A THESIS

entitled

THE VANADIUM PENTOXIDE-CATALYSED OXIDATION OF PENTENES

Submitted by

NASIR SAEED BUTT

for the degree of

DOCTOR OF PHILOSOPHY

in the

University of London.

CONTENTS.

ACKNOWLEDGMENTS.

The author wishes to express his deep sense of gratitude to Dr. C.F. Cullis and Dr. A. Fish for their invaluable advice, guidance and encouragement.

Grateful acknowledgment is made to Pakistan Petroleum Ltd. for the financial assistance which enabled the author to undertake this work.

Thanks are due to Mr R.W. Toft of the Analytical and Chemical Services Division, Shell Research Limited, Thornton Research Centre, for X-ray diffraction examination of the catalysts.

The author would also like to thank his colleagues in the Department for their genial companionship and help.

Department of Chemical Engineering and Chemical Technology, January 1965.
Imperial College,
London S.W.7.

ABSTRACT.

Studies are described of the heterogeneous catalytic oxidation over vanadium pentoxide of the five acyclic C_5 olefins. The investigations were carried out with particular reference to the role of the catalyst itself and the mode of initial attack on the olefin.

In the Introduction (Section I) various physicochemical properties of catalysts are outlined and the factors governing catalytic activity and selectivity are described. General theories of catalysis, applicable to most heterogeneous catalytic reactions and the oxidation-reduction mechanism operative with certain metallic oxides, are reviewed. Modes of adsorption of reactants and subsequent reactions of the adsorbed species are discussed.

The Experimental Techniques used are described in Section II. This includes accounts of the preparations of the pentenes and the catalyst and description of the gas flow system and methods of analysis. Gas-liquid chromatography was the main analytical technique used for the estimation of volatile products, infra-red spectroscopy for the analysis of the solid products and carbon oxides and spectrophotometry for determination of formaldehyde. The crystallographic structure of the catalyst itself was studied by X-ray diffraction and its surface area was measured by low-temperature adsorption techniques.

The Experimental Results are described in Section III. A detailed study has been made of the oxidation of the various

isomeric pentenes over vanadium pentoxide and special attention has been paid to the fate of the catalyst itself during reaction. The results show that the oxidation of all straight-chain pentenes resemble the oxidation of pent-2-ene and that of all branched-chain pentenes resemble that of 2-methyl but-2-ene because the terminal pentenes invariably tend to isomerize to non-terminal pentenes. As the main oxidation products found from pent-2-ene are acetaldehyde and propionaldehyde and the major products of 2-methyl but-2-ene are acetaldehyde and acetone, it is concluded that the attack of the oxygen is predominantly at the double bond. The presence of the corresponding epoxy compounds in the products also supports this conclusion.

A reaction scheme, involving RH^+ (RH=olefins) and O_2^-, O^- and O^{2-} is postulated in the Discussion (Section IV). The changes of activity and selectivity of the catalyst during reaction are explained on the basis of phase changes taking place in consequence of the electron transfer processes involved.

SECTION I.

INTRODUCTION.

SECTION I.

A. GENERAL.

Organic compounds, especially fairly low molecular weight oxygenates, are very useful as starting materials for the production of a wide range of important industrial chemicals such as polymers, lacquers and resins. The basic starting materials from which these oxygenates are prepared, are usually paraffinic, olefinic or aromatic hydrocarbons, which are obtainable from crude oil or coal. These compounds can be allowed to react with oxygen in the gas-phase, in the absence of catalysts but reaction under these conditions generally gives a large number of diverse products, the separation of which often makes the process industrially impracticable. Furthermore, the complex mixtures of products obtained often render the reaction mechanism, difficult to elucidate. The use of heterogeneous catalysts helps to overcome some of these difficulties by making the oxidation more selective. Furthermore the reaction temperatures are lowered in the presence of a catalyst and this not only helps to minimise side reactions but also lowers the "wear and tear" in a chemical plant.

In order to facilitate the choice of catalyst for a particular reaction, it is obviously essential to know the mechanism by which such heterogeneous catalytic oxidation proceeds. A knowledge of the physicochemical properties of such catalysts proves very useful and great stress has been laid in recent work on the interrelationship between such properties and catalytic activity. Studies on catalysts with known physicochemical properties help to throw light on the mechanism of heterogeneous gas reactions.

The uncatalysed gaseous oxidations have been quite widely investigated and, although this knowledge may be generally helpful, the mechanism of reactions over heterogeneous catalysts is quite distinct. Indeed in recent years it has increasingly become the practice to investigate the mechanism of catalytic oxidation more from the point of view of the catalyst itself than of the reacting gases.

B. HETEROGENEOUS CATALYSIS.

1. The relationship between physicochemical properties and catalytic activity of solids.

As a result of studies of heterogeneous catalysis, repeated suggestions have been made that distinct relationships exist between the physical, chemical, electrical and mechanical properties of a solid and its catalytic activity. As early as 1939, Huttig, (1) found that catalytic activity could be roughly correlated with various physical changes in the catalyst such as those of colour, crystal structure and magnetic susceptibility. Subsequently Elovich et.al. (2) investigated the catalytic activity of various oxides with respect to their colour and observed the lack of any appreciable activity in the case of colourless oxides whereas the binary oxides containing at least one transitional element, capable of forming coloured compounds, generally displayed high catalytic activity. More recently many other workers have made similar suggestions.(3)(4). These differences in the colour of various catalysts can often be related to the presence or absence of foreign ions in the lattice of the solid. In some cases phase changes occur in the catalyst during its use, which produce concurrent changes in colour and activity. Other physical characteristics, such as pore size, affect the activity of a catalyst (5). Similarly, magnetic properties bear a relationship to catalytic activity, as shown by the increase in activity with increasing paramagnetic susceptibility (4)(6).

All these physicochemical properties are strongly linked with the electronic properties of the solid. These electronic properties play an important role in determining the qualitative and quantitative aspects of adsorption. As there is now sufficient evidence to prove that catalysis involves the adsorption of reactants and subsequent desorption of products, it can be reliably concluded that electronic properties and catalytic activity are related to one another.

In the past decade there have been repeated attempts to link, qualitatively and quantitatively, semiconductivity and catalytic activity. The qualitative aspect of this relationship is now well-established but doubts have been expressed (7) as to the feasibility of the use of semiconductivity as a measure of activity. It is largely through developments in the theory of the solid state that the phenomena of semiconductivity and catalysis have been related. In the field of heterogeneous catalysis the focus moved from the study of the reaction kinetics alone to that of mechanistic implications of kinetic and solid state studies. One of the main centres of interest in this field is currently the catalyst itself.

2. Factors governing the selectivity and the activity of heterogeneous catalysts.

In considering the action of heterogeneous catalysis two factors in particular have been investigated and accepted as participatory in governing the selectivity and activity of catalysts.

(a) The electronic factor.

(b) The geometrical factor.

(a) The electronic factor.

Catalytic processes comprise a number of consecutive elementary steps involving scission and formation of chemical bonds in reactant and product molecules. Transfer of electrons between reactant species and the solid catalyst is involved in such steps and it is reasonable to assume that electronic properties of the solid therefore play a leading role in heterogeneous catalysis.

As early as 1928, Roginskii and Schulz (8) raised this point in explaining the catalytic decomposition of solids but further development of the idea at this stage was hindered by the inadequacy of the atomic theory of solids. Researches in the field of adsorption led to further discoveries regarding the importance of electronic factors.

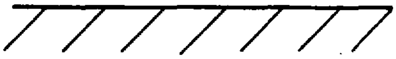
Langmuir (9) showed that the attractive forces between adsorbed gas and the solid catalyst are often similar in character to those which exist in the solid itself. In general, however the forces involved were classified either as van der Waals forces (physical adsorption) or as chemical forces (chemisorption). Physical adsorption is characterised by low heats of adsorption (1-5 kcal/mole), takes place at low temperatures and involves forces which are non-directional. The second type of adsorption, chemisorption is characterised by much higher heats of adsorption (20-100 kcal/mole) and involves forces which are more specific, and approximate much more nearly to chemical bonds. This gives rise to slower adsorption which is temperature-dependent (as are other processes with a high activation energy) and occurs only at elevated temperatures. This type of adsorption was indeed first termed "activated adsorption". A theoretical foundation was given to these concepts by Lennard-Jones (10), who showed that a gas molecule may have to overcome a potential barrier during adsorption onto a solid. It was shown experimentally that the heat of adsorption varied with the extent of coverage and, on this basis, Taylor (11) postulated the presence of "active centres" on the surface of solids undergoing adsorption. These "active centres" were considered to be specific points on the surface, notably peaks and edges, which were capable of adsorbing molecules and were favoured both energetically and geometrically as sites for the initiation of chemical reaction. The two concepts of "activated adsorption" and "active centres" have been substantially modified in recent years but they played a most important part in establishing a relationship between semiconductivity and adsorption. "Activated adsorption" emphasised the importance of the electronic factor while the concept of "active centres" helped to establish the role of surface geometry.

At this stage, it is worth while to discuss the causes of the electronic conductivity of semiconductors. In the case of solid semiconductors the theory of the solid state, based on a model incorporating a regular lattice of ions or atoms, has been used extensively to explain the observed properties. The method most commonly used is the band approach (12), which is analogous to the molecular-orbital method, each electron being described by a wave function extending throughout the lattice. The energy states of the free electrons, assumed to be the outermost electrons, are separated into bands which may either overlap or be separated by gaps of "forbidden energies". Wilson (13) described semiconductors as having a filled band of bound electrons at absolute zero, which is separated by an energy gap from a conduction band, empty at absolute zero but able to accommodate electrons of suitable energy at other temperatures. In insulators, which do not function as oxidation catalysts, the energy gap between the conduction band and the filled band is so wide that at normal temperatures all the electrons possess insufficient energy to bridge it. Imperfections in the crystal lattice have, however, the effect of introducing additional discrete levels into the energy gap. These imperfections may be due to a variety of causes, the presence of impurities being an important one. The impurity atom may have electrons associated with it which are available for excitation into the conduction band more easily than the electrons in the filled band. Alternatively the impurity may give rise to empty energy levels into which electrons from the filled band can be excited more easily than into the conduction band. On the basis of this band method, semiconductors can therefore be divided into intrinsic (i-type) and extrinsic (defect type) semiconductors. The extrinsic type of semiconductor is further subdivided into n-type and p-type. These different types of semiconductor are schematically represented in Fig. I. 1. In the case of an intrinsic type semiconductor (e.g. germanium, silicon and lead sulphide), the energy gap is of such width that at reasonable temperatures a small proportion of the electrons in the filled band is excited across it. Thus excitation places an electron in the conduction band and leaves a vacancy in the filled band.

Key to FIG. I.1

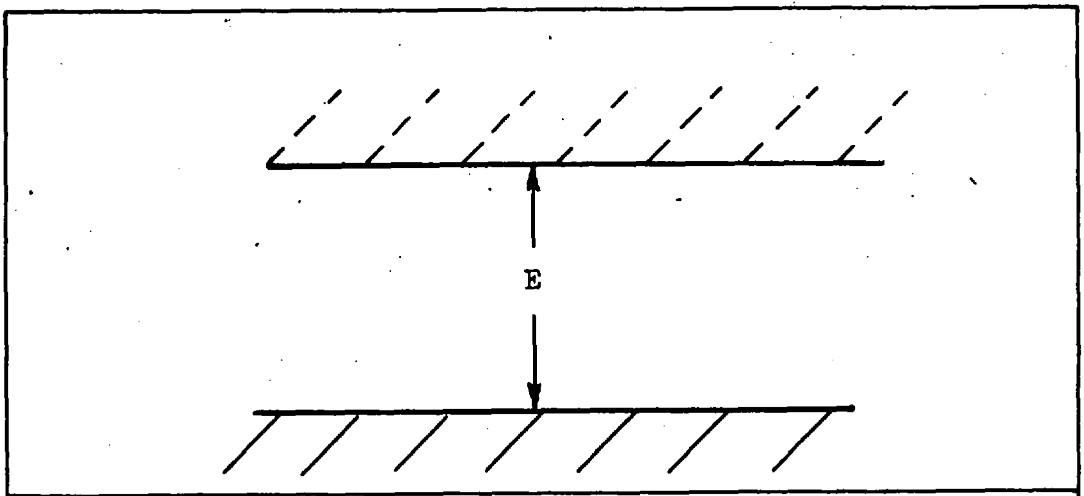
= conduction band

E = energy gap

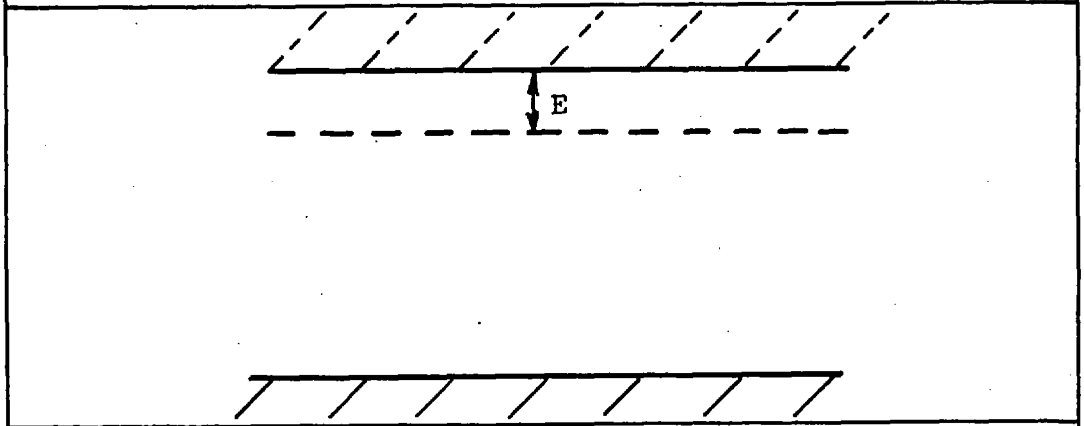


= filled band

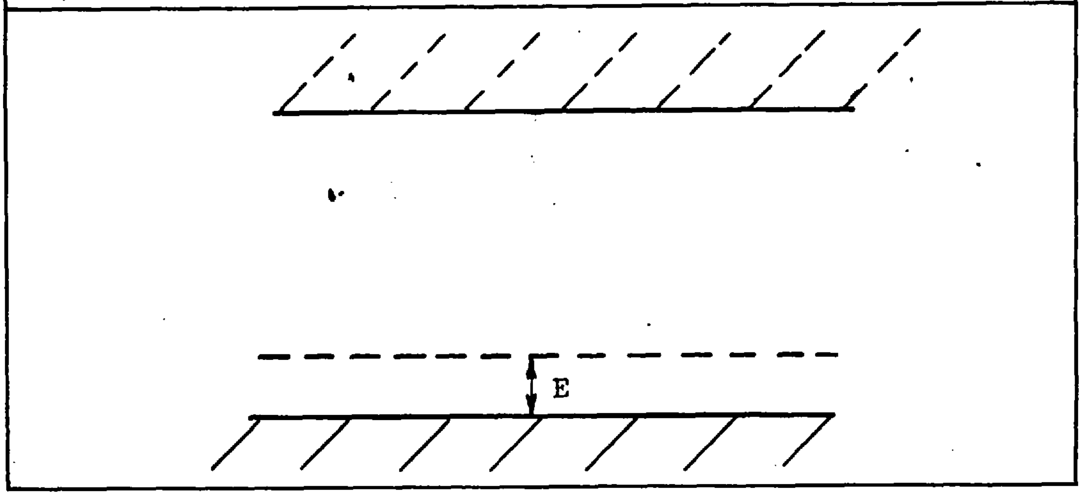
FIG. I.1 TYPES OF SEMICONDUCTOR.



(a) Intrinsic



(b) Extrinsic, n-type



(c) Extrinsic, p-type

Movements of the conduction electrons, and of electrons in the no-longer-filled band now both contribute to conduction. The latter contribution is referred to as "positive hole" conduction and is equivalent but of opposite sign to the movement of the electrons themselves. The extrinsic types of semiconductor (metal oxides and most metal sulphides) depend for their conduction on the existence of energy levels arising from imperfections in the crystal lattice. In n-type (excess) conductors, the energy levels of the impurity atoms are close to the conduction band into which the electrons associated with the impurity atoms are excited or donated. In p-type (deficient) semiconductors, the impurity levels are empty and close to the filled band, electrons from which are excited into the discrete impurity levels. This leaves positive holes in the filled band which in turn give rise to conduction.

(b) The geometrical factor.

The possibility of operation of geometric factors in heterogeneous catalysis was originally discussed by Raschig (14). The subsequent advance in the understanding of crystallization processes and of crystallographic structures provided impetus to this idea. Differences in the chemisorptive properties of different faces of single crystals (15)(16) was a further proof of the role played by the geometric factor. The postulation of "active centres" (11) at the edges of crystals explained in principle how imperfections in the lattice of a solid could provide specific points at which adsorption is favoured leading to a surface-catalysed reaction. It is pertinent to point out, at this stage, how the surface area of heterogeneous catalysts affects the activity. It would be expected that the activity of a catalyst would increase with surface area, and although correlations of this kind have been observed (17), deviations have also been pointed out (18)(19). The two commonest causes of such deviations are firstly that it is the "active centres" which are important rather than the total accessible area and secondly that it is possible that some of the surface area might not be available to the reactant due to small pore size.

The lattice imperfections which govern the catalytic activity are of two types (12), reversible and irreversible. Reversible imperfections exist in crystals at all temperatures above the absolute zero, as their presence minimises the total free energy. They consist of Frenkel defects which are described as interstitial units, occurring in the lattice with or without vacant sites, and Schottky defects, which are vacant lattice sites. The particular type of reversible defect present depends on the respective energies of formation of the substances concerned. Irreversible imperfections depend, however, primarily on the history of the sample and include flaws and Smekal cracks, the presence of which relieves strain. Dislocations on the surface of the crystal consisting of displacements of planes of the crystal lattice from their normal positions, are also important.

Imperfections may have chemical origins and depend largely on non-stoichiometric chemical compositions or the presence of foreign ions as impurities in interstitial or lattice positions. Such imperfections are common in metal oxide catalysts and are responsible for their semiconductivity which in turn is responsible for the catalytic activity. Geometric factors are capable then of affecting profoundly the electronic properties of the catalyst. Non-stoichiometry, giving rise to conduction, can be due to either excess of metal or oxygen in the lattice. Zinc oxide (Fig. I. 2a) is a typical case of an oxide having excess of metal, giving rise to an n-type conduction in which the electrical conductivity is due to the mobility of quasi-free electrons. On the other hand, cuprous oxide (Fig. I. 2b) represents a case where non-stoichiometry exists due to excess of oxygen, and the conductivity is due to quasi-free positive holes in the lattice.

Lattice imperfections due to the presence of foreign ions in the lattice structure are especially important when these impurities are cations of a valency different from that of the main cationic constituent of the lattice. The physicochemical properties of such solids and consequently their catalytic properties, are greatly affected by the valency, size and ionization potential of these impurities (20). Such an imperfection is illustrated by means of hypothetical example of vanadium pentoxide (12). The valency requirement of the predominant vanadium ion in vanadium pentoxide is five (V^{5+}). When an impurity (e.g. a tungsten ion having six valence electrons) is introduced (Fig. I. 3a), the extra electron, being loosely bound migrates by thermal vibration through the vanadium pentoxide lattice and acts as a carrier of electrical current, influencing the extent of oxygen adsorption. The electrical neutrality of the crystal is maintained due to the excess positive charge on the impurity ion. However the positive charge remains localized while the excess electrons can migrate and an n-type semiconductor results. In contrast, when an impurity having less than five valence electrons (e.g. a titanium ion) is introduced into the vanadium pentoxide lattice (Fig. I. 3b), the extra electrons necessary to maintain the valence structure of the crystal are contributed by the vanadium ions, thereby forming "positive holes". In this case, the electrical conduction is due to these positive holes (p-type semiconductor)

When gases are adsorbed on such semiconductors, the energy diagram (Fig. I. 1) is modified near the surface. For example, when oxygen is adsorbed on an n-type semiconductor, electrons are transferred from donor electron sites of the catalyst to the oxygen (See Section I. B. 2(b)).

FIG. I.2 2-DIMENSIONAL REPRESENTATION OF ZINC OXIDE AND COPPER OXIDE.

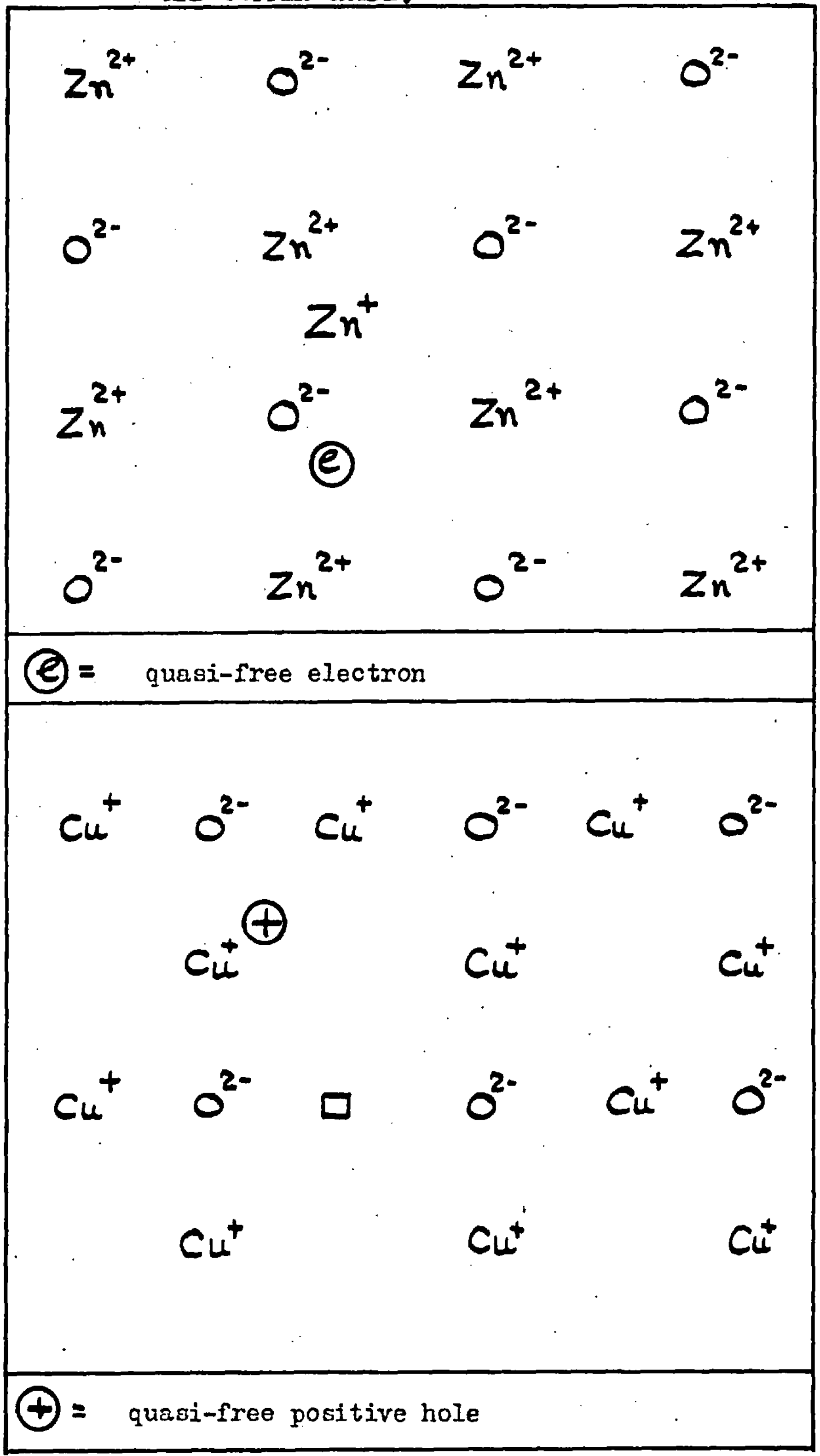
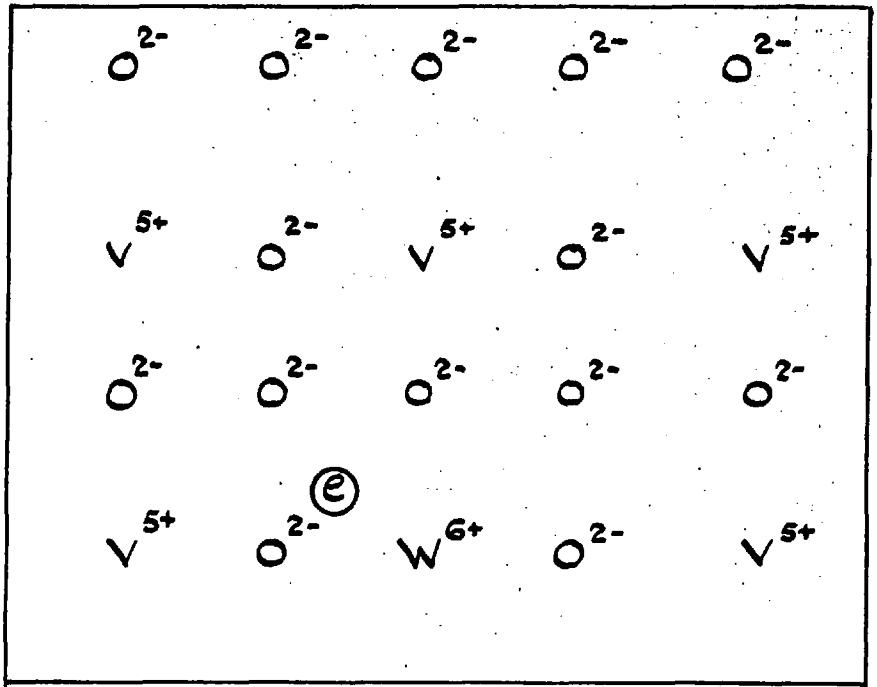
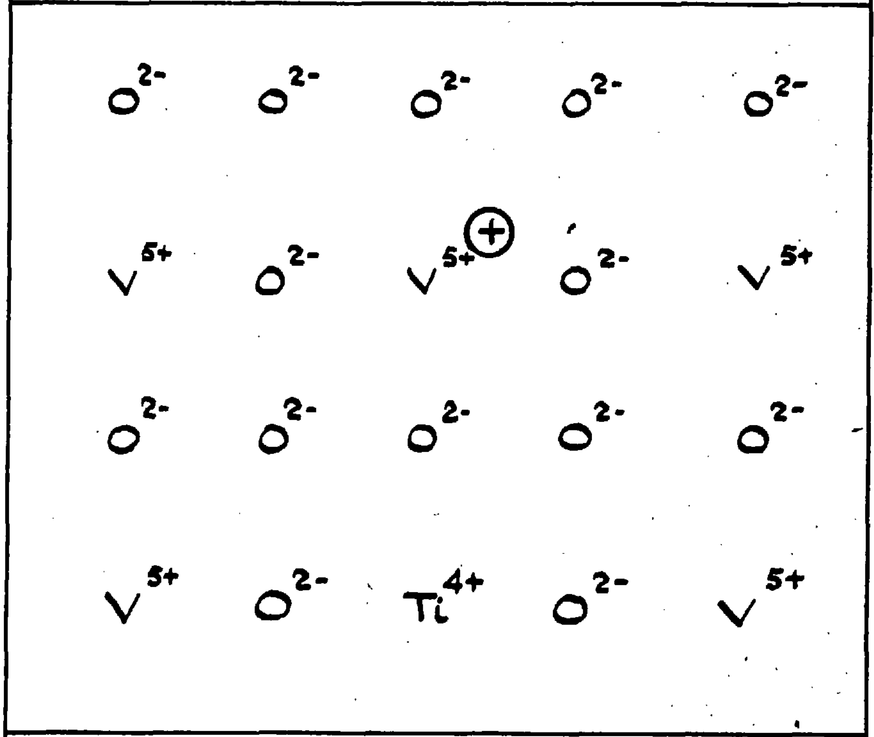


