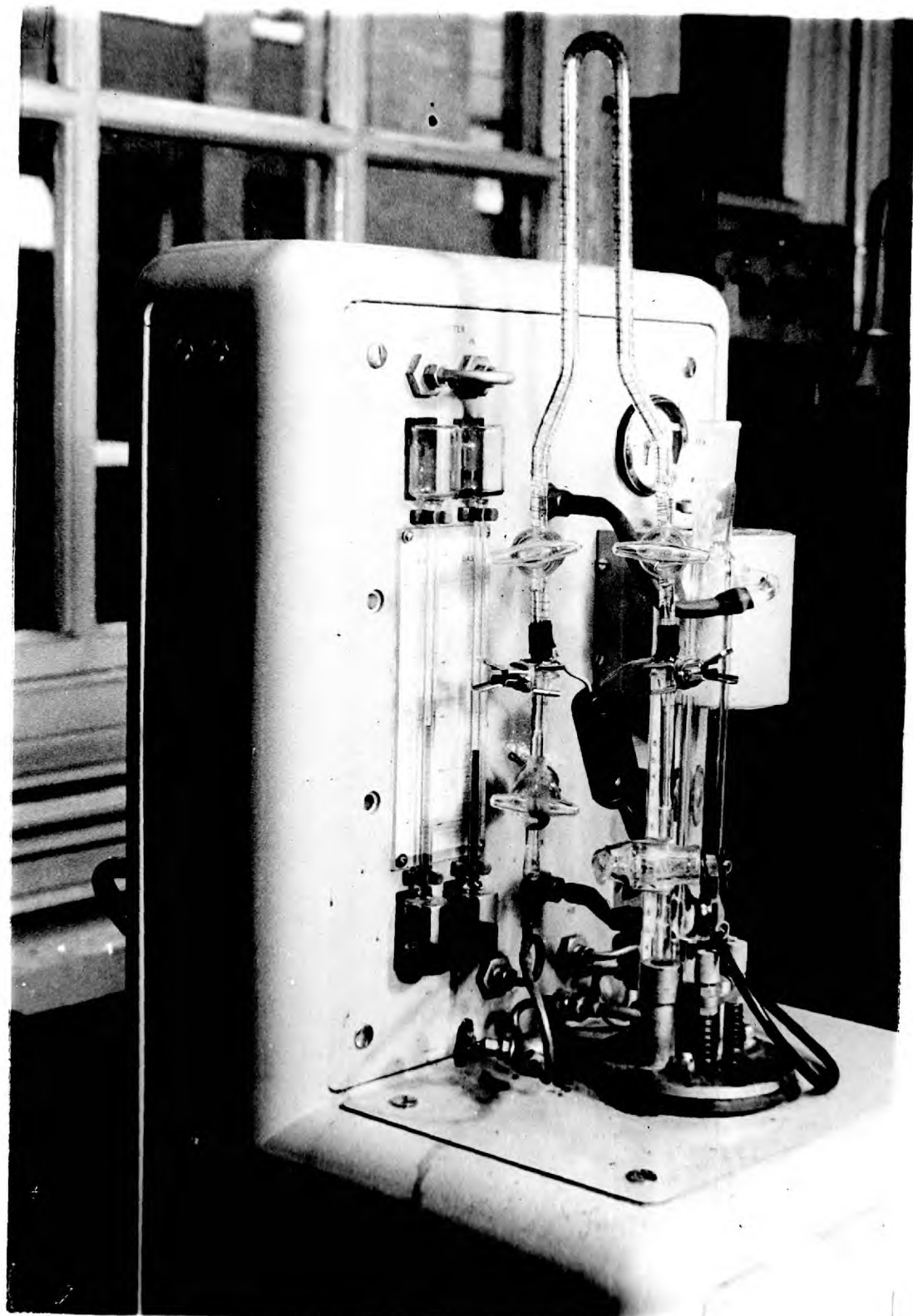
Johns-Manville C22 fire-brick, graded and acid washed, was found, despite its excellent packing properties and chemical inertness⁸², to give highly irreproducible results for aldehydes and higher alcohols and badly tailing peaks for the former compounds. These effects were attributed to adsorption on the fire-brick followed by polymerisation of the aldehydes (which was particularly marked with iso-butyraldehyde) and dehydration of the alcohols. In all the work reported herein therefore 40-60 mesh 'Embacel' (May and Baker Ltd.), a specially treated form of kieselguhr, has been used as the supporting material. This shows little or no signs of catalytic activity and the difficulties mentioned are largely eliminated.

(c) Preparation of the column.

The polyethylene glycol column used was a 12 ft. column working at a temperature of 56.2°C with a gas flow rate of 50 ml/minute. It was prepared as follows.

FIG. 2.8

(41)



'Embacel' as purchased was found to range from approximately 40 to 100 mesh (B. S.). As this would have necessitated an inconveniently high gas pressure to attain the optimum flow rate, it was wet sieved with water and only the 40-60 fraction was used. It was then washed with concentrated hydrochloric acid to remove traces of iron, rinsed several times with distilled water and dried at 120°C . 25g. of the 'Embacel' were then impregnated with 2.5g. of polyethylene glycol dissolved in 20ml. of pure methyl alcohol. The slurry was dried by warming on a hot-plate with continuous gentle stirring to ensure uniformity of impregnation and to avoid abrasion of the particles. The superficially dry packing was then transferred to a vertical tube one metre high and 4 cm. in diameter, and dry air was passed upwards through the tube. By adjusting the flow rate it was possible to blow the dust out of the top of the tube leaving a free flowing dry powder. This was packed into the heat-worked deoxidised copper column with continuous shaking and tapping.

The column was found to hold 22g. of the mixture of which 2.0g. was polyethylene glycol.

II Pressure-time studies.

(a) Standard manometric studies.

(i) Determination of the lower temperature limit of reaction.

2-methyl-but-2-ene (200 mmHg, measured on manometer M_1) from B, and oxygen (200 mmHg) from A, were introduced into the pre-mixing vessel V_2 which was heated electrically to ca. 100°C . After five minutes, the mixture was 'shared' between V_2 and the reaction vessel R_1 , the sharing factors for these vessels and also for vessel V_1 having been determined for various temperatures of the furnace F_1 .

by preliminary experiments with oxygen alone.

The temperature of R_1 , originally 100°C , was now increased at a rate of ca. $1^\circ\text{C}/\text{minute}$, and the resulting rate of pressure change noted from M_1 . Deviations from Charles' Law were first noticed at 230 to 240°C and on further heating to 400°C and subsequent cooling the original pressure-temperature curve was not reproduced. Reaction has thus occurred and the lower limit of such reaction is ca. 230°C .

(ii) The form of the pressure-time curve and its variation with reactant ratio.

Two series of pressure-time measurements were made at 246°C in order to determine the general shape of the pressure-time curve at this temperature and its variation with reactant ratio. In the first series, the initial pressure of 2-methyl-but-2-ene was kept constant at 200 mmHg, the initial oxygen pressure being varied, while in the second series the initial oxygen pressure was kept constant at 200 mmHg, that of 2-methyl-but-2-ene being varied. Representative pressure-time curves from these studies are shown in figs.

2.9 and 2.10. A consideration of these curves shows that the slow combustion reaction has two definite regions:

- 1) An abnormally large fall in pressure (compared with those obtained in previous studies of olefin oxidation eg. . ref. 23) probably due to the formation of intermediates such as peroxides, and
- 2) A subsequent autocatalytic rise in pressure, probably due to the breakdown of intermediates.

The extent of the initial pressure decrease increases with the amount of oxygen available until the oxygen:olefin ratio is ca. 0.5; thereafter further increase in oxygen concentration affects mainly the magnitude of the subsequent pressure rise.

Fig. 2.9. The influence of oxygen pressure on the oxidation of 2-methyl-but-2-ene.

temperature = 246°C

olefin pressure = 200 mmHg

oxygen pressure (mmHg.):

(1) 56.6	(2) 89.0	(3) 110.0
(4) 125.0	(5) 141.4	(6) 165.4
(7) 182.0	(8) 209.0	(9) 258.4
(10) 357.0		

Fig. 2.10. The influence of olefin pressure on the oxidation of 2-methyl-but-2-ene.

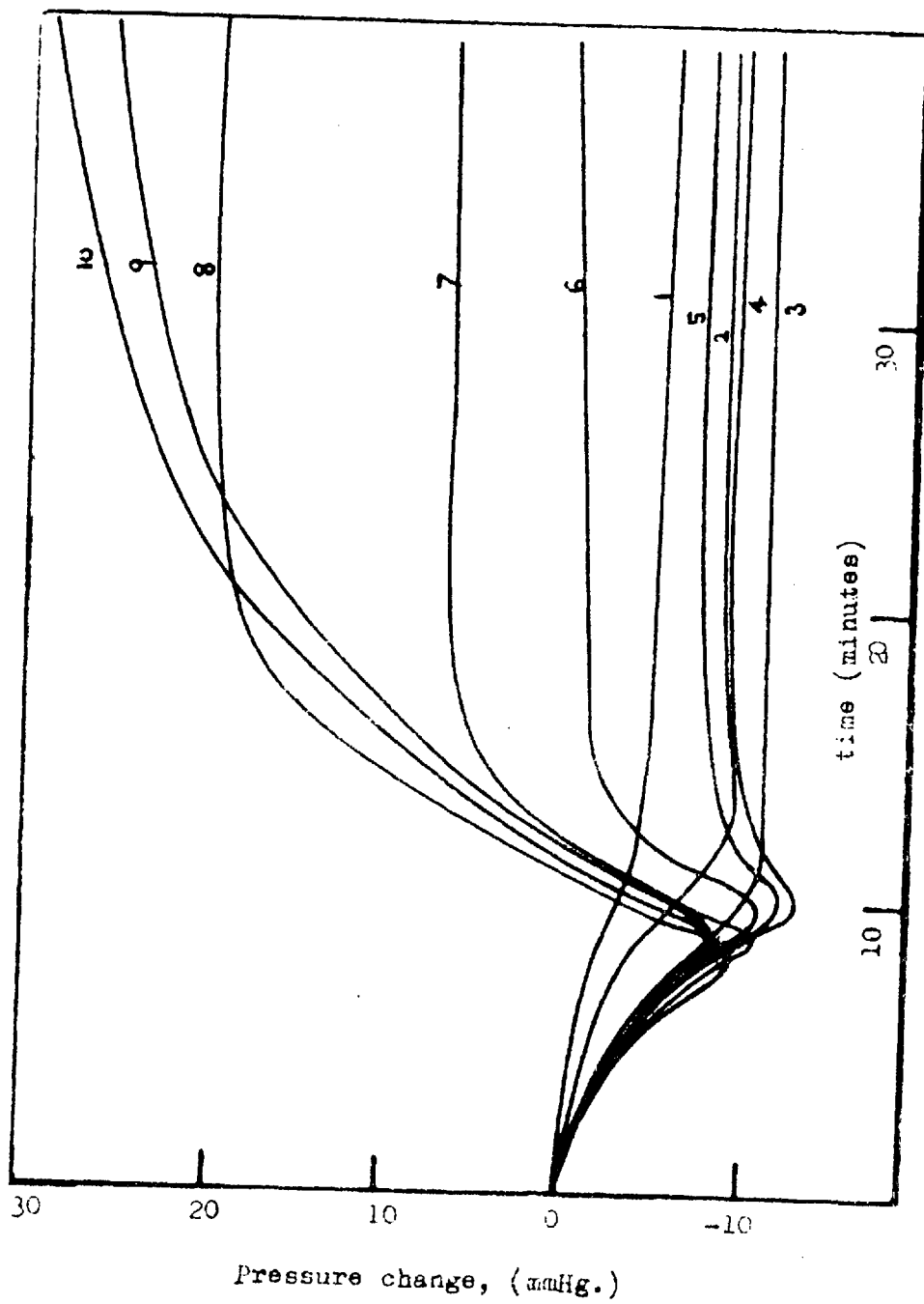
temperature = 246°C

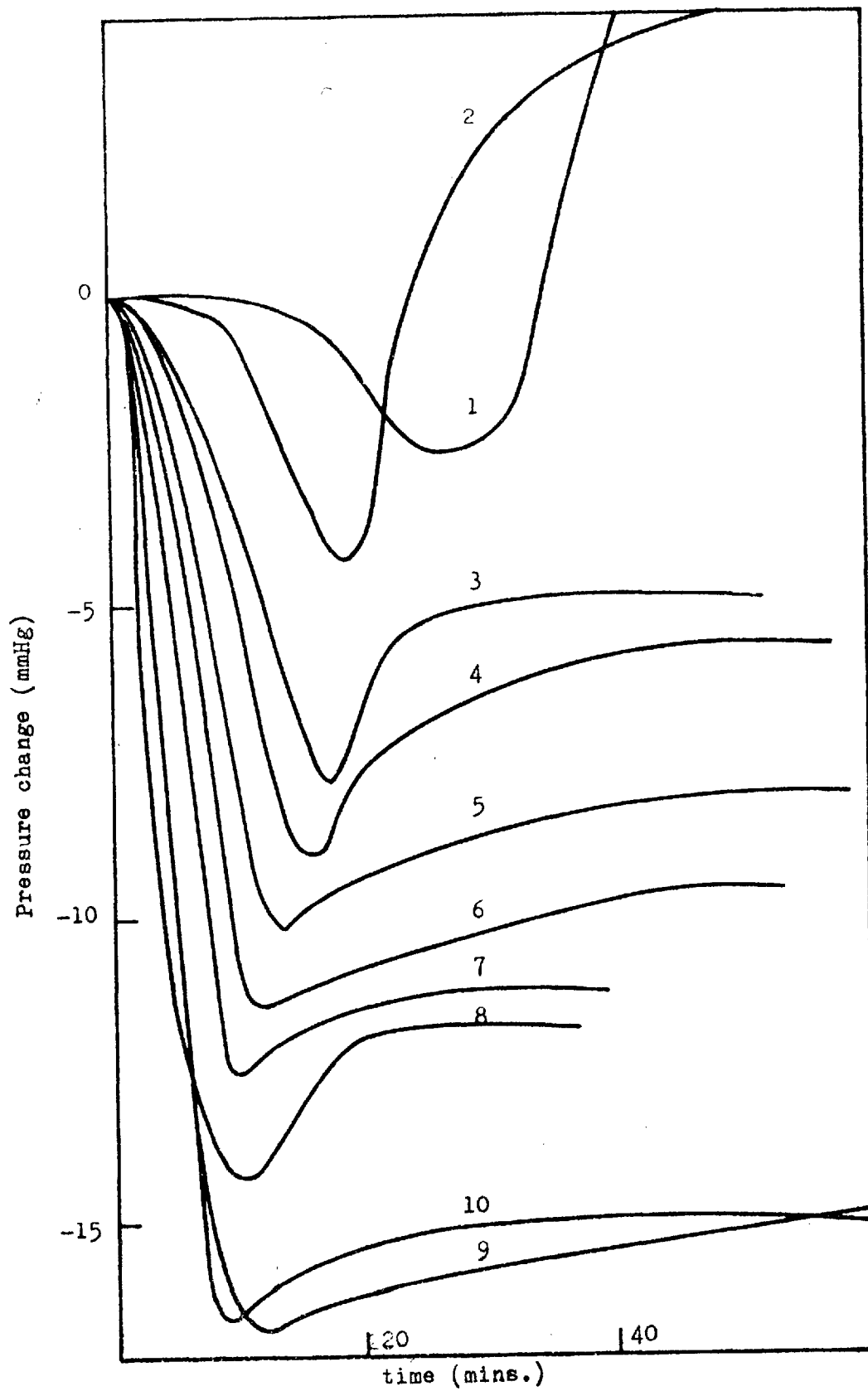
oxygen pressure = 200 mmHg

olefin pressure (mmHg.):

(1) 35.6	(2) 60.4	(3) 90.1
(4) 121.3	(5) 180.2	(6) 235.2
(7) 312.5	(8) 357.1	(9) 416.6
(10) 444.3		

FIG. 2.9.





For each series of pressure-time measurements, the maximum rate of the first stage of reaction (pressure decreasing) has been plotted against the initial pressure of the reactant of which the initial pressure was varied (fig. 2.11).

(iii) The variation of the pressure-time curve with temperature.

The variation in shape of the pressure-time curve with temperature was investigated, the oxygen:olefin ratio being maintained constant at 1.02. Such studies were carried out at thirteen different temperatures in the region 240–340°C. Similar series of measurements were carried out using five other oxygen:olefin ratios between 0.2 and 1.4. Typical results are presented in figs. 2.12. It is evident from these results that the reaction has an explosive region and a region of cool flames. The lower limits of these regions are shown in fig. 2.13. In regions just below the explosion limit, and in which oxygen:olefin $\nearrow$ 1.5, a region of slow combustion with large positive ultimate pressure change (ca. 200 mmHg) was discovered.

From the results in the slow combustion region, for each oxygen:olefin ratio used an Arrhenius plot for the initial reaction was made (fig. 2.14); from these curves, activation energies may be calculated for the pressure-decreasing reaction. The values of E_A thus obtained were plotted against the oxygen:olefin ratio and the curve extrapolated to zero oxygen pressure, at which point stage 2 of the reaction (pressure increasing) would not interfere, masking the true value of E_A (fig. 2.15). It should be pointed out that the rate constants from which E_A was calculated were derived from maximum rates, not initial rates, so that the significance of the value of E_A is doubtful.

FIG. 2.11. THE VARIATION OF THE MAXIMUM RATE OF
PRESSURE DECREASE WITH PRESSURE OF REACTANTS. (246°C)

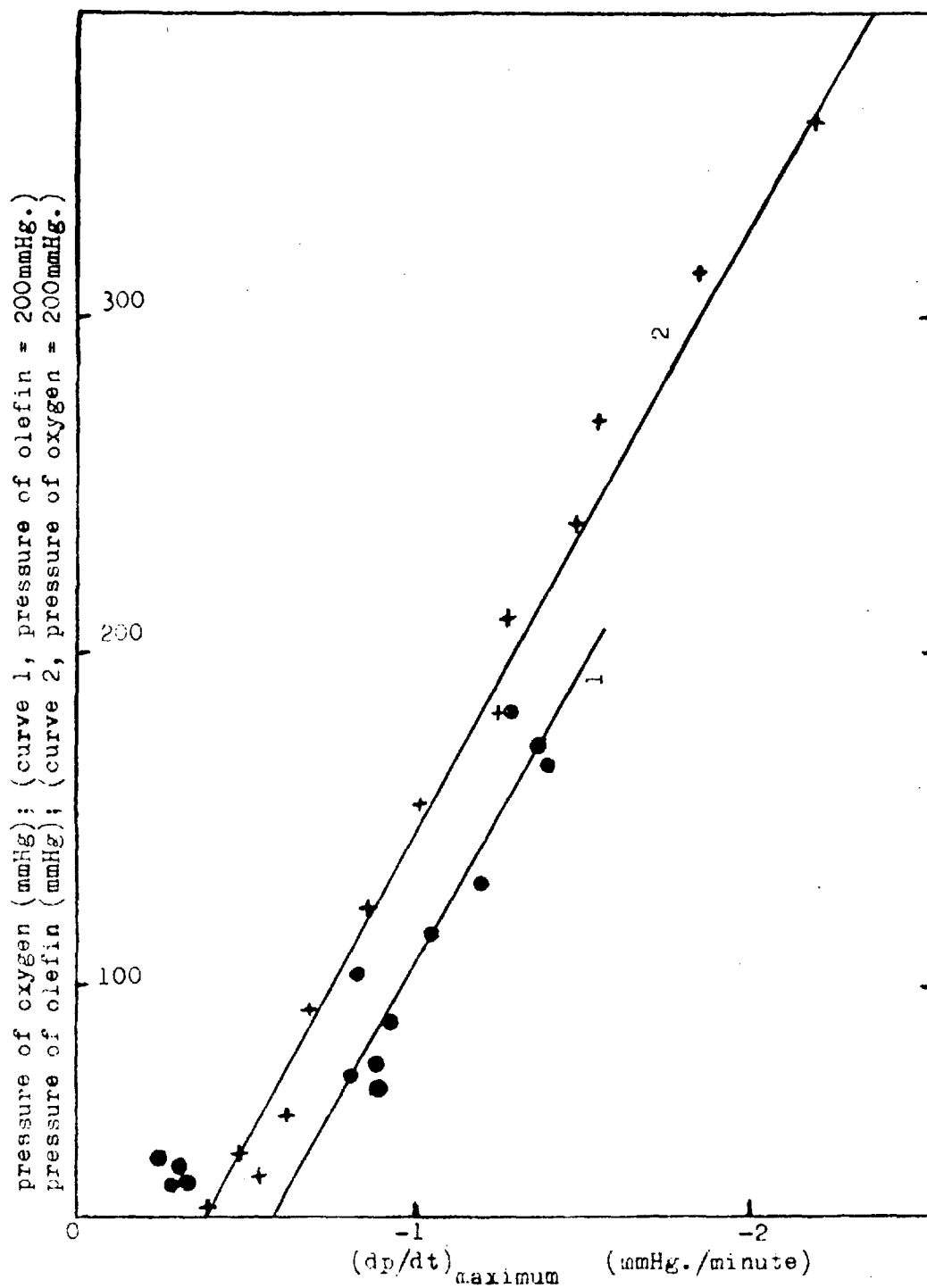


Fig. 2.12. The influence of temperature on the
oxidation of 2-methyl-but-2-ene.

olefin pressure = 200 mmHg

Fig. 2.12(a) oxygen pressure = 182 mmHg
temperature ($^{\circ}\text{C}$):

(1) 246	(2) 264	(3) 272	(4) 301
(5) 307	(6) 324	(7) 340	(8) 351

Fig. 2.12(b) oxygen pressure = 204 mmHg
temperature ($^{\circ}\text{C}$):

(1) 246	(2) 250	(3) 268	(4) 297
(5) 300	(6) 306	(7) 308	(8) 312

Fig. 2.12(c) oxygen pressure = 230 mmHg
temperature ($^{\circ}\text{C}$):

(1) 246	(2) 256	(3) 265	(4) 281
(5) 288			

Fig. 2.12(d) oxygen pressure = 270 mmHg
temperature ($^{\circ}\text{C}$):

(1) 246	(2) 255	(3) 267	(4) 270
---------	---------	---------	---------

FIG. 2.12(a)

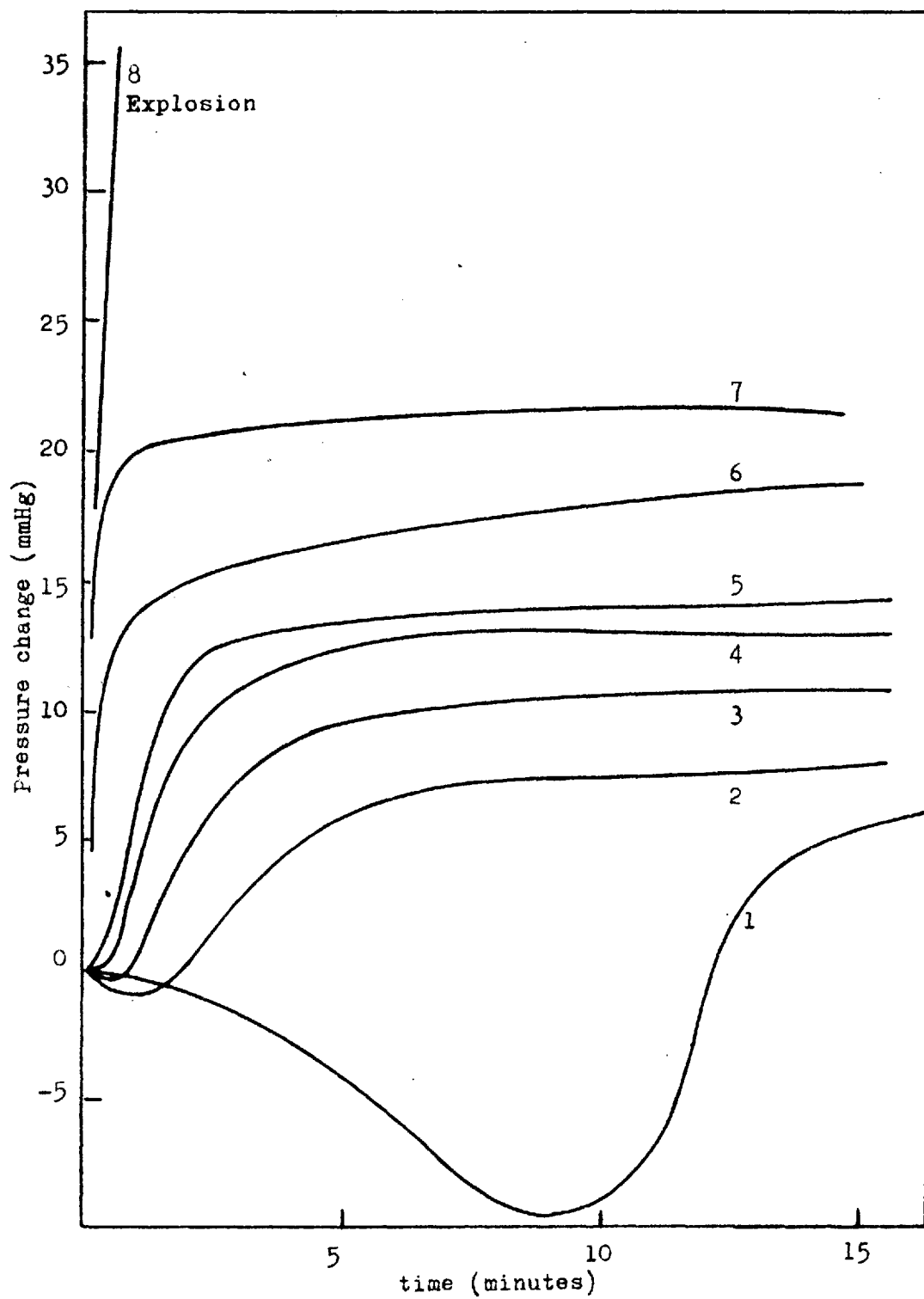


FIG. 2.12.(b)