FIG. I.3. IMPURITIES IN THE VANADIUM PENTOXIDE LATTICE: 2-DIMENSIONAL REPRESENTATION.



ⓔ = quasi-free electron



⊕ = quasi-free positive hole

$$O_2 \rightleftharpoons 2O_{(ads)} \rightleftharpoons 2O^-_{(ads)} + 2\oplus$$

A negative charge is therefore built up on the surface, compensated for by a positive charge extending some distance below the surface, and the potential barrier for further electron-transfer to oxygen, i.e. for further adsorption, is raised. The semiconductivity is also altered, the increased concentration of positive holes will increase the semiconductivity of p-type semiconductors but decrease that of n-type semiconductors. This type of adsorption is known as anionic chemisorption. On the other hand, donation of electrons from adsorbate to the solid accompanies cationic chemisorption. The increase in electron concentration will lead to increased semiconductivity in n-type semiconductors and decreased semiconductivity in p-type semiconductors. It is noteworthy in this respect that p-type semiconductors are better oxidation catalysts and that n-type semiconductors are better hydrogenation catalysts.

3. Theories of catalysis.

There are three main theories of catalysis, namely intermediate surface compound theory, the multiplet theory and the electronic theory, all of which are, in general, complementary. All of them, stress the importance of the physicochemical properties of solid surfaces in relation to the phenomenon of catalysis.

(a) The intermediate surface compound theory.

This theory regards catalysis as due to chemical forces, under the influence of which many intermediate surface structures are obtained. It can be regarded, as a modernised version of Sabatier's original idea (21). The main postulates of the theory are as follows.

Activated adsorption (chemisorption) of reactants, forming strong bonds between the surface and the adsorbed species, precedes catalysis and is followed by the formation of intermediate surface compounds which decompose to give adsorbed reaction products. These reaction products are then desorbed. According to Balandin (22) the major weakness of this theory is the lack of any detailed explanation of the mechanism by which the intermediate surface compounds decompose to give the products. Furthermore it does not take into account the electronic properties of the compounds involved and it has failed in cases where the intermediate surface compounds could not be isolated.

(b) The multiplet theory.

The multiplet theory stresses the importance of geometry as a factor influencing the interaction of atoms and molecules. Burk (23) postulated that a surface could accomplish separation of atoms A and B of the molecule A-B, only if the atoms were attracted by different atoms to the surface of the catalyst, and were separated by a distance greater than the normal length of the bond A-B. This condition would cause the original bonds in the reactant molecule to stretch and eventually rupture. Balandin (24) has discussed this postulate more precisely and has thus formulated the multiplet theory. To the above condition for the catalytic rupture of a bond in the reactant, Balandin has added a condition for the formation of a new bond, namely that atoms between which the new bond is to be formed should be attracted to the same catalyst atom in the vicinity of which they will then react. The catalytic reactivity is determined therefore by the forces of attraction of the reactant molecule for different catalyst atoms. As such forces operate only over short distances (10^{-7} - 10^{-8}cm.), the interaction is determined solely by the relative spacing of surface and reactant atoms.

The main drawbacks (25) of the multiplet theory are the lack of an entirely satisfactory explanation of catalyst specificity and poisoning, and the failure to take into account the unsaturated nature of the catalyst surface. Balandin (25) has made an attempt, based on the work of Maxted (26)(27), to explain the first drawback by pointing out that the poisoning of a catalyst results from "screening" of its surface (or at least of the active sites); in other words the poison molecule prevents the reactant molecules from coming into contact with the catalytic surface.

(c) The electronic theory.

In recent years an electronic theory of catalysis has been evolved which has a wide applicability to semiconductors. The fundamental postulates (28) of this theory are as follows.

Firstly chemisorption must necessarily precede catalysis and the adsorbed particles and the lattice of the adsorbent may be treated as a single quantum-mechanical system. The electrons of the crystal lattice are accordingly direct participants in the chemical changes taking place on the surface of the catalyst. The chemisorbed species are considered to be equivalent to "biographical" structural defects of the surface, the only difference being that the chemisorbed species are mobile between the surface and the gas-phase, while the defects are not. Each chemisorbed species therefore serves as a centre of localization either of free electrons or of free positive holes.

Secondly a chemisorbed molecule possesses different reactivities in different "forms" of chemisorption i.e. the reactivity depends upon whether the species concerned is adsorbed as a molecule, as an anion, as a cation or as a radical.

Thirdly due to the localization or delocalization of a free positive hole or a free electron near an adsorbed species, the latter can change the character of its bonding to the surface. Thus a radical for example may react with a free electron to give an anion with consequent change in the reactivity of the adsorbed species.

Fourthly the relative amounts of a substance chemisorbed in each form (ions, molecules and radicals) are determined by the position of the Fermi level, which is also postulated to be responsible for the adsorption capacity of the surface, other factors being equal.

Lastly the bulk properties of a solid are related to the properties of its surface since the position of the Fermi level of the surface depends upon the position of the Fermi level in the bulk of the solid.

4. The oxidation-reduction mechanism of heterogeneous catalytic oxidation.

Catalytic oxidation on metallic oxides has been widely explained on the basis of an oxidation-reduction mechanism, the metallic constituent of the catalyst existing in at least two valency states and the oxygen from the gas-phase replenishing the oxygen anions in the oxide lattice as these are used up as a result of oxidation of the fuel. Farravano (29), on the basis of work on the oxidation of ammonia over oxide catalysts, concluded that this particular oxidation does not involve such an oxidation-reduction mechanism but proceeds by means of the excess oxygen present on the surface. On the other hand Karpacheva (30) indicated the possibiltiy of the oxidation of carbon monoxide proceeding through reduction of the oxidized contact surface. Similar reductions have been frequently reported by other workers (31)(32). Half the vanadium pentoxide in the upper layers of the catalyst has been known to have been converted to vanadium tetroxide (V_2O_4) while being in industrial operation as an oxidation catalyst for two years. The most conclusive proof in the support of this mechanism has been given by Mars and Van Krevelen (32), who have shown that a vanadium pentoxide catalyst, when it is in contact with a mixture of an oxidizable substance and air, will be partly in a reduced state. Good yields of anthraquinones from anthracene were obtained without using any source of oxygen, proving that the oxygen ions of the crystal lattice itself were independently taking part in the oxidation process. This catalyst however soon showed a sharp drop in activity, indicating that reduction of the catalyst to a lower oxide was taking place. The phenomenon of re-oxidation of the deactivated reduced catalyst was investigated (33). It was pointed out that, for a wide range of fuels, the operating temperature for a given conversion is independent of the compounds being oxidized and these findings justify the postulate that the rate of oxidation is determined by the rate of re-oxidation of the catalyst by oxygen. The structure of crystalline vanadium pentoxide (34), induced Mars and Van Krevelen to attribute its catalytic action to certain specific oxygen ions. According to present ideas regarding the structure of this compound, about three fifths of the oxygen ions are present in about the same planes as the vanadium ions, with about two fifths of the oxygen arranged in a series of planes parallel to but alternating with the other planes. It was the latter set of oxygen ions, which were assumed to interact with the molecule being oxidized on the surface. On this basis the rate of oxidation would depend on the concentration of these oxygen ions and on that of organic molecules adsorbed on the surface. The degree of surface coverage would automatically be fixed at a certain value, depending on the rate of reaction of the oxygen ions on the surface with the substance to be oxidized and on the rate of re-oxidation of the reduced surface by molecular oxygen. Such a mechanism was in agreement with the experimental results since, when a low partial pressure of oxygen or a high partial pressure of fuel was used, a considerable proportion of V^{5+} was reduced to V^{4+}. The process can be depicted as having two distinct steps:

I. organic fuel + oxidized catalyst ⟶ oxidation products + reduced catalyst

II. reduced catalyst + oxygen ⟶ oxidized catalyst

This idea developed further and some workers now visualize an oxide catalyst as a dynamic surface of oxygen and metal ions in continuous and varying valence state. Simard et al. (35) regard vanadium pentoxide as having V^{4+}, V^{5+} and O^{2-} ions. It thus exhibits features characteristic of the phase $V_2O_{4.34}$ in certain areas and features characteristic of the phase V_2O_5 in others, changes of structure corresponding to the interchange of valency of vanadium ions. This change of valency has been associated with the production of lower oxide phases during the oxidation of organic fuels on vanadium pentoxide, and may also be responsible for changes of semiconductivity noted in such systems. For example, the exposure of V_2O_5 to an olefin air stream lowers the electrical resistance as the oxide is reduced to $V_2O_{4.34}$ or V_2O_4 (36) and this increase in semiconductivity is consistent with the increase in catalytic activity often noted during use of vanadium catalysts. Reöxidation of the catalyst will restore the resistance to its original value. Again when naphthalene is oxidized on vanadium pentoxide gradual reduction of the oxide to tetravalent vanadium oxide produces a gradual increase in the reaction velocity. Eventually the phase $V_2O_{4.34}$ separates out and a sharp increase in reaction velocity occurs simultaneously (37)(38).

C. THE OXIDATION OF OLEFINS.

1. The uncatalysed gas-phase oxidation.

In the uncatalysed gaseous oxidation of olefin hydrocarbons, two modes of initiation of the reaction are believed to operate.

(a) Abstraction of a hydrogen atom .

(b) Addition of an oxygen molecule at the double bond.

(a) Hydrogen abstraction as the initiating step.

This mode of initiation is similar to the initial step in the gaseous oxidation of the paraffins. According to

Tipper (39) the initiation step in the oxidation of paraffins is abstraction by oxygen of a hydrogen atom to produce a reactive alkyl radical:

$$RH + O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet}$$

This is followed at low temperatures by attachment of molecular oxygen to this radical at the site of the free valency,

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$$

and reaction of the resulting $RO_2^{\bullet}$ radical with another fuel molecule to give a hydroperoxide, ROOH and another alkyl radical $R^{\bullet}$ which continues the chain

$$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$$

In the case of olefinic hydrocarbons, the preferred point of attack is the allylic carbon atom, particularly when tertiary or secondary hydrogen is attached thereto as the proximity of the double bond weakens α-C-H bonds. The resulting allyl radical reacts, by a linear chain mechanism, to give an $\alpha\beta$-unsaturated hydroperoxide. This mode of reacton has been investigated by many workers.

Mulcahy and Ridge (40) suggested a mechanism based on α-hydrogen abstraction as the initiation step to explain the course of the gaseous oxidation of propylene.

<u>Initiation</u>: $CH_2{=}CH{-}CH_3 + O_2 \longrightarrow CH_2{=}CH{-}CH_2^{\bullet} + HO_2^{\bullet}$

<u>Propagation</u>: $CH_2{=}CH{-}CH_2^{\bullet} + O_2 \longrightarrow CH_2{=}CH{-}CH_2OO^{\bullet}$

$CH_2{=}CH{-}CH_2OO^{\bullet} + CH_2{=}CH{-}CH_3 \longrightarrow CH_2{=}CH{-}CH_2^{\bullet} + CH_2{=}CH{-}CH_2OOH$

The hydroperoxide formed acts as a degenerate branching agent

$$CH_2{=}CH{-}CH_2OOH \longrightarrow CH_2{=}CH{-}CH_2O^{\bullet} + OH^{\bullet}$$

$$CH_2{=}CH{-}CH_2O^{\bullet} \longrightarrow CH_3CHO,\ HCHO,\ CH_2{=}CH{-}CHO$$

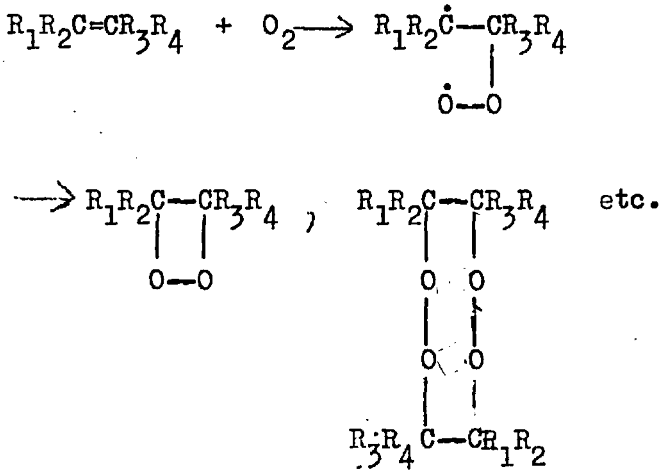
If these reactions were the only ones taking place, it might be expected that the induction period would end when the hydroperoxide concentration reached some critical value. Batten and Ridge (41) proved experimentally, however, that this was not so.

The pressure-time curves during the gas-phase oxidation of propylene at 300-400°C. are sigmoid (42), being similar to those obtained during the slow oxidation of paraffins, in support of the mechanism proposed by Mulcahy and Ridge (40). Acetaldehyde and not hydroperoxide was however postulated as the species responsible for degenerate chain branching.

The results of Blundell and Skirrow (43) on the oxidation of but-2-ene give no clear indication of the initiation reaction but are compatible with initiation by hydrogen abstraction. As these workers found no crotonaldehyde in the reaction products, they suggested that the radical $CH_3{-}CH{=}CH{-}CH_2^{\bullet}$ isomerizes to $CH_3{-}\dot{C}H{-}CH{=}CH_2$ before reacting with oxygen. The kinetics of hex-1-ene oxidation (44) are also compatible with such a scheme.

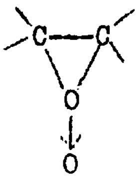
(b) Addition of an oxygen molecule at the double bond as the initiating step.

The possibility of addition of molecular oxygen at the double bond of an olefin has long been considered as an initiation mechanism. The reaction scheme may be represented as:-

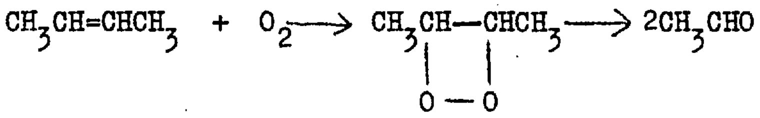


Inevitably the study of such reactions is complicated by competition from initiation by hydrogen abstraction. Thus deviations from the results which would follow if the hydrogen abstraction mechanism were the only one operative have often been used as evidence of oxygen addition. Direct evidence has however more recently become available.

Lenher (45)(46) postulated that oxygen could activate the double bond of ethylene or propylene and thus react to give a compound of the form.



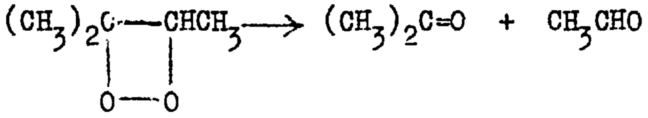
Lucas, Prater and Morris (47) found acetaldehyde to be the major product of the oxidation of but-2-ene and postulated its formation, via a cyclic peroxide.



$$CH_3CH{=}CHCH_3 + O_2 \longrightarrow CH_3\underset{|}{C}H{-}\underset{|}{C}HCH_3 \ (\text{O—O}) \longrightarrow 2CH_3CHO$$

A similar mechanism was suggested for oxidation of but-2-ene by Dobrinskaya and Neiman (48) who considered that the more usual hydroperoxylation mechanism was concurrently operative. These workers, in contrast to Blundell and Skirrow (43), found some crotonaldehyde among the reaction products.

Cullis, Fish and Turner (49)(50), showed that equivalent amounts of acetaldehyde and acetone resulted from the oxidation of 2-methyl but-2-ene at 263°C. and that these two products were formed at equal rates. It was suggested that these two compounds arose from the simple breakdown of the cyclic peroxide.



$$(CH_3)_2\underset{|}{C}{-}\underset{|}{C}HCH_3 \ (\text{O—O}) \longrightarrow (CH_3)_2C{=}O + CH_3CHO$$

The formation of this peroxide as an unstable intermediate was supported by reduction of oxidation products with lithium aluminium hydride to give 2-methyl butan-2,3-diol. The origins of the products were investigated by specific skeletal labelling using carbon-14 and shown to be consistent with the postulated cyclisation-cleavage mechanism. On the basis of this mechanism, the overall extent of oxidation will depend markedly on the nature of the carbonyl scission products, the formation of aldehydes leading to extensive autocatalytic development of the reaction but ketones being relatively stable. In the same way however, autocatalytic development of the reaction may be due to the fact that the normal hydroperoxylation mechanism is also operative. The presence of large amounts of methyl isopropyl ketone and the absence of isovaleraldehyde and 2-methyl butyraldehyde in the products lead to the conclusion that hydrogen abstraction takes place mainly at the vinyl group, unless the radical formed by attack at the methyl group rearranges completely before reacting with oxygen. Certain mechanisms involving co-polymerisation of olefin and oxygen, proposed for liquid-phase oxidation (51), were considered unsatisfactory when applied to the gas-phase oxidation; for the formation of the large involatile peroxide molecules involved would entail a pressure decrease corresponding to the disappearance of at-least two molecules for every peroxidic linkage formed, which is not the case experimentally.

2. The heterogeneous catalytic oxidation of olefins.

The study of the mechanism of heterogeneous catalytic oxidation of olefins is more complex than similar studies of the uncatalysed oxidation, since in the former case, the catalytic surface plays an important part in determining both qualitative and quantitative aspects of the reaction. The role played by surfaces in uncatalysed gaseous reactions, is widely recognized and it has been pointed out that the type of material used for constructing a reaction vessel and the "ageing" of such vessels have a marked effect on the reaction. The role of the surface becomes even more important in the case of catalytic surfaces, since these are, by definition, highly active during the reaction.

Adsorption of the reacting species generally precedes catalysis and important physicochemical changes take place in the adsorbate and the adsorbent (Section I. B. 2.(b)) during adsorption, which throw light on the initial stages of heterogeneous catalytic oxidation reactions. The behaviour of oxygen and of hydrocarbons on typical oxidation catalysts (metals and metal oxides) has been widely investigated. The general similarity of such behaviour has been noted and it has been pointed out that this probably arises from the fact that metal surfaces are covered by a thin oxide film during their action as oxidation catalysts (52).

(a) The adsorption of oxygen on catalytic surfaces

Benton et al. (53) postulated that, in a silver-oxygen system, "activated adsorption" of oxygen on silver was very slow at 0°C. but became quite rapid at higher temperatures. Similar adsorption of oxygen on smooth silver has also been reported at temperatures from -78 to 20°C. and at low pressures (54).

Twigg (55) during his work on the catalytic oxidation of ethylene on silver, demonstrated by its effect in lowering electrical resistance, the chemisorption of oxygen on silver.

The existence was postulated of complexes such as  to explain the results.

Later work was done to show more specifically the form in which oxygen exists on these catalysts. Garner et al. (56) found, while studying the reaction between carbon monoxide and oxygen on cuprous oxide, that oxygen is not only adsorbed on the catalytic surface but is also <u>incorporated in the crystal lattice</u>. It was suggested that the adsorption of oxygen on cuprous oxide involves electron-transfer from Cu^+ ions to oxygen, producing oxygen ions (O^-, O^{2-} and O_2^-) and positive holes at the surface. The oxygen ions will confine themselves to the surface but the positive holes may distribute themselves into the interior leaving an excess negative charge at the surface. ([illegible]). In the case of nickel oxide (57), however, the dissolution of oxygen is not considered significant, chemisorption being the only important step.

Following the suggestions made by Weisz (58), Clark and Berets(36), who studied the electrical properties of vanadium pentoxide, postulated the existence of negative species such as O^{2-} and O^-. According to these workers, oxygen vacancies in the crystal lattice form electron donor levels below the conduction band and are present in sufficient concentration to be a source of electrons. In the presence of an electron-donating molecule like ethylene or a xylene, the formation of the barrier layer is prevented. Similar electron transference leading to the presence of these negatively charged oxygen species occurs on the surface of zinc oxide (59).

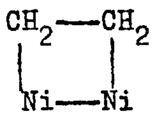
The most likely species present on a catalytic surface, during adsorption of oxygen are O_2^- and O^- at low temperatures and O^{2-} at higher temperatures, since under the latter conditions there would be more energy available for the transfer of a second electron to oxygen (60)(61). The isotopic exchange reaction,

$$^{18}O_2 + {}^{16}O_2 \longrightarrow 2\,{}^{16}O^{18}O$$

which is catalysed by zinc oxide, suggests that monatomic oxygen ions are important species as it is unlikely that a molecular entity such as O_2^- would participate in the above exchange reaction (61).

(b) The adsorption of hydrocarbons on catalytic surfaces.

Studies have been made by various workers on the adsorption of various hydrocarbons on metals and metal oxides. Steacie (62) points out that nickel-ethylene systems exhibit the criteria of "activated adsorption", and has discounted the possibility that the ethylene is "dissolved" in the nickel lattice. Twigg et al. (63) agree with these suggestions and postulate the adsorption of ethylene as taking place between the two carbon atoms and two nickel atoms to give a complex of the form:-



Adsorption of ethylene on a silver surface (55) is relatively weak but ethylene is shown to be chemisorbed at room temperatures on zinc oxide, zinc chromite and cuprous oxide (64).

It is difficult to be certain whether a defect structure is formed during adsorption of hydrocarbons on these solid surfaces but the work of Thomas (65) is of interest inasmuch as a change in the colour of nickel oxide from green to grey is observed during adsorption of ethane, suggesting the incorporation of a defect structure. It has been suggested (66) that such a structure represents a potential unit for surface bonding and that surface bonds can be designated by indicating the defects involved without specifying participation of surface metal or oxygen ions.

In 1950, Dowden (20) introduced the concept of the formation of charged radical-ions on the catalytic surface during the hydrogenation of olefins

$$\underset{\text{(olefin)}}{RH} \longrightarrow RH^{+} + e$$

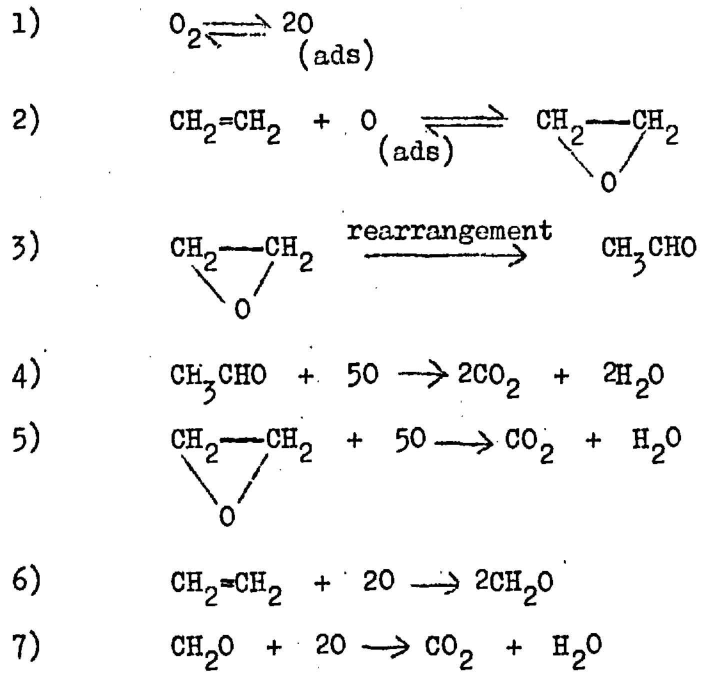
Lately the trend has been towards the formulation of adsorption reactions in terms of these charged radical-ions. Margolis, (67) while studying the chemisorption of ethylene, propylene and propane on oxidation catalysts (vanadium pentoxide, cuprous oxide, nickel oxide, manganese dioxide and chromium oxide), proved the existence of such charged radical-ions, RH^{+}, by measuring the electrical conductivity of these surfaces. Many other workers (68) have explained the adsorption of olefins as being due to donation of an electron from the π-bond of the olefin, with the resulting opening of this bond, the other free valency of which is then available for adsorption. Ioffe(69) found oxide catalysts to be both σ- and π- active, the former being responsible for breaking C-H bonds and the latter for the rupture of C=C bonds.

(c) <u>The reactions of the adsorbed species</u>.

Much of the work on the catalytic oxidation of olefins has consisted of attempts to produce highly selective processes leading to desirable products. On the other hand, efforts have been made to elucidate the basic nature of the reaction mechanism. A major general problem which needs to be studied is (as in the case of uncatalysed gaseous oxidation) the mode of attack of oxygen on the olefin, viz. whether the initial attack by molecular or ionic oxygen consists of addition across the double bond or of hydrogen abstraction.

A great deal of the work on ethylene oxidation does not in fact elucidate this particular aspect of the problem, although it helps to throw light on other points of mechanistic interest.

Twigg (55) obtained ethylene oxide, acetaldehyde, water and carbon dioxide as the main products during oxidation of ethylene on silver at 263°C. The following mechanism was proposed:



1) $O_2 \rightleftharpoons 2O_{(ads)}$

2) $CH_2{=}CH_2 + O_{(ads)} \rightleftharpoons \underset{\diagdown O \diagup}{CH_2{-}CH_2}$

3) $\underset{\diagdown O \diagup}{CH_2{-}CH_2} \xrightarrow{\text{rearrangement}} CH_3CHO$

4) $CH_3CHO + 5O \rightarrow 2CO_2 + 2H_2O$

5) $\underset{\diagdown O \diagup}{CH_2{-}CH_2} + 5O \rightarrow CO_2 + H_2O$

6) $CH_2{=}CH_2 + 2O \rightarrow 2CH_2O$

7) $CH_2O + 2O \rightarrow CO_2 + H_2O$

This mechanism suggests which is the most probable rearrangement process involved during such oxidation (viz step 3) and underlines the parallel (steps 6 and 7) and consecutive (steps 2, 3 and 4) modes of formation of the ultimate product, carbon dioxide.

The results obtained by McBee (70) (ethylene on silver oxide) and Murray (71) (ethylene on silver containing 10% barium carbonate), agree with the mechanism put forward by Twigg (55). More recently Margolis (72) has proposed a mechanism for ethylene oxidation based on electron-transfer processes, involving charged radical-ions. The basic contention of Margolis is that ethylene and water act as electron-donors while oxygen and carbon dioxide behave as electron-acceptors.

The postulated mechanism is as follows:

$$Ag + O_2 \longrightarrow Ag\text{-}(O_2)^-$$

$2Ag + O_2 \longrightarrow 2Ag\text{-}(O_2)^-$

$Ag\text{-}O_2^{\bullet} + C_2H_4 \longrightarrow Ag\text{-}(O_2\text{-}\dot{C}_2H_4)$ charged complex I

$Ag\text{-}O_2\text{-}\dot{C}_2H_4 + O_2 \longrightarrow (CO_2) + 2(H_2O)^+ + Ag$

$Ag\text{-}O_2\text{-}\dot{C}_2H_4 \longrightarrow (C_2H_4O)^+ + Ag\text{-}(O)^-$

$Ag\text{-}O_2\text{-}\dot{C}_2H_4 + C_2H_4 \longrightarrow Ag\text{-}O_2C_2H_4$

$Ag\text{-}O + \dot{C}_2H_4 \longrightarrow Ag\text{-}(O\text{-}C_2H_4)$ charged complex II

$Ag\text{-}O\text{-}C_2H_4 + O_2 \longrightarrow (CO_2) + 2(H_2O)^+$

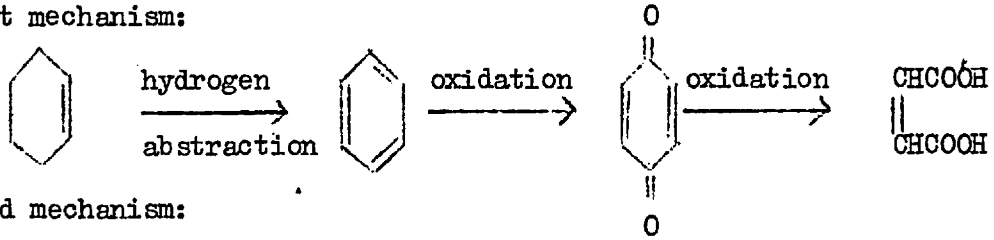
$Ag\text{-}(C_2H_4O)^+ + e \longrightarrow Ag + C_2H_4O$

$Ag\text{-}(CO_2)^- - e \longrightarrow Ag + CO_2$

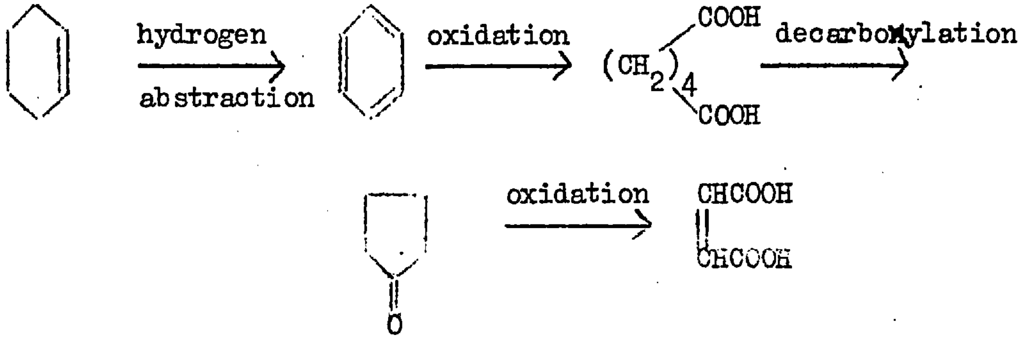
$Ag\text{-}(H_2O)^+ + e \longrightarrow Ag + H_2O$

Cyclohexene oxidation on pumice-supported vanadium pentoxide resulted in the formation of maleic acid. Benzene and quinone were found as intermediates (73). Since, however, adipic acid is also found as an intermediate in liquid-phase oxidation of cyclohexene to maleic acid, two mechanisms were put forward to explain the results.

1st mechanism:

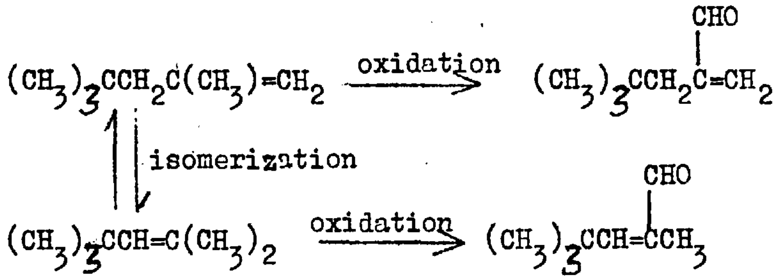


2nd mechanism:



The intermediate cyclopentanone is oxidized to maleic acid under these conditions.

Hadley et al. (74) studied the heterogeneous catalytic oxidation of isomeric mextures of di-isobutenes and concluded that the attack by oxygen took place at the α-methyl group.



$$\begin{tikzcd}(CH_3)_3CCH_2C(CH_3){=}CH_2 \arrow[r, "\text{oxidation}"] \arrow[d, shift left, "\text{isomerization}"] & (CH_3)_3CCH_2\overset{\overset{\displaystyle CHO}{|}}{C}{=}CH_2 \\ (CH_3)_3CCH{=}C(CH_3)_2 \arrow[u, shift left] \arrow[r, "\text{oxidation}"] & (CH_3)_3CCH{=}\overset{\overset{\displaystyle CHO}{|}}{C}CH_3\end{tikzcd}$$

Bretton, Wan and Dodge, (75) have postulated a mechanism for the oxidation of C_4 olefins on vanadium pentoxide based on the corresponding liquid-phase oxidation mechanism. The surface is assumed to act primarily as a hydrogen abstractor and donor.

(1) $RH + \underset{\text{(catalyst)}}{X} \longrightarrow HX + R^{\bullet}$

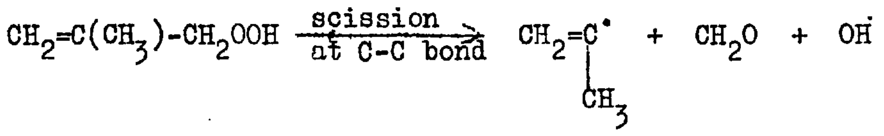
(2) $R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$

(3) $RO_2^{\bullet} + HX \longrightarrow ROOH + X$

The presence of α-methyl acrolein and methyl vinyl ketone in the catalytic oxidation of isobutylene and but-1-ene respectively led to the suggestion that the initial point of attack in olefin oxidation is the α-methyl or α-methylenic carbon atom. The mechanism proposed for isobutylene oxidation is as follows, the hydroperoxide being formed by steps (1), (2) and (3).

(4) $CH_2{=}C(CH_3){-}CH_2OOH \xrightarrow[\text{C-H bond}]{\text{scission at}} CH_2{=}C(CH_3){-}CHO + \dot{H} + O\dot{H}$

If the scission at the adjacent C-C bond occurs rather than at C-H, then step (5) would follow step (3)

(5)


$$CH_2{=}C(CH_3){-}CH_2OOH \xrightarrow[\text{at C-C bond}]{\text{scission}} \underset{\displaystyle CH_3}{CH_2{=}\overset{\bullet}{C}} + CH_2O + O\dot{H}$$

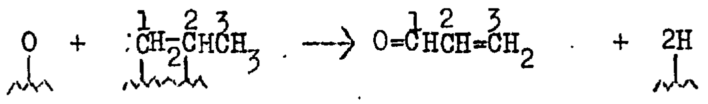
This new radical can then be converted to hydroperoxide by steps (2) and (3)

(6) $CH_2{=}C(CH_3)OOH \longrightarrow CH_2{=}C{=}O + \dot{C}H_3 + O\dot{H}$

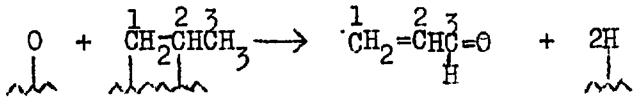
(7) $CH_2{=}C{=}O \xrightarrow{\text{hydration}} CH_3COOH$

In cases where the olefins are converted to unsaturated carbonyl compounds, efforts have been made to elucidate the mechanism by isotopic tracer methods (82). Two mechanisms are possible.

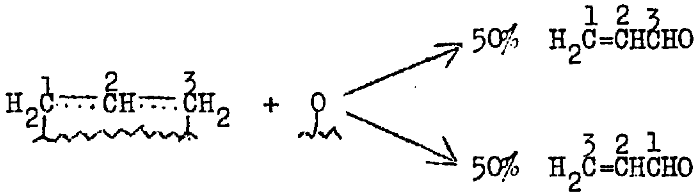
In the first mechanism, either the π-complex reacts with adsorbed oxygen, followed by release of two hydrogen atoms and migration of the double bond; or the release of two hydrogen atoms precedes the interaction of the π-bonded complex with adsorbed oxygen, without migration of the double bond taking place.



or



In the second mechanism, the dissociative chemisorption of propylene on the catalyst surface is postulated to form a symmetrical allyl group, providing an equal chance for both the terminal carbon atoms to form a C=O bond.



In order to distinguish between the two mechanisms, propylene samples enriched respectively in [1-^{14}C] -propylene, [2-^{14}C] -propylene, and [3-^{14}C]-propylene were used as starting materials to give acrolein which was then decomposed photochemically to ethylene and carbon monoxide (76). From the results it was concluded that, during oxidation of propylene, the two terminal carbon atoms become equivalent.

The overall picture of catalytic oxidation can thus be envisaged as taking place in five stages:

(1) Adsorption of reactants.

(2) Migration of adsorbed reactants to sites active for electron transfer.

(3) Electron transfer processes

  (a) $RH_{(ads)} - e \longrightarrow RH^{+}_{(ads)}$

  (b) $O_{2(ads)} + e \longrightarrow O^{-}_{2(ads)}, O^{-}_{(ads)}, O^{2-}_{(ads)}$

(4) Reaction of these adsorbed species:

$$\left.\begin{matrix} RH^{+}_{(ads)} \\ \text{or} \\ RH^{+}_{(ads)} \end{matrix}\right] + \left[\begin{matrix} O_{2(ads)} \\ O_{(ads)} \\ O^{-}_{2(ads)} \\ O^{-}_{(ads)} \\ O^{2-}_{(ads)} \end{matrix}\right. \longrightarrow \begin{matrix}\text{activated} \\ \text{complex}\end{matrix} \longrightarrow \text{products}$$

(5) Desorption of products

$$P_{(ads)} \longrightarrow P_{(g)}$$

A further type of unwanted reaction which may take place is further oxidation of $P_{(ads)}$. The selectivity of oxidation will depend on the number of possible routes by which reaction (4) may proceed. Surfaces which restrict the predominant ionic form present to a single anionic and cationic species should be highly selective. Step (3) will often be rate-determining and the oxidation scheme of Mars and van Krevelen (33) is in fact an alternative way of writing steps (3) and (4).

D. THE PRESENT STUDIES.

In the light of the above mechanisms postulated by different workers, it was considered of interest to study the mechanism of oxidation of acyclic C_5 olefins over vanadium pentoxide. This substance was chosen because its behaviour as a catalyst and its other properties have already been fully studied and it has been widely used for the production of industrially important oxygenates.

Since, in some cases, gas-phase oxidation schemes have been applied to explain the results obtained on catalytic surfaces, particular attention was paid to evaluating the role played by the catalyst during the oxidation of olefins.

The experimental methods are described in Section II, the experimental results are presented in Section III and the mechanistic interpretation of these results is discussed in Section IV.

SECTION II.

EXPERIMENTAL TECHNIQUES.

SECTION II

A. PREPARATION AND PURIFICATION OF PENTENES.

Olefinic compounds are in general prepared by two simple methods, viz, dehydration of hydroxy compounds and dehydrohalogenation of halides. The former method is of more general application since alcohols are more readily available than halides. The mechanism of formation of olefins by dehydration of corresponding alcohols has been studied by various workers (77)(78)(79)(80). A variety of dehydrating agents has been used and these include hydrogen iodide, hydrogen bromide, aniline hydrochloride, iodine, sulphuric acid and zinc chloride. Dehydration has also been effected by a pyrogenic catalytic method but this is normally used only for the manufacture of olefins in large quantities. It is desirable to use the dehydrating agent which will give the highest yield without causing the formation of polymers, isomers or cleavage products. Sulphuric acid in varying concentrations, depending upon the type of alcohol being dehydrated, has been found to be very suitable for this purpose.

In the present studies, pent-2-ene and 2-methyl but-2-ene were prepared by dehydration of the appropriate alcohol with sulphuric acid, while pent-1-ene, 3-methyl but-1-ene and 2-methyl but-1-ene were obtained from Light & Co. and were purified as described below.

1. Pent-1-ene.

Pent-1-ene was treated with 5% sodium hydroxide solution to remove any sulphur dioxide. The olefin was then dried overnight over anhydrous calcium chloride and fractionally distilled; the fraction having a boiling range of 30-30.5°C. was collected and was shown by gas-liquid chromatography to contain less than 0.5% of other isomeric pentenes. The product had a boiling point of 30.2°C. and a refractive index (at 20°C.) of 1.3718. (cf. literature B.P. = 30.1°C.; n_{20}^{D} = 1.3715)

2. Pent-2-ene

Pent-2-ene was prepared by the dehydration of pentan-2-ol. Unfortunately pentan-3-ol, which is a far better starting material since its use excludes the possibility of formation of the isomeric pent-1-ene, was not available in sufficient quantities. Pentan-2-ol 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 10 inch fractionating column. The fraction boiling between 118°C. and 120°C. was collected and analysed by gas-liquid chromatography, confirming the absence of appreciable quantities of volatile impurities. To 200 ml. of 50% V/V sulphuric acid at 0°C. were added slowly 107 ml. of purified pentan-2-ol. When the mixture was gently heated, a product distilled over with boiling range of 30-45°C. This crude fraction was refractionated witn 40 ml. of 50% V/V sulphuric acid and the fraction distilling between 35°C. and 41°C. was collected. This product was shaken with 25 ml. of a 5% solution of sodium hydroxide to remove any traces of sulphur dioxide. The hydrocarbon layer was separated, dried over anhydrous calcium chloride, and redistilled, the fraction boiling between 36°C. and 36.5°C. being collected. Gas-liquid chromatographic analysis showed that pentan-2-ol was absent and that the impurity content was less than 1%. The product, which was obtained in 75% yield had a boiling point of 36.2°C. and had a refractive index (at 20°C.) of 1.3794. (cf. literature b.p. = 36.4°C.; n_{20}^{D} = 1.3797)

3, 4. <u>2-Methyl but-1-ene and 3-methyl but-1-ene</u>.

These two olefins were obtained from Light & Co. They were purified using methods similar to those described for pent-1-ene. The purified sample had the following boiling points and refractive indices:-

2-methyl but-1-ene: b.p. = 31.2°C.; n_{20}^{D} = 1.3780
(cf. literature, b.p. = 31.05°C.; n_{20}^{D} = 1.3777)
3-methyl but-1-ene: b.p. = 20.7°C.; n_{20}^{D} = 1.3646
(cf. literature, b.p. = 20.9°C.; n_{20}^{D} = 1.3643)

5. <u>2-Methyl but-2-ene</u>.

The methods of preparation and purification of 2-methyl but-2-ene were similar to those used for pent-2-ene. The alcohol used was tert-amyl alcohol and 33% v/v sulphuric acid was employed as the dehydrating agent. After the final distillation, the product was found to contain ca. 5% of the isomeric 2-methyl but-1-ene. Preparative gas-liquid chromatographic techniques have been used to separate this impurity which is difficult to separate by fractional distillation. In the present studies it was not necessary to resort to this technique since ca. 15% of 2-methyl but-2-ene rapidly isomerized to 2-methyl but-1-ene under the conditions used during catalytic oxidation. The product was obtained in 68% yield and had a boiling points of 37.9°C. and $n_{20}^{D} = 1.3868$. (cf. literature: b.p. 38.42°C.; $n_{20}^{D} = 1.3874$)

B. STORAGE OF PENTENES.

The oxidative deterioration of olefins on storage in air is a possible source of error in this kind of work (81). In the temperature range 20-50°C., however the oxidation in air of 2-methyl but-2-ene is very slow, less than 0.5% peroxide being detected after one year. All the olefins used were in fact kept under air in closed glass vessels at 0°C. and were generally used within three months of their preparation.

C. PREPARATION OF THE CATALYST.

1. General techniques.

A large number of specialized techniques have been described for the preparation of catalysts. The final choice of the method of preparation depends on the form in which the catalyst is required, the stability of the catalyst, the desired homogeneity of the product, the ease of preparation and of exact duplication of the method. The various methods generally used are precipitation, gel formation, impreganation and wet mixing. Other methods having a limited application are thermal fusion, chemical reaction and evaporation of metals. Certain metals e.g. silver, can be used as catalysts in the form of foils or of thin films. The unit processes involved in catalyst preparation are, chemical preparation, washing, drying, sizing and activation. It is essential to avoid any contamination by foreign ions or impurities as these have a marked effect on the selectivity and the activity of the catalyst.

2. Preparation of vanadium pentoxide.

The catalyst chosen for the present studies was vanadium pentoxide. The oxidative properties of this compound are well known and standard methods of preparation are readily available. Different workers have used as starting materials vanadic acid, organic esters of vanadic acid, vanadyl chloride, sulphate or oxalate and alkali or ammonium vanadates (82)(83) (84)(85).

The method of preparation used in the present work was that recommended by Milas and Walsh (83).

To a solution of 25 gm. of ammonium metavanadate (B.D.H.; Analar; containing less than 0.002% chloride and 0.01% of sulphate) in 100 ml. of water were added 100 gm. of the support (pumice or alumina) of the required mesh size. The mixture was evaporated to dryness with continuous stirring, until the evolution of ammonia ceased. The temperature was not allowed to exceed 350°C. The impregnated support was then sieved to the required mesh size. Great care was taken to avoid the introduction of any foreign ions during sieving. Thus, cloth sieves were used throughout, since metallic sieves (e.g. brass) were liable to introduce impurities, giving a catalyst of completely different activity. The solid thus obtained was heated in the reaction vessel at 350°C. under vacuum for four hours to remove adsorbed ammonia. The catalyst was activated with oxygen at 350°C. for four hours and was then ready for use.

3. Supports.

Pumice and alumina were the two supports used. The pumice was obtained from B.D.H. while the alumina was obtained from Peter Spence Ltd. (Specification pure y-Al_2O_3, less than 1% sulphate, only parts per million of other impurities.) The supports were heated at 200°C. for 2-3 hours to remove any diffused air and moisture before they were impregnated with vanadium pentoxide.