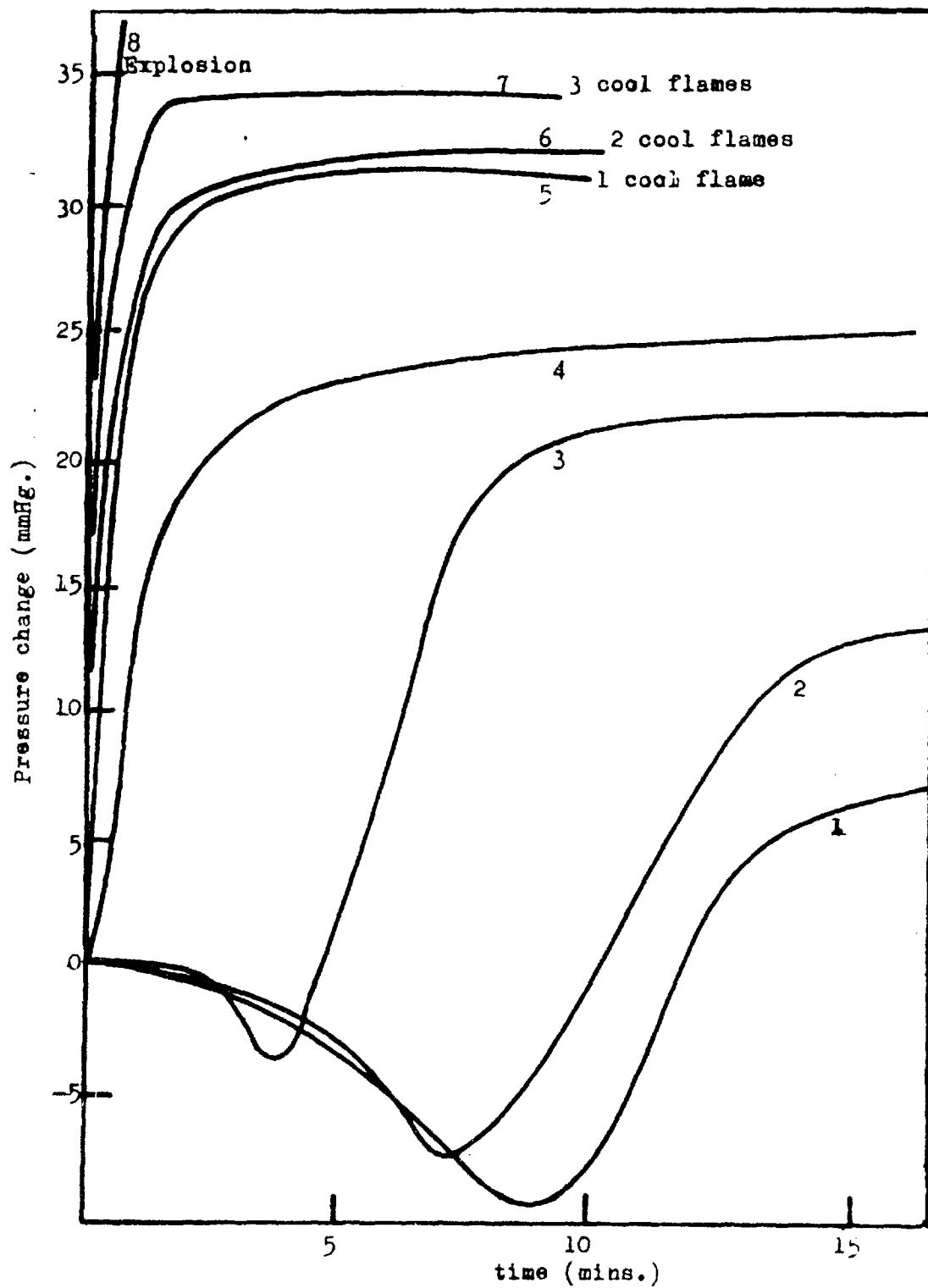


FIG. 2.12(c)

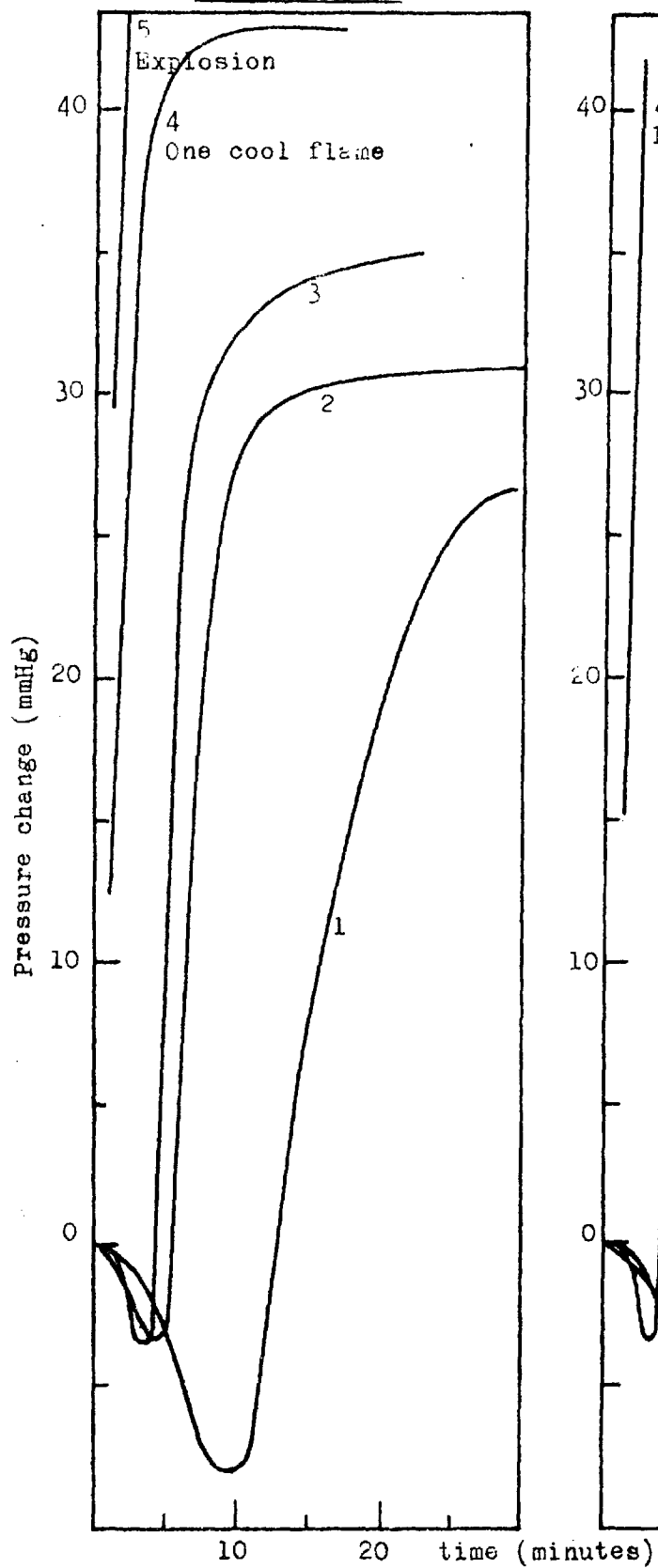


FIG. 2.12(d)

(52)

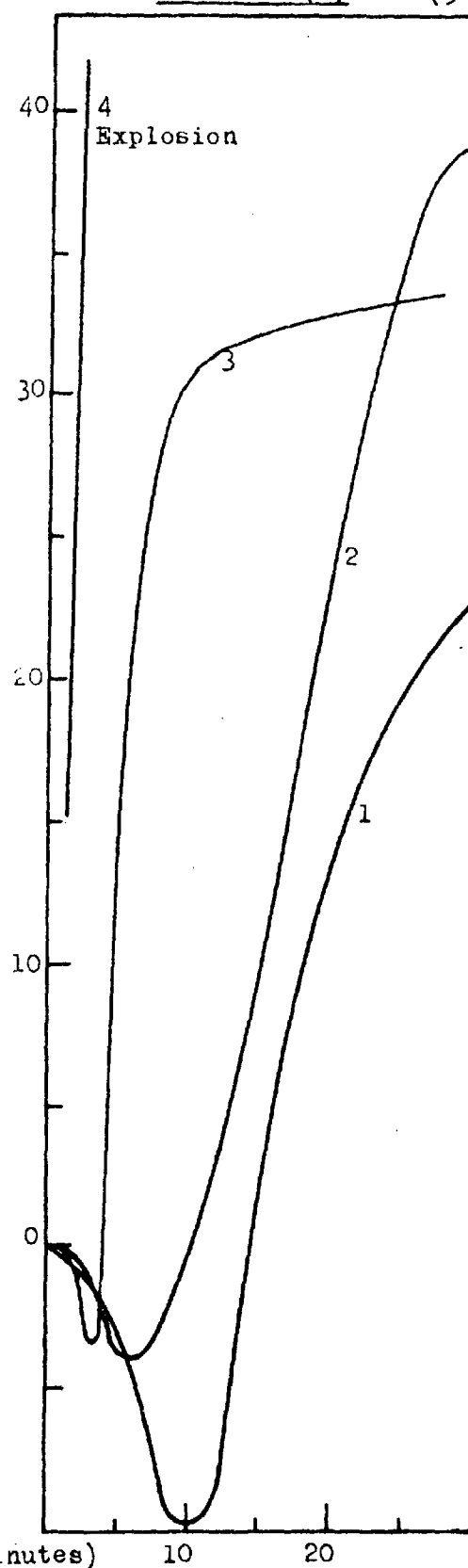


FIG. 2.13. IGNITION DIAGRAM.

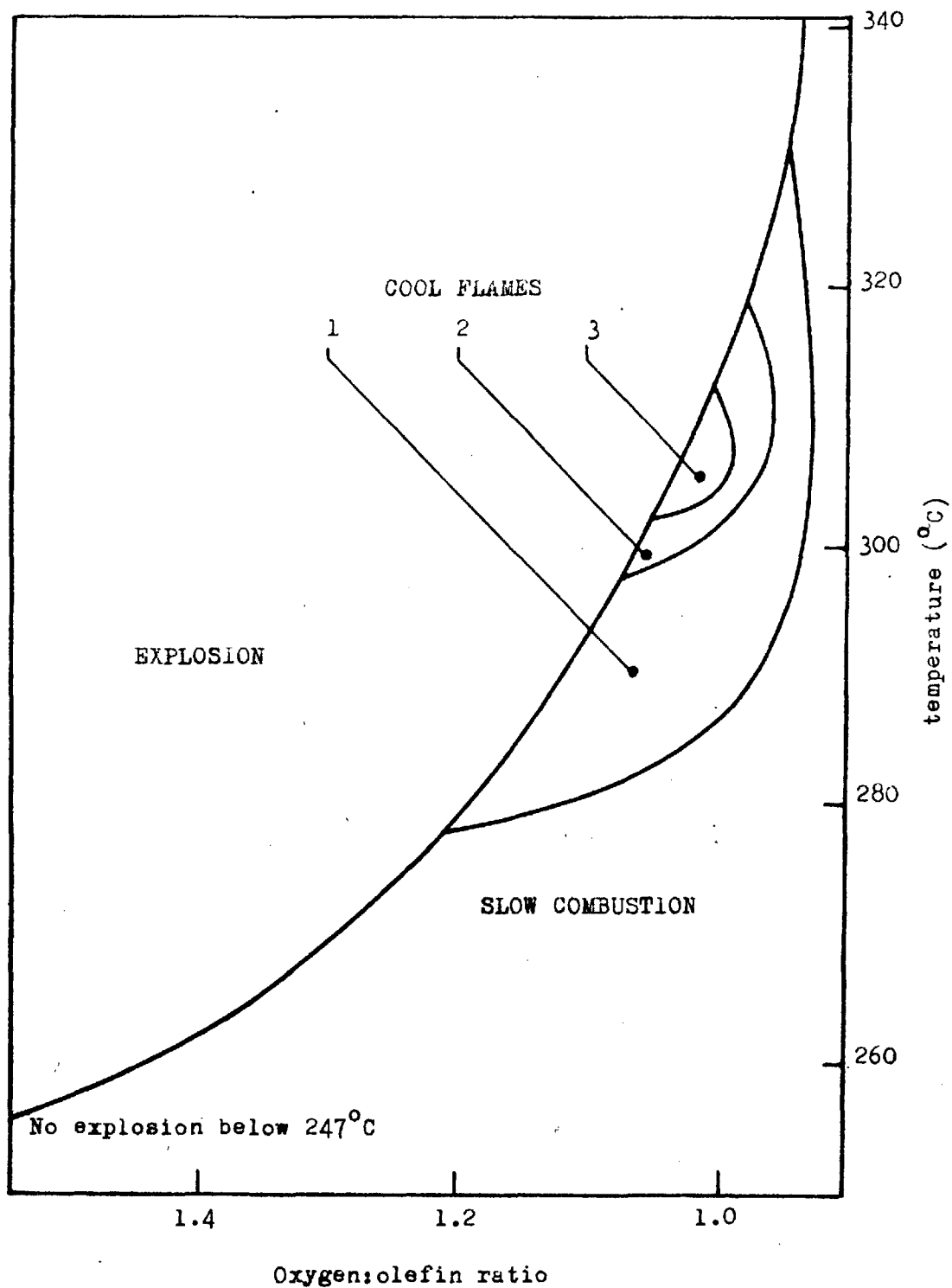


FIG. 2.14. ARRHENIUS PLOTS FOR THE
PRESSURE-DECREASING REACTION.

(54)

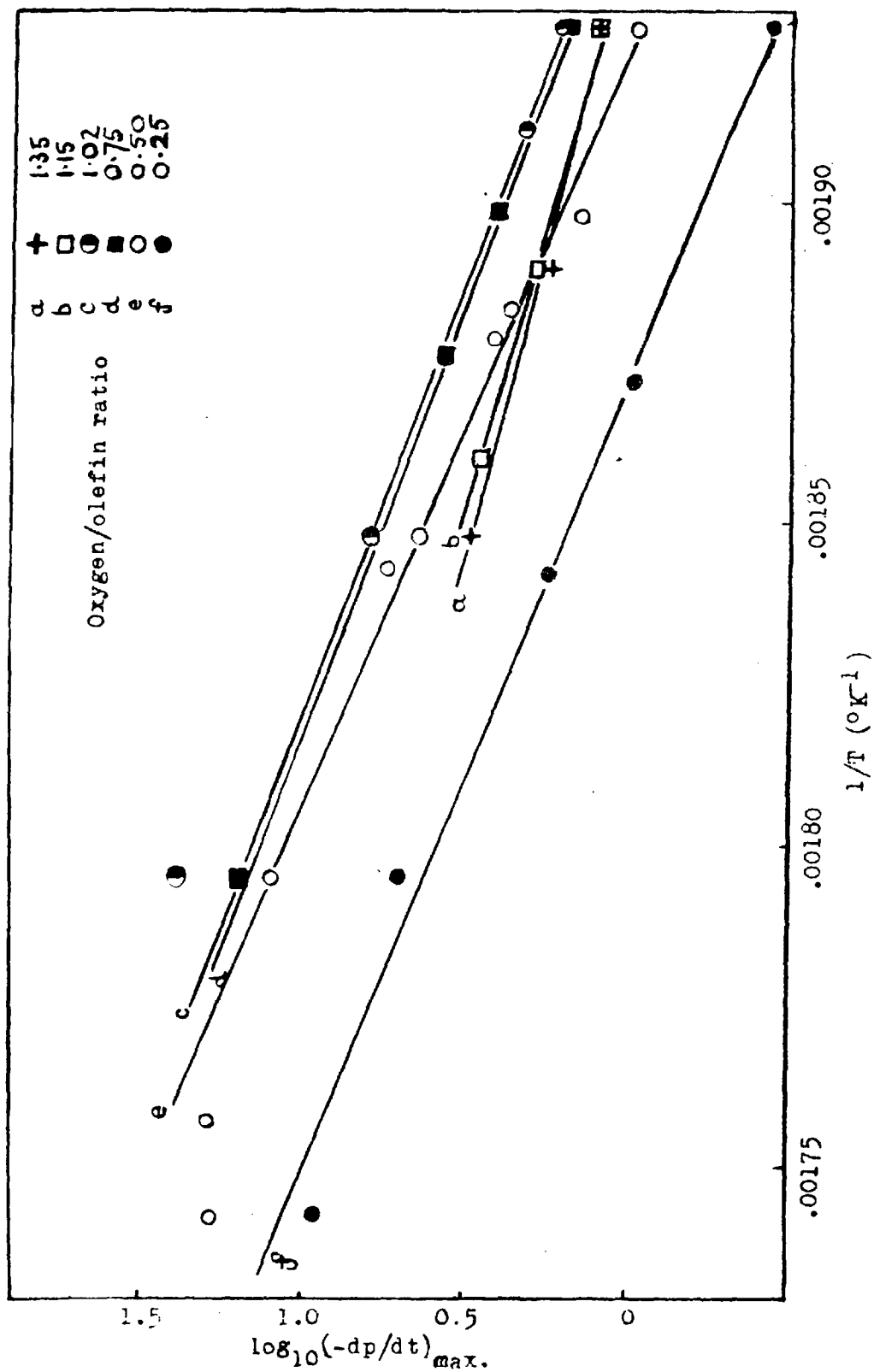


FIG. 2.15. VARIATION OF APPARENT ENERGY OF ACTIVATION
WITH REACTANT RATIO.

(55)

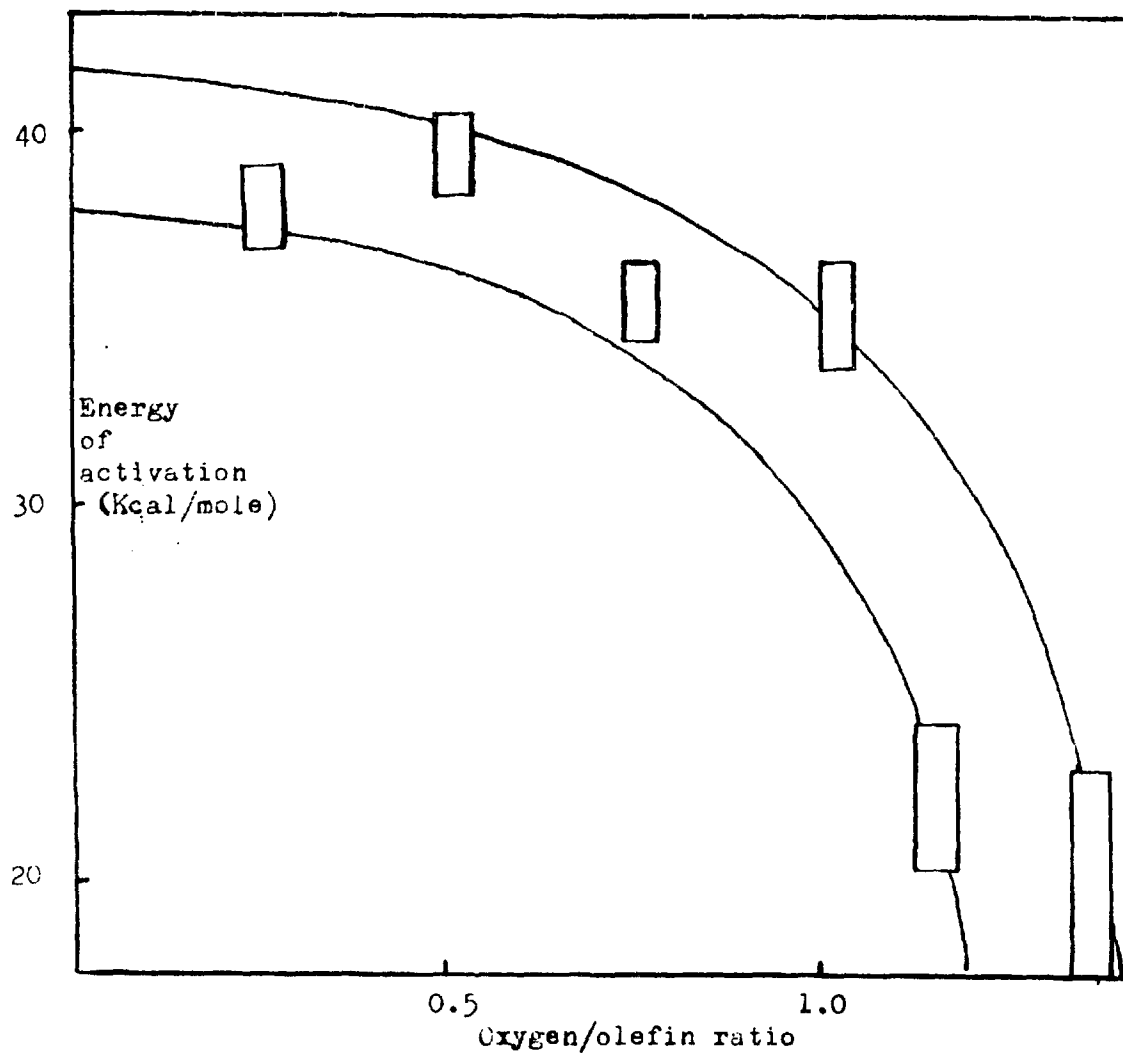
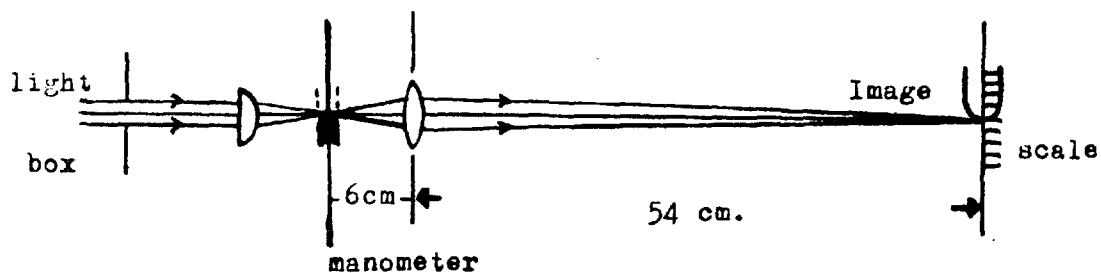


FIG. 2.16. OPTICAL SYSTEM USED FOR ACCURATE PRESSURE
MEASUREMENTS.



magnification = 9.0

(b) Accurate studies of the initial region of reaction.

In an attempt to measure $dp/dt)_{\text{initial}}$ for the gaseous oxidation of 2-methyl-but-2-ene an optical device producing a nine times magnified image of the mercury meniscus (fig. 2.16.) was set up. The manometer was thoroughly cleaned and dried, and fresh triple-distilled mercury was used. The experiments were carried out with the laboratory in darkness. This system enabled pressure changes of 0.02 mmHg to be detected and from the pressure-time curves obtained for the first minute of reaction, approximate values of $dp/dt)_{\text{initial}}$ were calculated at temperatures of 246°C and 282°C with oxygen:olefin ratios of 1.00 and 0.50. These results are tabulated and compared with values of $dp/dt)_{\text{maximum}}$ in table 2.1. Rate constants were derived from values of $dp/dt)_{\text{initial}}$ and an activation energy calculated.

III Product analysis.(a) Gas chromatography.(i) Gas-liquid chromatography: polyethylene glycol as stationary phase.

The majority of the analytical results were obtained using the gas-liquid chromatographic apparatus described in section B.I(e).

(α) Calibration of the apparatus.A) Adjustment of thermocouple height.

Before accurate quantitative calibrations can be carried out with a flame detector it is necessary to place the thermocouple at its optimum height above the jet. This height was determined in the following way. A constant mass of a suitable substance (acetone) was introduced onto the column with the thermocouple set at various heights (differing by 0.5 mm.) for each sample, the amount of sample

TABLE 2.1.

THE SLOW COMBUSTION OF 2-METHYL-BUT-2-ENE: THE INITIAL AND MAXIMUM RATES OF THE PRESSURE-DECREASING REACTION.

Oxygen:olefin	0.5	1.0	0.5	1.0
temperature °C	246	246	282	282
$-dp/dt)_{\text{initial}}$ (mmHg/minute)	0.025	0.041	0.101	0.197
$-dp/dt)_{\text{maximum}}$ (mmHg/minute)	0.98	1.53	10.7	20.0
$\frac{dp/dt)_{\text{initial}}}{dp/dt)_{\text{maximum}}}$	0.023	0.027	0.0095	0.0098
$k \text{ (mmHg}^{-1}\text{sec}^{-1})^{\#}$	1.9×10^{-8}	1.7×10^{-8}	8.4×10^{-8}	8.1×10^{-8}
$k \text{ (moles}^{-1}\text{sec}^{-1})^{\#}$	4.10×10^{-3}	3.67×10^{-3}	1.94×10^{-2}	1.87×10^{-2}

$\#$ calculated from $dp/dt)_{\text{initial}}$

used being sufficient to give a large deflection using the sensitivity to be used during the analysis. It was found that only over a small range of thermocouple settings was the response constant and also a maximum. The thermocouple height was finally set at an intermediate height in this range.

B) Qualitative calibration.

The number of substances present in the reaction products was ascertained by taking representative samples of these products and identifying the peaks on the chromatograms by comparison of the retention times with those of known compounds. Most of the substances were readily identified since their formation was expected on theoretical grounds; the presence of other, less obvious, products such as methyl ethyl ketone, propionaldehyde and tertiary butyl alcohol, was confirmed in the following way. A small amount of the suspected substance was added to the reaction products prior to their introduction onto the column. The corresponding peak was then examined for any deformity of shape. If any change in the shape of the peak was noticed clearly the substance added was different from that present in the products. If, on the other hand, no such change was evident, the effect on the retention times of changing the column temperature was checked. The solubility of any vapour in the fixed phase varies with temperature according to a relation of the Clausius-Clapeyron type; the variation is thus dependent upon the heat of solution of the vapour in the fixed phase. All different vapours therefore exhibit different temperature dependences. Thus if the retention times of a reaction product and the added sample change identically with temperature, there is little reason to doubt that they are identical.

C) Quantitative calibration.

Known pressures (and hence known masses) of

pure degassed reaction products were introduced into the calibrated sharing vessel V_1 from small ampoules at B. For pressures less than 10 mmHg, a larger pressure was introduced and diluted with a known pressure of nitrogen. A measured pressure of the mixture was then pumped out, the residue being retained in V_1 . The gasses in V_1 were next pumped slowly through the detachable U-tube T_1 (maintained at -196°C) and were then introduced onto the column as previously described.

For each substance calibrated, mass was plotted against peak area and in all cases a linear plot passing through the origin was obtained. The relative sensitivities of the substances are shown in fig. 2.17., plotted against their molar heats of combustion. Straight lines are obtained for each group of substances, cutting the y-axis at a value equal to the heat of combustion of the carrier gas used. Aldehydes show significantly lower sensitivities than all other substances, an effect probably attributable to adsorption of the aldehydes on the column (confirmed by the fact that their chromatograms exhibit tailing) followed by polymerisation.

D) Correction of retention volumes.

Considerable attention has been given in the literature⁸³ to the correction of retention volumes to standard conditions in the hope that retention data obtained in certain circumstances may be of quantitative value to others working under different conditions.

The measured retention times were corrected for 'dead' space in the column by subtracting the time for an inert gas to pass through the column from that taken for a vapour to elute, i.e. retention time = $(t_{\text{vapour}} - t_{\text{gas}})$. Retention times were converted to volumes by multiplying by the gas flow rate, f , at atmospheric pressure but at the temperature of the column. Thus, Retention Volume = $(t_{\text{vapour}} - t_{\text{gas}}) f$.

Pressure drop along the column produces a velocity gradient, for which the correction factor

$$\frac{V_r}{V_r^0} = \frac{2(p_i/p_o)^3 - 1}{3(p_i/p_o)^2 - 1}$$

was applied⁸⁴.

(p_i = pressure at inlet.

p_o = pressure at outlet

V_r = retention volume at pressure p_o

V_r^0 = corrected retention volume i.e. the retention volume with zero pressure drop).

Finally V_r^0 was corrected for the weight (w) of fixed phase present in the column by dividing by w .

The corrections can thus be expressed in the form:

$$V_g = (t_{\text{vapour}} - t_{\text{gas}})_f \frac{2(p_i/p_o)^3 - 1}{3(p_i/p_o)^2 - 1} \cdot \frac{1}{w}$$

V_g , the specific retention volume, has physical significance, being the volume of gas at the column temperature which has passed through a hypothetical ideal column, containing lg . of fixed phase, when the peak maximum occurs. This ideal column has a constant pressure (equal to the pressure at which the volume of gas is measured) throughout its length, and zero dead volume.

The retention times and specific retention volumes are tabulated for twenty-three substances in table 2.2.

(β) Analysis of samples of condensable combustion products (including unconsumed 2-methyl-but-2-ene).

At a given stage of the reaction, as characterised by pressure change and time, a sample was withdrawn from the

TABLE 2.2.THE SPECIFIC RETENTION VOLUMES OF VARIOUS SUBSTANCES.