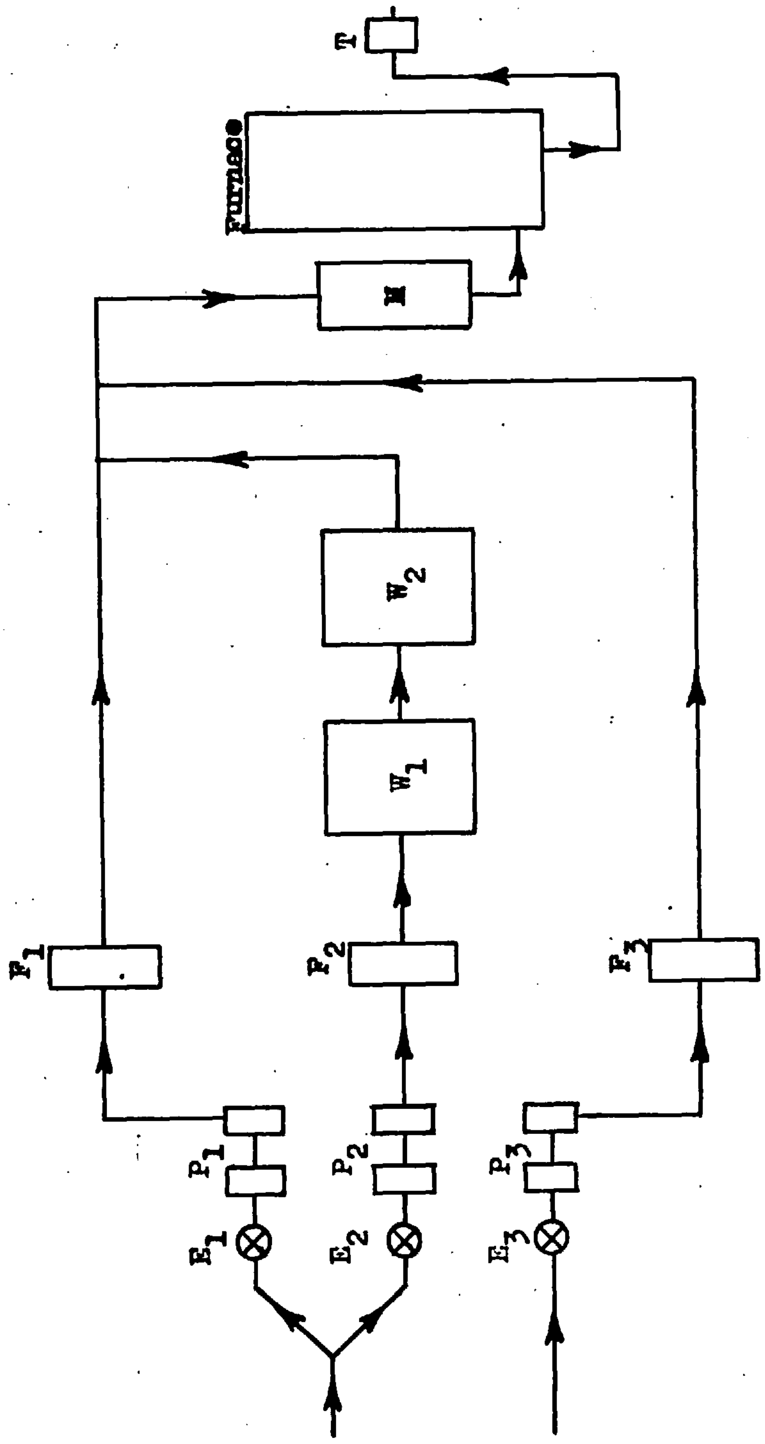
D. STUDIES OF THE CATALYTIC REACTIONS OF PENTENES.

1. Apparatus.

(a) The flow system.

A flow apparatus of conventional design was employed and its design is shown diagrammatically in Fig. II.1 and Plate II.1. Oxygen and "oxygen-free" nitrogen from cylinders were purified from carbon dioxide and water vapour by passage through purgers, P_1, P_2 and P_3, which consisted of two-feet-long cylindrical glass columns containing sofnolite (ca. 15% sodium hydroxide in calcium oxide) to remove carbon dioxide and anhydrone (magnesium perchlorate), with silica gel as an indicator, to remove water. The flow rates of the gases were regulated by needle valves, E_1, E_2, E_3 and measured by capillary flow meters F_1, F_2 and F_3 which were fitted with adjustable and interchangeable capillaries, which had previously been calibrated by the soap bubble method. A typical calibration curve is shown in Fig. II. 2. One of the nitrogen streams (i.e. that flowing through needle valve E_2) was allowed to bubble through a U-tube, in which was incorporated a sintered glass disc at the base of a bulb containing the liquid fuel. The saturator was in a thermostat, W_1 the temperature of which was controlled to within ± 0.1°C. The fuel-containing nitrogen was passed through a series of U-tubes which were kept in another thermostat, W_2, at a temperature slightly lower than that of the first. Fuel spray was removed in this second saturator, ensuring the production of a saturated, but not supersaturated, mixture of fuel vapour in nitrogen at the required temperature. This was premixed with oxygen flowing through needle valve E_3, in the vessel M, which was a 1 foot-long cylindrical glass column, packed with glass wool, and covered with asbestos paper. This also served as a flame trap to prevent any explosion

FIG. II.1 THE FLOW SYSTEM.



E = needle valve; P = purgers; F = flowmeter; W = thermostat;
M = flame trap; T = cold trap.

FIG. II.2. A TYPICAL FLOWMETER CAPILLARY CALIBRATION

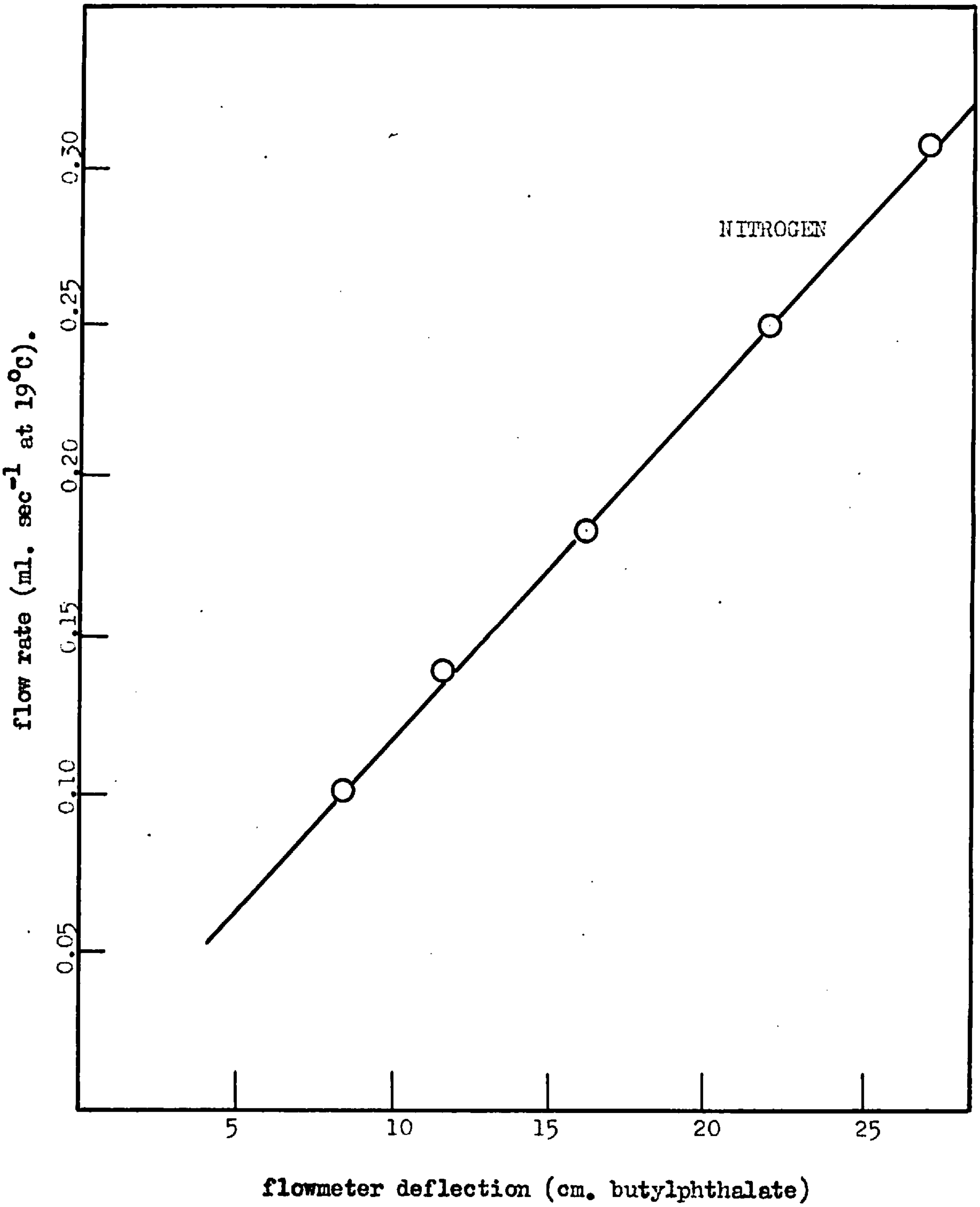
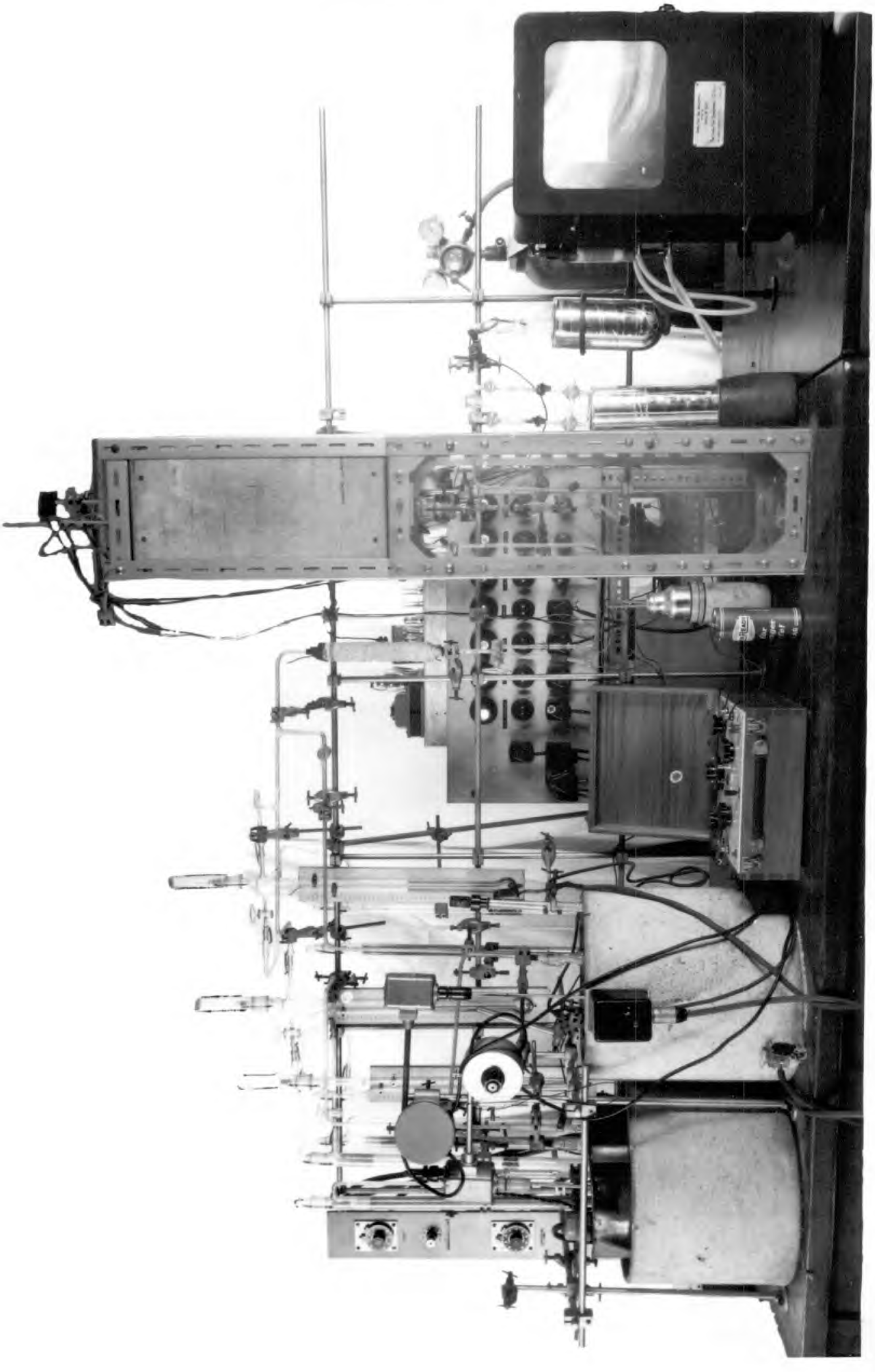


PLATE II.1.



that might occur in the reaction vessel, from propagating into fuel reservoirs. The nitrogen passing through the needle valve, E_1, was used as an auxiliary gas stream, being introduced in order that the contact time and oxygen:olefin ratio could be varied without altering the flow rate of the fuel itself. Thereafter, the reactants entered the reaction vessel which is shown diagrammatically in Fig. II. 3. This reactor was constructed of pyrex glass and consisted of an outer jacket (diam.=3.2cm.) and an inner tube (diam.=2.4cm.), the upper end of which served as a container for the catalyst. The inlet and outlet were made of narrow glass tubing (diam. = 0.3mm.), so that their combined volume was small compared with that of the main body of the reactor. The inlet and the outlet tubes were fitted with ball joints to facilitate the interchange of reactor and of analytical apparatus.

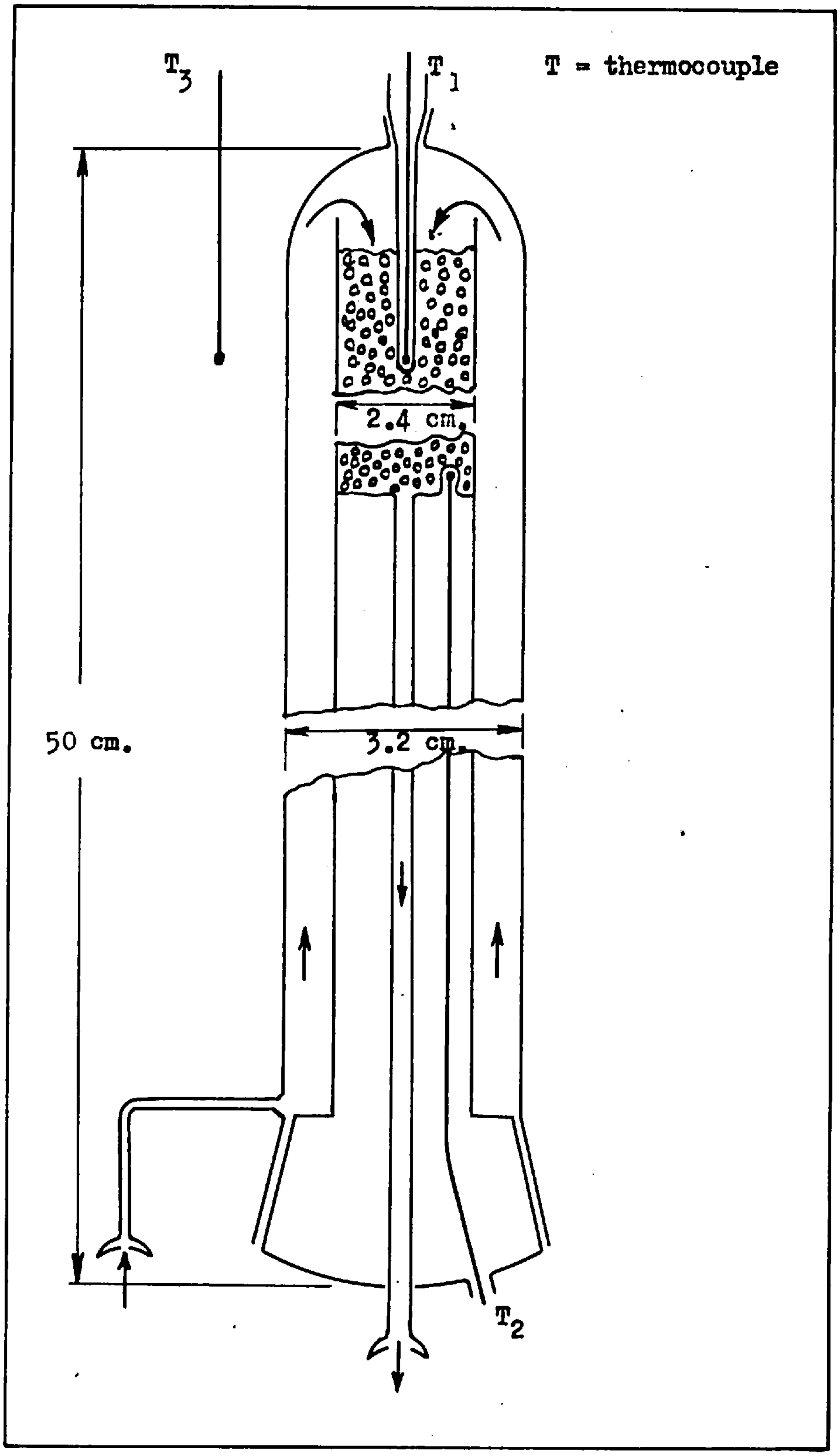
The reaction products were collected in the cold trap T. Samples for gas-liquid chromatographic analysis were collected in capillary U-tubes, fitted with a special by-pass device between the reaction vessel and cold trap T.

To prevent condensation of relatively involative products, all parts of the apparatus between the outlet of the reaction vessel and the cold trap were heated electrically to ca. 100°C. with nichrome wire (17 ohms per yard).

(b) The furnace.

The reaction vessel was mounted vertically in an

FIG. II.3. THE REACTOR.



electric furnace which consisted essentially of a vitreosil tube (length = 46cm.; diam. = 6.5cm.) supported in a sendanyo casing, the intervening space being packed with a mixture of magnesium oxide and kieselguhr. The furnace tube was lined with a copper sheath (1/16 inch thick), to provide a more uniform temperature distribution along its length and to protect the tube against the effect of possible explosion. The ends of the furnace tube were fitted with thick sendanyo plugs to minimise heat losses. The tube was wound in three separate sections in parallel, all of which were connected through variacs to the 230-volt a.c. mains.

(c) Temperature measurement and control.

(i) Measurement.

The temperature at various points in the reaction vessel and adjacent to it, were measured by chromel/alumel thermocouples, T_1, T_2 and T_3 (Fig. II. 3.). The thermocouple, T_1, measured the temperature of the catalyst bed itself, T_2 that of the gases leaving the catalyst and T_3 that of the furnace at the same height as the centre of the catalyst bed. The leads from these hot junctions were individually sheathed in thin pyrex tubing which was contained in a wider pyrex tube sealed at the junction end. The leads from the cold junctions were enclosed in similar pyrex tubes which were immersed in melting ice. The e.m.f. developed was measured on a potentiometer reading to ± 0.05mv. (equivalent to ca. 0.25°C. in the temperature range used). All these thermocouples were calibrated periodically against a standard 87% platinum - 13% rhodium thermocouple over a temperature range of 100-400°C.

The distribution of temperature along the length of the furnace, and hence the most suitable position for the 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 axial position (Fig. II. 4.). The reaction vessel was then placed so that the temperature difference between the ends of the tube containing the catalyst was a minimum.

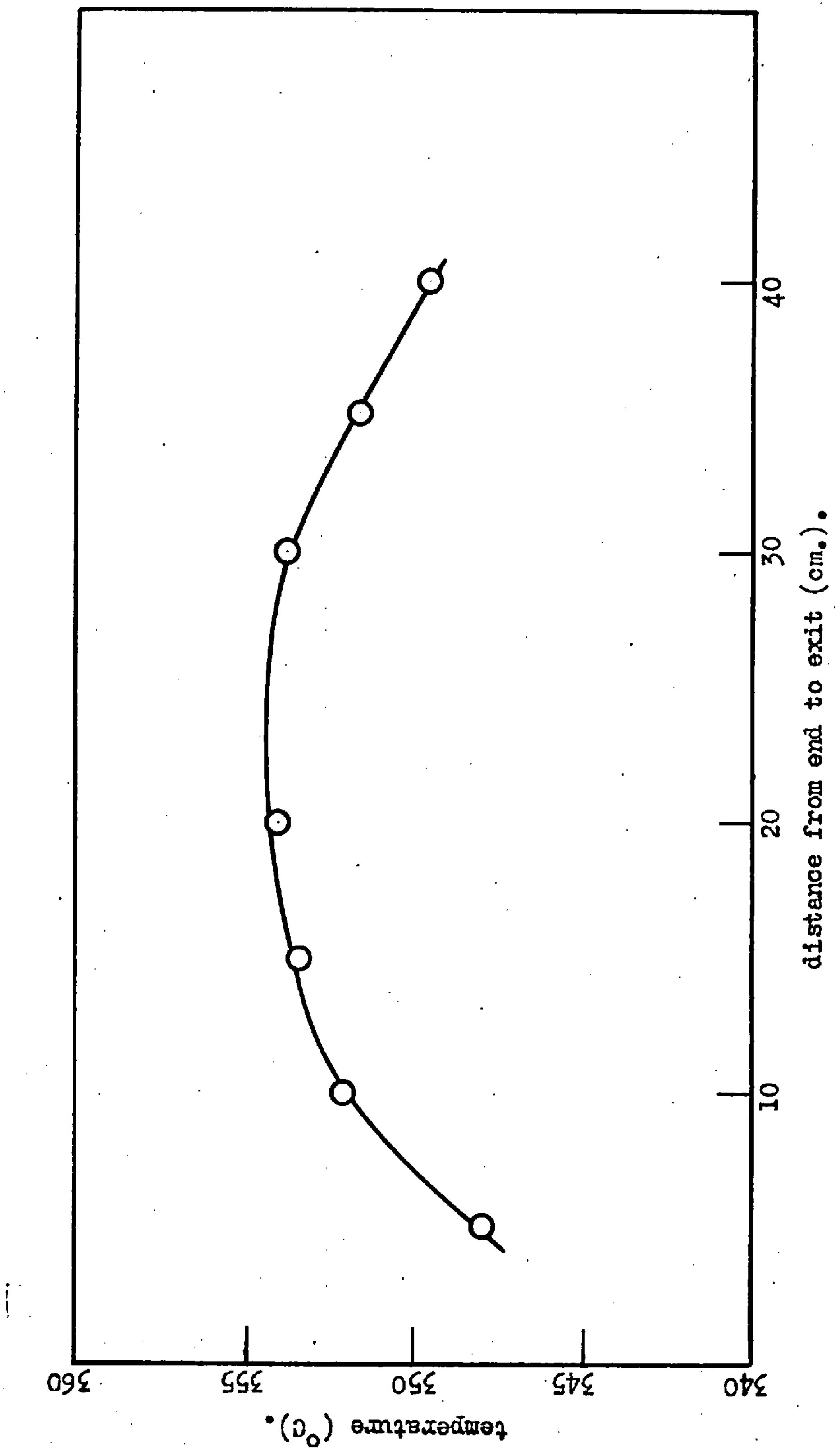
(ii) Control.

The power supplied to the furnace windings was controlled by a platinum resistance thermometer. This was situated in the furnace close to the centre of the catalyst bed and incorporated into one arm of a Wheatstone's bridge circuit, the out-of-balance current through which was fed to a hot wire switch The operation of this switch varied the current through the centre furnace winding. The circuit diagram is shown in Fig. II. 5.

2. Experimental procedure.

(a) Kinetic methods.

FIG. II.4. TEMPERATURE DISTRIBUTION IN THE FURNACE.



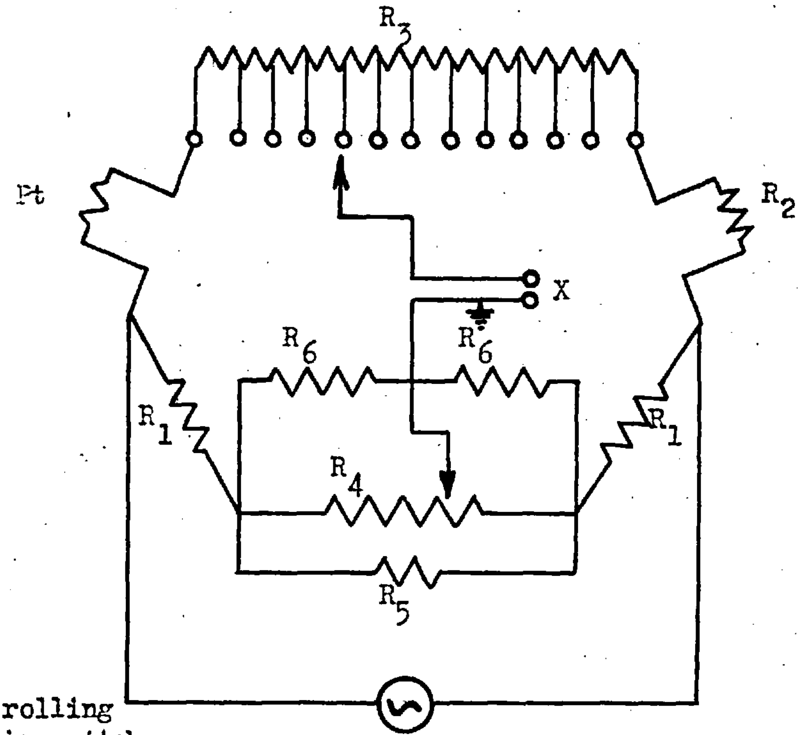
Before the start of a run, the apparatus was tested for leaks by opening the valves E_1, E_2 and E_3 (Fig. II. 1.) so that the flowmeters each recorded a reading of about 3 cm. difference. When the outlet for the gases was closed, the rapid return of the flowmeter readings to zero confirmed the absence of leaks. To commence an experiment, valve E_1 was opened, allowing a stream of nitrogen to bubble through the liquid fuel and to be expelled without passing through the reactor. The amount picked up by the nitrogen was determined gravimetrically (duplicate) by condensing in a weighed U-tube fitted with two taps the fuel which had been picked up in a specified time and then reweighing. The oxygen and auxiliary nitrogen were now admitted and the mixed gases were allowed to pass through the reactor. Catalytic oxidation was allowed to proceed at the specified temperature for 45 minutes before the first sample was taken for analysis.

(b) <u>Sampling</u>.

Samples for gas chromotographic analysis were collected in specially designed U-tubes with spring-loaded taps (Fig. II.6.). The total effluent from the reactor during a given time (20 sec.) was passed into the U-tube while this was maintained at -195.8°C. The nitrogen and oxygen were then removed by pumping on the cold products and the tube now containing the condensable products of oxidation was detached from the flow apparatus. From such tubes, samples could be introduced directly into the gas

FIG. II.5. THE FURNACE TEMPERATURE CONTROL.

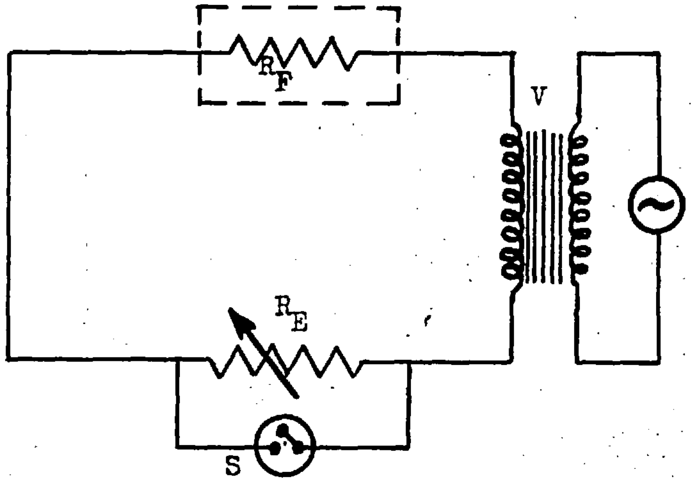
The Temperature Controller.



KEY:

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.



KEY:

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.

chromatography apparatus, after being warmed to room temperature.

Samples for determination of formaldehyde and of total acids were collected for 30min. in a conventional trap, the inlet of which was connected through a three-way tap to both the reactor outlet and a 20ml. funnel from which solvent was subsequently introduced to wash down the condensable products through the central stem into the flask.

For analysis of carbon dioxide the effluent gases were passed through a series of ice-cooled traps and finally through a U-tube containing magnesium perchlorate, before being allowed to pass into an infra-red carbon dioxide analyser. (Type SC, The Infra-red Development Company Ltd.)

Solid products collected near the outlet of the reaction vessel in minute quantities over a large number of runs. Although quantitative estimation was not possible, the main species present were identified by infra-red spectroscopy.

(c) Calculation of contact time.

The time for which the reactants were in contact with the catalyst was calculated using the following equation.

$$\text{Contact time} = \frac{VT_1}{FT_2} \text{ sec.}$$

where

T_1 = Room temperature (^{o}K)

T_2 = Temperature of catalyst bed (^{o}K)

F = Flow rate of the gases at room temperature (cm^3 sec^{-1})

V = Volume of the tube occupied by the catalyst (cm^3)

These contact times are arbitrary inasmuch as they are dependent on the overall dimensions of the tube containing the catalyst. In order that all contact times should be strictly comparable, it is necessary that the mesh size be kept constant.

3. Analytical methods.

The majority of the analytical results, both qualitative and quantitative, were obtained by gas chromatography. It was, however, found advantageous to make certain preliminary tests, employing chemical methods, to derive general qualitative information regarding the products before these were subjected to gas chromatographic analysis.

Other analytical methods used to determine specific products were infra-red spectroscopy, ultra-violet spectrophotometry and conventional volumetric analysis.

(a) Qualitative analysis.

Preliminary qualitative tests were made to facilitate the choice of a stationary phase for subsequent analysis by gas chromatography and also gave information regarding other qualitative analytical techniques which could usefully be employed. These tests were as follows.

(i) Detection of acetic acid.

One drop of an aqueous solution of the products was mixed on a spot plate with one drop of a 5% aqueous solution of lanthanum nitrate and one drop of 0.01N aqueous iodine solution. One drop of N. ammonia was then added. After a few minutes a blue-brown ring developed around the drop of ammonia. This test is specific for acetic acid (86) (limit of identification = 50 γ).

(ii) Detection of aldehydes.

The chromotropic acid method (87), described on page 84 was used to detect formaldehyde (limit of identification = 0.14γ).

Acetaldehyde was identified by placing one drop of the test solution on a spot plate and adding one drop of sodium nitroprusside solution containing a trace of piperidine. The development of a blue colour indicates the presence of acetaldehyde (88) (limit of identification = 1 γ).

Ninhydrin reagent (1,2,3-triketohydrindene in 5% sodium bisulphite solution) gave a blue colour in the presence of propionaldehyde (89) (limit of identification = 1-3 γ).

(iii) Detection of peroxides.

A few ml. of test solution were mixed with 5 ml. of slightly acid potassium iodide solution at 0°C. One drop of starch solution was added as indicator and the solution was slowly heated to 40°C. The appearance of a blue colour at 0°C. indicates the presence of peroxy acids, while appearance of the same colour at 5°C. and at 40°C., is characteristic of hydrogen peroxide and alkyl hydroperoxides respectively (90).

(b) Quantitative analysis.

(i) Gas chromatography.

Apparatus.

The gas-chromatographic apparatus used was a commercial model manufactured by the Shandon Scientific Co., and incorporated the hydrogen flame detector originally devised by Scott (91).

The carrier gas was hydrogen containing 25% nitrogen in order to reduce the degree of longitudinal diffusion of organic vapours in the gas stream. This gas was introduced through a special reducing valve to a capillary flowmeter and thence to the column (Fig. II. 6.). The copper column was attached both to the gas inlet pipe and to the combustion chamber by standard petrol-pipe connections. Both the column and the combustion chamber were immersed in a vapour jacket, maintained at a given temperature. The gas passed from the column, through the centre of the base of the combustion chamber and then through a short length of pipe to the jet. Air was led from a needle-valve through another capillary flowmeter and a pipe situated in the vapour jacket, and then through a further orifice in the base of the chamber, being finally allowed to diffuse through porcelain beads to the hydrogen flame at the jet (Fig. II. 7.).

The thermocouple was situated a few mm. above the

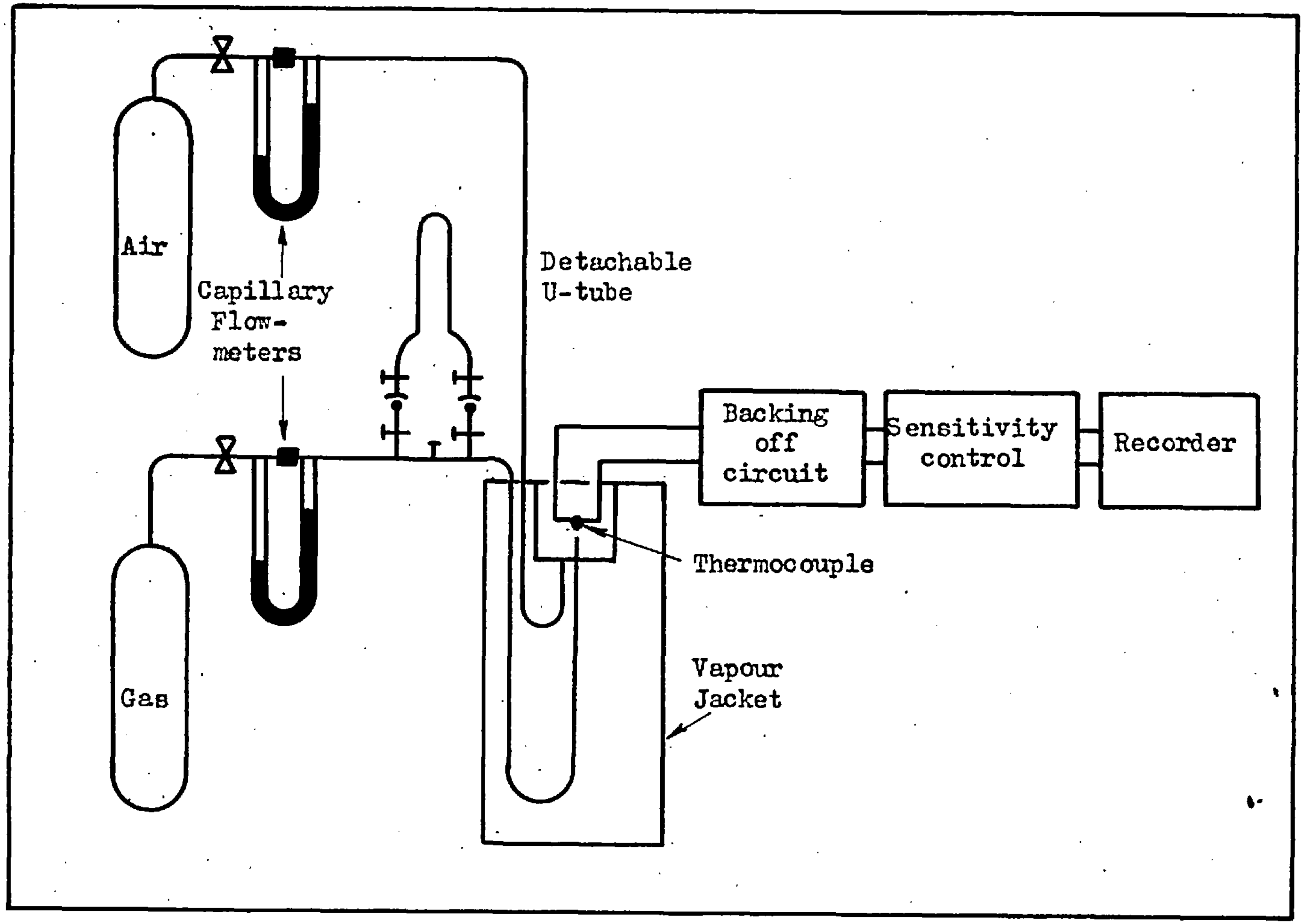


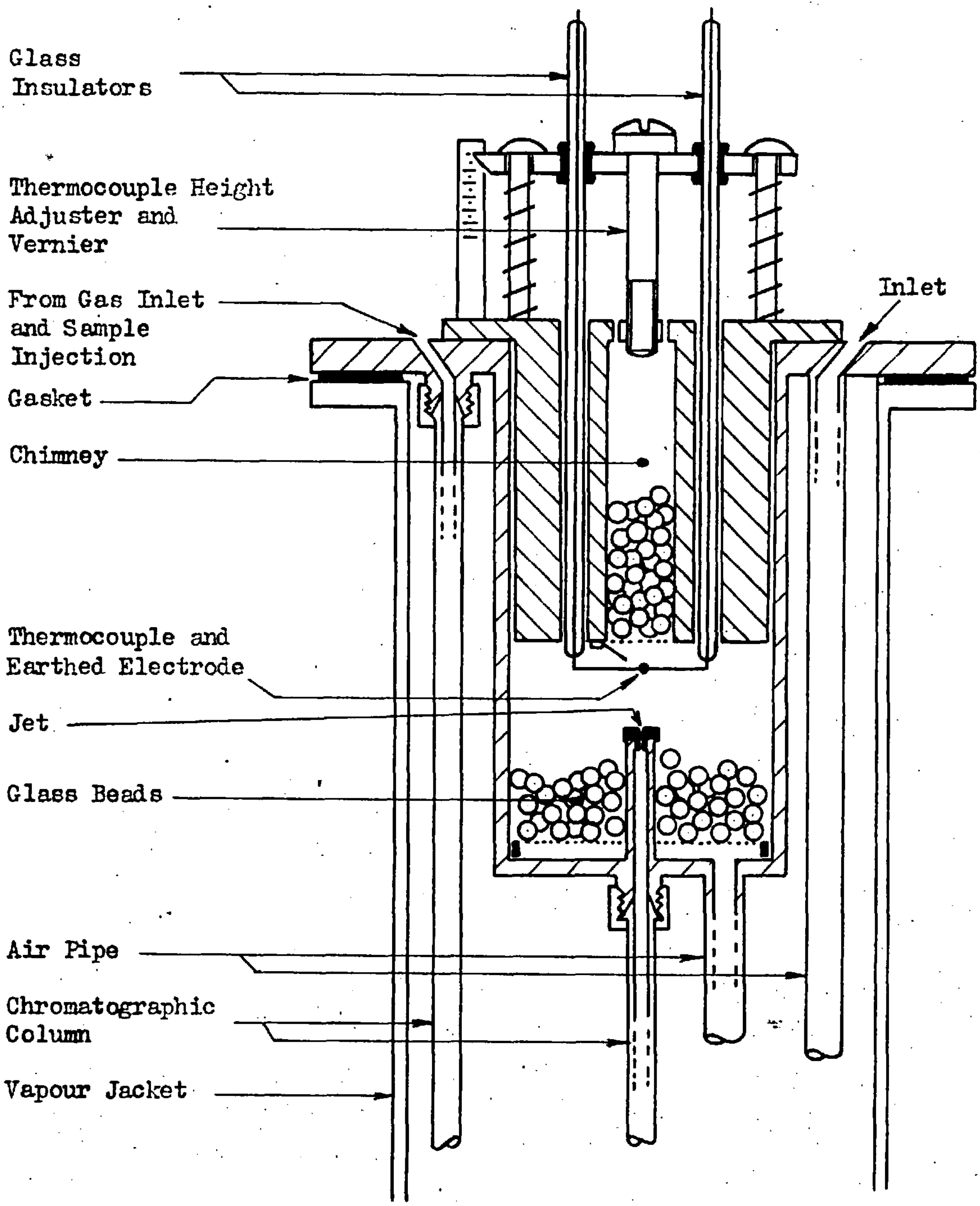
FIG. II.6. THE GAS-CHROMATOGRAPHY APPARATUS.

jet and the effluent gas was ingited by momentarily passing a high voltage electrical discharge from the thermocouple to an earthed electrode 1.mm. away. The thermocouple (gold-palladium/platinium-iridium) was supported by 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 was itself bolted through a gasket to the top of the vapour jacket.

The thermocouple leads were connected by a cable covered with an earthed sheath to a simple potentiometer fed by a 1.5 V. Mallory cell against which the thermocouple output was balanced, and the out-of-balance voltage was 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 an A.E.I. high speed potentiometric recorder (full scale deflection = 12" = 1.0 mv.; response time = 1 sec.).

The gas-chromatographic apparatus as manufactured used micropipettes for the injection of samples. This system was unsuitable for the present work and was replaced by the capillary glass U-tube (volume ca. 1 ml.) and the by-pass arrangement shown in the photograph (Plate II. 2.) which

FIG. II.7. THE THERMOCOUPLE DETECTOR.



enabled the gaseous contents of the U-tube to be swept directly and rapidly onto the column.

The column.

The stationary phase.

Polyalcohols, such as diglycerol (92), polyethylene glycol (93)(94)(95) and polypropylene glycol (93)(94) have been found to be useful for the separation of a wide range of hydrocarbons and, especially, oxygenated organic compounds. Similarly, esters of high molecular weight, such as diethyl hexyl sebacate (96) and dibutyl phthalate (97) have proved useful for such analyses. Silicone oil (98) and di-(2-cynoethyl)-ether (95) have been widely used as stationary phases for the separation of hydrocarbons. The stationary phases used in the present work are given in Table II. 1.

The supporting material.

In all the work reported herein 60-100 mesh (B.S.), Embacel (May and Baker Ltd.), a specially treated form of kieselguhr, has been used as it has previously been found (99) to show no signs of catalytic activity and to give reproducible results. Embacel as supplied, however, was found to cause slight tailing of aldehyde peaks when polyethylene glycols were used as stationary phases. Pre-treatment of this Embacel with 5% alcoholic potash helped to eliminate this tailing effect (100).

PLATE II.2.

TABLE II. 1. SPECIFICATIONS OF THE GAS CHROMATOGRAPHY COLUMNS.

Column	1	2
Packing	20% P.E.G.(1500) on 60-100 mesh alkali-washed Embacel.	27% propylene carbonate and 2.7% squalene on 60-100 mesh acid-washed Embacel; followed by 30% silicone oil (M.S. 550) on 60-100 mesh acid-washed Embacel.
Length (feet)	12	19.5 + 4.5
Inlet pressure (cm.Hg)	231	231
Outlet pressure (cm.Hg)	76	76
Flow rate (ml.min.$^{-1}$)	47	47
Temperature (^{o}C)	81	35.5

Carrier gas: 75% hydrogen + 25% nitrogen.

Preparation of the column.

Embacel (60-100 mesh; B.S.) was washed with concentrated hydrochloric acid to remove traces of iron, rinsed several times with distilled water and dried at 120°C. A given amount of the solid was then impregnated with a specified amount of the stationary phase, dissolved in a suitable solvent (Table II. 1.). The resulting 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 (100cm. high and 4mm. in diameter) and dry air was passed upwards through the tube. By adjustment of 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.

Calibration of the apparatus.

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 (e.g. acetone) was introduced onto the column, and the thermocouple was set at various heights (differing by 0.5mm.), for each sample. The amount of sample added was sufficient to give a large deflection at the sensitivity to be to be used during the analysis. It has been found that over only a small range of thermocouple setting was the response constant and maximal. The thermocouple height was finally set at a value within this range.

Qualitative calibration.

The substances present in the reaction products were identified by taking representative samples of these products and comparing the retention times of the peaks on their chromatograms with those of authentic compounds. Most of these were readily identified, since their formation was expected on theoretical grounds; the presence of other, less obvious, products, such as epoxy compounds and methyl ethyl ketone, 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 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 took place, the effect on the retention times of changing the column temperature was investigated. 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 on the heat of solution of the vapour in the fixed phase. All different vapours therefore exhibit different dependences on temperature. Thus if the retention times of a reaction product and the added sample change in exactly the same way with temperature, there is little reason to doubt that they are chemically identical. Further confirmation of the nature of the products was obtained by use of the other stationary phases.

Quantitative calibration.

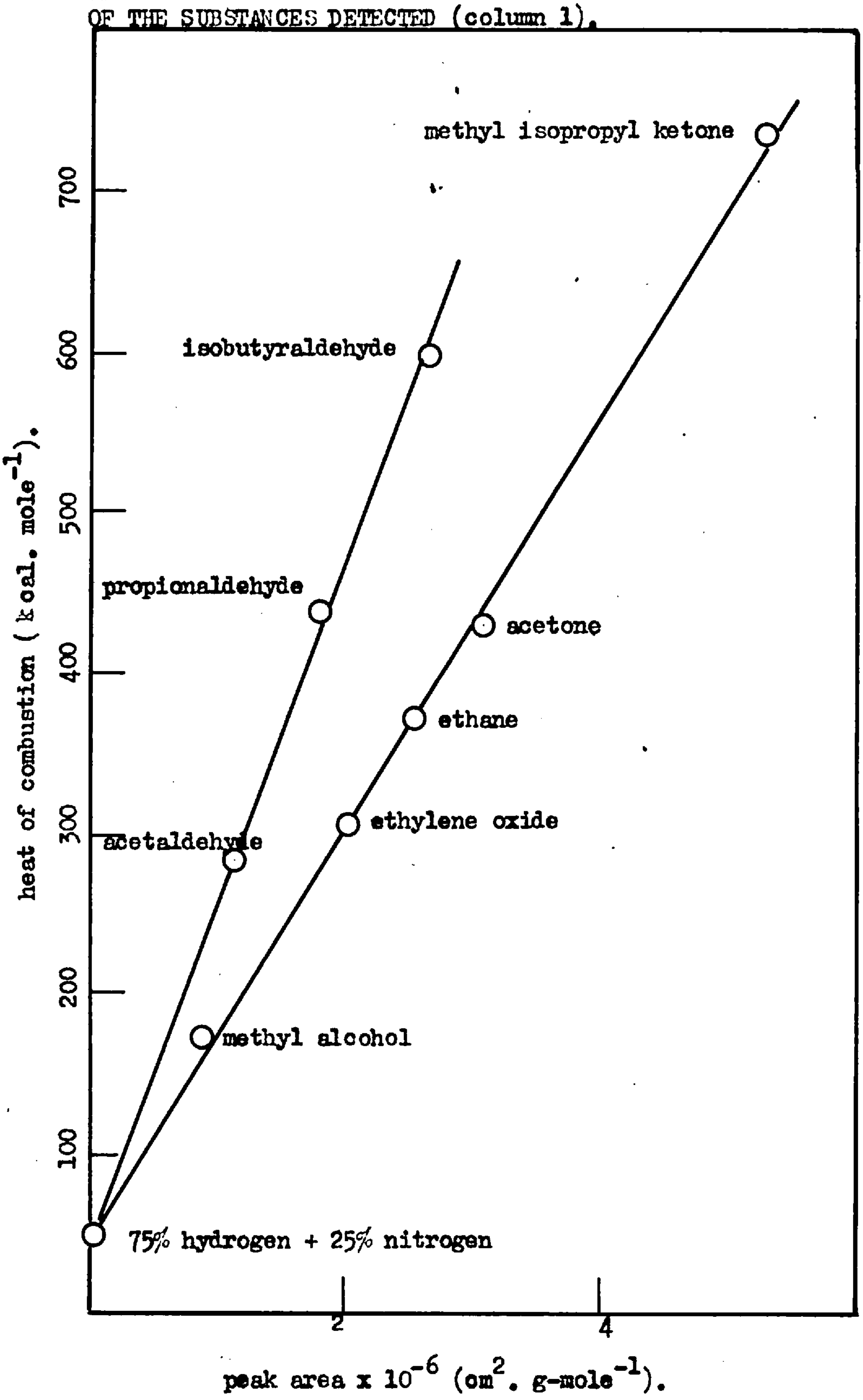
For each substance, a known weight was introduced onto the column (99). Graphs were plotted of weight of subatance against peak area and in all cases a linear plot passing through the origin was obtained. The relative sensitivities of the substances are shown in Fig. II. 8. in which they are plotted against their molar heats of combustion. Straight lines are obtained for each group of substances, cutting the axis of ordinates 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 possibly attributable to partial adsorption of the aldehydes on the column followed by their polymerisation (99).

(ii) Infra-red spectroscopy.

Solid products.

The method used was a modification of the Nujol mull method (101). A disc of pure potassium bromide and a disc containing 0.1%-0.5% of the solid sample in potassium bromide was prepared as follows. One mg. of the solid sample was ground to a fine powder in a mortar. To this was added 300 mg.

FIG. II.8 THE RELATION BETWEEN THE SENSITIVITY OF THE THERMOCOUPLE DETECTOR AND THE MOLAR HEAT OF COMBUSTION OF THE SUBSTANCES DETECTED (column 1).



of Analar crystalline potassium bromide which had been dried overnight at 110°C. and the solids were intimately mixed. The resulting mixture was then placed in a cylindrical steel die which was enclosed in a larger cylinder connected to a vacuum pump. Slight pressure was applied to the die and the air was then evacuated by pumping. The pressure on the die was then increased to 10,000-12,000 lb./in.^{2} After ca. 1 min. the pump was disconnected from the die. The mull was then kept under pressure for a further 10-15 min., after which the pressure was slowly released and the die was carefully dismantled. A reference disc of pure potassium bromide was similarly prepared.