Inlet pressure = 2,310 mmHg

Outlet pressure = 760 mmHg

Flow rate = 47 ml/minute

Temperature = 56°C

Weight of polyethylene glycol on column = 2.0g

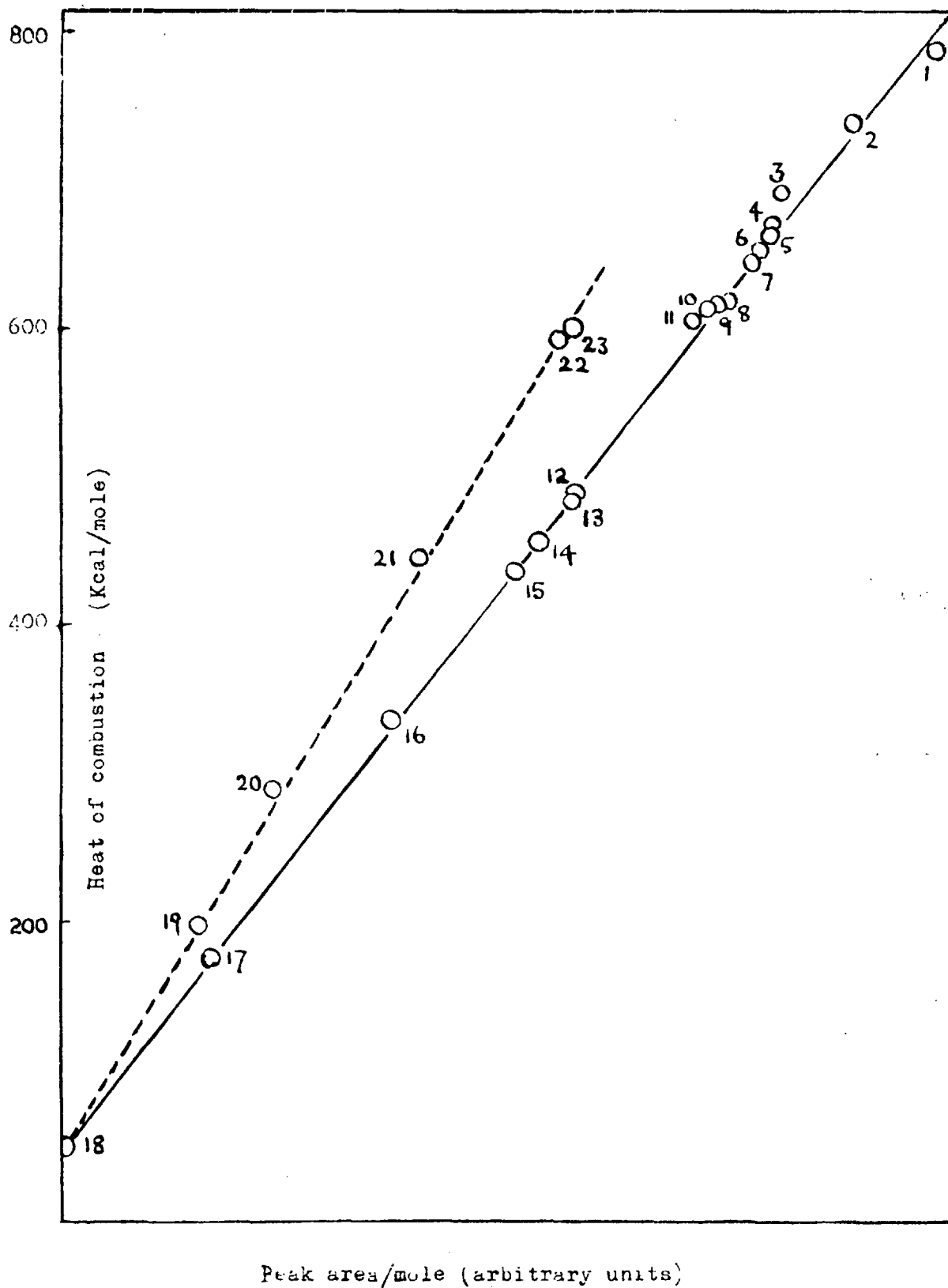
James and Martin correction factor = 0.48

Substance	Retention time $t_{\text{vap}} - t_{\text{air}}$ minutes	Volume V_g ml.
diethyl ether	1.3	14.6
acetaldehyde	2.4	27.0
epoxy-propane	3.3	37.0
2-methyl-epoxy-propane	3.6	41.0
trans-2,3-epoxy-n-butane	4.3	48.5
1,2-epoxy-n-butane	4.3	48.5
propionaldehyde	4.7	53
isobutyraldehyde	5.3	60
acetone	6.5	73
glyoxal	8.0	90
2-methyl-2,3-epoxy-butane	8.7	98
n-butyraldehyde	9.7	109
methyl ethyl ketone	11.7	132
methyl isopropyl ketone	13.9	157
t-butyl alcohol	18.4	208
methyl alcohol	18.6	210
diacetyl	20.5	231
isopropyl alcohol	21	237
ethyl alcohol	24	270
sec-butyl alcohol	41	460
n-propyl alcohol	46	520
iso-butyl alcohol	69	780
n-butyl alcohol	103	1160

Key to Fig. 2.17.

- 1 2-methyl-2,3-epoxy-butane
- 2 methyl isopropyl ketone
- 3 diethyl ether
- 4 iso-butyl alcohol
- 5 n-butyl alcohol
- 6 sec-butyl alcohol
- 7 t-butyl alcohol
- 8 2-methyl-epoxy-propane
- 9 1,2-epoxy-n-butane
- 10 trans-2,3-epoxy-n-butane
- 11 methyl ethyl ketone
- 12 iso-propyl alcohol
- 13 n-propyl alcohol
- 14 epoxy-propane
- 15 acetone
- 16 ethyl alcohol
- 17 methyl alcohol
- 18 carrier gas (75% H₂, 25% N₂)
- 19 glyoxal
- 20 acetaldehyde
- 21 propionaldehyde
- 22 n-butyraldehyde
- 23 iso-butyraldehyde

FIG. 2.17. THE RELATION BETWEEN THE SENSITIVITY OF THE THERMOCOUPLE DETECTOR AND THE MOLAR HEAT OF COMBUSTION OF THE SUBSTANCE DETECTED.



reaction vessel R_1 by sharing into the evacuated vessel V_1 . The temperature of R_1 was sufficiently high to prevent serious fractionation during this process. The absence of any such fractionation was checked by sampling and analysis of mixtures of pure reaction products of known composition. The contents of V_1 were then pumped slowly through the U-tube T_1 , which was immersed in liquid nitrogen. The condensables are thus retained in T_1 which was closed, removed, and attached to the gas-liquid chromatographic apparatus. The contents of T_1 were then analysed.

The slow combustion of 2-methyl-but-2-ene at 265°C was fully studied using this analytical technique. With an oxygen:olefin ratio of 1:1, samples were withdrawn and analysed at many stages of reaction, enabling a curve to be constructed with amount of product formed as ordinate against time as abscissa (figs. 2.19). These measurements were repeated for oxygen:olefin ratios of 0.5 (figs. 2.20 (a,b,c)) and 1.5 (figs. 2.20 (a,d,e)).

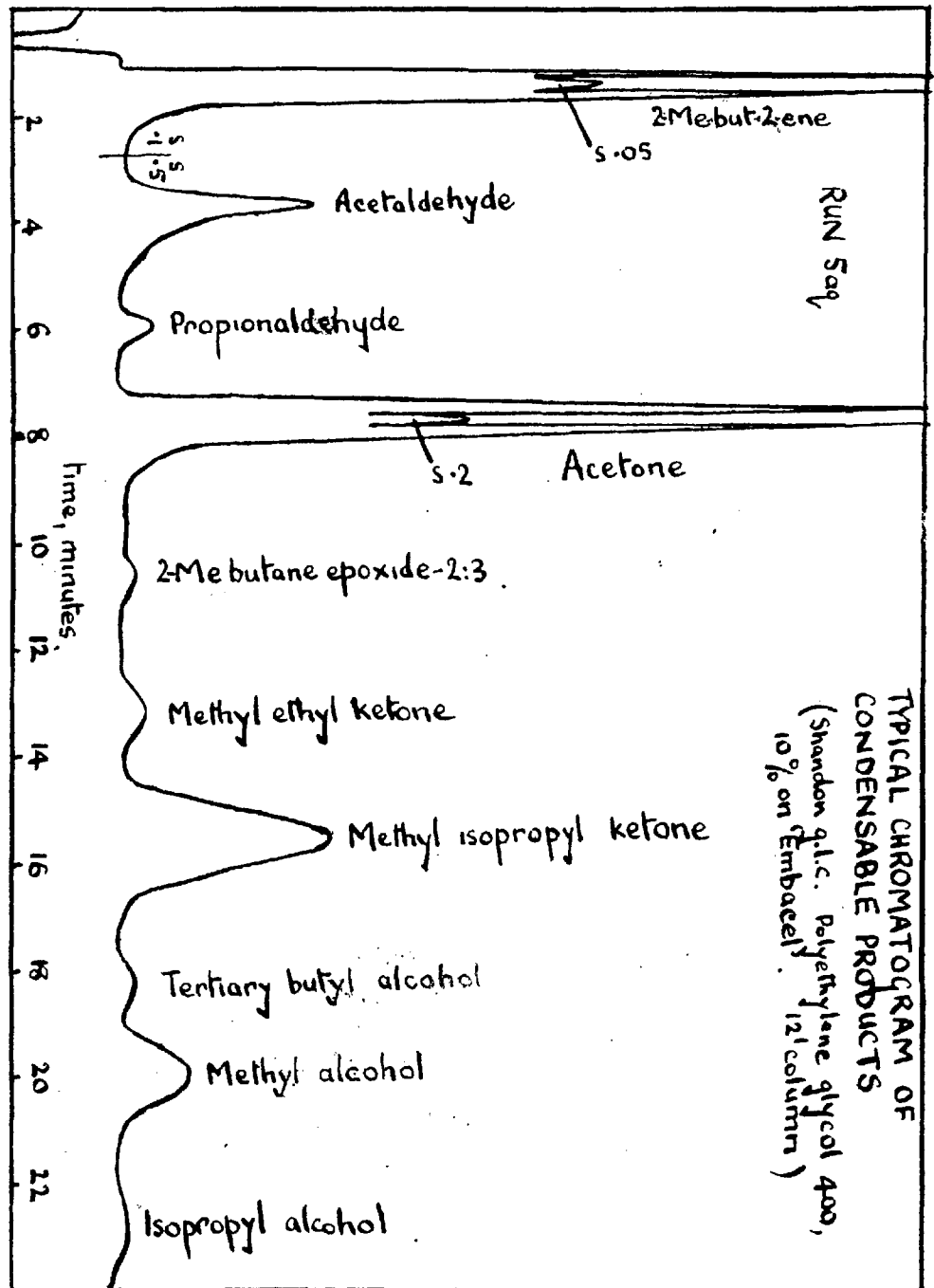
Similar, though less extensive, measurements were made in the explosive region of reaction, and showed that the amount of condensable products present after explosion is very small compared with the amounts found in slow combustion. Subsequent to the explosion, these amounts slowly increase, no doubt due to the occurrence of some slow combustion.

Similar analytical studies of the cool-flame regions of reaction showed that the products formed are similar to those produced during slow combustion. Somewhat greater amounts are however formed in the cool-flame region. A typical chromatogram is shown in fig. 2.18.

(ii) Gas-solid chromatography: Linde sieve
as stationary phase.

Permanent gases (oxygen, hydrogen, carbon

FIG. 2.18. SPECIMEN ANALYSIS OF COMBUSTION PRODUCTS.



KEY TO FIGS. 2.19, 2.20.

Fig. 2.19(a).

- 2-methyl-but-2-ene
- oxygen
- pressure change

Figs. 2.19(b), 2.20(b), 2.20(d).

- acetone
- acetaldehyde
- ⊙ methyl isopropyl ketone
- × methyl alcohol
- ◻ carbon monoxide
- ⊕ carbon dioxide
- pressure change

Figs. 2.19(c), 2.20(c), 2.20(e).

- propionaldehyde
- tertiary butyl alcohol
- ⊙ isopropyl alcohol
- × methyl ethyl ketone
- 2-methyl-2,3-epoxy-butane
- ◻ glyoxal

FIG. 2.19.(a) CONSUMPTION OF REACTANTS.

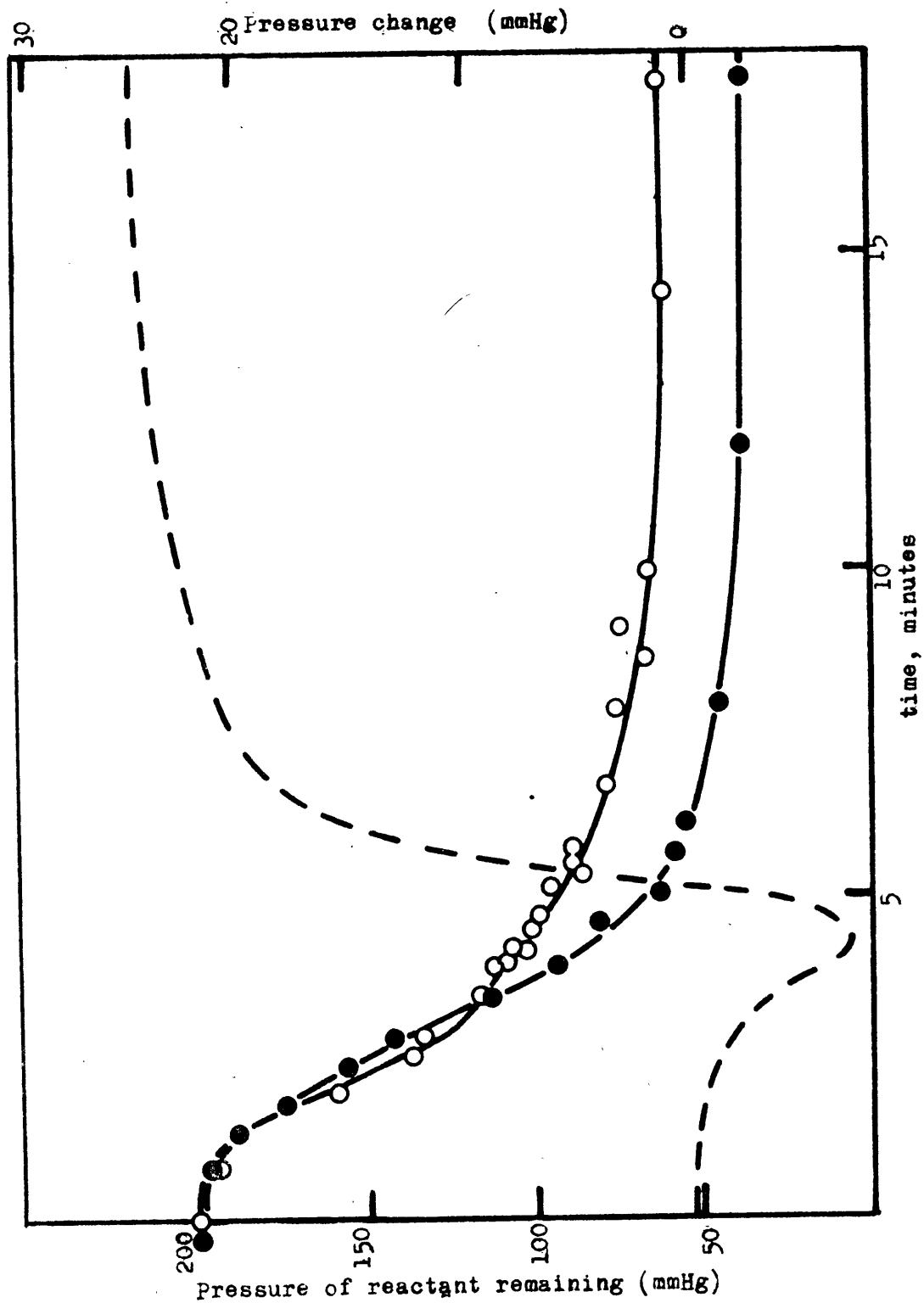
Oxygen:olefin = 1, temperature = 265°C 

FIG. 2.19.(b) THE FORMATION OF MAJOR PRODUCTS.

(68)

Oxygen:olefin = 1, temperature = 265°C

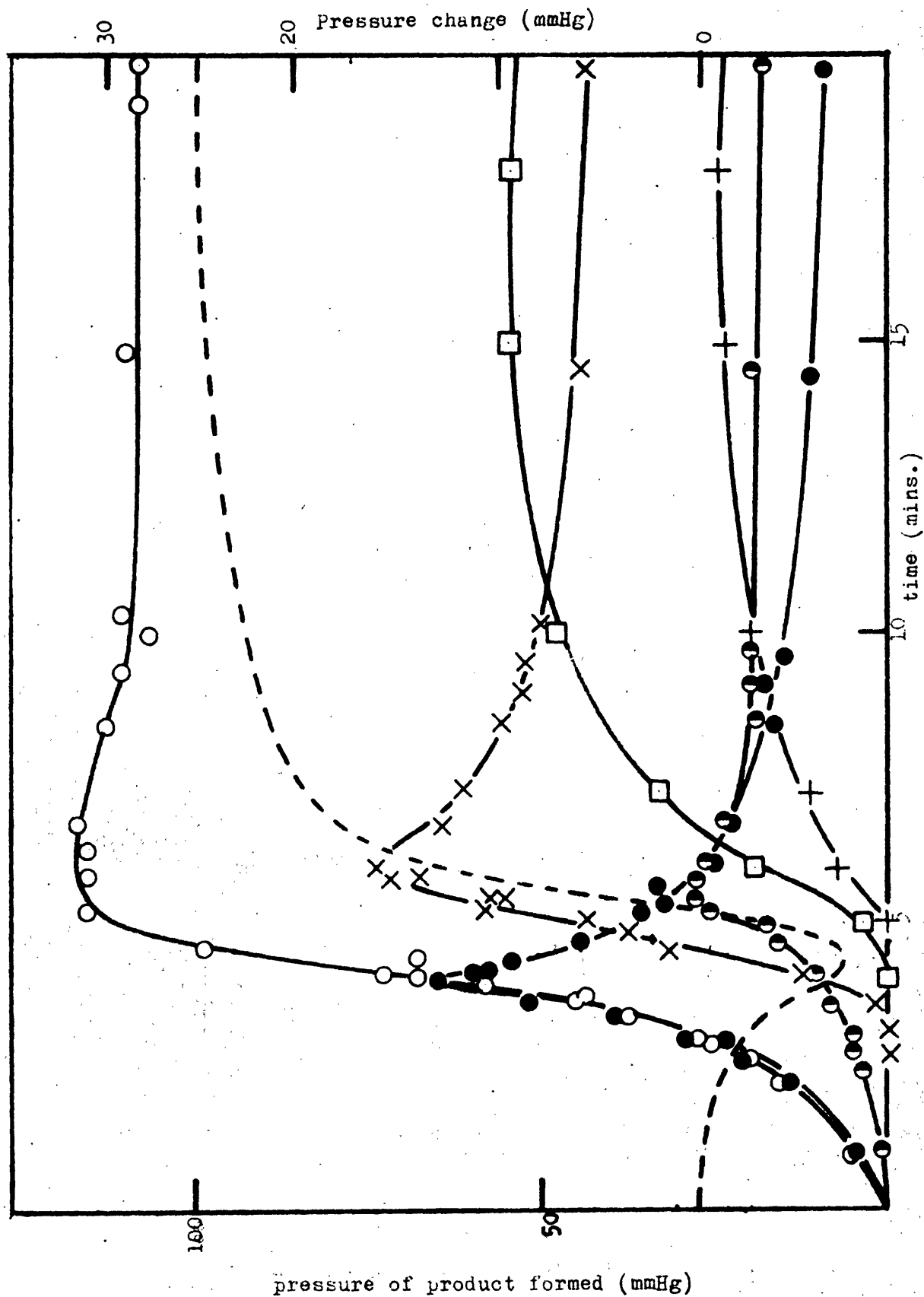


FIG. 2.19.(c) THE FORMATION OF MINOR PRODUCTS.

(69)

Oxygen:olefin = 1, temperature = 265°C

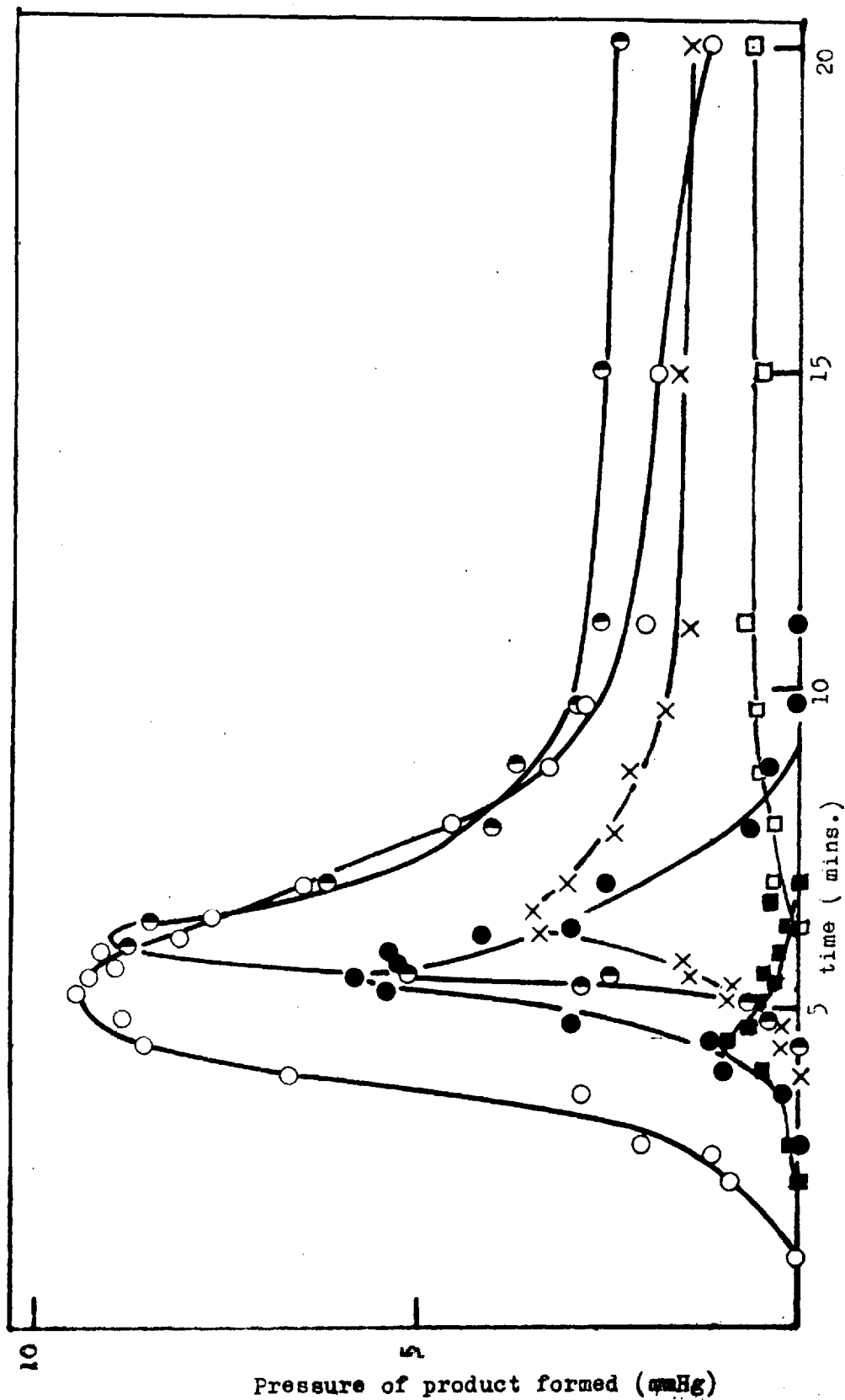


FIG. 2.20.(a) COMPARATIVE CONSUMPTION OF 2-METHYL-BUT-2-ENE
AT VARIOUS OXYGEN:OLEFIN RATIOS. (TEMPERATURE = 265°C)

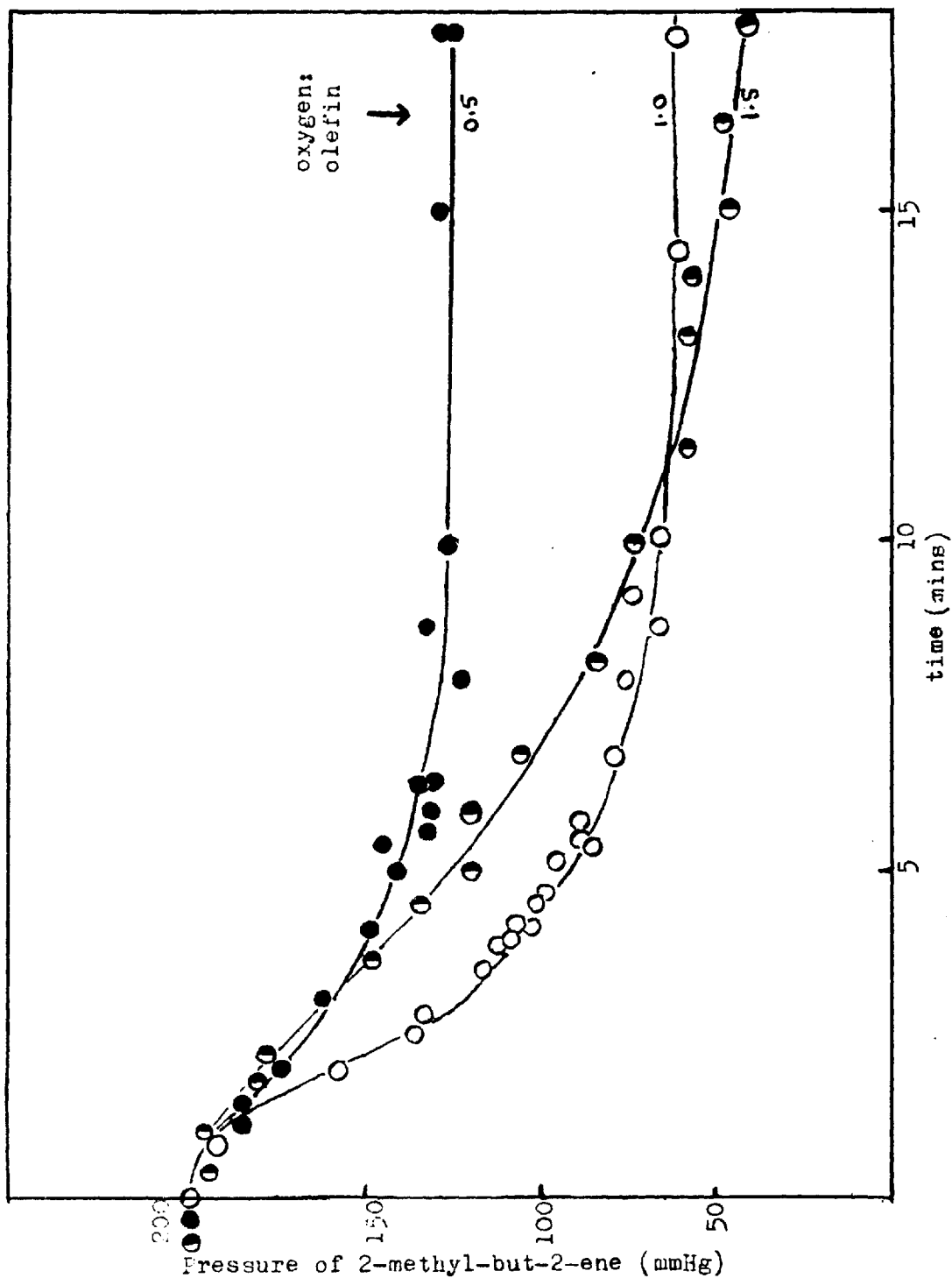


FIG. 2.20.(b) THE FORMATION OF MAJOR PRODUCTS.