Infra-red spectra were obtained using a Perkin Elmer Infracord apparatus (model 137).

Carbon dioxide.

Carbon dioxide was estimated by passing the effluent gases through a series of cold traps (at 0°C.) and a U-tube containing magnesium perchlorate and then through an infra-red gas analyser (Type Sc.). The instrument was calibrated by passing streams of air containing known amounts of carbon dioxide through it.

(iii) Estimation of formaldehyde.

Formaldehyde was determined colorimetrically by the chromotropic acid method (87). The following procedure was adopted.

A 1 ml. sample of the aqueous test solution (containing between 1 and 4 x 10^{-7}g. moles of formaldehyde) was treated with a small quantity of magnesium powder and several drops of concentrated hydrochloric acid. This treatment reduced any formaldehyde-peroxide complex which may have been formed by the reaction

$$HCHO + H_2O_2 \longrightarrow HCH(OH)OOH$$

in the sample solution. However it also reduces formic acid to formaldehyde and the method therefore estimates formaldehyde plus formic acid. After the magnesium had dissolved, the solution was cooled in ice and 10 drops of a freshly prepared 10% aqueous solution of chromotropic acid, followed by 10 ml. concentrated sulphuric acid, were added. The stoppered flask was then heated at ca. 60°C. for 30 min. and cooled to room temperature. The solution was diluted to 50 ml. in a calibrated flask. The colour intensity was then measured spectrophotometrically using a Unicam SP 500 spectrophotometer and a tungsten source ($\lambda = 500$ mμ).

A calibration curve was constructed using standard solutions of formaldehyde of various concentrations, these solutions being standardised previously by Romijn's iodometric method (102). Blank tests were carried out with the fuel used each giving a negative test for formaldehyde.

(iv) Estimation of total acids.

An aliquot of the sample was titrated under nitrogen with 0.1N aqueous sodium hydroxide using phenolphthalein as indicator. The alkali titre represented the total acids present in the mixture.

E. METHODS FOR INVESTIGATING PROPERTIES OF THE CATALYST.

1. Surface area measurement.

The surface areas of supports and catalysts were determined by a gas adsorption method. The gas sorption apparatus used was of the conventional Brunauer-Emmett-Teller type. It consisted of a 100 cm^3 gas burette immersed in a water thermostat at 25°C., a wide-bore manometer (which, in combination with a cathetometer, was used to measure equilibrium pressures up to 80 mm. Hg), a capillary manometer and standard gas-storage and sample bulbs.

The volume of the apparatus was calibrated with helium. n-Butane was employed for surface area measurements as it is adsorbed to a convenient extent at 0°C. and on account of its close resemblance to the hydrocarbons being used in the catalytic studies. This gas (99.5% n-butane) was supplied by the British Petroleum Company Ltd. and was further purified by bulb-to-bulb distillation.

Preliminary ~~expertimets~~ experiments were carried out to elucidate the effects on surface area of particle size, of the method of preparation of the catalyst and the temperature at which the sample was degassed prior to adsorption.

Routine surface area measurements were made by adsorption of n-butane at 0°C. after degassing the sample of catalyst at 350°C. and were repeated after desorption and degassing at 500°C.

2. X-ray crystallography.

Preliminary X-ray crystallographic measurements, designed to elucidate phase changes taking place in the catalyst during the oxidation of pentenes, were carried out in the Chemistry Department of Imperial College using a Guinier camera (with a copper target, operating at 50kV and 10mA). Samples of vanadium pentoxide catalyst were exposed to radiation for 360 min. and control experiments were carried out by exposing the pumice support to similar conditions for 480 min.

These samples of vanadium pentoxide and pumice were also studied by X-ray crystallography in the Analytical and Chemical Services Division, Thornton Research Centre, by the Debye-Scherrer powder method using a chromium anode X-ray tube and Phillips cameras.

SECTION III.

RESULTS.

SECTION III.

A. THE CATALYTIC OXIDATION OF STRAIGHT-CHAIN PENTENES.

1. Pent-2-ene.

(a) The effect of temperature.

The lowest temperature at which appreciable oxidation of pent-2-ene occurred was determined by gradually raising the temperature and periodically analysing the emerging gases while a given mixture of the fuel, oxygen and diluent nitrogen was allowed to flow at a known rate through a fixed amount of a freshly prepared and activated pumice-supported vanadium pentoxide catalyst (8-10 mesh (B.S.)). The lowest temperature at which pent-2-ene underwent appreciable oxidation was found to be ca. 300°C. (with an oxygen:olefin ratio of 1.25 and contact time of 33.6 sec.).

Determinations were made of the variations in the consumption of pent-2-ene and in the formation of products with the reactor temperature under otherwise constant conditions and the results obtained are shown in Fig. III. 1. The consumption of pent-2-ene and the formation of the majority of the products reach maximum values at ca. 360°C. Acetaldehyde, one of the major products, acquires its highest concentration at a lower temperature (ca. 280°C.) and methyl alcohol, which begins to be formed above 300°C., reaches a maximum at ca. 320°C., at which temperature the acetaldehyde concentration is decreasing rapidly. Propionaldehyde and acetone attain their maxima at ca. 360°C. The other important oxygenates were 2,3-epoxypentane and pentanones. The latter begin to form at higher temperatures (ca. 300°C.) than the former, reaching their maxima at 355°C. and 345°C respectively. The extent of formation of lower hydrocarbons, ethylene and propylene, showed an appreciable increase with temperature.

In comparison, Fig. III. 2. shows the variations with temperature of the consumption of pent-2-ene and of the formation of products for oxidation in the gas-phase. The lowest temperature at which any appreciable homogeneous oxidation of the olefin takes place was ca. 325°C. All the oxygenated products reach maximum concentrations at ca. 330°C. at which temperature the amounts of pent-2-ene reacting have also reached maximum values. Further increase of temperature causes further oxidation of the primary products. The concentrations of lower hydrocarbons increase steadily with rising temperature. No traces of dimeric (C_{10}) hydrocarbons or of n-butryaldehyde were found in the absence of the catalyst.

(b) The effect of contact time.

The effect of contact time on the catalytic oxidation of pent-2-ene was investigated systematically using catalysts of two different "ages". Fig. III. 3. shows the products formed and the variation with contact time of the amount of each when the catalyst is "new" (i.e. used for less than 5 hours)

The major oxygenated products are acetaldehyde, and propionaldehyde. Their concentrations increase with contact time up to a value of ca. 33 sec. after which their concentrations start to decrease again. At contact times less than ca. 33 sec., the consumption of pent-2-ene increases rapidly but with larger values the further increase is small illustrating the predominance under the latter conditions of side reactions involving further oxidation of primary products. The products of the lower contact time range (0-33 sec.) are thus the important ones from the point of view of elucidation of the mechanism. The oxygenates formed in small quantities include trans-2,3-epoxypentane and acetone. The variations with contact time of the amounts of these compounds are similar to those of the principal oxygenated products. The lower hydrocarbons formed are ethylene and propylene. Ethylene reaches a maximum at ca. 33 sec. contact time while propylene reaches a miximum at ca. 50 sec.

The analogous results of contact time variation for pent-2-ene on an "old" catalyst (i.e. one that has been used for more than 5 hours) are given in Fig. III. 4. The comparison of these two sets of results shows clearly the rise in activity and the drop in selectivity which takes place as the catalyst "ages". Under otherwise similar conditions the consumption of pent-2-ene is considerably greater on an "old" than on a "new" catalyst. The production of the major oxygenates such as acetaldehyde and propionaldehyde on an "old" catalyst is again highest at 33 sec. contact time but at higher values these compounds undergo more extensive secondary oxidation than on a "new" catalyst. At a contact time of 33 sec. on an "old" catalyst the amount of trans-2,3-epoxypentane formed was again a maximum but on further increase in contact time the concentration of the epoxide decreases concurrently with the gradually increasing formation of pentanones, the total concentrations of which reach a maximum value at a contact time of ca. 50 sec. In addition to pentanones, several other oxygenates which were not produced on a "new" (selective) catalyst are now formed. The formation of methyl alcohol begins at ca. 28 sec. contact time and reaches a maximum at ca. 70 sec., at which point the other products are all decreasing while the pent-2-ene consumption is substantially constant. Carbon dioxide production increases steadily with rising contact time, even at high values, showing that side-reactions of the intermediates formed during oxidation of pent-2-ene again predominate in this region. Pent-1-ene and hydrocarbons of low molecular weight (methane, ethylene and propylene) are also produced but are not shown in Fig. III. 4.

It is evident therefore that, as the catalyst ages, its activity increases and the products proliferate.

(c) The effect of oxygen:olefin ratio.

Mixtures of pent-2-ene with nitrogen, at the same total flow rate and containing the same concentration of the fuel but varying proportions of oxygen, were allowed to react on a pumice-supported vanadium pentoxide catalyst. Again two sets of results were obtained, one on a "new" catalyst and the other on an "old" catalyst.

On a "new" catalyst (Fig. III. 5.) the formation of the major products, acetaldehyde and propionaldehyde, reach maxima at an oxygen:olefin ratio of ca. 1.4 and then decrease as further oxygen is introduced. The minor products, acetone, propylene, ethylene and methane exhibit a similar behaviour. At higher oxygen:fuel ratios there is obviously a greater probability of secondary oxidation.

The results obtained on an "old" catalyst are given in Fig. III. 6. The production of acetaldehyde attains a maximum at an oxygen:olefin ratio of ca. 1.3 and declines rapidly with any further increase in oxygen content. Methyl alcohol begins to form when the oxygen:olefin ratio is equal to 0.75 and reaches a maximum at a value of 1.55. Propionaldehyde reaches a maximum at a value of ca. 1.6. The production of trans-2,3-epoxypentane at first increases with the oxygen: olefin ratio and then begins to decline, the decrease in its concentration coinciding quantitatively with the rise in the formation of pentanones. The other minor products ethylene oxide, propylene oxide, methyl ethyl ketone, isobutene oxide and 2,3-epoxybutane show an increase in concentration which coincides quantitatively with the decrease of the major products, showing the predominance of side reactions at this stage. On "old" catalysts n-butyraldehyde, pent-1-ene and dimeric (C_{10}) hydrocarbons were detected in small quantities but the values are not shown in Fig. III. 6. Comparison of the variation with reactant ratio of the formation of products on "old" and "new" catalysts again illustrates the greater activity but lower selectivity of an aged catalyst.

(d) Solid products of the catalytic oxidation.

During the catalytic oxidation of pent-2-ene over a pumice-supported vanadium pentoxide catalyst, very small amounts of solid products condensed at the reactor outlet. The solid deposits resulting from a large number of runs at various contact times and with different reactant ratios were collected as a single sample. The solid was analysed by infra-red spectroscopy (Section II. D. 3.) and the spectrum obtained is shown in Fig. III. 7. On comparison of this with the spectrum of maleic acid it is evident that this compound is a major constituent of the solid in question. The absorption band appearing at a frequency number of 1470 cm^{-1} (Fig. III. 7.) shows also the presence of an anhydride linkage. Minute traces of crotonic acid and citraconic acid are indicated by the bands at 800 cm^{-1} and 859 cm^{-1} respectively.

KEY TO FIGURES III.1 - III.16

⊗	C_4 hydrocarbons
○	pent-2-ene
●	2-methyl but-2-ene
⊕	2-methyl but-1-ene
⦶	pent-1-ene
⊖	3-methyl but-1-ene
◑	methane
◐	ethylene (+ ethane)
◓	propylene (+ propane)
◒	C_{10} hydrocarbons
▭	acetone
■	propionaldehyde
◩	n-butyraldehyde
◪	isobutyraldehyde
◩	methyl ethyl ketone
⧅	methyl isopropyl ketone
◩	acetaldehyde

⊠	3-pentanone + 2-pentanone
⧗	crotonaldehyde
⬘	ethylene oxide
⬙	propylene oxide
⬖	isobutene oxide
⬗	2,3-butene oxide
◇	trans-2,3-epoxy pentane
◆	2,3-epoxy-2-methylbutane
×	sec-butyl alcohol
+	methyl alcohol
✱	ethyl alcohol
▼	carbon dioxide

FIG. III.1(a). THE OXIDATION OF PENT-2-ENE ON AN "OID" CATALYST : THE EFFECT OF TEMPERATURE ON MAJOR PRODUCTS. (contact time = 33.6 sec; oxygen:olefin = 1.25)

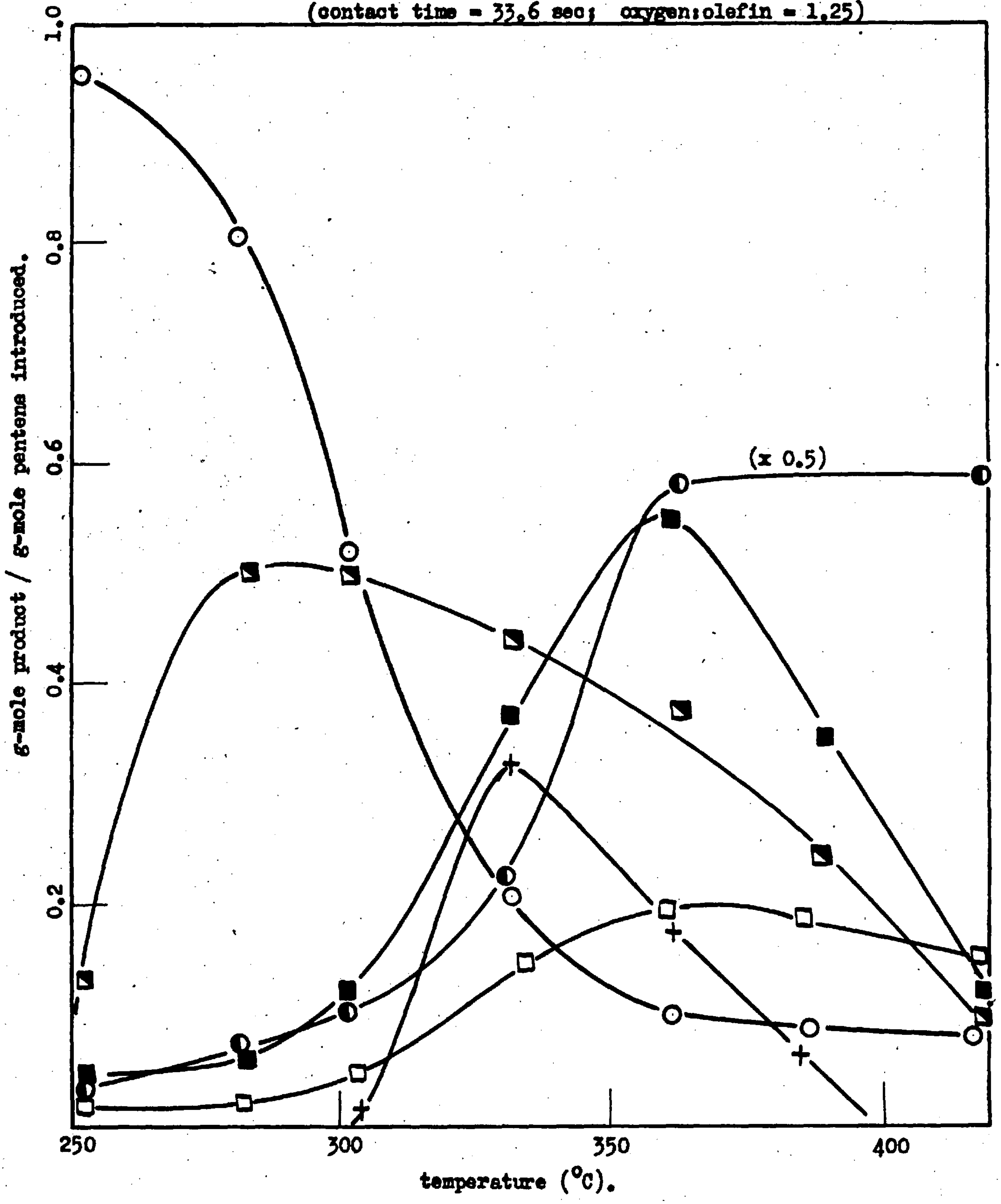


FIG. III,1(b). THE OXIDATION OF PENT-2-ENE ON AN "OLD" CATALYST; THE EFFECT OF TEMPERATURE ON MINOR PRODUCTS. (contact time = 33.6 sec; oxygen:olefin = 1.25)

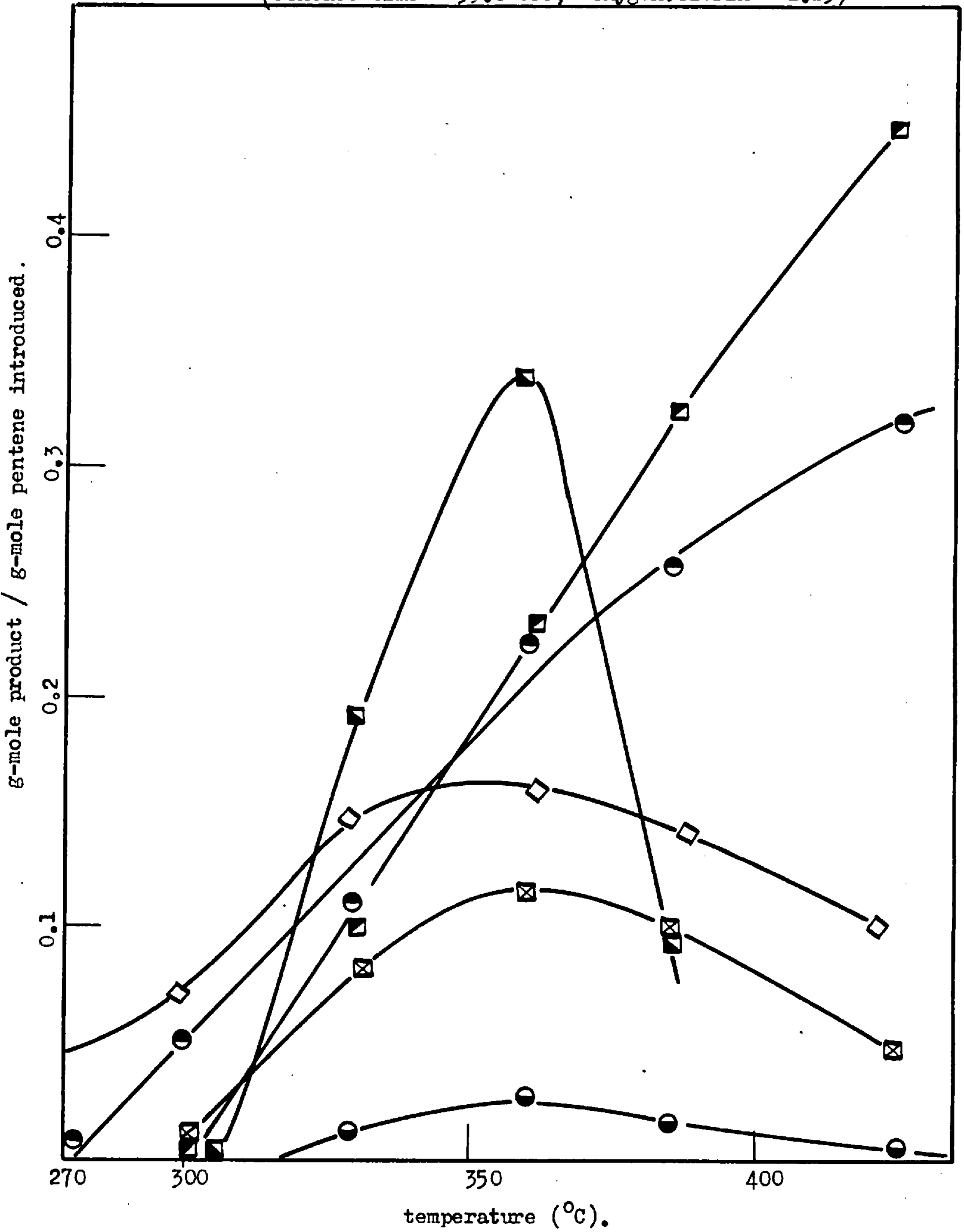


FIG. III.2(a). THE OXIDATION OF PENT-2-ENE IN THE GAS PHASE : THE EFFECT OF TEMPERATURE ON MAJOR PRODUCTS. (contact time = 33.6 sec; oxygen:olefin = 1.25).

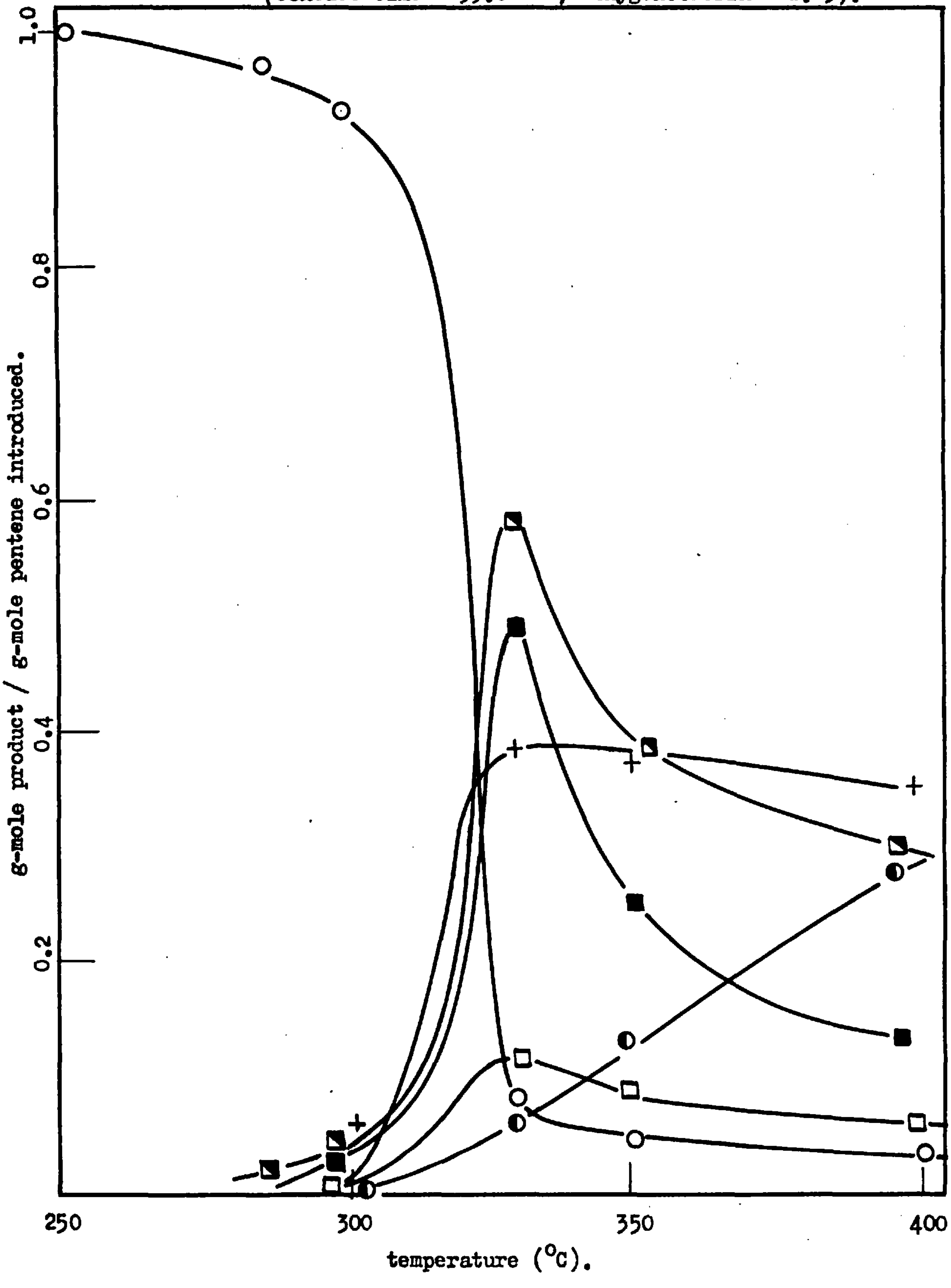


FIG. III.2(b) THE OXIDATION OF PENT-2-ENE IN THE GAS PHASE: THE EFFECT OF TEMPERATURE ON MINOR PRODUCTS. (contact time = 33.6 sec; oxygen:olefin = 1.25)