(71)

(Oxygen:olefin = 0.5, temperature 265°C)

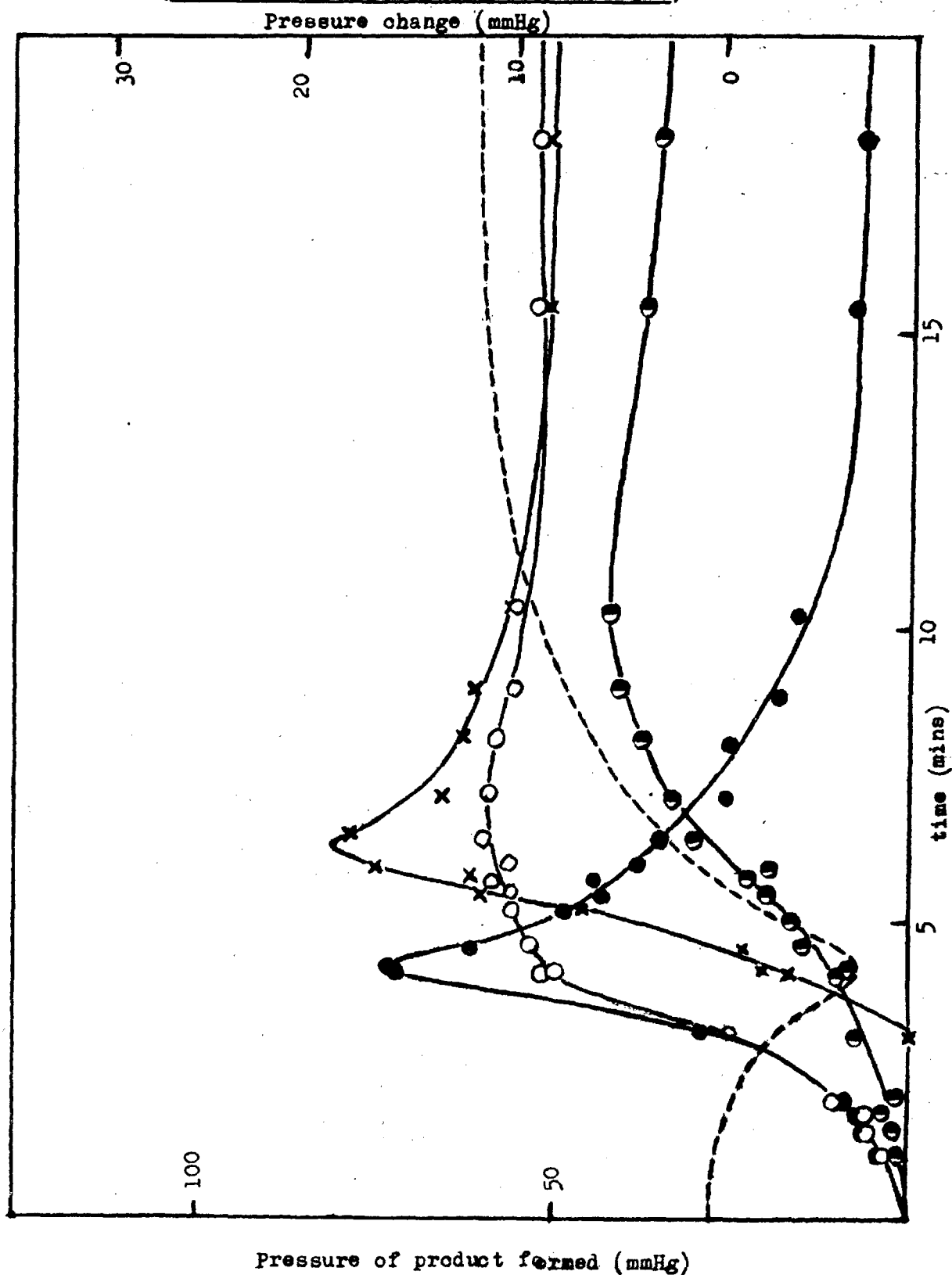


FIG. 2.20.(c) THE FORMATION OF MINOR PRODUCTS.

(72)

(Oxygen:olefin = 0.5, temperature 265°C)

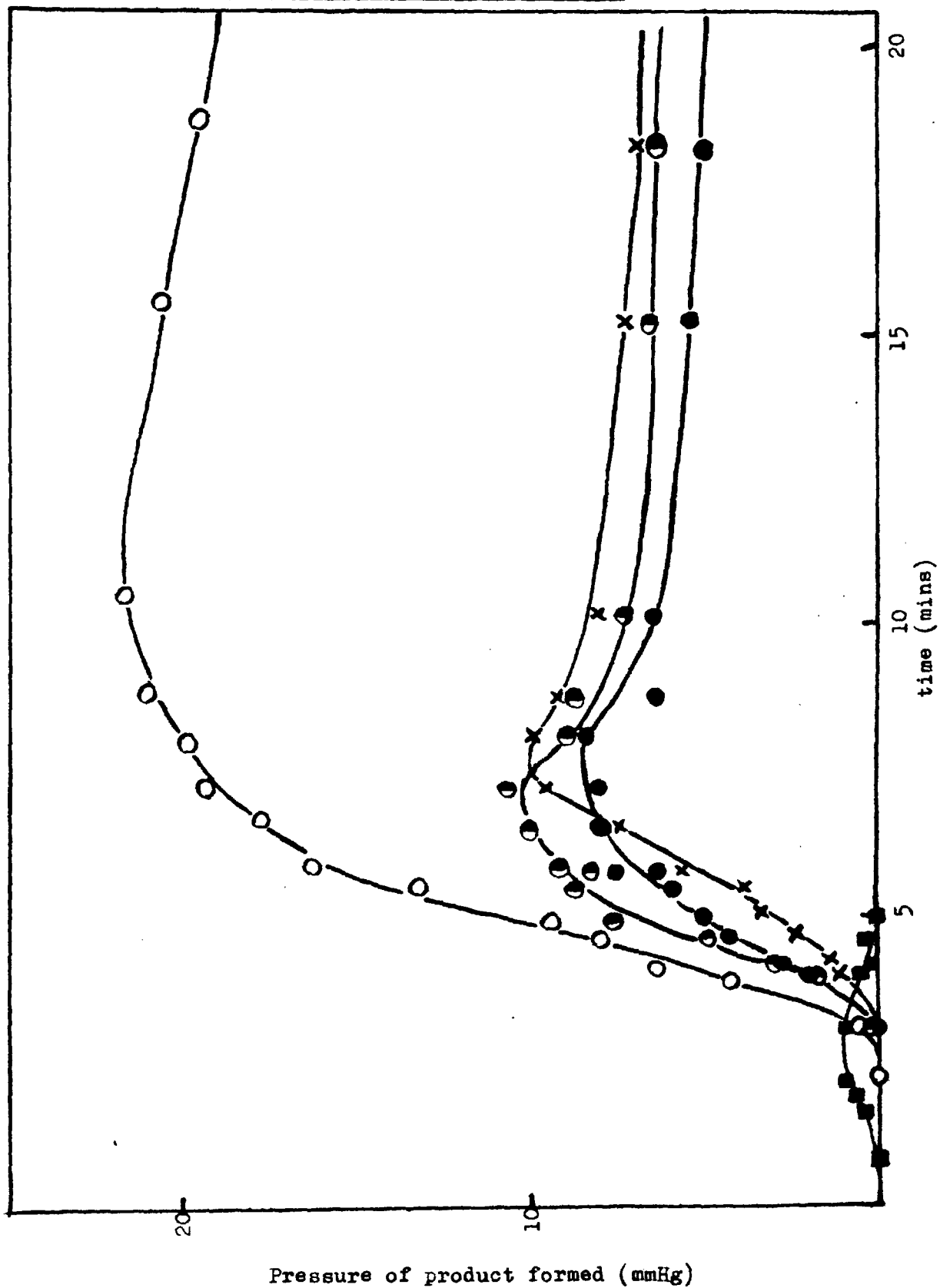


FIG. 2.20.(d) THE FORMATION OF MAJOR PRODUCTS.

(73)

(Oxygen:olefin = 1.5, temperature 265°C)

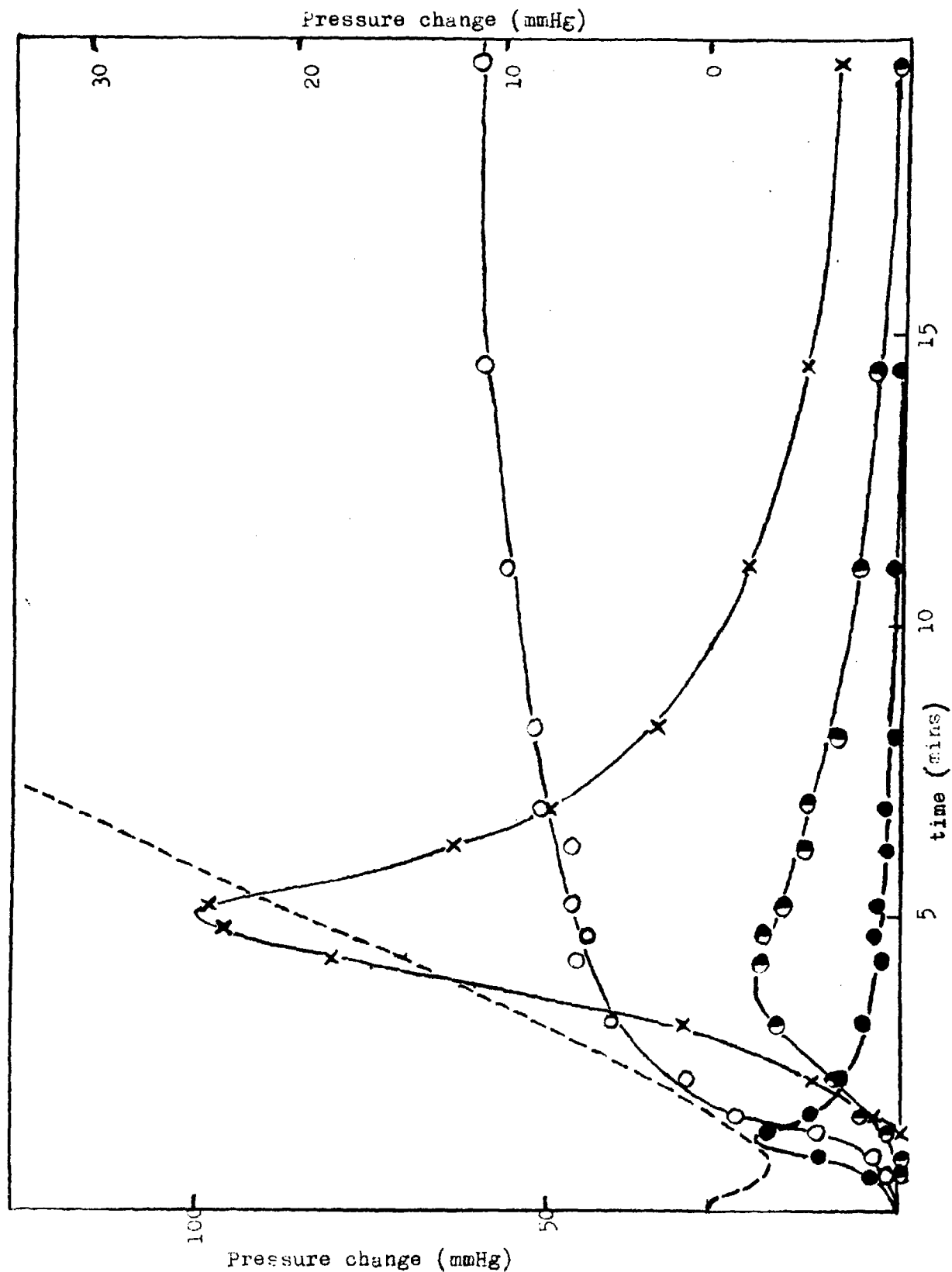
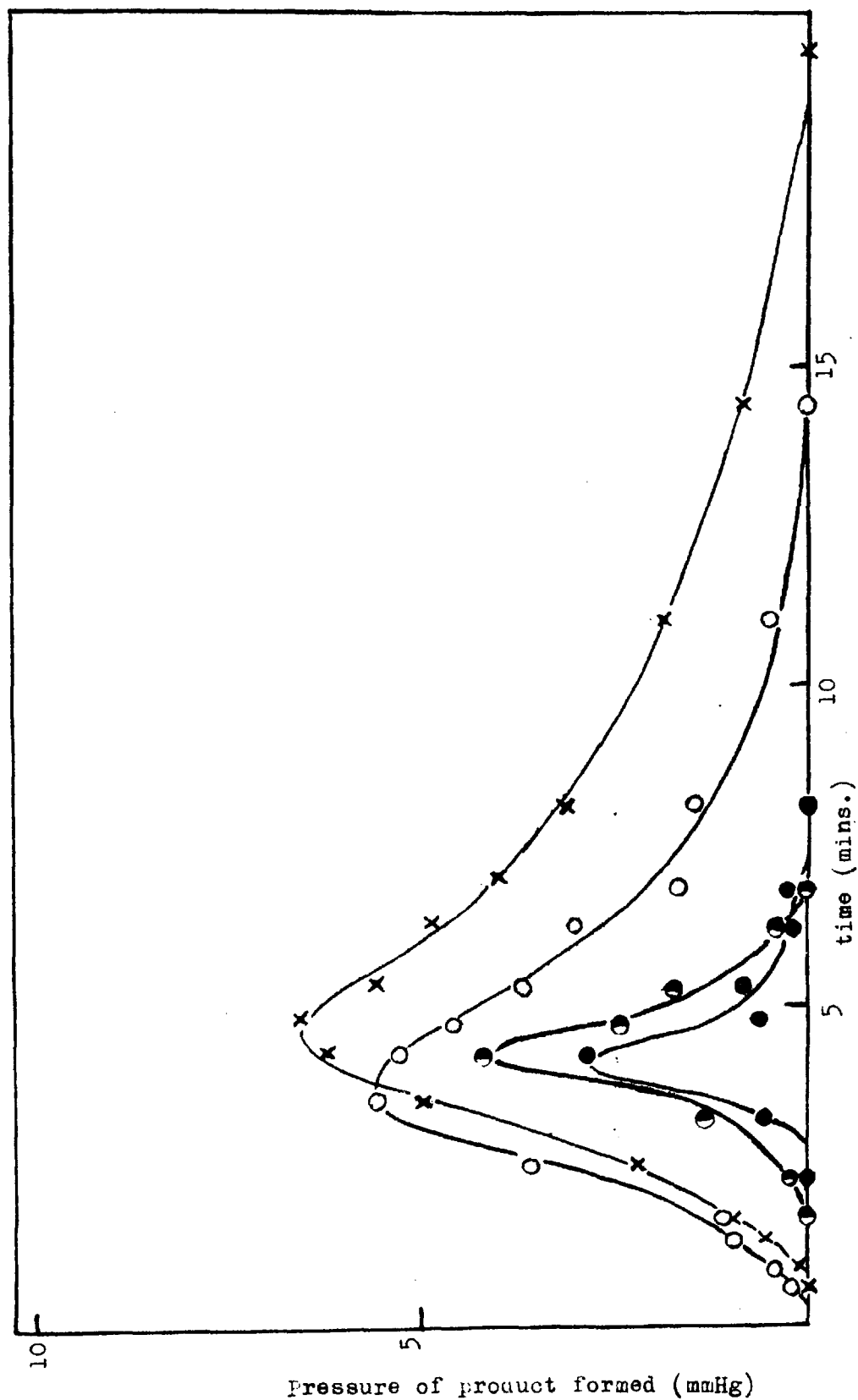


FIG. 2.20.(e) FORMATION OF MINOR PRODUCTS.

(74)

(Oxygen:olefin = 1.5, temperature 265°C)



monoxide and methane) were analysed, by courtesy of Dr. J.A. Barnard, University College, London, on a Griffin and George gas chromatographic apparatus with a Linde 5A sieve column, maintained at 20°C , using a katharometer detector and argon as carrier gas (flow rate = 2.0 litres/hour). These studies show that, during slow combustion of a 1:1 oxygen:olefin mixture at 265°C , no methane and only very small quantities of hydrogen are formed. From the results were also obtained an oxygen consumption/time curve (fig. 2.19(a)), and a curve of carbon monoxide formed against time (fig. 2.19(b)). It should be mentioned that carbon monoxide and oxygen were not completely separated under these conditions. The analysis of carbon monoxide by this method is therefore somewhat unsatisfactory.

(b) Infra-red spectroscopy.

Infra-red spectroscopy, using a Hilger H800 spectrophotometer, was used for two purposes.

- 1) Qualitative infra-red analysis of samples of reaction products taken directly from the reaction vessel as gas samples confirmed the presence of carbonyl compounds, carbon monoxide and carbon dioxide. It is therefore certain that the oxygenated hydrocarbon derivatives estimated by gas-liquid chromatography are indeed formed in the reaction vessel during gas-phase reaction, and are not products of any reaction which may occur in the condensed phase (in trap T_1) during gas-liquid chromatographic sampling.
- 2) Quantitative analysis of carbon oxides in the products of slow combustion at 265°C of a 1:1 oxygen:olefin mixture confirmed the carbon monoxide/time curve obtained previously (to within the accuracy of the experiments) and enabled a semi-quantitative estimation of the extent and time of

formation of carbon dioxide to be made.

(c) Carbon dioxide analysis.

The above semi-quantitative estimation of carbon dioxide was checked, and the accuracy increased, by the following procedure. Condensable products of slow combustion were collected in trap T_1 which was immersed in liquid oxygen. The trap was now allowed to warm up to -80°C by surrounding it with a cardice/acetone mixture. Under these conditions, the carbon dioxide present alone evaporates, and was estimated manometrically. The curve showing the variation of pressure of carbon dioxide formed with time, during the reaction of a 1:1 mixture at 265°C , obtained by this method is incorporated in fig. 2.19(b).

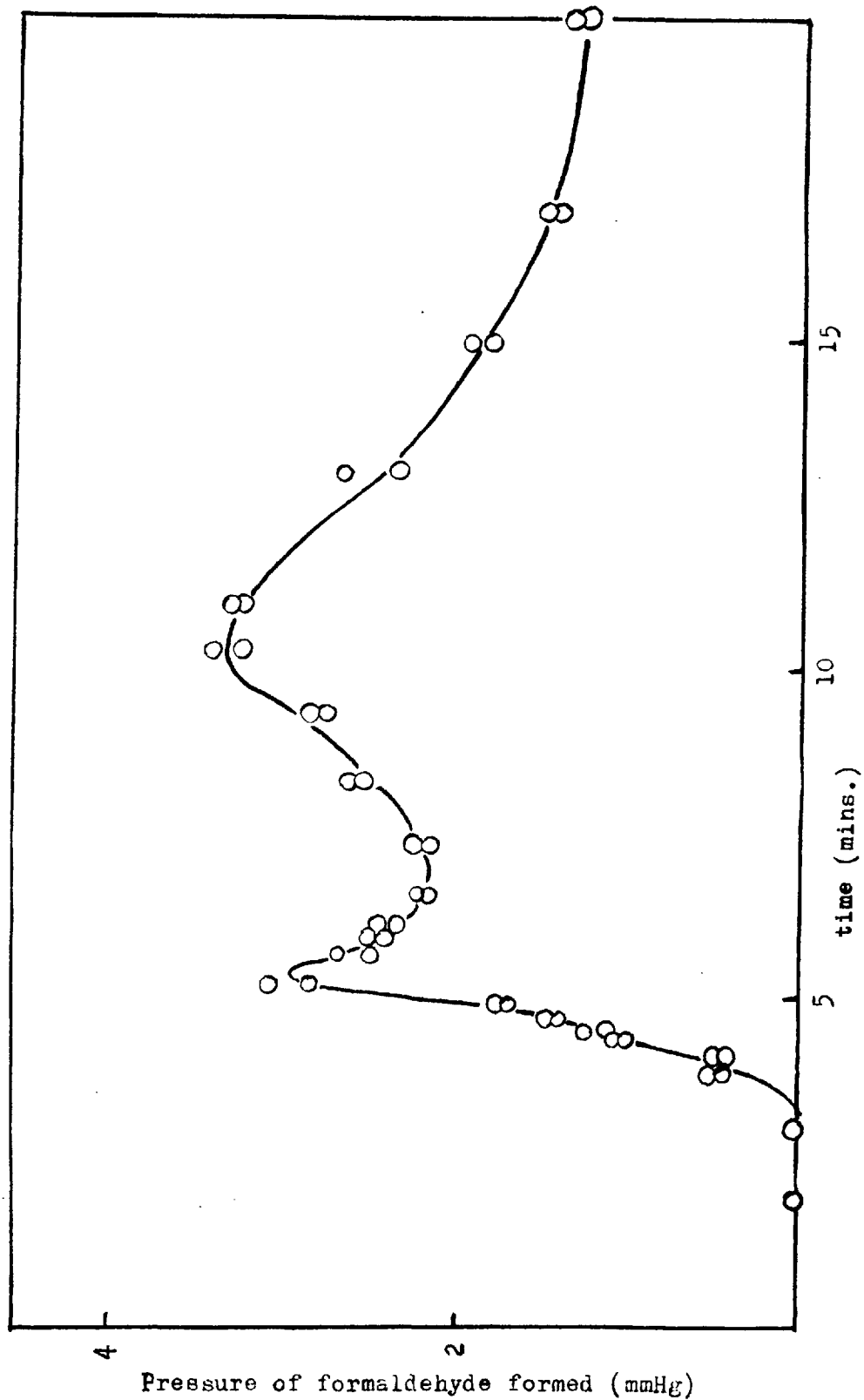
(d) Chemical analysis.

(i) Colorimetric determination of formaldehyde.

Formaldehyde was estimated by the colorimetric method due originally to Bricker and Johnson⁸⁵ and modified for the direct estimation of formaldehyde in the presence of peroxides⁸⁶. The whole of the reaction products was withdrawn from the reaction vessel and frozen into two consecutive traps, T_2 and T_3 , maintained at liquid nitrogen temperature. The frozen products were dissolved in 25.0 ml of water. 1 ml of this solution was transferred to a 50 ml calibrated flask containing ca. 0.05g of magnesium turnings. A few drops of concentrated hydrochloric acid were added and the flask shaken until the magnesium had dissolved. This was done in order to reduce the peroxides present and to reverse addition reactions which occur between hydrogen peroxide and formaldehyde⁸⁸.

0.2 ml of a 5% solution of chromotropic acid in water were then added, followed by 10 ml of concentrated sulphuric

FIG. 2.21. THE FORMATION OF FORMALDEHYDE.

(Oxygen:olefin = 1, temperature 265°C)

acid (slowly with cooling). The solution was heated at 60°C for 45 minutes, then cooled and diluted to 50 ml. with water. The intensity of the violet colour developed was measured, against a reagent blank, using 1 cm. absorption cells in a Unicam SP500 spectrophotometer. A wavelength of 500 m μ , selected from the spectrum of a tungsten source, was used. Each such determination was duplicated. A calibration curve was constructed by preparing a series of standard formaldehyde solutions by diluting Analar formalin solution, standardising by Romijn's iodometric method, and measuring the transmission density for these standard samples. An approximately linear relationship was obtained between the concentration of formaldehyde and the transmission density over the range of concentrations employed for the analysis of combustion product samples.

From these studies a curve was obtained showing the variation with time of the amount of formaldehyde produced in the slow combustion of a 1:1 mixture of 2-methyl-but-2-ene and oxygen at 265°C (fig. 2.21.). Determinations of formaldehyde after explosive reaction were also carried out, the amount present being low (< 1 mmHg).

(ii) Reductive cleavage of peroxides.

(α) By iodide ion.

An iodometric method which permits a distinction to be made between peroxyacids, hydrogen peroxide and organic peroxides⁸⁹ was used in a modified form⁸⁶.

The whole of the reaction products was frozen into traps T₂ and T₃, dissolved in 25 ml water, and immediately transferred to a conical flask containing 10 ml of a saturated aqueous solution of potassium iodide, 5 ml of 2N sulphuric acid and three drops of starch solution, all of which had been frozen just previously by the addition of liquid nitrogen. The

iodine that was liberated after a few seconds was titrated with standardised sodium thiosulphate solution (ca. 0.01N). This titre was equivalent to the amount of peroxyacids present, for these compounds liberate iodine immediately under such conditions. The solution was now allowed to warm to 5°C and the freshly liberated iodine was titrated, the titre being equivalent to the amount of hydrogen peroxide present. The stoppered flask was then warmed to about 40°C, and maintained at this temperature for 60 minutes (until liberation of iodine had ceased). The iodine liberated under these conditions, which was produced mainly by reduction of organic peroxides, was then titrated.

The accuracy of this method depends largely on the speed at which it can be carried out after the products are mixed with water, since hydrogen peroxide reacts at an appreciable speed with any aldehyde, olefin or carboxylic acid present. By this method, the variation with time of the amounts of peroxides formed in the slow combustion of 2-methyl-but-2-ene at 265°C was calculated. Oxygen:olefin ratios of 0.25, 0.50, 0.75, 1.00, 1.25 and 2.00 were used, the initial pressure of 2-methyl-but-2-ene being kept constant at 200 mmHg. The resulting curves are shown in fig. 2.22. The maximum pressure of organic peroxide titrated is compared with the experimentally found pressure decrease in fig. 2.23.

(B) By lithium aluminium hydride.

A solution of 0.14g of lithium aluminium hydride in 20 ml of dry ether was prepared, and frozen into the trap T₂ which was surrounded with liquid nitrogen. A slow combustion of 2-methyl-but-2-ene was now carried out, and at the time of the pressure minimum, the total contents of the reaction vessel were pumped into trap T₂, where they froze on top of the lithium aluminium hydride solution.