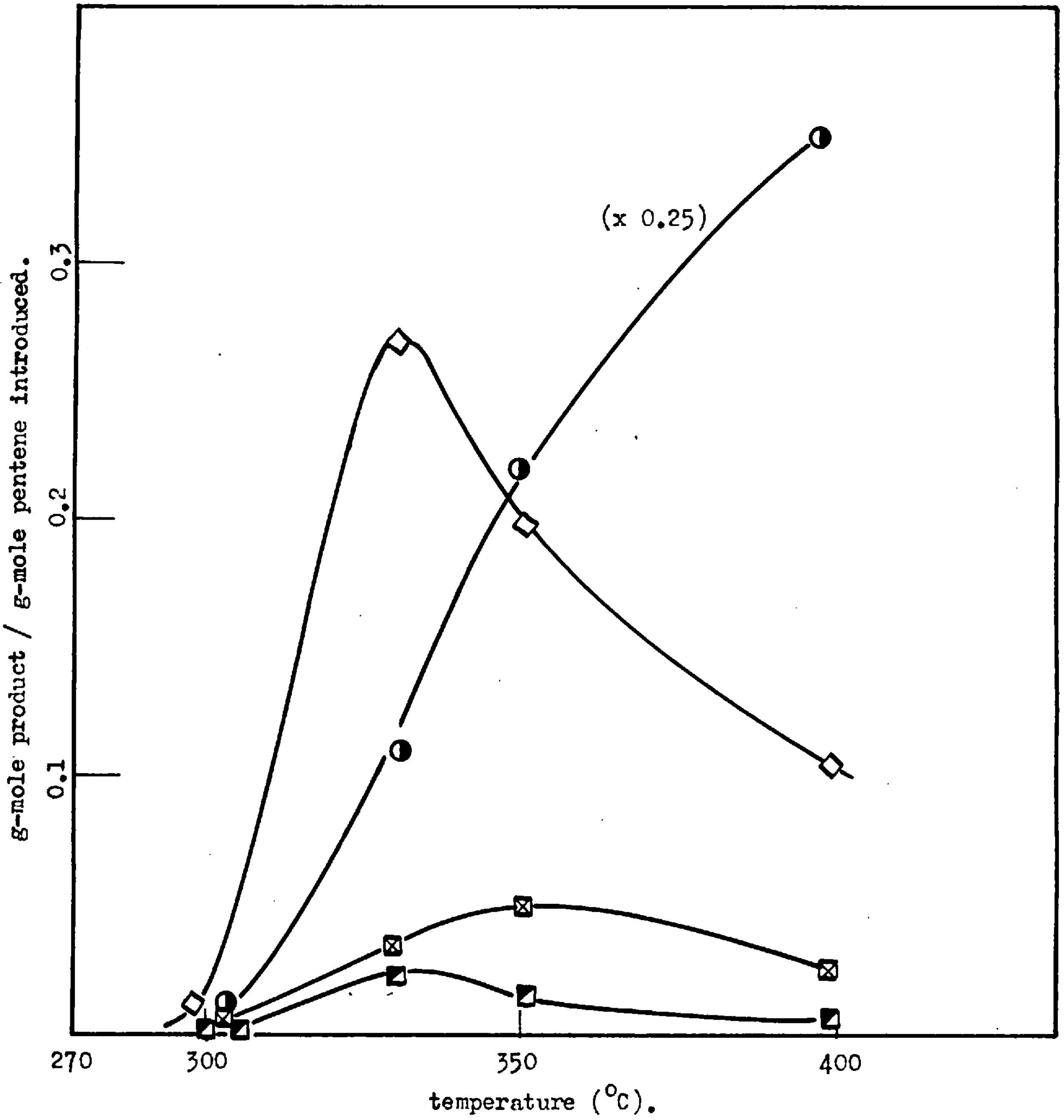


FIG III.3(a) THE OXIDATION OF PENT-2-ENE ON A "NEW" CATALYST : THE EFFECT OF CONTACT TIME ON MAJOR PRODUCTS. (oxygen:olefin = 1.25; temperature = 300°C).

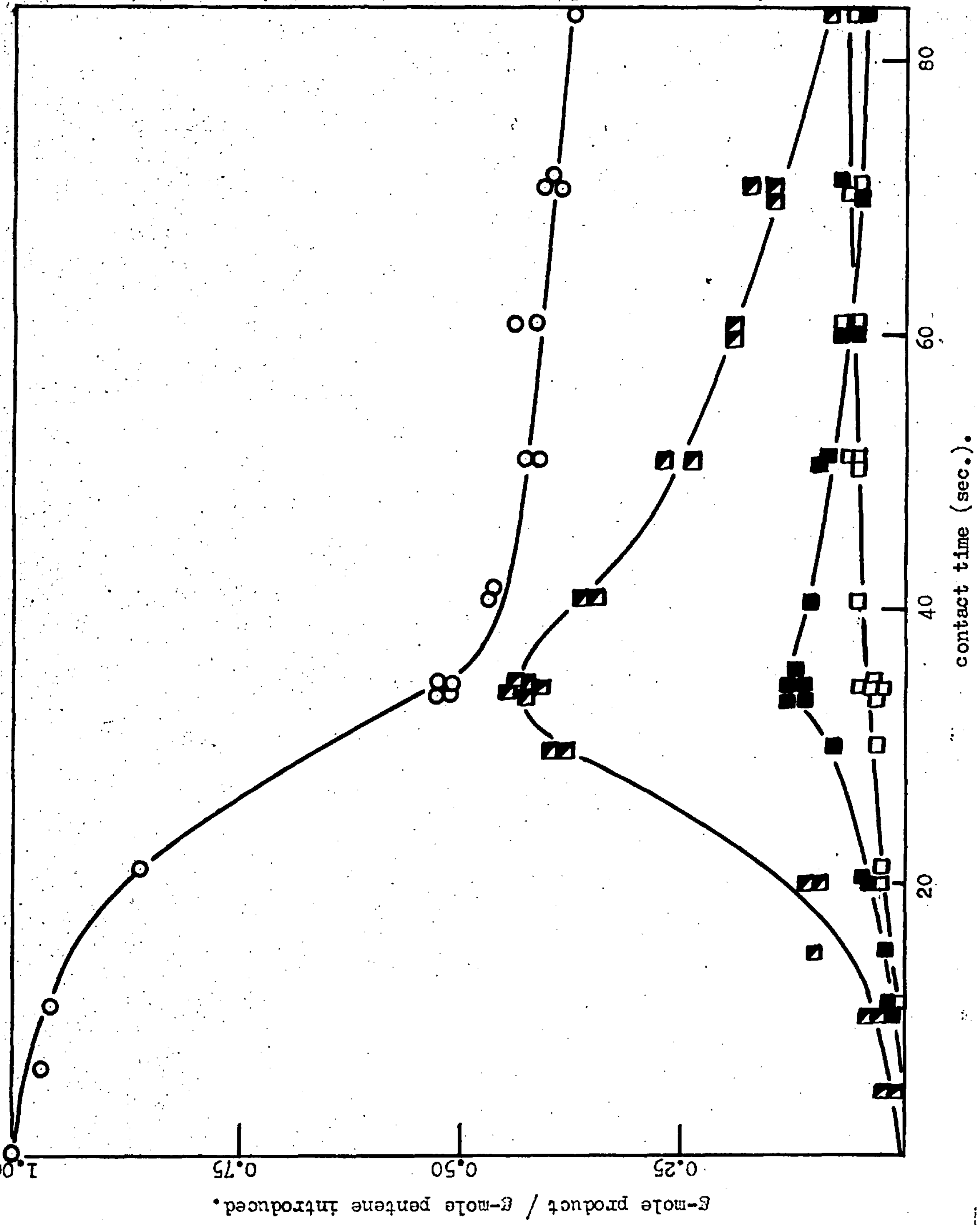


FIG III.3(b) THE OXIDATION OF PENT-2-ENE ON A "NEW" CATALYST : EFFECT OF CONTACT TIME ON MINOR PRODUCTS.
(oxygen:olefin = 1.25; temperature = 300°C)

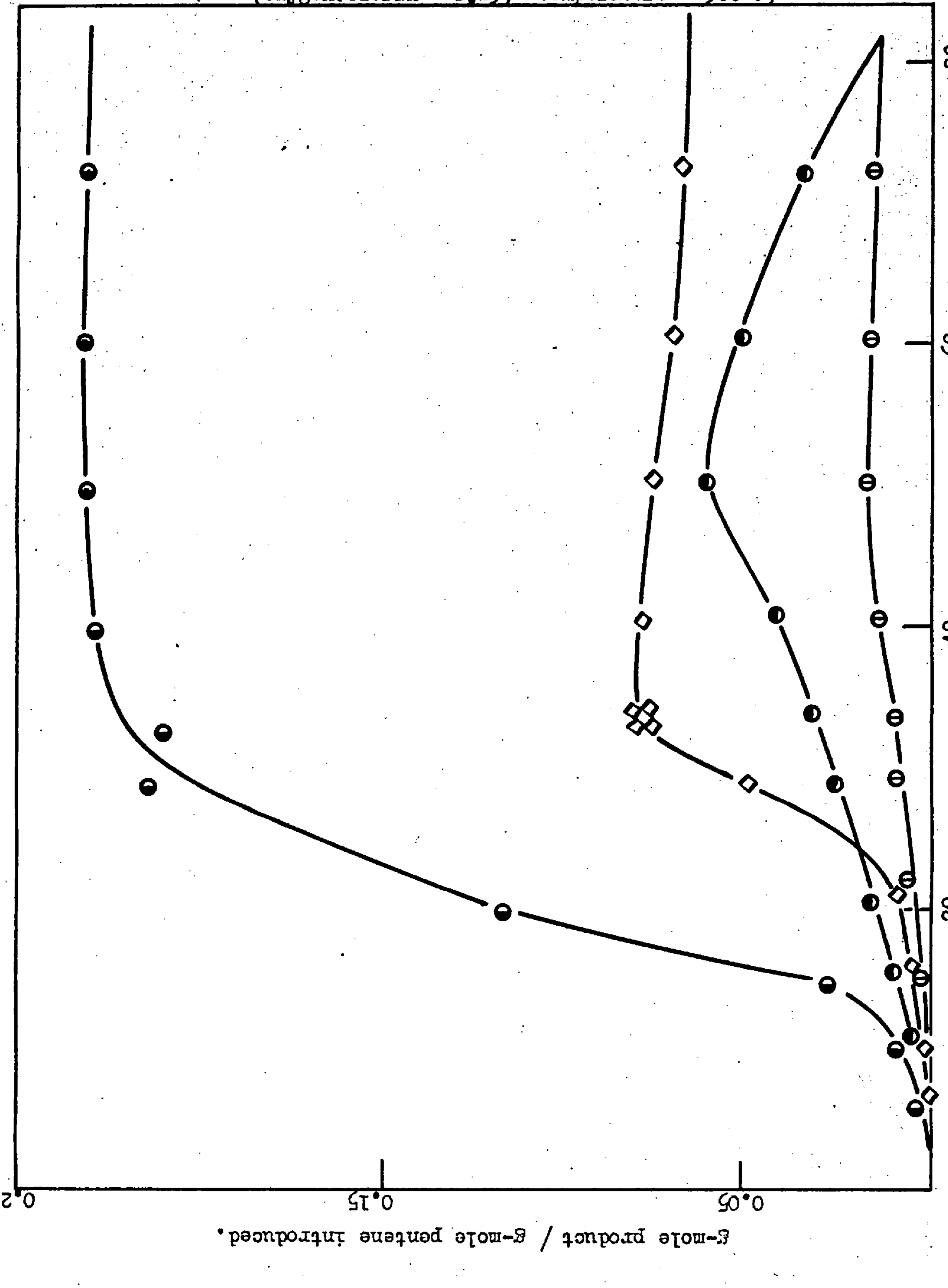


FIG. III.4(a). THE OXIDATION OF PENT-2-ENE ON AN "OID CATALYST : THE EFFECT OF CONTACT TIME ON MAJOR PRODUCTS. (oxygen:olefin = 1.25; temperature = 300°C)

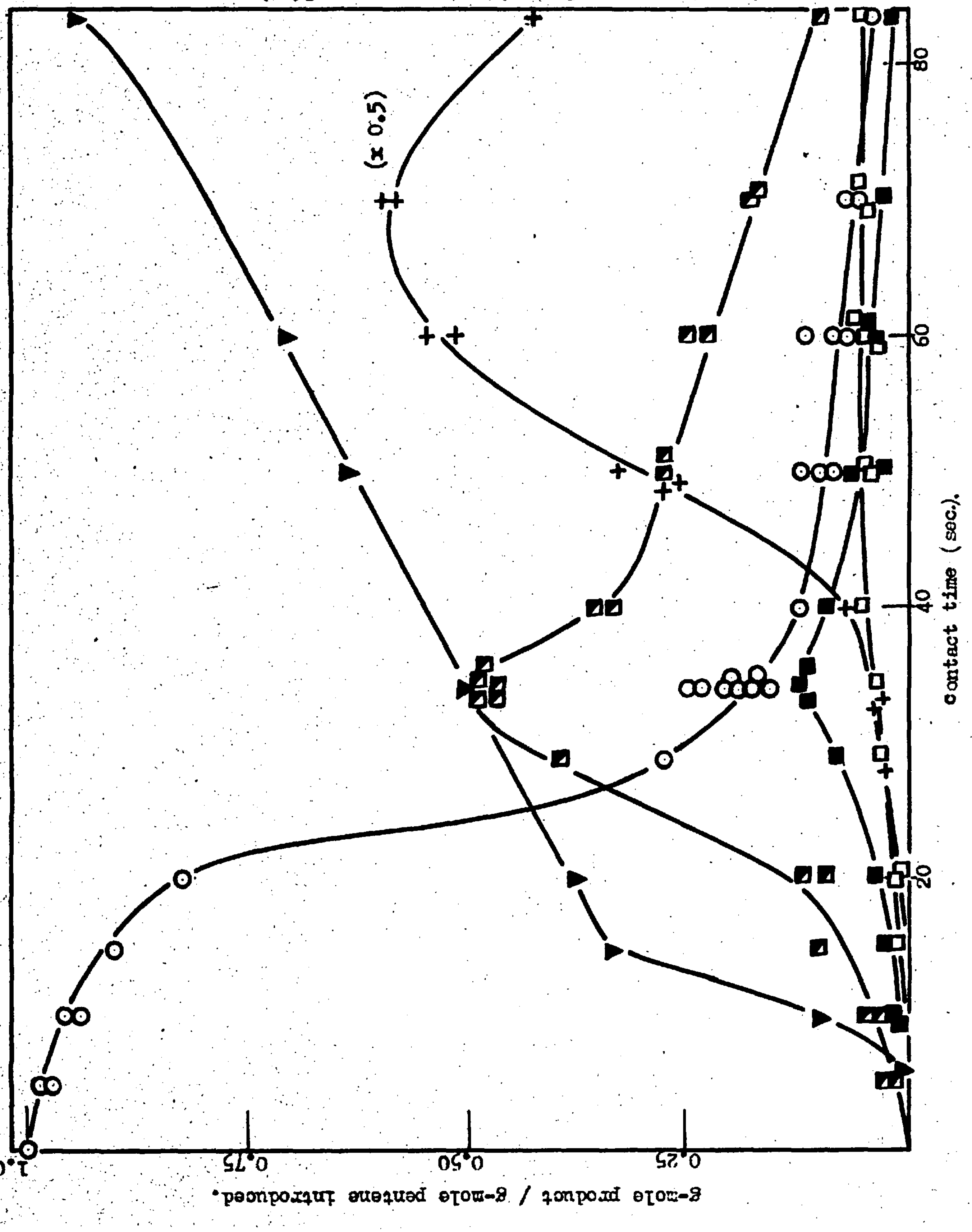


FIG. III.4(b). THE OXIDATION OF PENT-2-ENE ON AN "OLD" CATALYST: THE EFFECT OF CONTACT TIME ON MINOR PRODUCTS.
(oxygen:olefin = 1.25; temperature = 300°C)

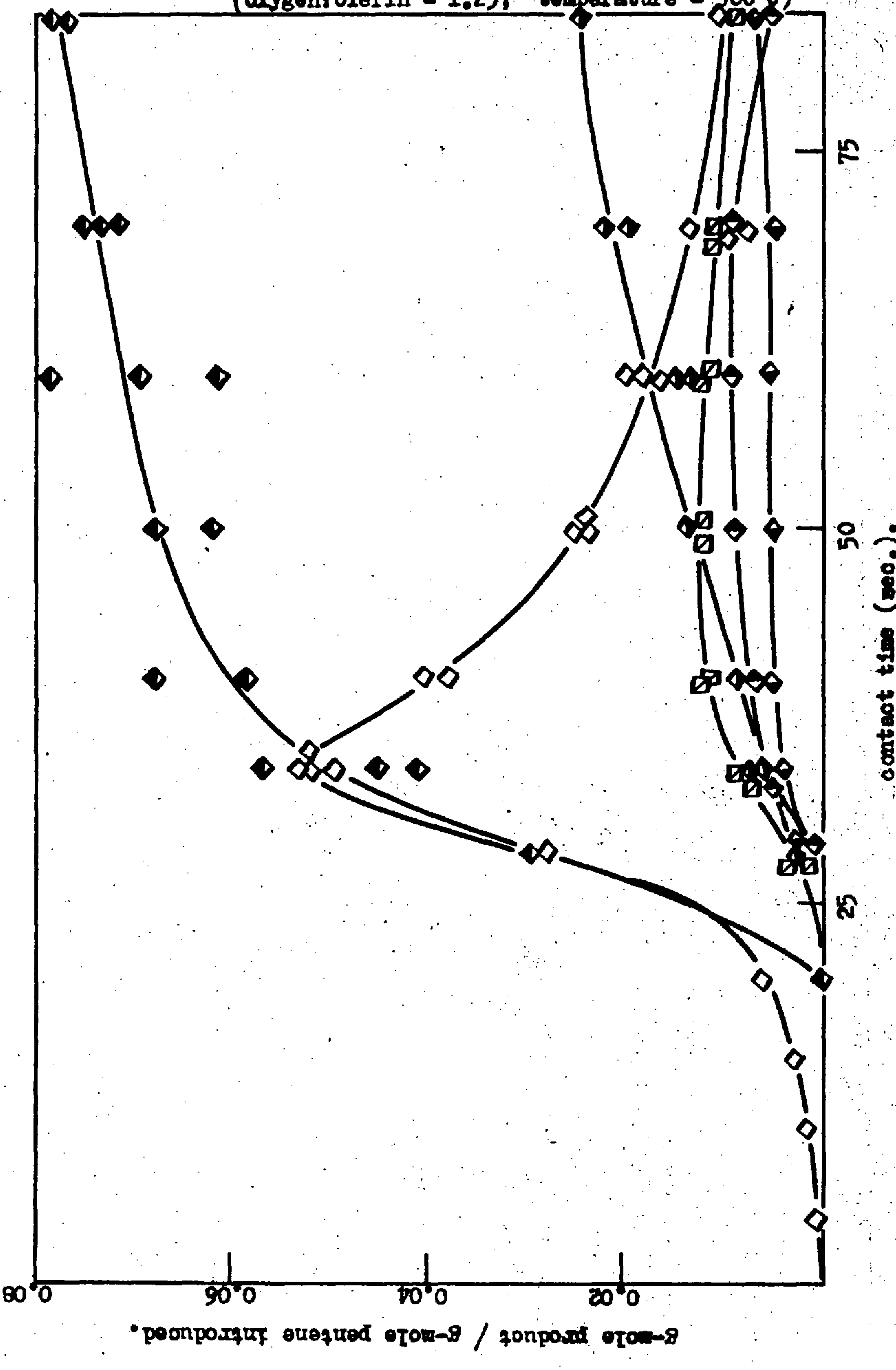


FIG. III.4(c). THE OXIDATION OF PENT-2-ENE ON AN "OID" CATALYST : THE EFFECT OF CONTACT TIME ON MINOR PRODUCTS. (oxygen:olefin = 1.25; temperature = 300°C)

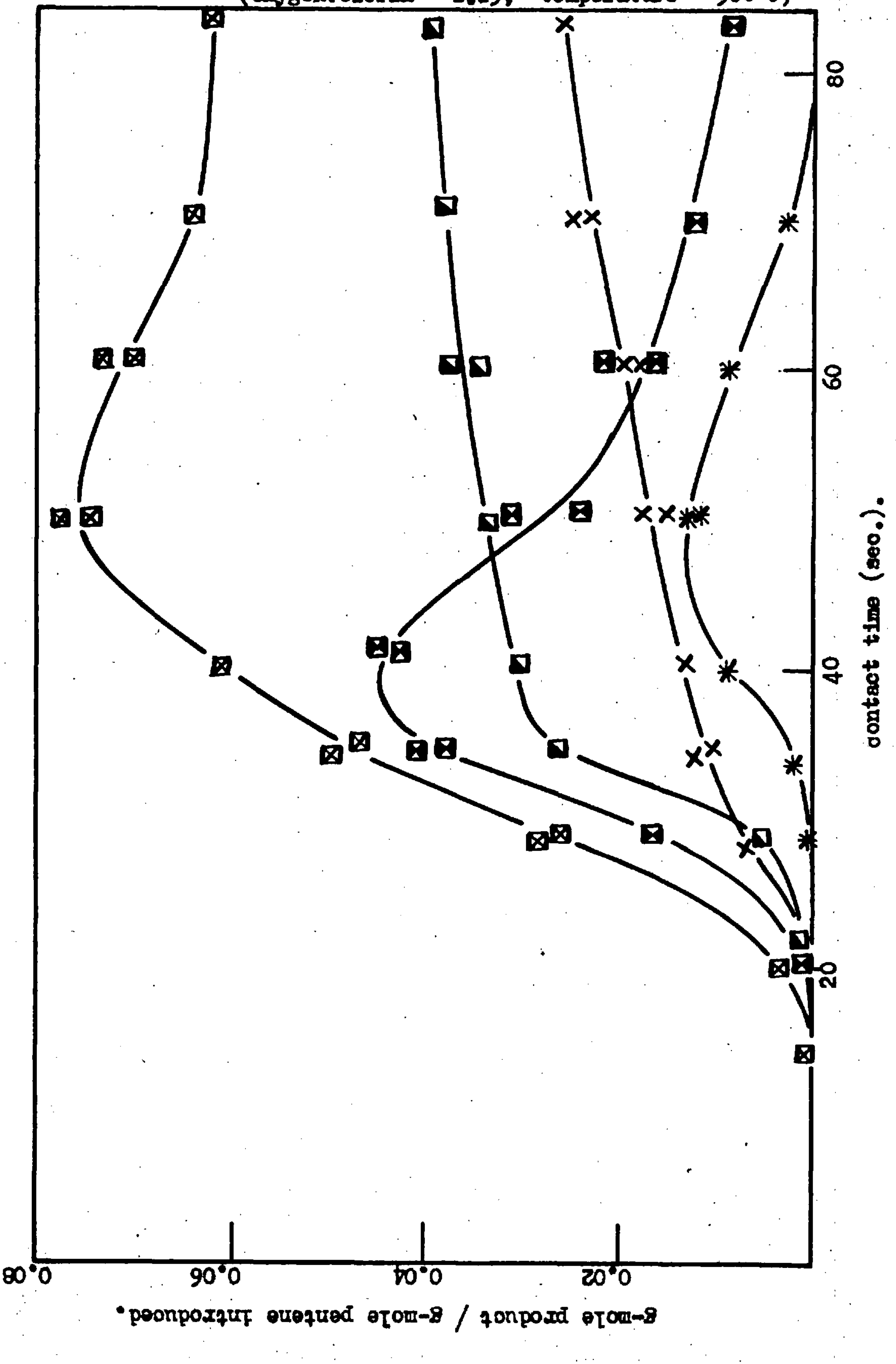


FIG. III.5(a). THE OXIDATION OF PENT-2-ENE ON A "NEW" CATALYST: THE EFFECT OF OXYGEN:OLEFIN ON MAJOR PRODUCTS.