FIG. 2.22.(a) THE FORMATION OF PEROXIDES.
(Oxygen:olefin = 1, temperature 265°C)

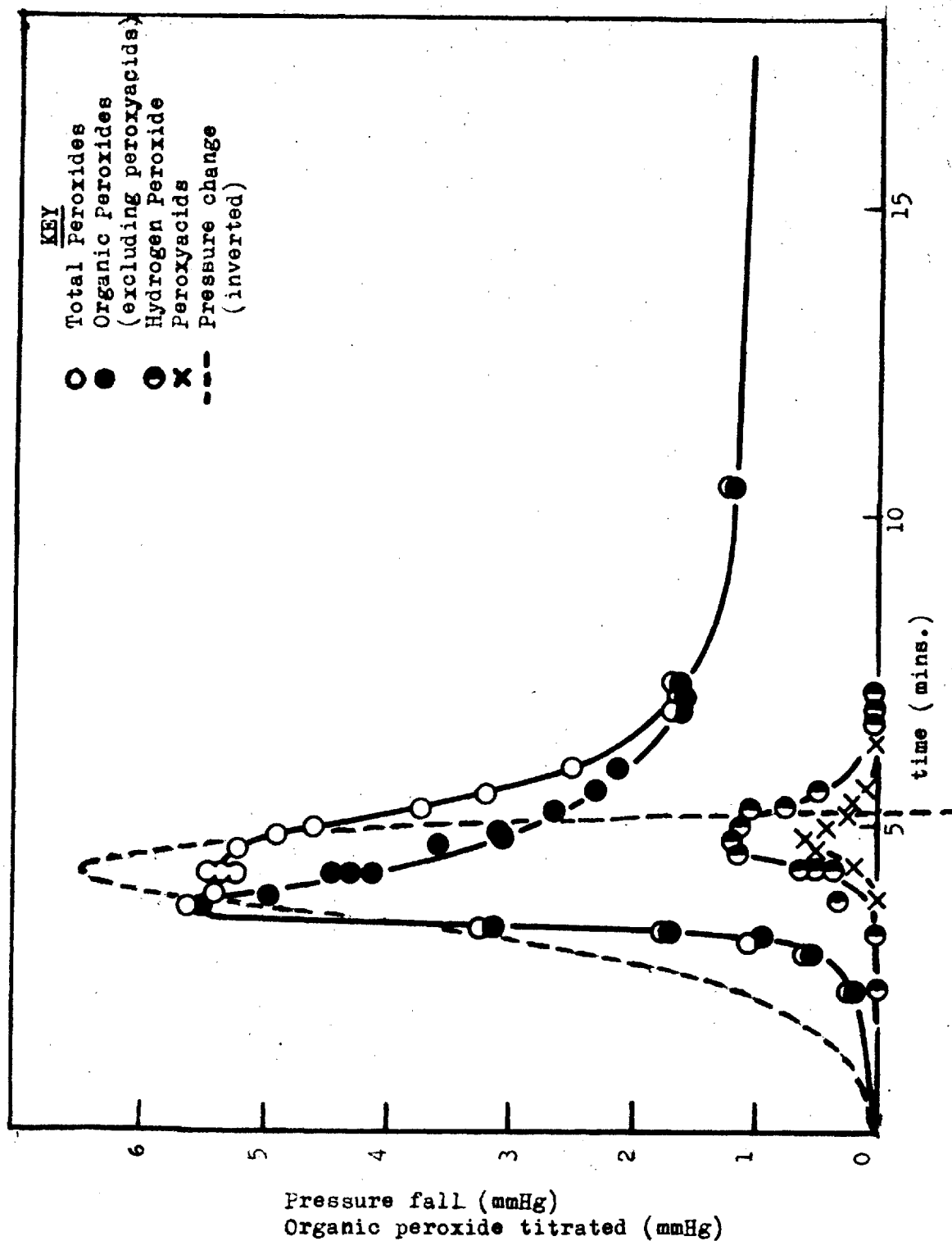


FIG. 2.22(b) THE FORMATION OF ORGANIC PEROXIDES. (81)
VARIATIONS OF PEROXIDE YIELD WITH REACTANT RATIO.
(Temperature 265°C)

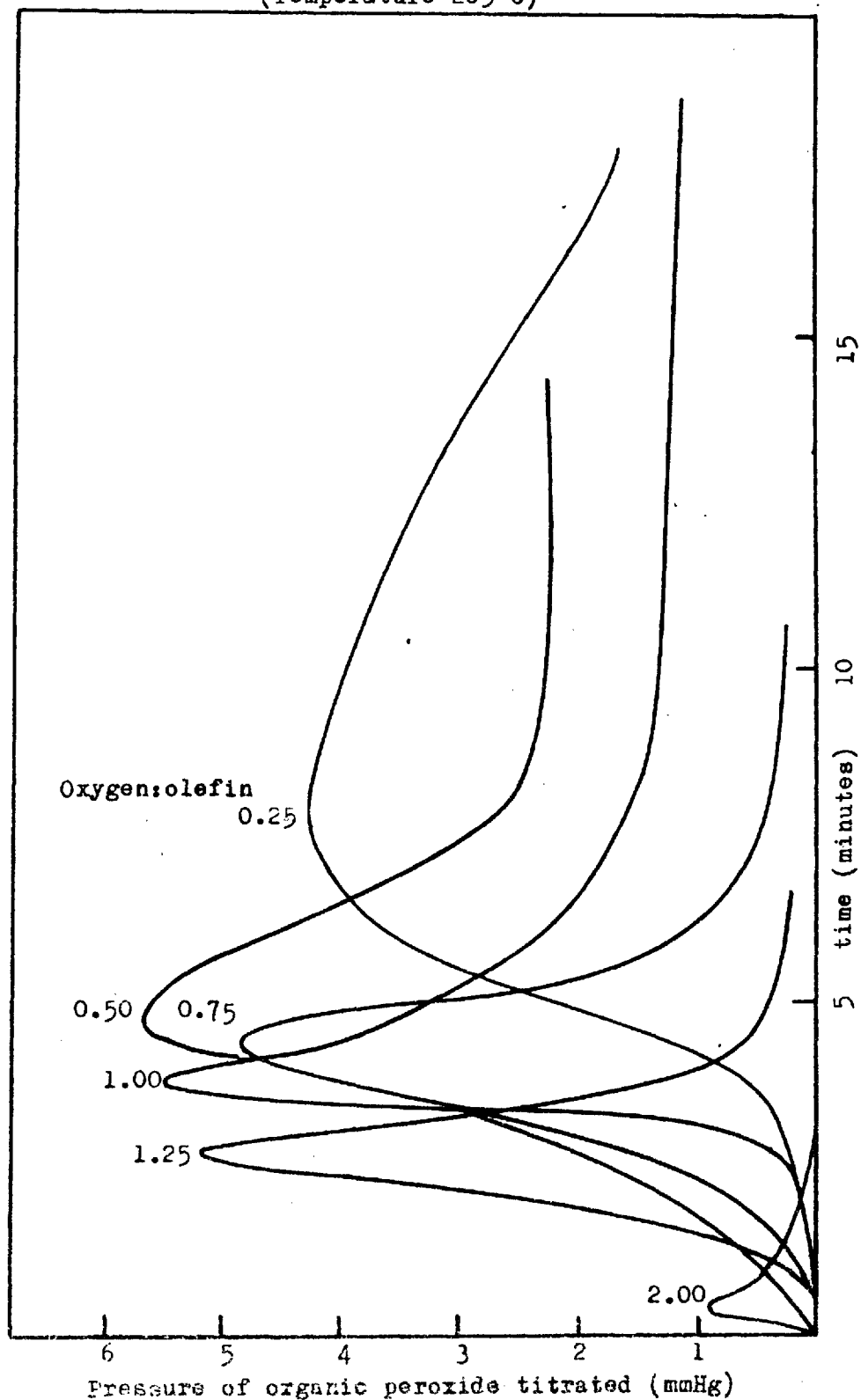
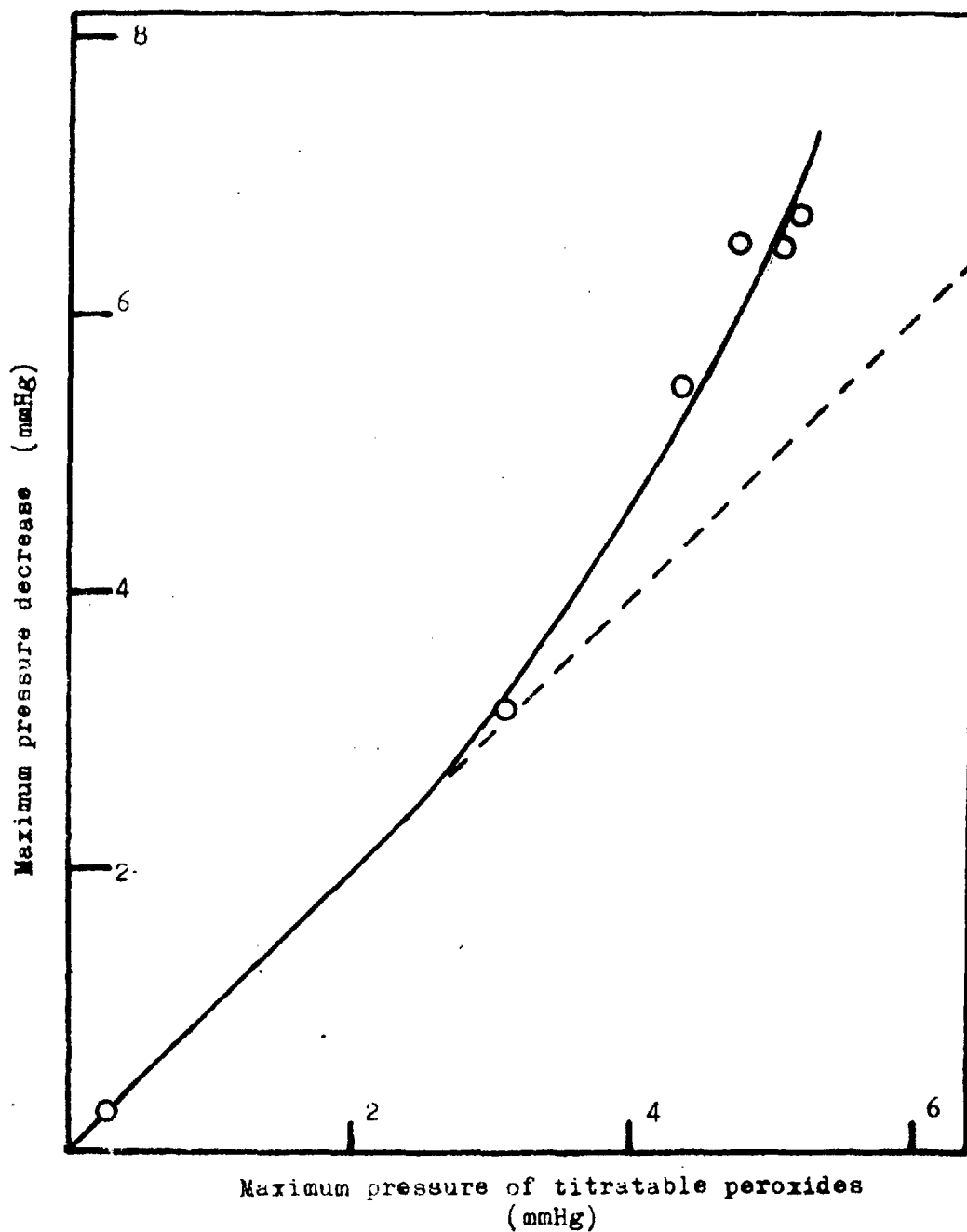


FIG. 2.23. COMPARISON OF THE MAXIMUM AMOUNT OF ORGANIC PEROXIDE TITRATED WITH MAXIMUM PRESSURE DECREASE.

(Temperature 265°C)



This solution was now allowed to warm very slowly, being magnetically stirred to ensure dissolution and reaction of the combustion products. The mixture was now cooled once more to -196°C , and the products (at the time of the pressure minimum) of another combustion reaction were pumped into the trap and allowed to warm. In all, this procedure was repeated fourteen times.

The lithium aluminium hydride complexes so formed were now hydrolysed by the very careful addition of ice-cold 10% sulphuric acid, whereupon all solid material present reacted or dissolved. The ethereal and aqueous layers were separated; the latter was extracted with ether and the extracts added to the ether layer. The ether was now distilled off, the last traces being removed on a microdistillation apparatus, and the products were re-distilled. Sharp fractions were not obtained but the products had a boiling range of $80-170^{\circ}\text{C}$.

The higher-boiling fractions of the reduction products were separated by a silicone gas-liquid chromatographic column at 75°C with a flow rate of 20 ml argon/minute, using an argon ionisation detector. As expected these products contained several alcohols, but they also contained a component which gave a badly tailing peak but nevertheless had a characteristic retention time. Comparison of these chromatograms with chromatograms under similar conditions of pure 2-methyl-2,3-dihydroxy-butane (which was prepared by the reaction of 2-methyl-but-2-ene with 100 volume hydrogen peroxide and 90% aqueous formic acid, and alkaline hydrolysis of the hydroxy formoxy compound so formed) showed that the badly tailing peak mentioned above was identical with that obtained for 2-methyl-2,3-dihydroxy-butane.

The reaction products of the slow combustion of 2-methyl-but-2-ene thus contained, at the time of the pressure minimum,

a component which is reduced by lithium aluminium hydride to 2-methyl-2,3-dihydroxy-butane.

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DISCUSSION OF KINETIC AND ANALYTICAL RESULTS.3A. GENERAL FEATURES.

Gaseous oxidation of 2-methyl-but-2-ene takes place at temperatures above 230°C . The shape of the pressure-time curves for reaction at 246°C (figs. 2.9, 2.10, pages 45-6) shows that an initial autocatalytic decrease in total pressure is followed eventually by an autocatalytic pressure rise. As the temperature is raised, the pressure decrease becomes progressively smaller until at ca. 300°C , the total pressure increases continuously throughout reaction (figs. 2.12, pages 50-2). Single or multiple cool flames are sometimes observed under these conditions and at slightly higher temperatures true ignition intervenes and is accompanied by a considerable increase in pressure (>200 mmHg). Changes in pressure cannot, except under restricted conditions, be used as a parameter for following the reaction, as the observed overall pressure change is the result of a concurrent decrease and increase and is clearly then of little significance as a criterion for following the progress of the oxidation.

A consideration of the analytical results also divides the slow combustion reaction into two regions. Initially, acetone, acetaldehyde, methyl isopropyl ketone and peroxides are the only products detected; during the period of pressure increase, several other (generally simpler) products are formed. It is therefore convenient to discuss the results of studies of the slow combustion reaction in two sections:

- i) The period of pressure decrease, and
- ii) The period of pressure increase.

3B. SLOW COMBUSTION: THE PERIOD OF PRESSURE DECREASE.

I Pressure-time characteristics.

At 246°C, the extent of the initial autocatalytic pressure decrease increases with the amount of oxygen available until the oxygen:olefin ratio is ca. 0.5; thereafter further increase in oxygen concentration affects mainly the magnitude of the subsequent pressure rise (fig. 2.9, page 45). The maximum rate of pressure decrease increases numerically with increasing pressure of each reactant; plots of $(dp/dt)_{\text{maximum}}$ against pressure of oxygen and against pressure of 2-methyl-but-2-ene (fig. 2.11, page 48) show that the relation

$$(dp/dt)_{\text{maximum}} = k_1 [O_2] [\text{olefin}]$$

is obeyed. It is probable that, in this low temperature region, the effect of the pressure-increasing reaction on the slope of the pressure-time curve for the pressure-decreasing reaction is quite small, and the above relation is therefore valid.

The results of accurate pressure-time studies of the initial rate of reaction (Table 2.1, page 57) show that, at a given temperature

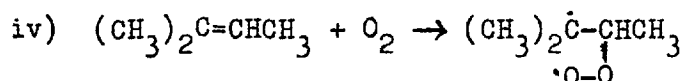
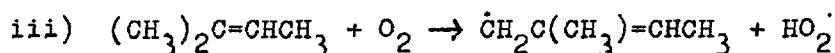
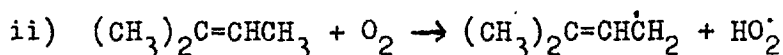
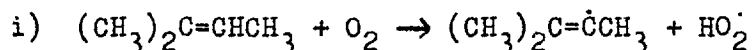
$$(dp/dt)_{\text{initial}} = k_2 (dp/dt)_{\text{maximum}} ,$$

the parameter k_2 being temperature dependent. Thus we have, at a given temperature,

$$(dp/dt)_{\text{initial}} = k_3 [O_2] [\text{olefin}] .$$

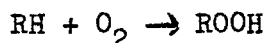
(The proportionality of the initial rate and the oxygen concentration is also suggested directly by the results in Table 2.1). It is suggested, therefore, that the initiation

step in the slow combustion of 2-methyl-but-2-ene involves one molecule of the olefin and one of oxygen. The steps



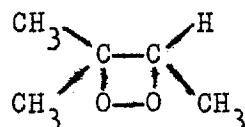
all satisfy this requirement.

Arrhenius plots for the reaction involving a decrease in pressure are shown in fig. 2.14. (page 54). All the points on any one line were obtained using the same concentrations of reactants, so that $\log_{10}(-dp/dt)_{\text{max}}$ may be plotted as $\ln k$. At low temperatures these plots are straight lines, but deviations occur at higher temperatures, particularly when the concentration of oxygen is relatively large, due probably to inaccuracies introduced by interference by the subsequent pressure-increasing reaction. From each Arrhenius plot, an energy of activation was calculated and the values thus obtained varied with oxygen: olefin ratio. A plot of E_A against this ratio (fig. 2.15, page 55) was extrapolated to zero oxygen pressure (near which point the pressure-increasing reaction will not interfere) giving $E_A = 40$ Kcal/mole. As maximum rates, not initial rates, were used for the calculation, and as the reaction is autocatalytic and of unknown chain length, this value of E_A may be without detailed significance. A value of E_A was also calculated from the rate constants calculated from $(dp/dt)_{\text{initial}}$ (Table 2.1), which results suggested a value of 26 ± 5 Kcal/mole

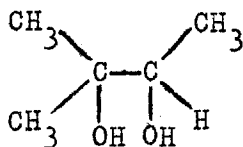


would result, if all the compounds concerned exhibit comparable approaches to ideal gas law behaviour, in a pressure decrease equal to the pressure of peroxides produced. Fig. 2.23 (page 82) shows that in the present system the experimentally observed pressure decrease is in fact somewhat greater than that expected from the total amount of peroxides detected. Since few processes other than peroxide formation involve a decrease in total pressure, this result suggests that more than one type of peroxide is formed. Apart from compounds, such as hydroperoxides, which liberate iodine quantitatively from potassium iodide, some other species, not determined by the analytical method used, are probably present at this stage.

One possible compound is the cyclic peroxide



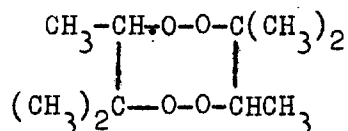
which could be formed by direct addition of oxygen to the excited olefin molecule followed by ring-closure of the bi-radical produced. As such a compound would presumably be unstable, no attempt was made to isolate and characterise it directly. Indirect evidence for its formation is provided however by the results of lithium aluminium hydride reduction of peroxides, the products of which contain the glycol



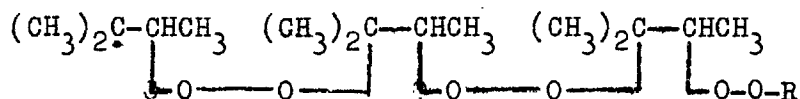
(page 83)

Other possible compounds which would give rise to this

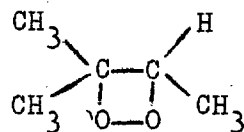
glycol under these conditions have polymeric structures such as



and



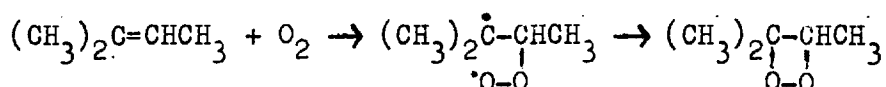
The behaviour of such compounds on iodometric titration cannot be predicted. The formation of such compounds would result however in a pressure drop of at least two millimetres for every millimetre of compound formed, whereas figure 2.23. shows that the experimental curve is tangential to a line of unit slope. Also, under oxygen-deficient conditions any long-chain co-polymer formed would contain some direct C-C bridges, leading to C_{10} units on breakdown. No such units were detected. The non-titratable peroxide most likely to be formed is thus



The actual mechanism of formation of this compound is unknown. It is possible that it involves transition of the olefin from the normal (N) state to the triplet (T) state, facilitating the addition of oxygen. Weak bands in the spectra of ethylene and alkyl-substituted ethylenes, including 2-methyl-but-2-ene, have been attributed to such transitions⁹¹ although this has been questioned by Mulliken⁹². Some calculations of the potential barrier for such transitions

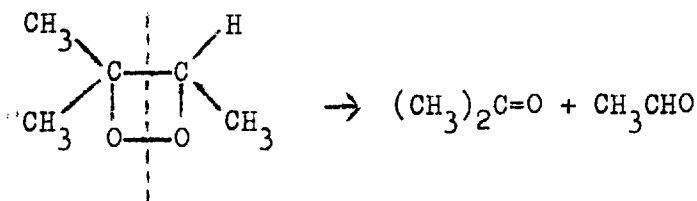
suggest a value of ca. 30 Kcal/mole⁹³ although other work suggests higher values⁹⁴. It has been shown by Evans⁹⁵ that singlet-triplet transitions in ethylenes, dienes, trienes and acetylenes are facilitated by oxygen under pressure. It is perhaps possible then that they may occur during the gas-phase oxidation of olefins, and be followed by oxygen addition at the double bond.

The formation of the cyclic peroxide may however be formally represented:



III The formation of acetone and acetaldehyde.

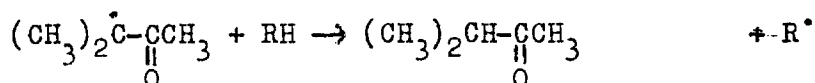
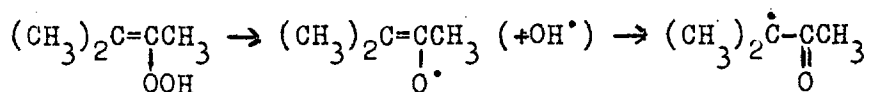
In the early stages of reaction at 265°C the main stable non-peroxidic products are acetone and acetaldehyde (figs. 2.19(b), 2.20(b),(d)). These two compounds are at first formed in closely parallel fashion and in equimolar amounts and their production appears to involve little overall pressure change in the system. It is therefore probable that they have a common precursor. The formation of the postulated cyclic peroxide (above) is consistent with the early and parallel formation of acetone and acetaldehyde, which could clearly arise by the following simple breakdown:



IV The formation of methyl isopropyl ketone.

The only other product detected in considerable quantity during the period of pressure decrease is methyl isopropyl ketone (figs. 2.19(b), 2.20(b)). This could clearly be

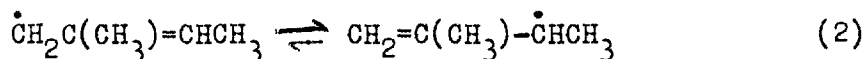
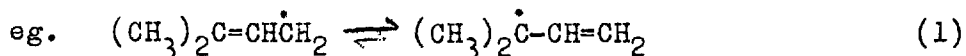
formed by the conventional breakdown of the hydroperoxide $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{OOH}$ produced by the hydroperoxylation chain mechanism (page 89):



methyl isopropyl ketone

This process is likely to be responsible for chain branching.

The absence of iso-valeraldehyde in the reaction products suggests that a hydroperoxylation chain leading to $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{OOH}$ does not occur, and the absence of 2-methyl-butylaldehyde precludes the formation of $\text{HOOCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_3$. This does not prove however that the initial hydrogen abstraction involves only the vinyl group, and that no hydrogen is removed from a methyl group. Some abstraction of hydrogen from methyl groups may occur, being followed by alkyl radical isomerisation,



(cf ref. 23), or by hydrogen migration, giving

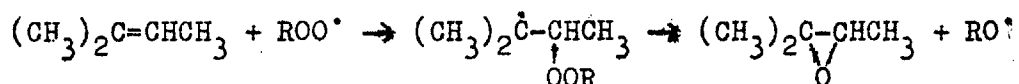


Oxygen addition to the radicals (2) and (3), for example, may well lead to methyl isopropyl ketone. Such radical isomerisations must occur to an almost complete extent however if no 1-hydroperoxy or 4-hydroperoxy 2-methyl-but-2-ene is

to be formed, and the simplest mode of formation of methyl isopropyl ketone is abstraction of hydrogen from the vinyl group, leading to the formation of $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{OOH}$ from which methyl isopropyl ketone is produced as shown on page 93.

V The formation of 2-methyl-2,3-epoxy-butane.

Small quantities of 2-methyl-2,3-epoxy-butane (< 1 mmHg) are formed during the reaction. A possible mode of formation of this compound involves oxidative attack of a further olefin molecule by a peroxy radical $\text{ROO}^\bullet$



The epoxide will tend to isomerise to methyl isopropyl ketone; this may well explain its rapid disappearance from the reaction products. {

3C. SLOW COMBUSTION: THE PERIOD OF PRESSURE INCREASE.I Pressure-time characteristics.

The period of pressure decrease is followed by a period of pressure increase which develops autocatalytically. At low values of oxygen:olefin and low temperatures (figs. 2.9, 2.10) the extent of pressure increase is very small, but at higher temperatures and oxygen:olefin ratios, it becomes the predominant feature of the reaction, Δp_m reaching values of the order of 40 mmHg (eg. fig. 2.12(d)). These results indicate that the principal reactions occurring during the autocatalytic pressure rise involve the participation of further oxygen.

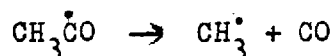
II The consumption of reactants.

During the reaction involving a decrease in pressure, the oxygen and olefin are used up in a closely parallel fashion (fig. 2.19(a)), their rates of disappearance reaching a maximum roughly when the total pressure in the system is a minimum. During the reaction which involves a pressure increase, however, the consumption of oxygen exceeds that of the olefin, indicating that the reactions occurring in this region involve more oxygen than 2-methyl-but-2-ene.

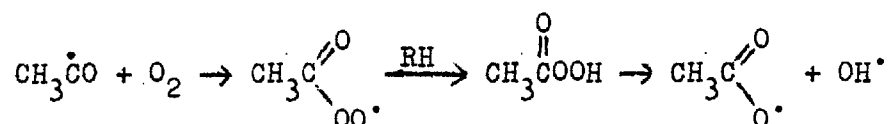
III The formation of methyl alcohol and carbon oxides.

Methyl alcohol is the fourth major condensable product of the combustion. It begins to be formed just before the time of the pressure minimum (figs. 2.19(b), 2.20(b),(d)) and its rate of formation closely parallels the subsequent pressure rise. It is a striking feature of each of these three figures that the methyl alcohol concentration increases as the acetaldehyde concentration decreases; it is therefore probable that acetaldehyde is the precursor of methyl alcohol:

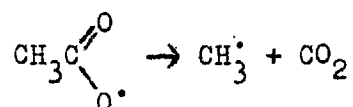




The methyl radicals so formed may produce methyl hydroperoxide by reaction with further oxygen to give a peroxy radical which will abstract hydrogen from further acetaldehyde or 2-methyl-but-2-ene. The resulting hydroperoxide will break down to the radical $\text{CH}_3\text{O}^\cdot$ which could produce methyl alcohol by further hydrogen abstraction. An alternative mode of reaction of the acetyl radical is



branching the chain



The formation of methyl alcohol from acetaldehyde and the production of oxides of carbon during the period of pressure rise (fig. 2.19(b)) thus have a relatively simple explanation.

The methyl alcohol formed suffers some further oxidation (probably to carbon oxides) although it is not completely destroyed.

IV The formation of minor products.

Quite small amounts of propionaldehyde, methyl ethyl ketone, isopropyl alcohol and tertiary butyl alcohol are detected during the later stages of the reaction involving a pressure decrease and throughout the period of pressure increase, but the maximum concentration of these products never exceeds 5%. The propionaldehyde, isopropyl alcohol and tertiary butyl alcohol suffer further oxidation or oxygen-catalysed pyrolysis, whereas the methyl ethyl ketone is relatively stable. The mode of formation of these products is not clear from the kinetic and

analytical results. The results of ^{14}C -tracer studies may elucidate the reactions involved. These results are presented in Part 4 and discussed in Part 5 of this thesis.

Very small amounts (< 1 mmHg) of glyoxal are found in the later stages of oxidation. The mechanism of formation of this product is not known, and the concentrations found are too small to enable an effective isotopic tracer study to be carried out.

V The self-inhibition of the reaction.

Despite the consumption of large amounts of oxygen during the later stages of reaction, oxidation of 2-methyl-but-2-ene appears to cease while considerable amounts of both the initial reactants are still present (fig. 2.19(a)), or in other words the reaction becomes self-inhibited. The reasons for this type of behaviour, which has been observed in other gaseous oxidation systems (eg. ref. 96), are still far from clear.

3D. THE REGION OF COOL FLAMES.

The combustion of 2-methyl-but-2-ene has a region of cool flames between the temperature limits 280°C and 330°C and at oxygen:olefin ratios of 0.95 to 1.2 (fig. 2.13, page 53). These limits vary as the reaction vessel ages. The products formed are similar to those found during slow combustion, although many of these are produced in somewhat greater amounts in the cool flame region. It therefore seems likely that the mechanisms of the reactions occurring in cool flames are akin to those postulated for the region of slow combustion.

3E. THE REGION OF EXPLOSIVE REACTION.

A region of explosive reaction, the limits of which are shown in fig. 2.13, has also been noted. Analysis of condensable products from explosive oxidation (including unchanged 2-methyl-but-2-ene) shows that such products are present in amounts which are small compared with those found in the slow combustion region. Explosion does not occur immediately on admission of the reactants to the reaction vessel and is thus presumably preceded by a short period (10 seconds to 3 minutes) of slow combustion, during which time characteristic pressure-time curves have been obtained. It is therefore probable that explosion results from the rapid further oxidation of the products of slow combustion to smaller, non-condensable fragments such as carbon monoxide. This postulate is consistent with the large pressure rise (> 200 mmHg) of the explosive reaction. As the oxidation of acetaldehyde is almost certainly the main chain propagating and branching reaction during the autocatalytic pressure rise of the slow combustion process, it is possible that this reaction is also responsible for rapid chain branching leading to explosion.

PART 4.CARBON-14 TRACER STUDIES: EXPERIMENTAL METHODS
AND RESULTS.

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CARBON-14 TRACER STUDIES: EXPERIMENTAL METHODS AND RESULTS.

4A. SYNTHESIS OF ^{14}C -LABELLED 2-METHYL-BUT-2-ENES.

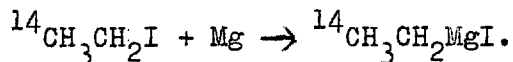
I Introduction.

In preparations involving the use of radioactive materials it is desirable to employ a closed system or vacuum line, firstly because this minimises the danger of inhalation of active material and secondly because any operation which involves the transfer of small quantities of volatile materials can be carried out with smaller loss on the vacuum line than by any other method. All the preparations of radioactive compounds were carried out in a suitably equipped radiochemical laboratory; the usual precautions were taken for handling soft β -emitters.

Syntheses were devised which incorporated labelled starting materials (ethyl iodide, acetone) obtained from the U.K.A.E.A. Radiochemical Centre, Amersham. The synthetic routes were first tested with inactive materials.

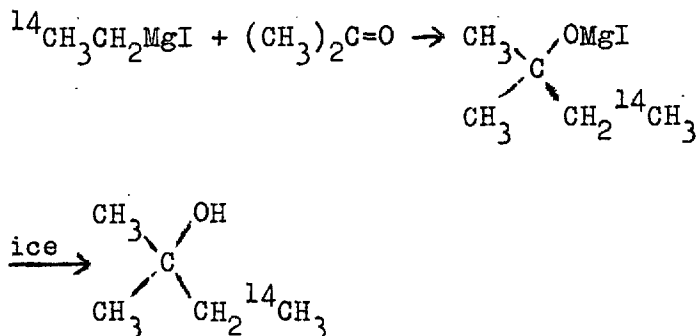
II $[4-^{14}\text{C}]$ 2-methyl-but-2-ene.

0.146g of magnesium turnings and 2.8 ml of diethyl ether were placed in a flask. 7.7mg (0.1 mc) of $[2-^{14}\text{C}]$ ethyl iodide followed by 0.966g of inactive ethyl iodide were distilled into the flask under vacuum, thus forming ethyl magnesium iodide labelled in the 2-position.



Successive portions of a solution of 0.428g acetone in 0.4 ml diethyl ether were vacuum-distilled into the frozen Grignard reagent and after the mixture had been stirred for three hours at room temperature the complex so formed was hydrolysed with 1.9g ice followed by 2.2 ml cold 10% v/v sulphuric acid which

dissolved the magnesium hydroxide present. When larger quantities of mineral acid were added (in trial preparations) the pH fell below five, causing considerable dehydration of the t-amyl alcohol formed and producing amylenes which were difficult to recover from the ether solution.



The aqueous layer was separated and extracted with diethyl ether (3 x 1 ml) and to the combined washings and ether layer 0.40 ml inactive t-amyl alcohol was added as carrier. The resulting solution was dried with anhydrous magnesium sulphate and potassium carbonate, and the desiccants were washed with an ethereal solution of 0.27 ml t-amyl alcohol. The solvent ether was removed by careful fractionation, leaving [4- ^{14}C] 2-methyl-but-2-ol. (Yield 64%; Analysis, C, 68.0%; H, 13.5%; $\text{C}_5\text{H}_{12}\text{O}$ requires C, 68.13%; H, 13.72%; $n_D^{20} = 1.4049$, cf. literature, $n_D^{20} = 1.4052$).

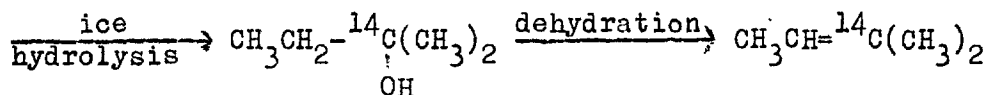
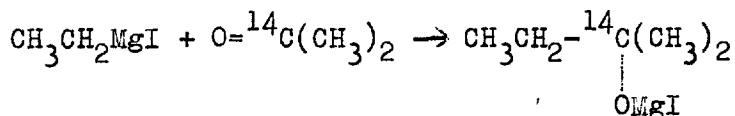
The [4- ^{14}C] 2-methyl-but-2-ol was next refluxed with 4.0 ml of 33% v/v sulphuric acid and the product was distilled in a special apparatus with a cardice-cooled condenser, the fraction boiling in the range 37-41°C being collected. This product was predominantly [4- ^{14}C] 2-methyl-but-2-ene but contained a small proportion of [4- ^{14}C] 2-methyl-but-1-ene. The latter was removed by gas chromatography on a silicone column (see Part 2, section A) leaving [4- ^{14}C] 2-methyl-but-2-ene (Overall yield 44%; analysis, C, 85.6%; H, 14.4%; C_5H_{10}

requires C, 85.63%; H, 14.37%; $n_D^{15} = 1.3909$, cf. literature, $n_D^{15} = 1.3908$).

After a small sample of the olefin had been removed for analysis and radioassay, the remainder was sealed in a break-seal ampoule.

III [2- ^{14}C] 2-methyl-but-2-ene.

The synthesis of [2- ^{14}C] 2-methyl-but-2-ene was achieved by a method similar to that described above for [4- ^{14}C] 2-methyl-but-2-ene. The source of carbon-14 was in this case [2- ^{14}C] acetone instead of [2- ^{14}C] ethyl iodide.



[2- ^{14}C] acetone having an activity of 0.8 mc was used in order to obtain an olefin with a higher specific activity than the [4- ^{14}C] 2-methyl-but-2-ene previously prepared, thus facilitating radioassay of the minor combustion products.

The yield of [2- ^{14}C] 2-methyl-but-2-ene was 39% (Analysis, C, 85.5%; H, 14.0%; C_5H_{10} requires C, 85.63%; H, 14.37%; $n_D^{15} = 1.3904$, cf. literature, $n_D^{15} = 1.3908$).

4B. GASEOUS OXIDATION OF ^{14}C -LABELLED 2-METHYL-BUT-2-ENES.

I Combustion experiments: kinetic procedure.

Duplicate combustion of $[4-^{14}\text{C}]$ 2-methyl-but-2-ene was carried out in exactly the same way as has been described for the inactive olefin (Part 2, section B II).

Oxygen and 2-methyl-but-2-ene vapour in a 1:1 ratio were used, the furnace temperature being 265°C . At a known stage of the reaction, the products of oxidation were withdrawn from the furnace, and trapped in a capillary U-tube surrounded by liquid oxygen, the amount of each product present at this time being calculated from the product-time curves obtained from gas-liquid chromatographic analysis of the products of the oxidation of the inactive olefin. To these products were added, by vacuum distillation, known amounts of pure inactive products to act as 'carriers'. The resulting mixture was separated by gas-liquid chromatography (section 4B II).

Similar experiments were carried out using $[2-^{14}\text{C}]$ 2-methyl-but-2-ene. The amounts of products taken from the reaction vessel and the amounts of carriers added are shown in Table 4.1.

II The separation and purification of products.

The combustion products (diluted with inactive carriers) were separated on a preparative-scale gas-liquid chromatographic column, using celite 545 impregnated with 20% by weight of polyethylene glycol (molecular weight = 400) as stationary phase. The dielectric constant detector⁷⁵ previously mentioned was used, the output being fed to a recorder. As each constituent was eluted it was trapped in the form of a derivative by passing through a suitable solution. For carbonyl compounds 2,4-dinitro-phenylhydrazine sulphate in methyl alcohol was used, and for alcohols, 3,5-dinitro-benzoyl chloride in dry benzene/pyridine.

TABLE 4.1.

OXIDATION OF $[4-^{14}\text{C}]$ 2-METHYL-BUT-2-ENE.

PRODUCT	No. of g-moles taken from reaction vessel	No. of g-moles of carrier added
acetaldehyde	7.46×10^{-5}	5.32×10^{-3}
acetone	2.33×10^{-4}	4.10×10^{-3}
propionaldehyde	$2.03 \times 10^{-5} \text{ }^{\#}$	4.17×10^{-3}
methyl ethyl ketone	3.01×10^{-6}	3.35×10^{-3}
methyl isopropyl ketone	6.15×10^{-6}	2.84×10^{-3}
methyl alcohol	5.70×10^{-5}	7.40×10^{-3}
isopropyl alcohol	5.4×10^{-6}	3.92×10^{-3}
t-butyl alcohol	6.87×10^{-6}	3.20×10^{-3}

[#] separate sample of reaction products used.

OXIDATION OF $[2-^{14}\text{C}]$ 2-METHYL-BUT-2-ENE.

PRODUCT	No. of g-moles taken from reaction vessel	No. of g-moles of carrier added
acetaldehyde	4.72×10^{-5}	8.87×10^{-4}
acetone	1.09×10^{-4}	1.06×10^{-3}
propionaldehyde	1.04×10^{-5}	4.17×10^{-4}
methyl ethyl ketone	1.66×10^{-6}	3.35×10^{-4}
methyl isopropyl ketone	2.73×10^{-5}	3.79×10^{-4}
methyl alcohol	6.26×10^{-5}	1.23×10^{-3}
isopropyl alcohol	5.13×10^{-6}	3.99×10^{-4}
t-butyl alcohol	2.83×10^{-6}	3.20×10^{-4}

The 2,4-dinitro-phenylhydrazones were precipitated immediately and were filtered off and washed with methyl alcohol. The solutions of 3,5-dinitro-benzoates were heated under reflux on a steam bath for 30 minutes (1 hour in the case of t-butyl alcohol) and poured into water. The esters were extracted with ether and the solutions were washed with sodium carbonate solution, dilute hydrochloric acid and finally water. They were then dried over sodium sulphate and the ether was removed by evaporation. The derivatives were recrystallised (2,4-dinitro-phenylhydrazones from ethyl alcohol, 3,5-dinitro-benzoates from carbon tetrachloride) and their melting-points were compared with literature values. The separation achieved was sufficiently good for most derivatives to be purified satisfactorily by two recrystallisations, although t-butyl 3,5-dinitro-benzoate was not well separated from methyl 3,5-dinitro-benzoate, six recrystallisations being necessary in this case.

III Radioassay equipment, technique and results.

(a) APPARATUS.

(i) The counter.

Radioactive decay of ^{14}C results in the emission of a continuous spectrum of β -rays with energies from zero up to a maximum of 0.15 MeV⁹⁷. The most energetic of these particles is absorbed by as little as 30 mg/cm² of aluminium and it is therefore essential to employ a counter of 'windowless' design if a high counting efficiency is to be obtained. The instrument used in the present work (described fully in ref. 98) is shown schematically in fig. 4.1. Essentially it comprised two brass cylindrical blocks C and D. The lower block D held the sample pans P and could be rotated so as to bring the pans successively into the pre-flushing

chamber B and the counting chamber A. The apparatus was continuously flushed with 99% methane from which carbon dioxide and water had been removed by passage over potassium hydroxide and anhydrous magnesium perchlorate respectively.

(ii) Associated electronic circuits.

These are shown diagrammatically in fig. 4.2. A power unit (type P200A) produced the 3000 volts positive collecting-potential applied to the centre wire of the counter. Output pulses (maximum amplitude ca. 1 mV) were applied to the H.F. head amplifier and a linear amplifier (type 1008) through a 50 pF blocking capacitor, this connection being kept very short in order to minimise pulse distortion by stray capacitance to earth. The main amplifier was operated 20 dB below maximum gain and with time constants of differentiation and integration of 0.15 and 0.5 microseconds respectively. Two germanium diodes introduced between the two sections of the amplifier limited 'overshoot' following the largest pulses. Output pulses from the amplifier were then fed to a scaler (type 1005A) followed by a dekatron register. A discriminator level of 15 volts rejected all valve noise and other interference which amounted to less than one volt with the amplifier settings given above. Normal operation of the counter tube was checked by means of an oscilloscope.

(iii) Coincidence correction.

As the dekatron register had a paralysis time of less than a millisecond, the maximum counting rate that could be recorded was limited only by the scaler paralysis time (5 microseconds). For the values normally recorded ($< 10^4$ counts/minute) no corrections were necessary.

(iv) Operating potential.

This was selected so that the counter

FIG. 4.1. SECTIONAL VIEW OF THE COUNTER.

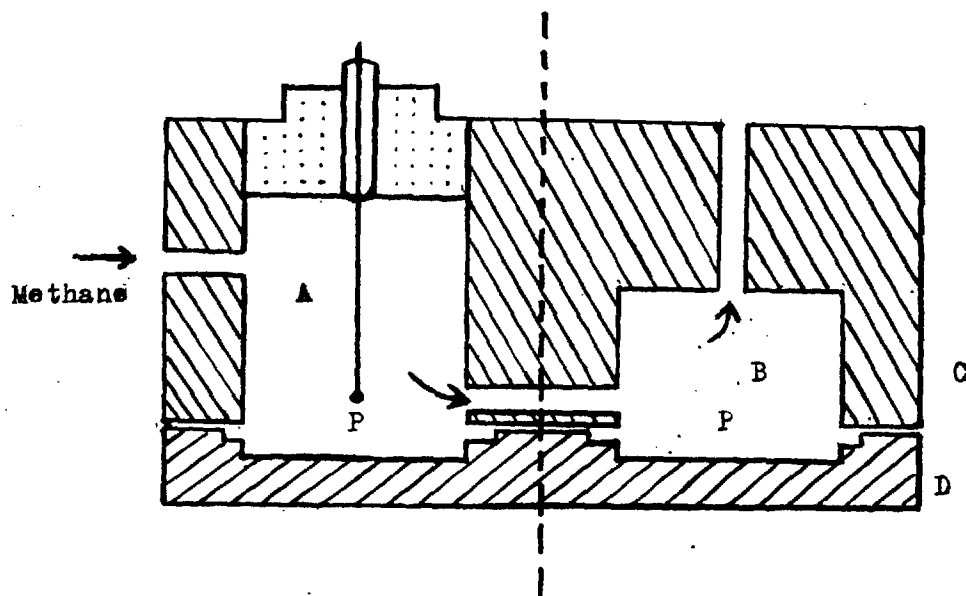


FIG. 4.2. COUNTER CIRCUIT.

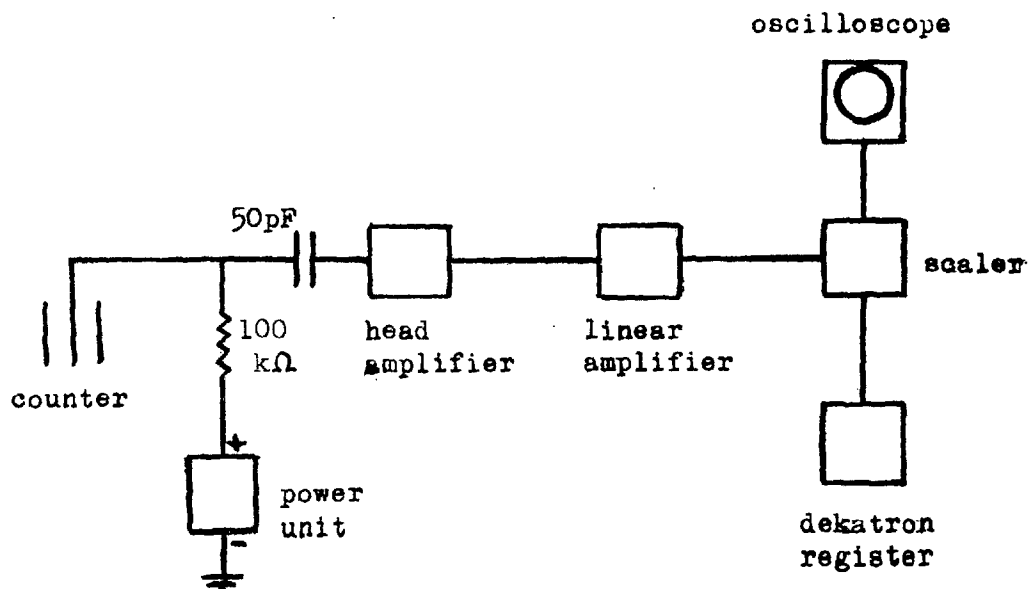
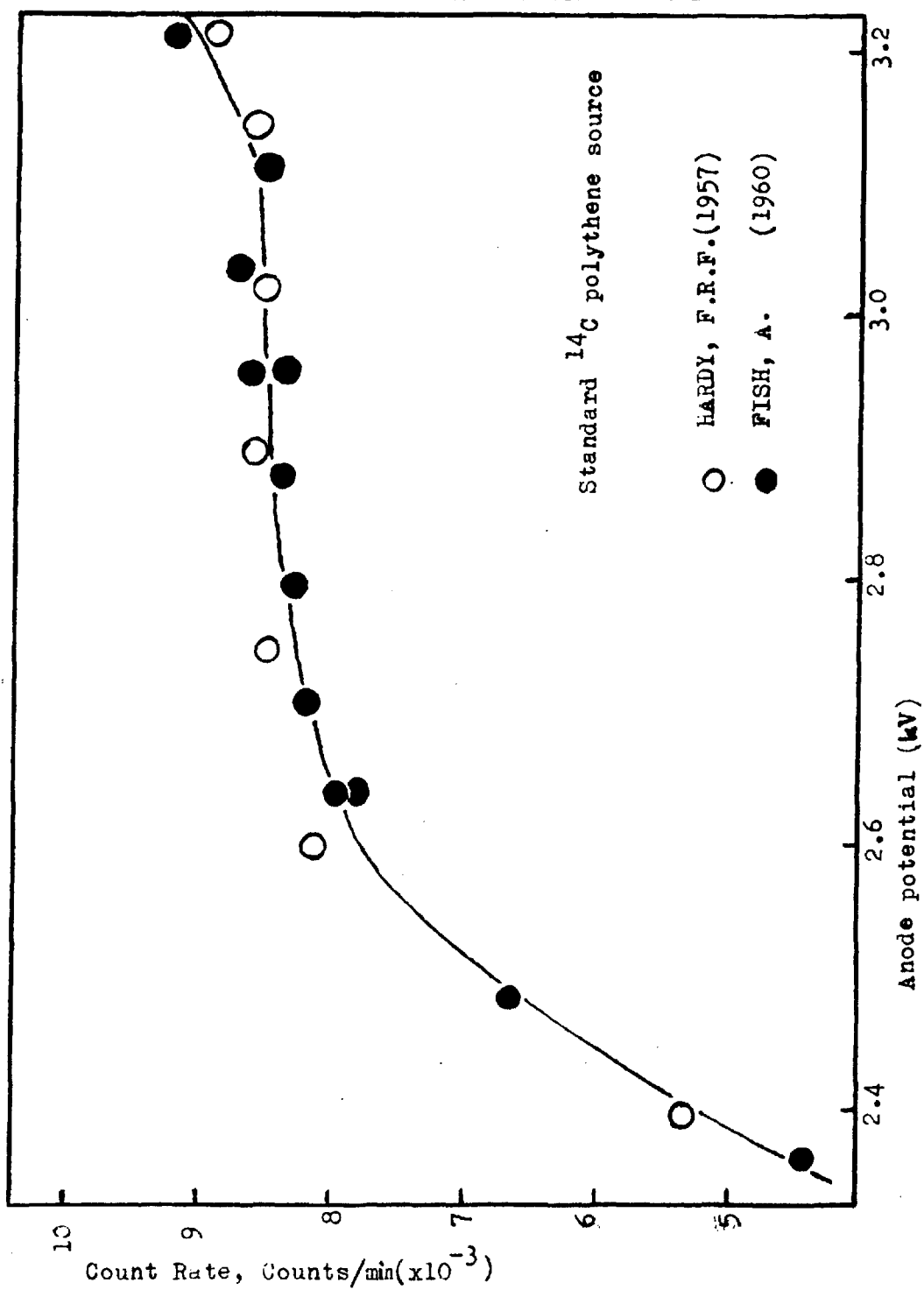


FIG. 4.3. COUNTER CHARACTERISTIC CURVEVARIATION OF COUNT RATE WITH ANODE POTENTIAL.

operated in the proportional region, i.e. pulse height is proportional to the magnitude of the initial ionising event. With the aid of a standard ^{14}C -polythene source, a graph was constructed of count rate against the potential applied to the counter wire (fig. 4.3). The final operating potential (2960 volts) was such that it was in the nearly level portion of this curve.

(v) Background count rate.

The counter was enclosed in a lead casing 2" thick and the background normally obtained was 10-20 counts/minute. However, this background tended to increase with prolonged use of the counter and, when backgrounds much above 20 counts/minute were obtained, the counter was completely dismantled and cleaned, first with organic solvents and finally by treatment with dilute nitric acid.

(vi) Linearity of counter response.

This was investigated by previous workers under conditions very similar to those used in the present work⁹⁹. Count rate was found to vary linearly with the concentration of active species in the sample.

(b) TECHNIQUE.

(i) Sampling.

The sample pans were nickel dishes 25 mm. in diameter and 2 mm. deep in which samples could be assayed either as thin solid films or in solution. For accurate work it is advisable to use a liquid sample since this can always be relied upon to give a uniform layer of even thickness and a reproducible surface. It has been found⁹⁸ that a liquid sample of ca. 0.3 ml. has an 'infinite' thickness when placed in one of the pans described above; in other words, for a liquid sample of given activity no increase in count rate is observed for sample volumes greater than 0.3 ml.

In the case of some of the highly isotopically diluted samples, however, the observed count rate was too close to the background count rate for accurate determinations if samples in solution were used. In these cases the samples were counted as thin films of 'infinite' thickness.

(ii) Choice of solvent for counting.

This was governed by two considerations: good solvent properties for the class of compounds being studied, and absence of interference of the solvent vapour with the operation of the counter. The latter requirement eliminates the more volatile solvents (B. Pt. $< 150^{\circ}\text{C}$), especially those such as water and alcohols which have a marked tendency to take part in negative ion formation.

The solvents used in the present work are discussed in section B III(c).

(c) MEASUREMENT OF THE SPECIFIC MOLAR ACTIVITY OF REACTANTS AND PRODUCTS.

(i) ^{14}C -labelled 2-methyl-but-2-enes.

Analysis and radioassay of the olefins may be attempted by two methods:

- (a) Preparation, analysis and radioassay of a non-volatile derivative of the olefin.
- (b) Complete combustion of the olefin to carbon dioxide, absorption of this carbon dioxide in a reagent of suitably low volatility and radioassay of the resulting solution.
- (a) Preparation of derivatives.

Direct derivatives of 2-methyl-but-2-ene, such as the dibromide, are too volatile to be used without contamination of the counter. Attempts were therefore made to synthesise 2,3-dimethyl-pent-2-ene-4-one from 2-methyl-but-2-ene by a Friedel-Crafts reaction followed by elimination (by the method of Sharefkin and Sulzberg¹⁰⁰). The ketone could then be

counted as its 2,4-dinitro-phenylhydrazone. This synthesis, however, gave an impure product in low yield and was therefore considered unsuitable.

Ozonolysis of the olefin followed by steam distillation and isolation of the resulting acetaldehyde as its dimedone adduct and of the resulting acetone as its 2,4-dinitro-phenylhydrazone was unfruitful, due to the dimedone adduct being produced in low yield. Precipitation of both aldehyde and ketone as 2,4-dinitro-phenylhydrazones gave better yields but separation of these derivatives by chromatography in a mixture of benzene and chloroform was also inefficient. Free acetaldehyde and acetone can of course be separated by gas-liquid chromatography but their regeneration from the 2,4-dinitro-phenylhydrazones with 1:1 pyruvic acid in water also gave low yields, particularly for the aldehyde.

(b) Complete combustion to carbon dioxide.

It was therefore decided to resort to complete combustion of the olefin as a method of radioassay (cf. ref. 99). Olefin was transferred by vacuum distillation into weighed narrow tubes, which were then carefully sealed with the blow torch and reweighed, thus giving samples suitable for complete combustion to carbon dioxide by standard microanalytical techniques. The results of these analyses have been quoted in sections A II and A III.

The carbon dioxide from a microanalytical combustion (in which hydrogen only was directly determined) was condensed in a spiral tube immersed in liquid oxygen. This tube was attached to the vacuum line, enabling the carbon dioxide to be transferred to a calibrated volume from which its uptake by a suitable reagent could be followed manometrically.

Lithium phenyl in diethylene glycol diethyl ether was used by previous workers⁹⁹ as a reagent for the quantitative

absorption of carbon dioxide, but was not entirely satisfactory due to its high rate of reactivity with atmospheric oxygen, water and carbon dioxide, and its tendency to form gelatinous products. Lithium n-octyl was prepared by refluxing a solution of lithium in anhydrous ether with n-octyl bromide, and investigated as a possible alternative reagent. Even when this reagent was stored under argon, however, a grey precipitate was continuously produced and the strength of the solution decreased quite quickly, making it impossible to calibrate accurately the extent of uptake of carbon dioxide by the solution.

The solubility of alkali metal hydroxides and tetra-alkyl-ammonium hydroxides in involatile solvents suitable for use in the counter was investigated. Concentrated solutions of potassium hydroxide in ethylene glycol were found to absorb carbon dioxide most satisfactorily, the amount of carbon dioxide absorbed being a linear function of the weight of potassium hydroxide/ethylene glycol solution used. This fact, together with the low volatility of such solutions, renders them most suitable for carbon dioxide radioassay. Such solutions were therefore used for absorption of the mixture of $[^{14}\text{C}]$ carbon dioxide and $[^{12}\text{C}]$ carbon dioxide produced during microanalysis of labelled olefins, the rate and extent of uptake of carbon dioxide being followed manometrically. The potassium hydroxide/ethylene glycol reagent was then saturated with inactive carbon dioxide as diluent and samples were radioassayed, thus enabling the specific molar activity of the carbon dioxide and hence of the original olefin to be calculated.

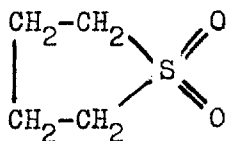
As a result of vigorous stirring of the assayed solutions in an atmosphere of pure inactive carbon dioxide and reassay after 15 minutes, it was found that no change in specific

activity had occurred, showing that the carbon dioxide had been absorbed in a form (probably CO_3^{--}) that does not rapidly undergo exchange.

The results of radioassay of the olefins are shown in Table 4.2.

(ii) Carbonyl compounds and alcohols.

The hydrogenated butadiene-sulphur dioxide adduct sulpholane,



is a polar solvent with a high boiling-point (202°C) and low volatility, and was discovered to be suitable for use in the counter. It was found to dissolve readily the 3,5-dinitrobenzoates of methyl, isopropyl and t-butyl alcohols and the 2,4-dinitro-phenylhydrazones of acetaldehyde, propionaldehyde and acetone, enabling counting in solution to be effected. The solubilities of methyl ethyl ketone and methyl isopropyl ketone 2,4-dinitro-phenylhydrazones were however sufficiently small to restrict seriously the count rate obtainable by this method in the case of the products of combustion of $[4\text{-}^{14}\text{C}]$ 2-methyl-but-2-ene. (In the case of the products of combustion of $[2\text{-}^{14}\text{C}]$ 2-methyl-but-2-ene the higher activity of the starting material was sufficient to overcome this disadvantage.)

The derivatives of the methyl ethyl and methyl isopropyl ketones produced during combustion of $[4\text{-}^{14}\text{C}]$ 2-methyl-but-2-ene were therefore counted as thin films. Such films should be amorphous for optimum results and, at least, must not have highly irregular crystalline surfaces. The best way of producing films of this kind was found to be by deposition from dimethylformamide solution of weighed amounts of derivative. Heating

TABLE 4.2.

ABSORPTION OF CARBON DIOXIDE BY POTASSIUM HYDROXIDE/
ETHYLENE GLYCOL SOLUTION AND RADIOASSAY OF THE
RESULTING SOLUTION.

- w = weight of olefin combusted to carbon dioxide (mg.)
 p_1 = pressure of carbon dioxide which should be produced in
 standard volume (50.0 ml. at N.T.P.) (mmHg)
 p_2 = pressure of carbon dioxide actually produced in standard
 volume (mmHg)
 p_3 = amount of this carbon dioxide absorbable by potassium
 hydroxide/ethylene glycol solution (mmHg)
 n = number of counts per minute corrected for background
 (average)
 A = specific activity of olefin (counts/minute/(g-mole/g soln.))

olefin	Inactive olefin (trial)		[4- ¹⁴ C] 2-methyl-but-2-ene			[2- ¹⁴ C] 2-methyl-but-2-ene		
w	12.20	12.03	5.38	4.57	6.95	13.50	14.30	14.75
p ₁	320	315	141	120	-	348	369	381
p ₂	317	313	139.5	118	78.5 [±]	351	372	377
p ₃	316	313	139	117	75.0 [±]	351	372	376
n	-	-	322.7	301.3	74.8	420.3	425.5	654.1
A x 10 ⁻⁷	-	-	1.387	1.365	1.345	5.43	5.33	5.24
A, average	-	-	(1.37±0.02)10 ⁷			(5.33±0.10)10 ⁷		

* In the case of this sample, complete combustion to carbon dioxide was effected using the copper oxide furnace (F_2 , fig. 2.1) on the combustion line, and the pressure of carbon dioxide measured using manometer M_2 . These pressures are thus not comparable with the others in this table.

from above, using an infra-red lamp, rather than from below ensured that the derivative was hotter than the nickel sampling pan, thus considerably decreasing the tendency of the hydrazones to decompose during deposition. The tendency of samples to be deposited round the outside of the pan, producing uneven layers, was counteracted by treating the pan rim with silicone grease which is not wetted by dimethyl-formamide. By use of one of these techniques the activity of a given sample in counts/minute (corrected for background) may be determined. Specific activities may then be calculated as below.

If x is the number of counts recorded per minute using a sample of y gms. of a compound of molecular weight M in $(z-y)$ gms. of a solvent (i.e. in z gms. solution), then the specific molar activity of the compound in counts/minute/ (g-mole/g. solution) (a) is given by

$$a = \frac{xzM}{y}$$

Now if m_1 g. of an active combustion product were isotopically diluted with m_2 g. of an inactive carrier, and the resulting isotopic mixture was used to prepare samples for radioassay, then the specific activity of the actual combustion product (b) is related to that of the sample (a) by

$$b = \frac{a(m_1 + m_2)}{m_1}$$

$$b = \frac{xzM}{y} \cdot \frac{(m_1 + m_2)}{m_1}$$

It is this specific activity, b , which must be compared with that of the reactant olefin in order to calculate the percentage retention of activity during the formation of the combustion product under consideration.

In this way, the specific activities of the carbonyl compounds and alcohols produced by combustion of ^{14}C -labelled 2-methyl-but-2-enes have been calculated. They are given and compared with the activities of the 2-methyl-but-2-enes in Table 4.3.

(d) DEGRADATION OF RADIOACTIVE COMBUSTION PRODUCTS.

(i) Degradation of oxidation products of $[4-^{14}\text{C}]$ 2-methyl-but-2-ene.

(α) Liberation of carbonyl compounds from their hydrazones.

A small portion (ca. 12 mg.) of acetaldehyde 2,4-dinitro-phenylhydrazone was weighed out into a small tube and to this was added a known weight of pure inactive acetaldehyde (ca. 100 mg.). One drop of concentrated hydrochloric acid was added to this mixture and the tube was sealed and heated in an oil bath at 70°C for sixteen hours. The free aldehyde was then distilled on the vacuum line, collected in a trap surrounded by liquid nitrogen and retained for degradative studies. To determine the extent of exchange that had taken place between the 'active' hydrazone and the inactive aldehyde, the hydrazone residue in the tube was dried, dissolved in dimethyl-formamide, deposited in a nickel sample pan and counted as a thin film. The activity of this hydrazone was then compared with that expected if exchange were complete. Similar experiments were carried out with the 2,4-dinitro-phenylhydrazones of methyl ethyl and methyl isopropyl ketones.

The results of these investigations are shown in Table 4.4(a). From comparison of the expected and actual activities of the final hydrazones, it is clear that the expected exchange has indeed taken place to the extent of at least 99%.

TABLE 4.3(a)

SPECIFIC ACTIVITIES OF OXIDATION PRODUCTS OF
[4-¹⁴C] 2-METHYL-BUT-2-ENE.

Product	Specific activity c/m/(g-mole/g. soln)	<u>specific activity</u> <u>specific activity</u> % of olefin (to nearest integer)
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	$(1.366 \pm 0.021) \times 10^7$	100 (by definition)
CH_3CHO	$(1.385 \pm 0.015) \times 10^7$	102 ± 4
$(\text{CH}_3)_2\text{C}=\text{O}$	$< 1.8 \times 10^3$	0
$\text{CH}_3\text{CH}_2\text{CHO}$	$< 4.6 \times 10^4$	0
CH_3OH	$(1.30 \pm 0.05) \times 10^7$	95 ± 7
$(\text{CH}_3)_2\text{CHOH}$	$< 5 \times 10^4$	0
$\text{CH}_3\text{C}_2\text{H}_5\text{C}=\text{O}$	$(1.37 \pm 0.08) \times 10^7$	101 ± 9
$\text{CH}_3\text{CCH}(\text{CH}_3)_2$ O	$(1.32 \pm 0.04) \times 10^7$	97 ± 6
$(\text{CH}_3)_3\text{COH}$	$(1.29 \pm 0.01) \times 10^7$	94 ± 7

TABLE 4.3(b).

SPECIFIC ACTIVITIES OF OXIDATION PRODUCTS OF
[2-¹⁴C] 2-METHYL-BUT-2-ENE.

Product	Specific activity c/m/(g-mole/g. soln)	<u>specific activity</u> <u>specific activity</u> of olefin (to nearest integer)
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	$(5.33 \pm 0.10) \times 10^7$	100 (by definition)
CH_3CHO	$< 5.4 \times 10^4$	0
$(\text{CH}_3)_2\text{C}=\text{O}$	$(4.78 \pm 0.17) \times 10^7$	90 ± 4
$\text{CH}_3\text{CH}_2\text{CHO}$	$(4.69 \pm 0.29) \times 10^7$	88 ± 6
CH_3OH	$< 2.3 \times 10^5$	0
$(\text{CH}_3)_2\text{CHOH}$	$(4.56 \pm 0.32) \times 10^7$	86 ± 7
$\text{CH}_3\text{C}_2\text{H}_5\text{C}=\text{O}$	$(5.22 \pm 0.26) \times 10^7$	98 ± 5
$\text{CH}_3\text{CCH}(\text{CH}_3)_2$ O	$(4.89 \pm 0.19) \times 10^7$	92 ± 4
$(\text{CH}_3)_3\text{COH}$	$(5.01 \pm 0.35) \times 10^7$	94 ± 7

(β) Degradative studies on carbonyl compounds:
the haloform reaction.

The sites of the carbon-14 in the acetaldehyde, methyl ethyl ketone and methyl isopropyl ketone formed from $[4-^{14}\text{C}]$ 2-methyl-but-2-ene were determined by degradation of these carbonyl compounds to iodoform.

The active carbonyl compound regenerated by the technique described in section (α) was dissolved in 15 ml. of N/2 sodium hydroxide solution to which was slowly added a solution of 1g. of iodine in 5 ml. of 10% aqueous potassium iodide. Iodoform was precipitated and after being left overnight was filtered off, washed well with water and dried in a vacuum desiccator, care being taken not to lose iodoform by sublimation. The iodoform was dissolved in ether and deposited onto a nickel sample pan by heating gently (as iodoform decomposes quite readily to iodine under these conditions) and counted as a thin film.

In the case of each of the three carbonyl compounds (acetaldehyde, methyl ethyl ketone and methyl isopropyl ketone), the iodoform was found to contain all the activity of the original compound. Now the iodoform is in each case derived from the methyl group in the α-position to the carbonyl group. In each case therefore, it is this position in the carbonyl compound which carries the carbon-14.

(ii) Degradation of oxidation products of $[2-^{14}\text{C}]$
2-methyl-but-2-ene.

(α) Liberation of carbonyl compounds from
their hydrazones.

The active carbonyl compounds produced during combustion of $[2-^{14}\text{C}]$ 2-methyl-but-2-ene are acetone, propionaldehyde, methyl ethyl ketone and methyl isopropyl ketone (Table 4.3). These carbonyl compounds were liberated from

TABLE 4.4(a).LIBERATION OF ACTIVE CARBONYL COMPOUNDS FROM THEIR
2,4-DINITRO-PHENYLHYDRAZONES BY EXCHANGE REACTIONS.(a) ACTIVE PRODUCTS OF COMBUSTION OF [4-¹⁴C]
2-METHYL-BUT-2-ENE.

	CH_3CHO	$\text{CH}_3\text{COC}_2\text{H}_5$	$(\text{CH}_3)_2\text{CHCOCH}_3$
Weight of hydrazone used (m_1 g.)	0.01213	0.03551	0.01206
Equivalent weight of carbonyl compound (m_2)	0.002383	0.01016	0.003901
Weight of inactive carbonyl compound added (m_3)	0.10994	0.25755	0.16170
Activity of original hydrazone ($c/m/(g-m/g. \text{ soln})(a)$)	1.94×10^5	2.15×10^4	3.85×10^4
Experimentally found activity of hydrazone after exchange (b)	4.59×10^3	8.96×10^2	1.08×10^3
Calculated activity of carbonyl compound and hydrazone if exchange were complete $am_2/(m_2 + m_3)$	4.115×10^3	8.15×10^2	9.07×10^2
Actual activity of carbonyl compound after exchange $(a-b)m_2/m_3$	4.10×10^3	8.13×10^2	9.03×10^2

TABLE 4.4(b).LIBERATION OF ACTIVE CARBONYL COMPOUNDS FROM THEIR
2,4-DINITRO-PHENYLHYDRAZONES BY EXCHANGE REACTIONS.(b) ACTIVE PRODUCTS OF COMBUSTION OF [2-¹⁴C]
2-METHYL-BUT-2-ENE.

	$(\text{CH}_3)_2\text{C}=\text{O}$	$\text{CH}_3\text{CH}_2\text{CHO}$	$\text{CH}_3\text{COC}_2\text{H}_5$	$(\text{CH}_3)_2\text{CHCOCH}_3$
Weight of hydra- zone used (m_1 g.)	0.02404	0.01146	0.04031	0.01241
Equivalent weight of carbonyl compound (m_2)	0.006006	0.002794	0.01153	0.004015
Weight of inactive carbonyl compound added (m_3)	0.20476	0.29746	0.28786	0.13348
Activity of original hydrazone ($c/m/(g-m/g.s.)(a)$)	4.44×10^6	1.15×10^6	2.58×10^5	3.28×10^6
Experimentally found activity of hydrazone after exchange (b)	1.78×10^5	1.91×10^4	1.70×10^4	1.09×10^5
Calculated acti- vity of carbonyl compound and hydr- azone if exchange were complete $am_2/(m_2 + m_3)$	1.266×10^5	1.07×10^4	9.93×10^3	9.58×10^4
Actual activity of carbonyl compound after exchange $(a-b)m_2/m_3$	1.25×10^5	1.07×10^4	9.93×10^3	9.56×10^4

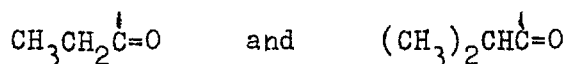
their hydrazones and the extent of exchange was determined by methods similar to those used with the active carbonyl compounds produced during the combustion of $[4-^{14}\text{C}]$ 2-methyl-but-2-ene. The results of these investigations are shown in Table 4.4(b) from which it is clear that the expected exchange has taken place to an extent of at least 99%.

(β) Degradative studies on ketones.

The haloform reaction.

Each active ketone (acetone, methyl ethyl ketone and methyl isopropyl ketone) was dissolved in 15 ml. of N/2 sodium hydroxide solution to which was added slowly a solution of 1g of iodine dissolved in 5 ml. of 10% potassium iodide solution. Iodoform was precipitated and after being left overnight was filtered off, washed with water and dried in a vacuum desiccator. The iodoform from each ketone was deposited from ether solution into a nickel sample pan and counted as a thin film. The iodoform was inactive in all cases (specific activity less than 0.1% of the specific activity of the original ketone), so that the α -methyl group of each ketone group is inactive.

In the case of acetone, then, the activity must be centred in the carbonyl group. The sites of carbon-14 in the methyl ethyl ketone and methyl isopropyl ketone are in the groups



respectively.

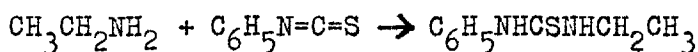
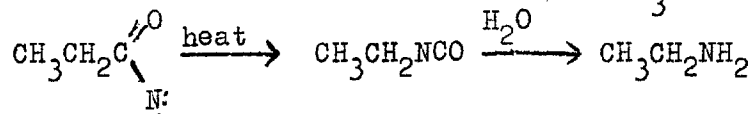
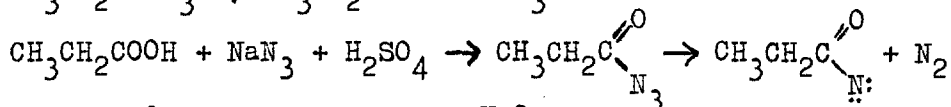
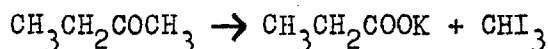
The Schmidt reaction.

The labelled methyl ethyl ketone was first degraded to iodoform and potassium propionate as described in preceding section. After removal of the iodoform, the residual alkaline solution was acidified with 2N sulphuric

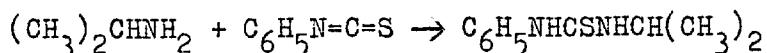
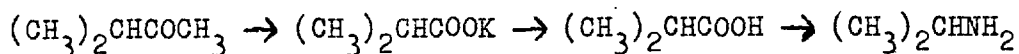
acid and then continuously extracted with ether for 24 hours. The ethereal solution of propionic acid was neutralised with methanolic potassium hydroxide and evaporated to dryness, leaving a pale purple solid, potassium propionate.

0.10g of the potassium propionate was mixed with 0.34g of sodium azide and 5 ml. of dry benzene in a 20 ml. 2-necked flask. The mixture was maintained at 45°C and 0.5 ml. of concentrated sulphuric acid was added slowly with constant stirring. After one hour the ethyl isocyanate produced was decomposed with 10 ml. of water and the mixture was heated at 80°C for 10 minutes. The aqueous layer was separated and made slightly alkaline with aqueous potassium hydroxide. 0.1g of phenyl isothiocyanate was added dropwise, the temperature of the solution being maintained near 0°C. A white granular precipitate of phenyl ethyl thiourea was formed. This precipitate was filtered off, washed with water to free it from unchanged phenyl isothiocyanate and recrystallised from aqueous methyl alcohol. The melting point of the phenyl ethyl thiourea was 130°C (lit. m. pt = 135°C). An insufficient yield was obtained to make further recrystallisation advisable.

The reactions which have taken place are



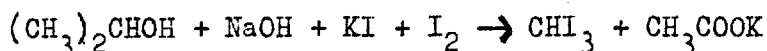
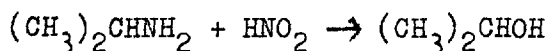
The experiments were repeated using the labelled methyl isopropyl ketone:



The phenyl isopropyl thiourea formed had a melting point of 98°C (literature melting point $=101^\circ\text{C}$).

The specific activity of the phenyl isopropyl thiourea derived from the methyl isopropyl ketone was measured by counting a solution of the derivative in sulpholane. The derivative was active, having a specific activity of 9.56×10^4 counts/minute/(g-mole/g. solution) i.e. 104% of that of the active methyl isopropyl ketone used as starting material for these degradations. The original specific activity of the methyl ethyl ketone (9.9×10^3 counts/minute/(g-mole/g. solution) was too low to enable counting of its degradation products in solution to be effected. The phenyl ethyl thiourea was thus dissolved in methyl alcohol, deposited on a nickel planchette by evaporation of this solvent and counted as a thin film. The activity found by this method was 8.79×10^3 counts/minute/(g-mole/g. solution) i.e. 88% of that of the methyl ethyl ketone used as starting material.

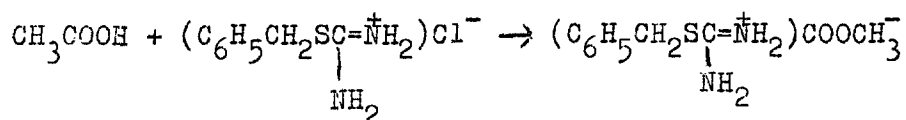
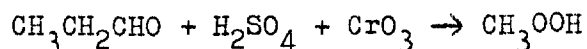
These degradative studies show that the activity of the methyl ethyl ketone is centred in the ethyl group, and that of the methyl isopropyl ketone in the isopropyl group. In each compound then there are two possible sites of carbon-14 (the two methyl groups of the isopropyl group being equivalent). It is possible, in principle, to degrade the compounds further, enabling the site of carbon-14 to be determined unambiguously. eg.



Further studies however would necessitate further isotopic dilution in order to maintain amounts of material sufficient for accurate manipulation. Such isotopic dilution would lower the count rates obtainable, rendering quantitative radioassay extremely difficult. Hence no further studies on the degradation products of methyl ethyl ketone and methyl isopropyl ketone were undertaken.

(γ) Degradative studies on propionaldehyde.

Preliminary experiments using inactive propionaldehyde showed that it is degraded to acetic acid on refluxing for one hour with chromium trioxide and 50% v/v sulphuric acid. The acetic acid so formed was isolated as S-benzyl-isothiuronium acetate.



0.24g. of the labelled propionaldehyde (which had been liberated from its 2,4-dinitro-phenylhydrazone by exchange, section (α)) was refluxed with lg. of chromium trioxide and 2 ml. of 50% v/v sulphuric acid for one hour. The fraction boiling below 150°C was distilled and neutralised by adding concentrated aqueous sodium hydroxide until the solution was just alkaline and then carefully neutralising with 2N hydrochloric acid. A solution of lg. of S-benzyl-isothiuronium chloride in 5 ml. of water was now added and the solution cooled in ice overnight. A pale yellow solid was precipitated. This was removed by filtration, washed with ice water, recrystallised from dilute aqueous alcohol, again washed with ice water and dried. (Yield 0.20g.; melting point 142°C). After further

recrystallisation, the melting point was 145°C (cf S-benzyl-isothiuronium acetate, 146°C).

The S-benzyl-isothiuronium acetate was deposited in a nickel planchette by evaporation to dryness of a solution in ethyl alcohol, and counted as a thin film. The specific activity found was 9.6×10^3 counts/minute/(g-mole/g. solution), i.e. 89% of that of the original propionaldehyde. The site of carbon-14 in the propionaldehyde is thus not in the carbonyl group (which has been removed by degradation). Further degradation is again possible in principle but the yield and specific activity of the material seriously restricts its accuracy and usefulness.

(8) Degradative studies on isopropyl alcohol.

0.02g. of the labelled isopropyl 3,5-dinitro-benzoate was refluxed with 5 ml. of 3N sodium hydroxide solution for 12 hours to liberate the alcohol. Preliminary experiments using inactive ester had shown that this procedure was effective. 0.042g. of inactive isopropyl alcohol were now added as carrier. The alkaline solution of isopropyl alcohol was diluted to half-normal and a solution of 1g of iodine in 5 ml. of 10% aqueous potassium iodide was added. A yellow solid was precipitated on being left overnight. This solid was removed by filtration, washed with water and dried overnight in a vacuum desiccator. (Yield ca. 50mg., melting point 117°C , cf. iodoform 119°C). The iodoform was counted both as a thin film (by deposition from ether solution) and as a solution in sulpholane. It was inactive.

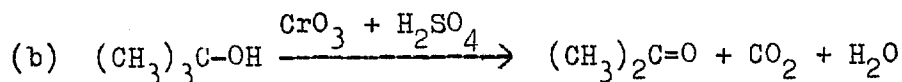
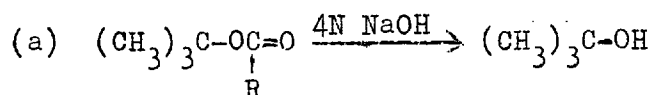
The site of carbon-14 in the isopropyl alcohol produced in the combustion of $[2-^{14}\text{C}]$ 2-methyl-but-2-ene is therefore the oxygenated carbon atom, the methyl groups being unlabelled.

(E) Degradative studies on tertiary butyl alcohol.

Preliminary experiments were carried out using inactive materials to investigate

- (a) the hydrolysis of t-butyl 3,5-dinitro-benzoate, and
- (b) the oxidation of t-butyl alcohol to acetone.
- (a) 0.2g. of t-butyl 3,5-dinitro-benzoate was refluxed for 24 hours with 5 ml. of 4N aqueous sodium hydroxide. The solid dissolved, leaving a brown solution which was fractionally distilled using a vacuum-jacketed 5" fractionating column. A fraction boiling in the range 84-87°C was obtained. It is likely that this fraction is an aqueous solution of t-butyl alcohol (B. Pt. = 83°C).
- (b) 0.2g. of t-butyl alcohol (inactive) was treated with 1g. of chromium trioxide and 2 ml. of 50% v/v sulphuric acid, and refluxed for 12 hours. The resulting black solution was distilled and a fraction boiling between 45°C and 50°C was obtained. This fraction was collected in a receiver containing methanolic 2,4-dinitro-phenylhydrazine sulphate (Brady's reagent), from which a dark orange precipitate was formed, indicating that a carbonyl compound had been produced by oxidation of t-butyl alcohol. The 2,4-dinitro-phenylhydrazone was removed by filtration and recrystallised from ethyl alcohol. The melting point of this derivative was 125-6°C (cf acetone 2,4-dinitro-phenylhydrazone, lit. M. Pt. = 126°C).

This experiment was repeated using the fraction collected from experiment (a) instead of t-butyl alcohol and concentrated instead of 50% v/v sulphuric acid, with similar results. The following reactions have thus taken place:



It is also possible that some isobutylene is produced in experiment (a); this too would be oxidised to acetone under the conditions of experiment (b).

These experiments were now repeated using 0.146g. of 'active' t-butyl 3,5-dinitro-benzoate as starting material. The fraction of hydrolysis products with a boiling range of 83-90°C was oxidised. Acetone 2,4-dinitro-phenylhydrazone (Yield 8mg., M. Pt. = 125°C, lit. M. Pt. = 126°C) was again produced. While the acetone-containing fraction was still being distilled, the receiver containing Brady's reagent was replaced by one containing ice-cold N/2 aqueous sodium hydroxide, in which further acetone was collected. To the resulting solution was added a solution of 0.1g. of iodine in 0.5 ml. of 10% aqueous potassium iodide. Iodoform was precipitated on being left for an hour and was filtered, washed with water and dried. (Yield ca. 10mg., M. Pt. = 118°C, lit. M. Pt. 119°C).

The acetone 2,4-dinitro-phenylhydrazone and the iodoform were each counted in solution in sulpholane. The acetone derivative was active, having a specific activity of 5.07×10^5 counts/minute/(g-mole/g. solution) i.e. 115% of that of the original t-butyl alcohol, but the iodoform was inactive. The site of carbon-14 in the t-butyl alcohol is thus the oxygenated carbon atom and not one of those in a methyl group.

IV Accuracy of results.(a) Radioactive purity of labelled hydrocarbons.

As well as being chemically pure, it is important that the ^{14}C -labelled hydrocarbons should have a high radioactive purity, that is their activity should be confined to particular known carbon atoms. Since it was difficult to prove directly that the radioactive compounds were pure in this respect, the only alternative was to ensure that the steps employed in their preparation did not involve the possibility of inter-molecular or intramolecular migration. The synthetic routes used in the present work were of a kind in which rearrangements involving rupture of carbon-carbon bonds are known not to occur.

(b) Influence of isotope effects.

The influence on the rate of reaction of the substitution of an isotopic atom in a molecule of reactant is known as the 'isotope effect', usually expressed as $(k/k' - 1)$ where k is the velocity constant for the reaction of the normal molecule and k' that for the corresponding isotopically labelled one. Except for the very simplest molecules, the isotope effect cannot be accurately calculated. However, examination of the calculated and experimental figures available for the isotope effects in ^{14}C -labelled compounds shows that these are quite small.

Stevenson, Wagner, Beeck and Otvos¹⁰¹ have studied the thermal decomposition of ^{13}C -labelled propanes and find that the ^{12}C - ^{12}C bond is ruptured about 8% more frequently than the ^{12}C - ^{13}C bond. Frey, Danby and Hinshelwood¹⁰² have studied the thermal decomposition of the ^{14}C -labelled propanes and have found a similar difference in the frequency of rupture of ^{12}C - ^{12}C and ^{12}C - ^{14}C bonds. Bigeleisen¹⁰³, from a consideration of the theory of absolute reaction rates, has deduced the

differences in the activation energies for a number of isotopic molecules. His results predict somewhat smaller differences in the ease of rupture of $^{12}\text{C}-^{12}\text{C}$, $^{12}\text{C}-^{13}\text{C}$ and $^{12}\text{C}-^{14}\text{C}$ bonds than those found above. The calculated isotope effect between $^{14}\text{C}-\text{H}$ and $^{12}\text{C}-\text{H}$ is even smaller than that between $^{12}\text{C}-^{14}\text{C}$ and $^{12}\text{C}-^{12}\text{C}$ 104.

It is evident from Table 4.3 that, in the present work, the specific activities of the combustion products fall into two well defined classes. The activities of the compounds in the one class approach 100% of that of the reactant olefin, while those of the compounds in the other class approach zero. The above isotope effects in ^{14}C -labelled compounds certainly cannot be responsible for differences of this magnitude. However, Table 4.3 also shows that the specific activities of certain members of the 'active' class of compounds are somewhat less than that of the starting material. Consideration of the postulated mechanism of oxidation (Parts 3 and 5) shows that this discrepancy is generally greater for products whose formation involves rupture of a $^{12}\text{C}-^{14}\text{C}$ bond (eg. methyl alcohol and t-butyl alcohol from $[4-^{14}\text{C}]$ 2-methyl-but-2-ene). It is therefore possible to suppose that an isotope effect of between 5% and 10% is weighting the results. This supposition is not however supported by all the results. For example, the activities of methyl ethyl and methyl isopropyl ketones from $[2-^{14}\text{C}]$ 2-methyl-but-2-ene are inconsistent with the occurrence of such an isotope effect. The above discrepancies, therefore, may be due to experimental error, and the isotope effect has been neglected in the discussions which follow.

(c) Statistical treatment of counting data.

Radioactive disintegration is a random process in which individual nuclei decay independently of one another

and as such it can be treated by the usual laws of probability. Thus the arithmetic mean, μ , of a series of activity readings $x_1, x_2, \dots, x_N$ is subject to a standard deviation, σ , given by

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (\mu - x_i)^2}{N(N-1)}}$$

Suppose that $\bar{n}$ is the average number of particles detectable in a given time interval, determined by a long period of counting. The probability, P_n , that n particles will actually be detected in this interval is given by the Poisson relation

$$P_n = \frac{(\bar{n})^n e^{-\bar{n}}}{n!}$$

If the error E in a single determination which involves the detection of n particles is

$$E = \sqrt{\sum_0^{\infty} (\bar{n} - n)^2 P_n}$$

$$\text{then } E = \sqrt{\bar{n}}$$

Thus the error is proportional to the square root of the number of particles detected so that the relative accuracy increases with $\bar{n}$.

If E is expressed as a function of n , the number of counts recorded,

$$E = \sqrt{\bar{n}} = k \sqrt{n} ,$$

when $k = 1$, E is the 'standard error'.

In the present work the number of counts recorded varied

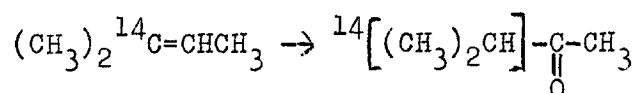
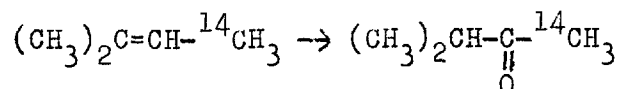
from about 2,000 to 10,000 counts per interval, and were thus subject to errors of 45 counts (2.2%) to 100 counts (1.0%) respectively. These 'counting' errors and errors associated with the calculation of the amounts of active products produced during combustion and of the amounts of inactive diluents added have been taken into account in determining the limits of accuracy of the specific activities of products stated in Table 4.3. From this table it can be seen that the total error involved in the determination of specific activities varies from about 4% to about 9%.

PART 5.DISCUSSION OF CARBON-14 TRACER RESULTS.

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DISCUSSION OF CARBON-14 TRACER RESULTS.5A. THE FORMATION OF MAJOR PRODUCTS.I The formation of methyl isopropyl ketone.

Measurement of the specific activities of the methyl isopropyl ketone produced by combustion of $[2-^{14}\text{C}]$ and $[4-^{14}\text{C}]$ 2-methyl-but-2-enes has shown that in each case the activity of the olefin is retained. The 'sites' of carbon-14 in the methyl isopropyl ketones have been found by degradation to be as follows:

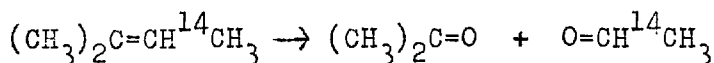
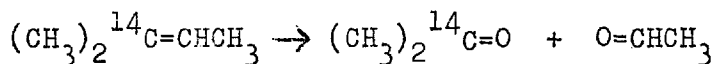


Although the site is not unambiguously determined in the latter case, it is almost certainly the tertiary carbon atom, since to account for one of the methyl carbon atoms being labelled it would be necessary to postulate several unlikely bond scissions and group replacements. The results show, then, that the methyl isopropyl ketone is most probably produced from 2-methyl-but-2-ene without a change in the carbon skeleton of the olefin. It is therefore likely that the methyl isopropyl ketone arises by conventional breakdown of the hydroperoxide $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{OOH}$ as suggested in Part 3 section B. IV. Although the results of carbon-14 labelling do not clarify the site of the initial attack on the olefin by oxygen to give an alkyl radical which is a precursor of the above hydroperoxide, they do ensure that alkyl radical rearrangements involving C-C bond fission do not take place to any significant extent during

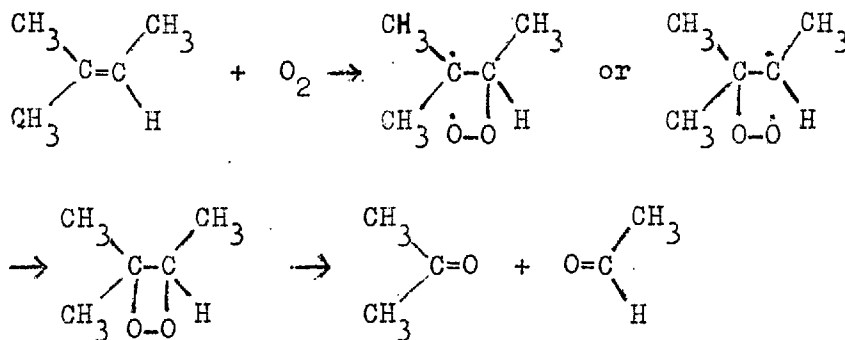
hydroperoxylation. The nature of the original alkyl radical or radicals formed could possibly be elucidated by an isotopic study involving deuterium or tritium.

II The formation of acetone and acetaldehyde.

The specific activities of the acetone and acetaldehyde, and of their degradation products, produced from $[2-^{14}\text{C}]$ and $[4-^{14}\text{C}]$ 2-methyl-but-2-enes show that the pattern of carbon-14 retention during combustion of the olefins to these products is as below.



This result strongly suggests that the acetone and acetaldehyde are produced by a mechanism involving oxygenation of both the carbon atoms involved in the double bond of the olefin and rupture of the bond between these carbon atoms. The results of the carbon-14 tracer studies, therefore, are consistent with the mechanism of production of acetone and acetaldehyde by the simple breakdown of a cyclic peroxide which was postulated in Part 3:



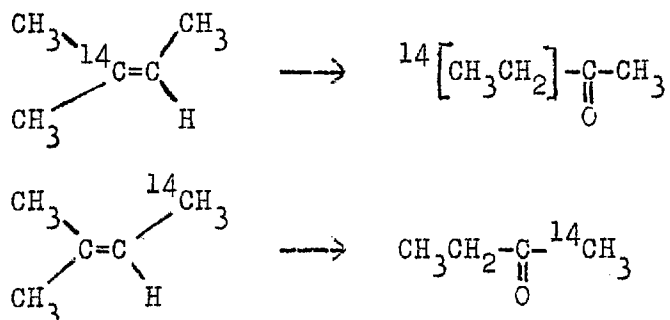
III The formation of methyl alcohol.

The methyl alcohol formed during gaseous oxidation of $[2-^{14}\text{C}]$ 2-methyl-but-2-ene is inactive, while that formed from $[4-^{14}\text{C}]$ 2-methyl-but-2-ene retains 95% of the activity of the olefin. The major source of methyl alcohol must therefore be the 4- position of the olefin. It is likely therefore that the methyl alcohol is indeed produced by breakdown of acetaldehyde (under the influence of oxygen) to acetyl radicals and hence methyl radicals, as suggested in Part 3. The high specific activity of the methyl alcohol produced by gaseous oxidation of $[4-^{14}\text{C}]$ 2-methyl-but-2-ene suggests that the production of methyl radicals from other parts of the olefin skeleton during combustion is unimportant.

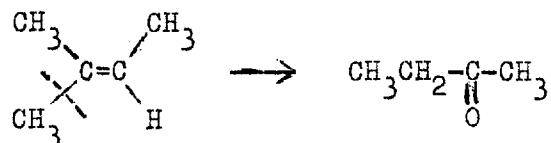
5B. THE FORMATION OF MINOR PRODUCTS.

I The formation of methyl ethyl ketone and propionaldehyde.

The methyl ethyl ketone produced during combustion of both $[4-^{14}\text{C}]$ and $[2-^{14}\text{C}]$ 2-methyl-but-2-enes retains the activity of the olefin, and degradative studies have shown the sites of carbon-14 to be as follows.

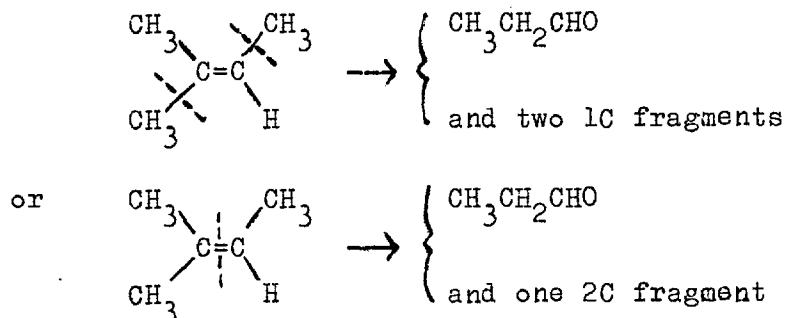


In the former case, it is likely that the site of carbon-14 is in fact the CH_2 group as several unlikely steps would be necessary to produce methyl ethyl ketone labelled at the β -methyl group. The formation of methyl ethyl ketone from 2-methyl-but-2-ene involves the loss of one carbon atom per molecule. The above pattern of retention of carbon-14 shows that it is likely that this carbon atom is the one in the 2-methyl group and that methyl ethyl ketone is produced from the resulting butene-2 skeleton.



The propionaldehyde produced from $[2-^{14}\text{C}]$ 2-methyl-but-2-ene is active, the carbon-14 being situated in the alkyl group, while that formed from $[4-^{14}\text{C}]$ 2-methyl-but-2-ene is inactive. In the formation of propionaldehyde from 2-methyl-but-2-ene

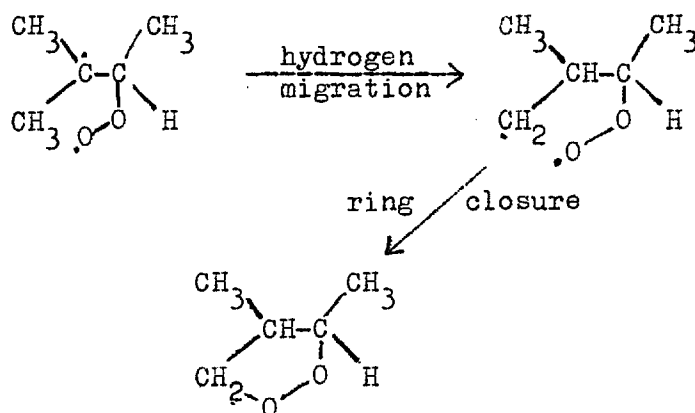
two carbon atoms per molecule have been lost, and the results of the tracer studies leave two possible pairs, as below.



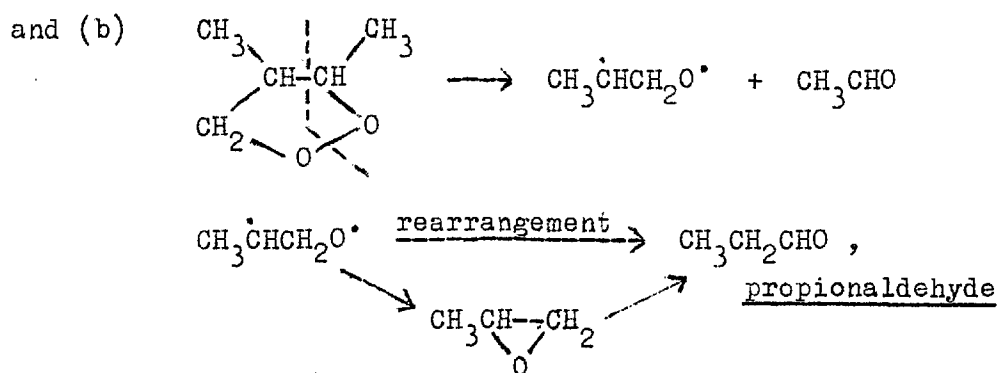
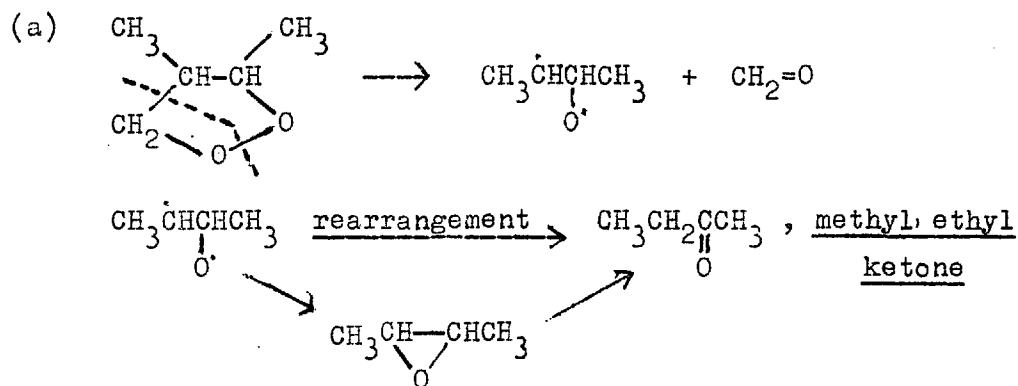
Even with the aid of the carbon-14 tracer results, then, it is difficult to determine unambiguously the modes of formation of methyl ethyl ketone and propionaldehyde. The postulated modes of formation of the major products (acetone, acetaldehyde and methyl isopropyl ketone) suggest however that the important peroxy radicals which are formed during the reaction are $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{OO}^\bullet$ and one or both of the bi-radicals



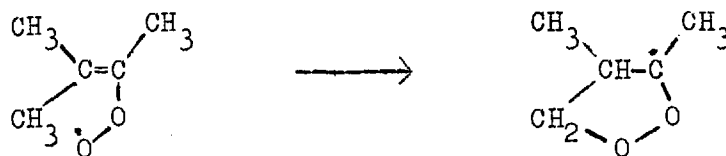
while other species such as $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{OO}^\bullet$ are absent. It is likely therefore that the minor products will be formed from one or more of the above three peroxy species rather than from others. Consideration of these species shows that any such mode of reaction must involve some radical rearrangement (cf. ref. 16). A possible sequence of reactions is as follows.



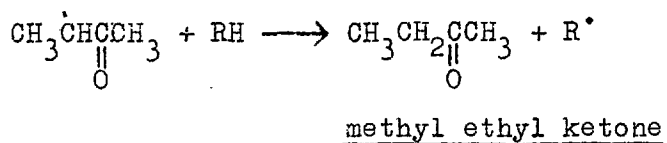
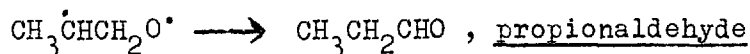
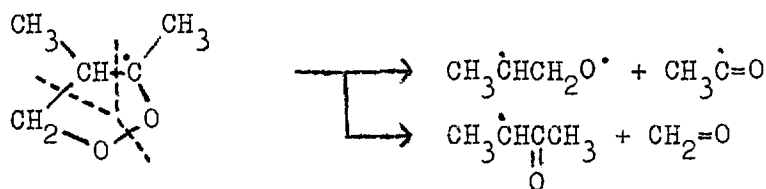
followed by



Alternatively the $\text{RO}_2^\bullet$ radical, $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{OO}^\bullet$, may be involved in a somewhat similar series of reactions:



followed by



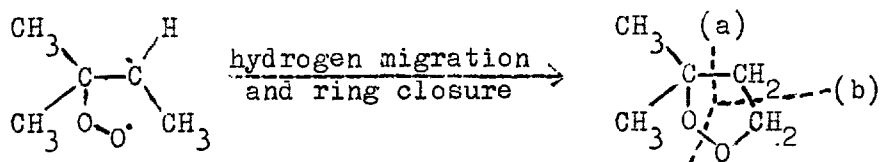
There are several reasons for favouring such a mechanism. $\text{RO}_2^\bullet$ radicals are believed to survive many collisions with other molecules before undergoing further reaction¹⁰⁵, so that there might be time for the above species to attain a conformation suitable for the occurrence of cyclisation. Furthermore, it has been suggested that $\text{RO}_2^\bullet$ radicals may be endowed with considerable excess vibrational energy¹⁰⁶, which could contribute to the activation energy required for cyclisation. Once the ring has been formed the bond most likely to break will be the O-O linkage, this being the weakest in the molecule. This would be followed by fission of one of the C-C bonds adjacent to the C-O $^\bullet$ groups, producing either methyl ethyl ketone and formaldehyde, or propionaldehyde and acetaldehyde, as in the above reaction scheme.

If such a series of reactions is indeed responsible for the production of methyl ethyl ketone and propionaldehyde, amounts of acetaldehyde and formaldehyde similar to those of the above products will be formed concurrently. The variation with time of the amount of formaldehyde (and formic acid) present in the products of combustion (fig. 2.21) shows two peaks. Formaldehyde therefore is probably produced by two different mechanisms. The earlier formaldehyde peak is similar in both height and 'time of appearance' to that of methyl ethyl ketone. These two compounds therefore may well have a common precursor. Formaldehyde formed in the later stages of combustion probably arises from oxidation of methyl alcohol. The acetaldehyde produced by the above mechanism will be formed in too small a quantity and appear too late in the reaction to affect the acetone-acetaldehyde equivalence noted early in the reaction and attributed to the breakdown of a cyclic peroxide with a four-membered ring (Sections 3B III, 5A II). Furthermore, the acetaldehyde produced by each of these two mechanisms contains the same two carbon atoms of the olefin skeleton (the 4-position being the methyl group and the 3-position the carbonyl group), so that the above mechanism is consistent with the experimentally found specific activities of acetaldehyde formed from $[4-^{14}\text{C}]$ and $[2-^{14}\text{C}]$ 2-methyl-but-2-enes.

The mode of formation of methyl ethyl ketone and propionaldehyde postulated above is therefore consistent with the experimental facts.

As the postulation of hydrogen migration in the biradical $(\text{CH}_3)_2\dot{\text{C}}-\text{CH}(\text{CH}_3)\text{OO}^\bullet$ leads to a consistent explanation of the formation of methyl ethyl ketone and propionaldehyde, it is interesting to consider the results of similar migrations in the other biradical which could be produced by direct addition

of oxygen to the olefin, i.e. $(\text{CH}_3)_2\text{C}(\text{OO}^\bullet)-\dot{\text{C}}\text{HCH}_3$:



Rupture of the O-O linkage followed by one of the C-C bonds adjacent to a C-O[•] group would in this case lead to

- (a) acetone and acetaldehyde, and
- (b) formaldehyde and isobutylene oxide.

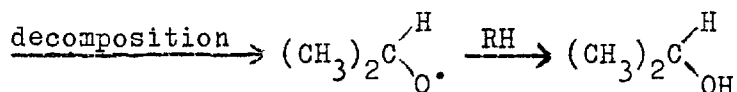
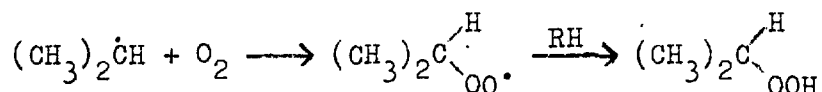
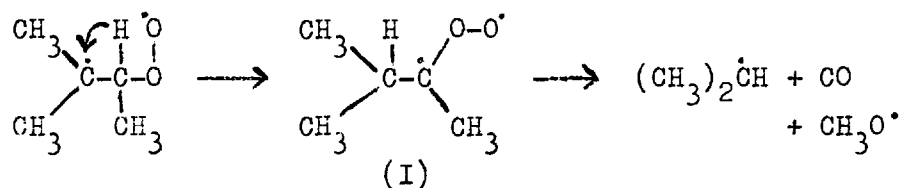
No isobutylene oxide has been detected in the combustion products, and any acetaldehyde produced in this way from $[4-^{14}\text{C}]$ 2-methyl-but-2-ene would be labelled in the carbonyl group, not the methyl group, which is contrary to the experimental findings. Rearrangement reactions of $(\text{CH}_3)_2\text{C}(\text{OO}^\bullet)-\dot{\text{C}}\text{HCH}_3$ therefore play little part in the combustion mechanism. There are two possible reasons for this. Either this biradical is not produced in any appreciable concentration, or it cyclises to a four-membered cyclic peroxide too quickly to allow hydrogen migration.

II The formation of isopropyl alcohol.

The isopropyl alcohol formed by gaseous oxidation of $[2-^{14}\text{C}]$ 2-methyl-but-2-ene is labelled, the site of carbon-14 being the oxygenated carbon atom, while that produced from $[4-^{14}\text{C}]$ 2-methyl-but-2-ene is inactive. During combustion then, the 2-carbon atom of the olefin becomes the oxygenated carbon of the isopropyl alcohol. It therefore seems reasonable to suppose that the two methyl groups of the isopropyl alcohol are the two methyl groups attached to the 2-carbon atom in the olefin molecule, and that these groups suffer no change during the reaction producing isopropyl alcohol.

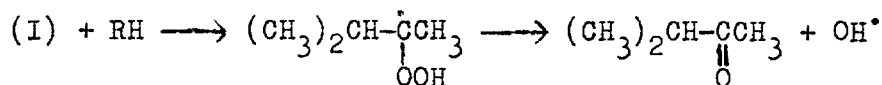
The C-C bond which must be ruptured during formation of

isopropyl alcohol is therefore that between the 2- and 3-carbon atoms of 2-methyl-but-2-ene. It is unlikely that the 2- carbon atom is oxygenated at this stage of the reaction, for this would lead to the formation of acetone, not isopropyl alcohol, when the C-C bond broke. It is possible that the formation of isopropyl alcohol again involves hydrogen migration in the biradical $(\text{CH}_3)_2\dot{\text{C}}-\text{CH}(\text{CH}_3)\text{OO}^\bullet$:



(Compare the production of methyl alcohol from methyl radicals).

Some of the methyl isopropyl ketone present in the combustion products could also be formed from (I):

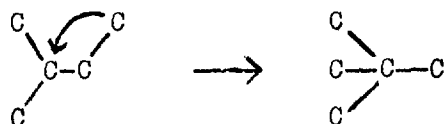


The mechanism of the formation of methyl isopropyl ketone by a conventional hydroperoxide 'route' (Part 3 Section B4) is however more straightforward.

III The formation of tertiary butyl alcohol.

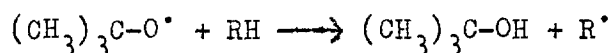
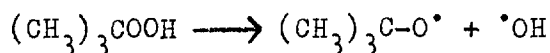
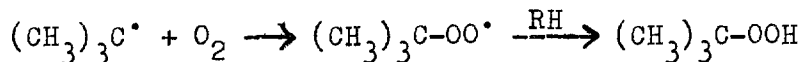
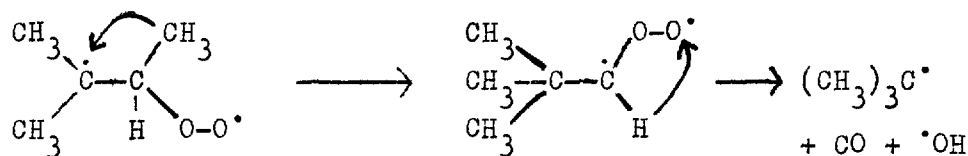
The t-butyl alcohol produced from both $[2-^{14}\text{C}]$ and $[4-^{14}\text{C}]$ 2-methyl-but-2-enes retains 94% of the activity of the olefin, and in the former case the site of the activity has been shown to be the oxygenated carbon atom. In the

latter case, then, the site of the activity must be a methyl group. The formation of t-butyl alcohol must therefore involve the intermolecular or intramolecular migration of the methyl group in the 4- position in the olefin skeleton so that this group becomes attached directly to the 2- position,



together with the loss of one carbon atom per molecule, this carbon atom being either the 1- or 3- carbon atom of 2-methyl-but-2-ene.

It is possible that such a methyl migration occurs in the biradical $(\text{CH}_3)_2\dot{\text{C}}-\text{CH}(\text{CH}_3)\text{OO}^\bullet$, this being formally similar to the hydrogen migrations leading to methyl ethyl ketone, propionaldehyde and isopropyl alcohol. t-butyl alcohol could then be formed by a sequence of reactions such as the following:



The t-butoxy radical $(\text{CH}_3)_3\text{C}-\text{O}^\bullet$ is known to decompose in the gas phase, giving acetone and a methyl radical¹⁰⁷, and if the mechanism of production of t-butyl alcohol is as suggested

above, small quantities of acetone and methyl radicals will no doubt be produced. The yield of t-butyl alcohol from slow combustion is however low enough to suggest that an insufficient number of t-butyl radicals is formed to cause the specific activities of the acetone and methyl alcohol produced during combustion of labelled olefins to be affected seriously. The counting techniques used are insufficiently accurate to detect reliably such small differences.

5C. CONCLUSIONS.

A rational explanation of the mechanism of formation of the four major condensable products of the slow combustion of 2-methyl-but-2-ene (acetone, acetaldehyde, methyl isopropyl ketone and methyl alcohol), consistent with the results of kinetic, analytical and isotopic studies, can therefore be provided by postulating two modes of initial attack of the olefin by oxygen:

- (1) Hydrogen abstraction followed by hydroperoxylation leading to methyl isopropyl ketone.
- (2) Oxygen addition at the double bond forming an intermediate cyclic peroxide the simple breakdown of which furnishes acetone and acetaldehyde.

Furthermore, simple rearrangements (by intermolecular and/or intramolecular hydrogen and methyl transfer) of the peroxy radicals and biradicals necessarily produced by these modes of attack furnishes a consistent explanation of the formation of the minor products (methyl ethyl ketone, propionaldehyde, formaldehyde, isopropyl alcohol and t-butyl alcohol), no additional modes of oxidative attack of the olefin itself being necessary to account for these products.

The results of the present work suggest therefore that during the slow combustion of 2-methyl-but-2-ene both the generally postulated mechanisms of initial attack of olefins by oxygen (see Part 1) are operative. The relative amounts of acetone and methyl isopropyl ketone formed indicate that in this system the 'additive' mode of attack is the more important. It is difficult however to make any quantitative estimation of the relative frequencies of hydrogen abstraction and oxygen addition, as such an estimate must necessarily be based on the concentrations of ketones formed (the cyclic

peroxide being far too unstable to estimate directly).

Such estimates would be weighted therefore according to

- (i) the relative ease of production of ketonic products from the initial unstable products of oxygen-olefin reaction,
- (ii) the chain length of the primary hydroperoxide-producing chain, and
- (iii) the relative stabilities of the ketones under the conditions of slow combustion.

Nevertheless, despite the uncertainty regarding the precise quantitative significance of the analytical data, the results clearly indicate the concurrent operation of both the addition and abstraction mechanisms of initial attack of olefins by oxygen. In the case of 2-methyl-but-2-ene, which contains no α -methylene group, it is evident that the addition mechanism is the predominant one.

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