(contact time = 33.6 sec; temperature = 300°C)

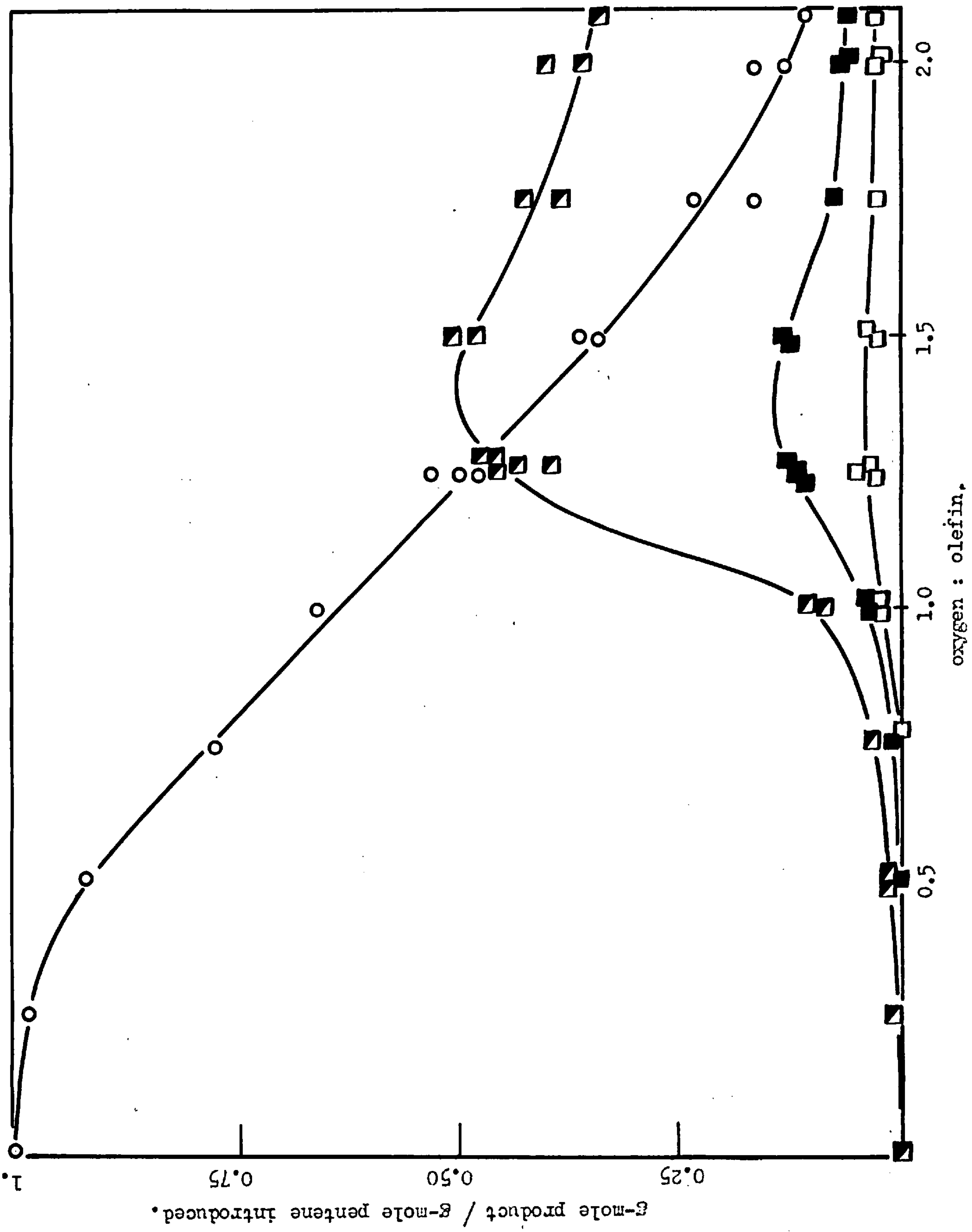


FIG III.5(b) THE OXIDATION OF PENT-2-ENE ON A "NEW" CATALYST : THE EFFECT OF OXYGEN:OLEFIN ON MINOR PRODUCTS.
(contact time = 33.6 sec; temperature = 300°C)

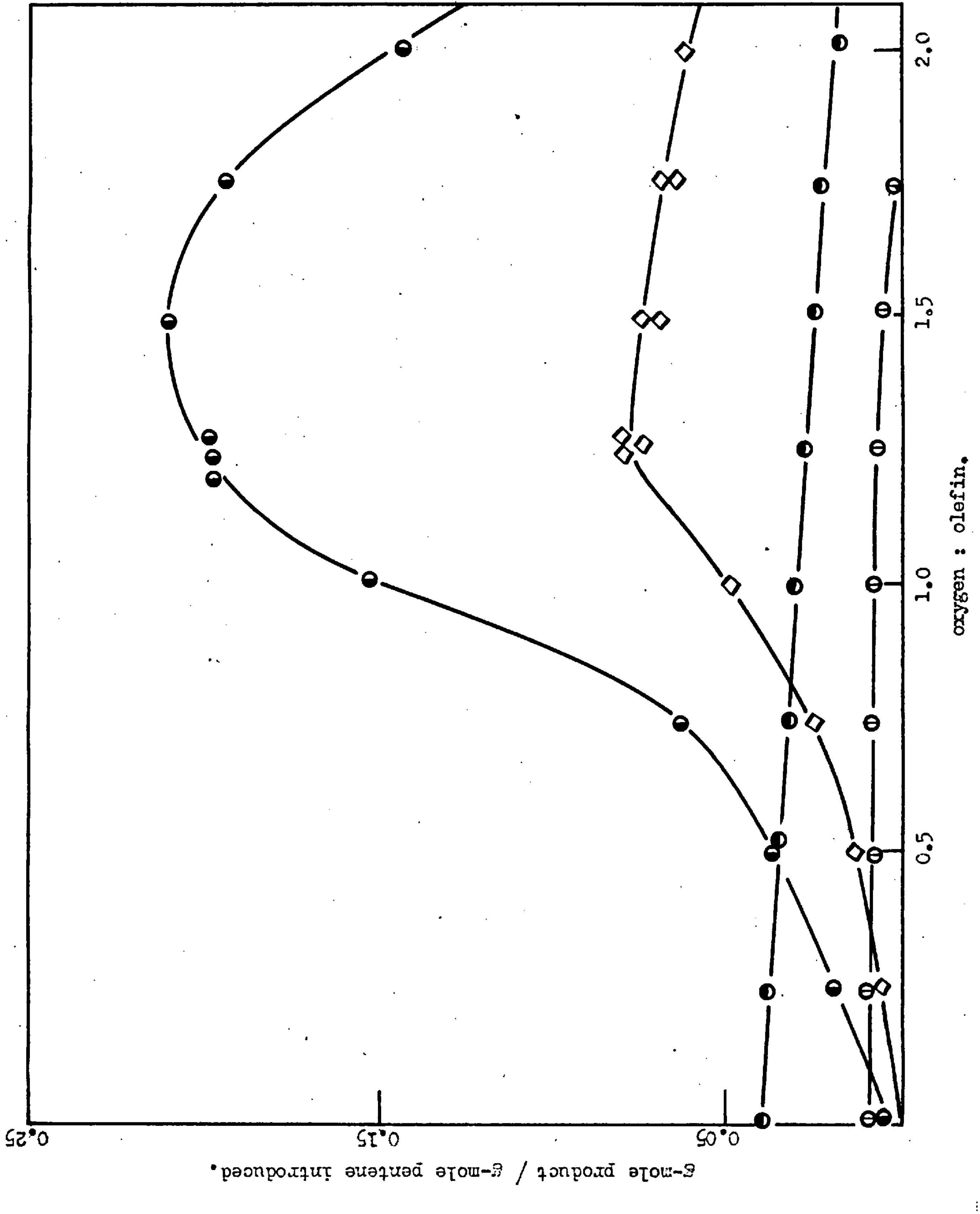


FIG. III.6(a). THE OXIDATION OF PENT-2-ENE ON AN "OLD" CATALYST : THE EFFECT OF OXYGEN:OLEFIN IN MAJOR PRODUCTS. (contact time = 33.6 sec.; temperature = 300°C.)

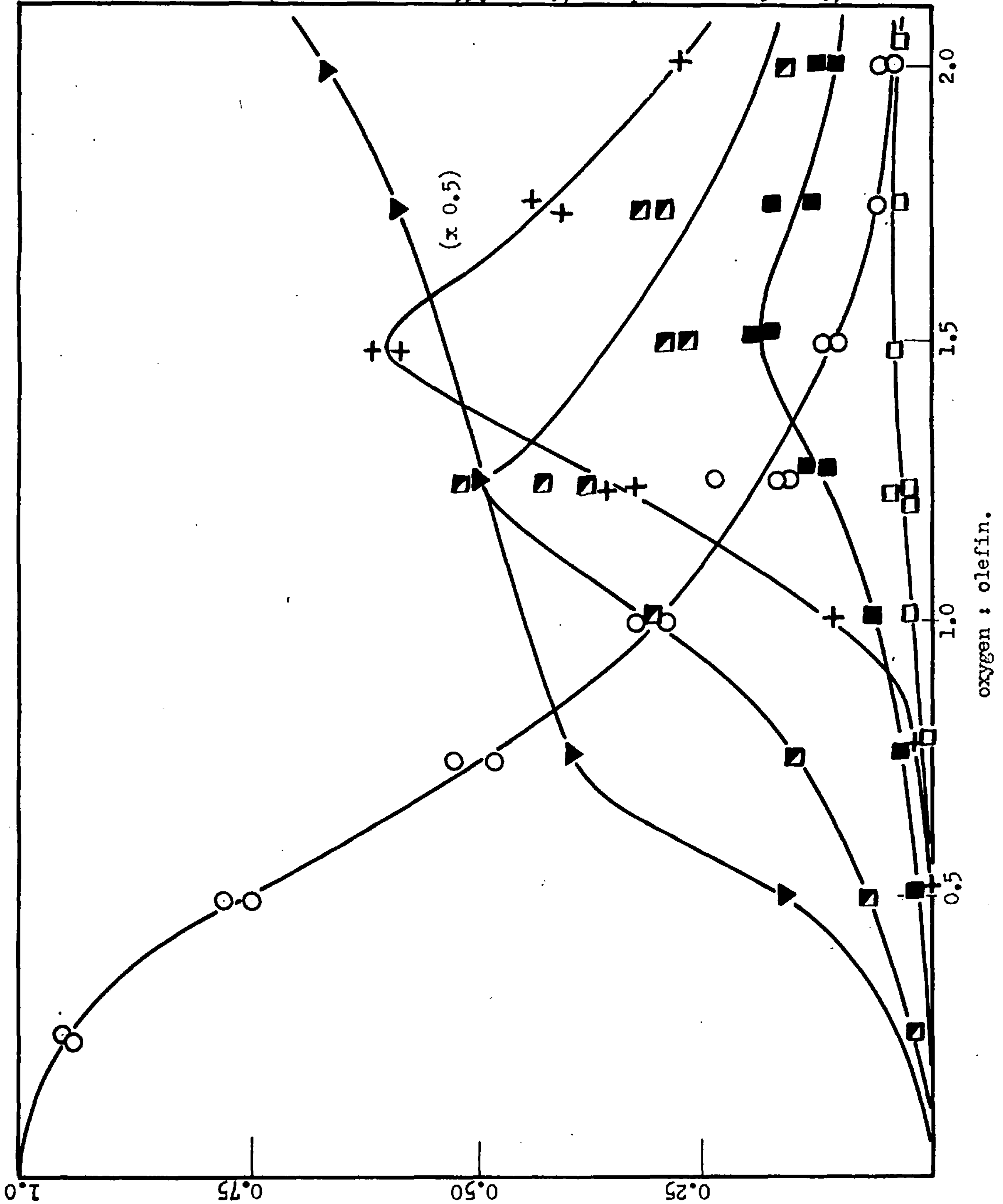


FIG. III.6(b). THE OXIDATION OF PENT-2-ENE ON AN "OLD" CATALYST: THE EFFECT OF OXYGEN:OLEFIN ON MINOR PRODUCTS.
(contact time = 33.6 sec.; temperature = 300°C)

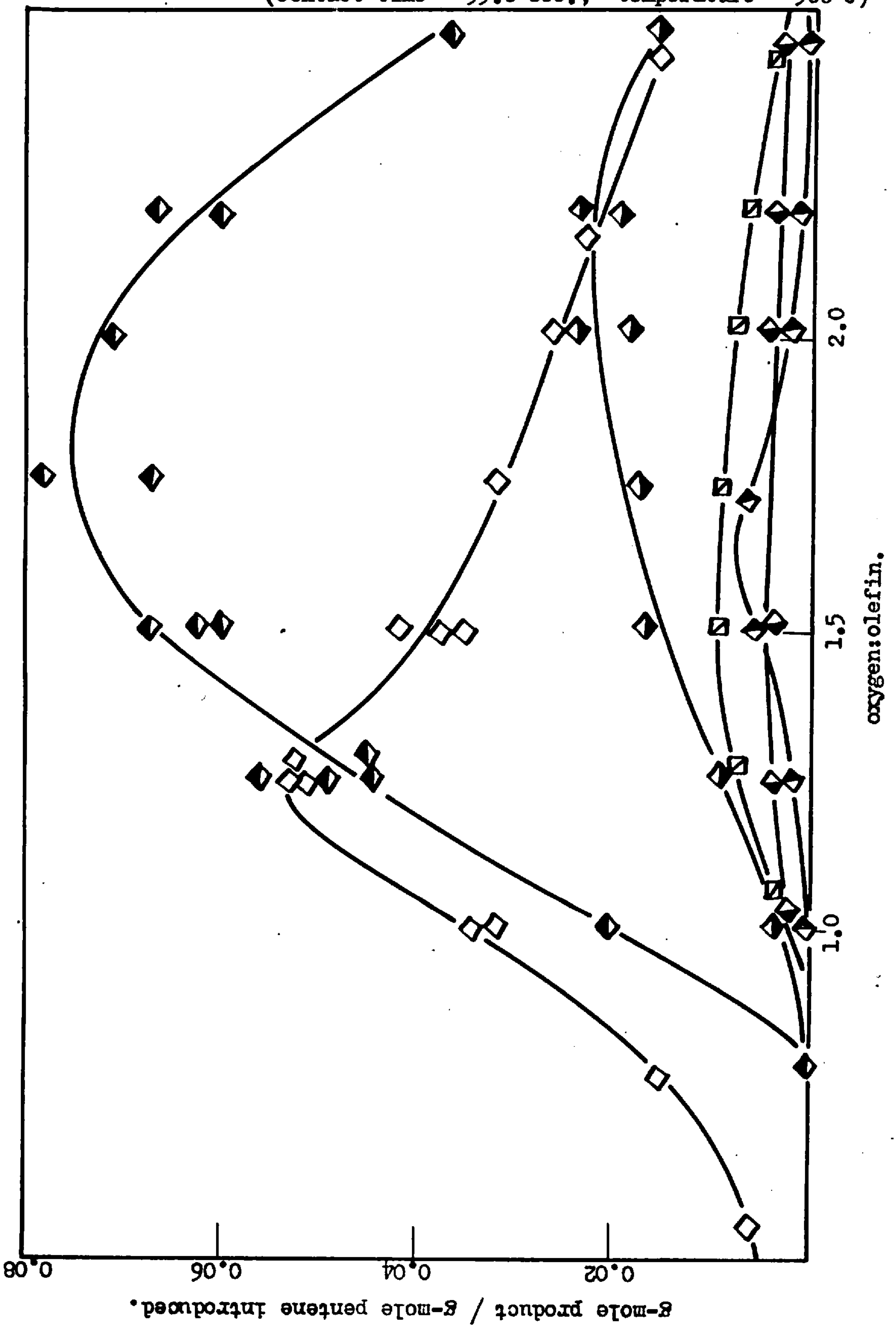


FIG. III.6(c). THE OXIDATION OF PENT-2-ENE ON AN "OLD" CATALYST: THE EFFECT OF OXYGEN:OLEFIN ON MINOR PRODUCTS. (contact time = 33.6 sec.; temperature = 300°C).

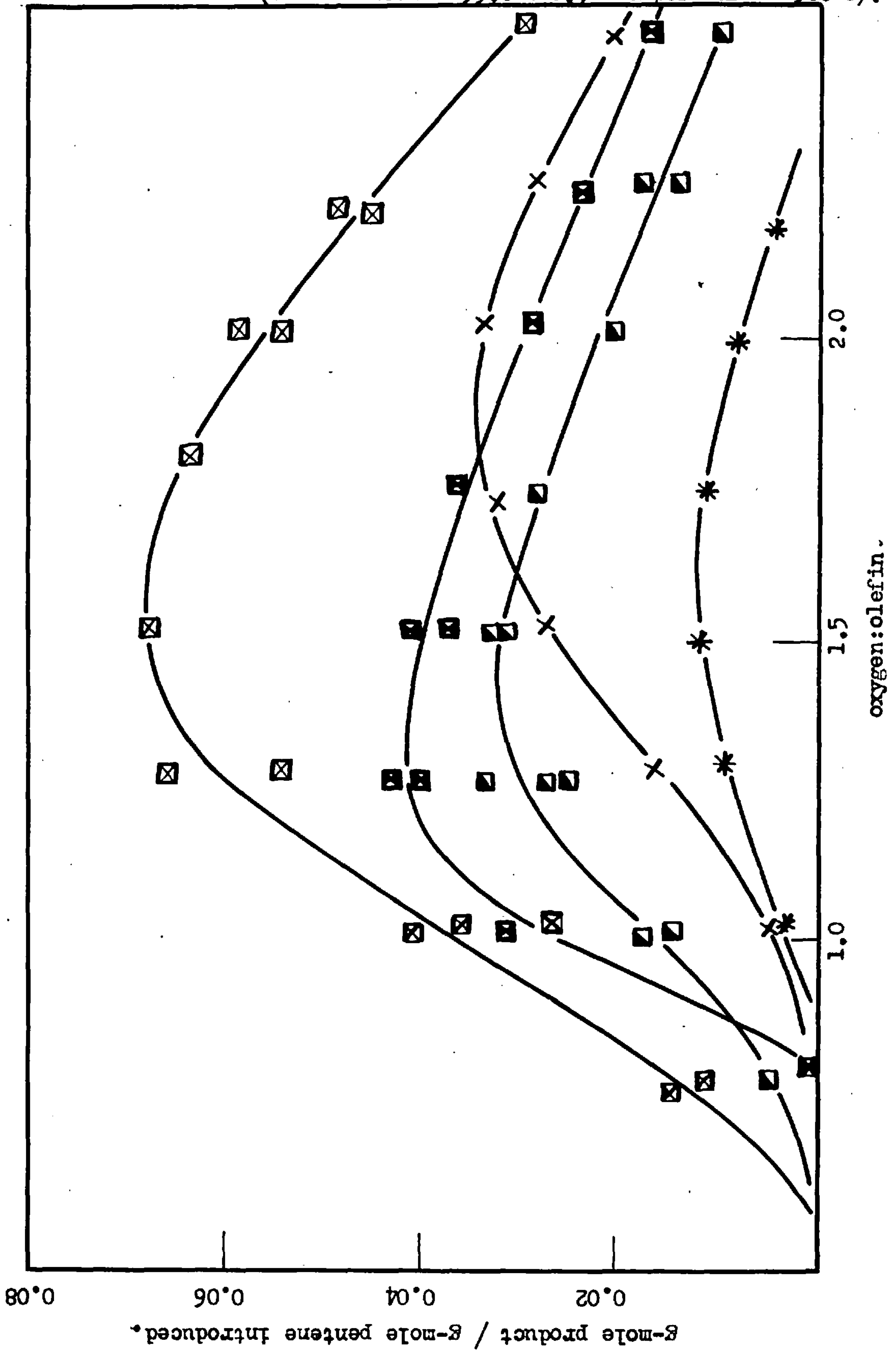
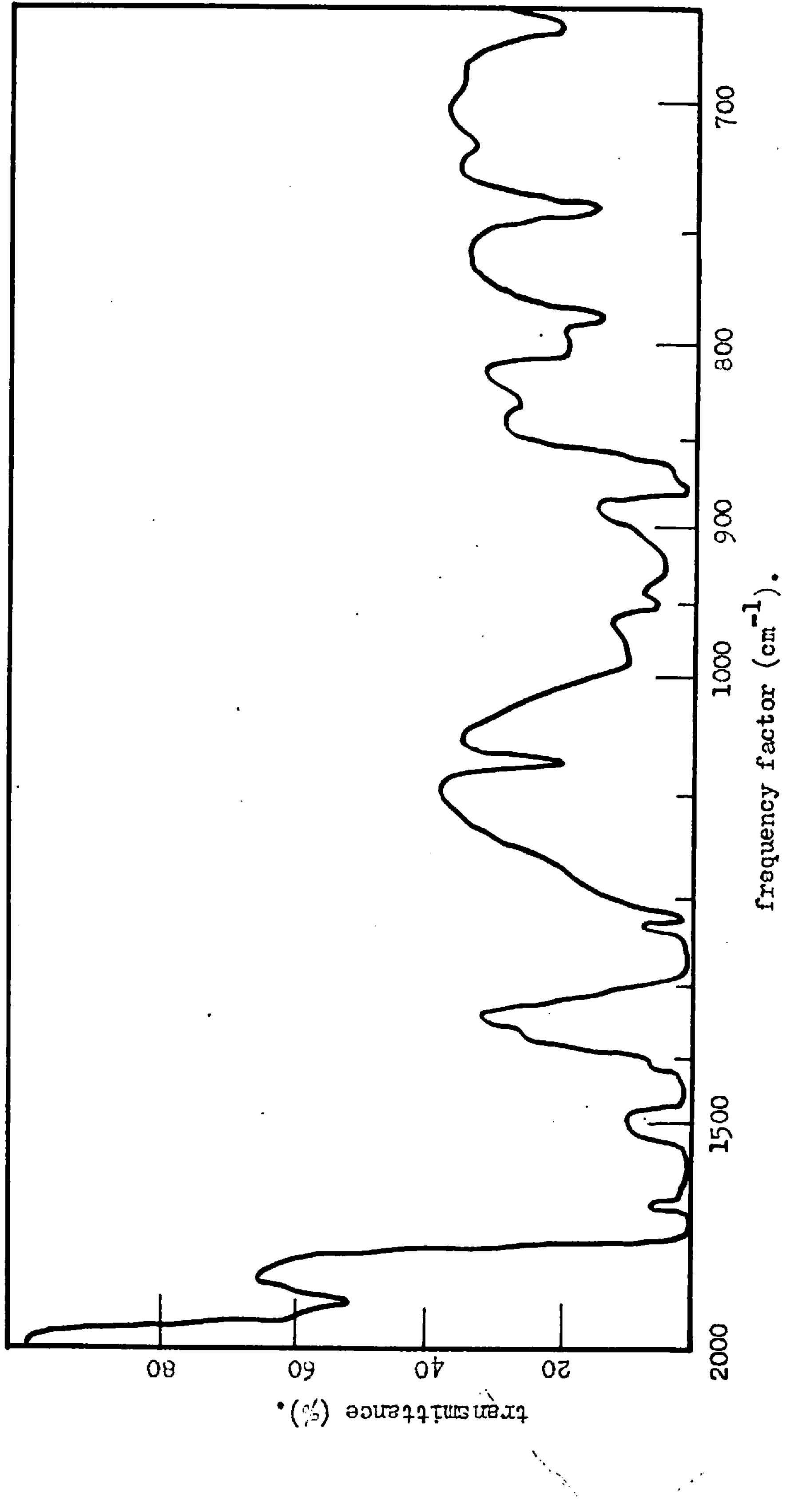


FIG. III.7. THE OXIDATION OF PENT-2-ENE:
INFRA-RED SPECTRUM OF SOLID PRODUCTS.



2. Pent-1-ene.

The effect of temperature on the gas-phase oxidation of pent-1-ene was studied by substituting, in the reactor, glass balls for the catalyst, and subsequently using temperatures in the range of 200-400°C. 50% of the olefin was consumed at 293°C. The major products were acetaldehyde and n-butryaldehyde (Fig. III. 8.), the concentrations of both of which attained maximum values at ca. 290°C.

The catalytic oxidation of pent-1-ene, on pumice-supported vanadium pentoxide was carried out at 300°C. so that the results could be meaningfully compared with those for pent-2-ene. The major products obtained from pent-1-ene (Table III. 1.) were the same as those from pent-2-ene. Studies of the isomerization of pentenes (Table III. 10.) show that isomerization of pent-1-ene to pent-2-ene takes place on pumice-supported vanadium pentoxide catalysts under these conditions. Since, qualitatively, no dissimilarity of products exists, no studies were made of the quantitative variations with temperature, contact time and reactant ratio of product formation during the oxidation of pent-1-ene.

FIG. III.8. THE OXIDATION OF PENT-1-ENE IN THE GAS PHASE : THE EFFECT OF TEMPERATURE.
(contact time = 33.6 sec; oxygen:olefin = 1.25)

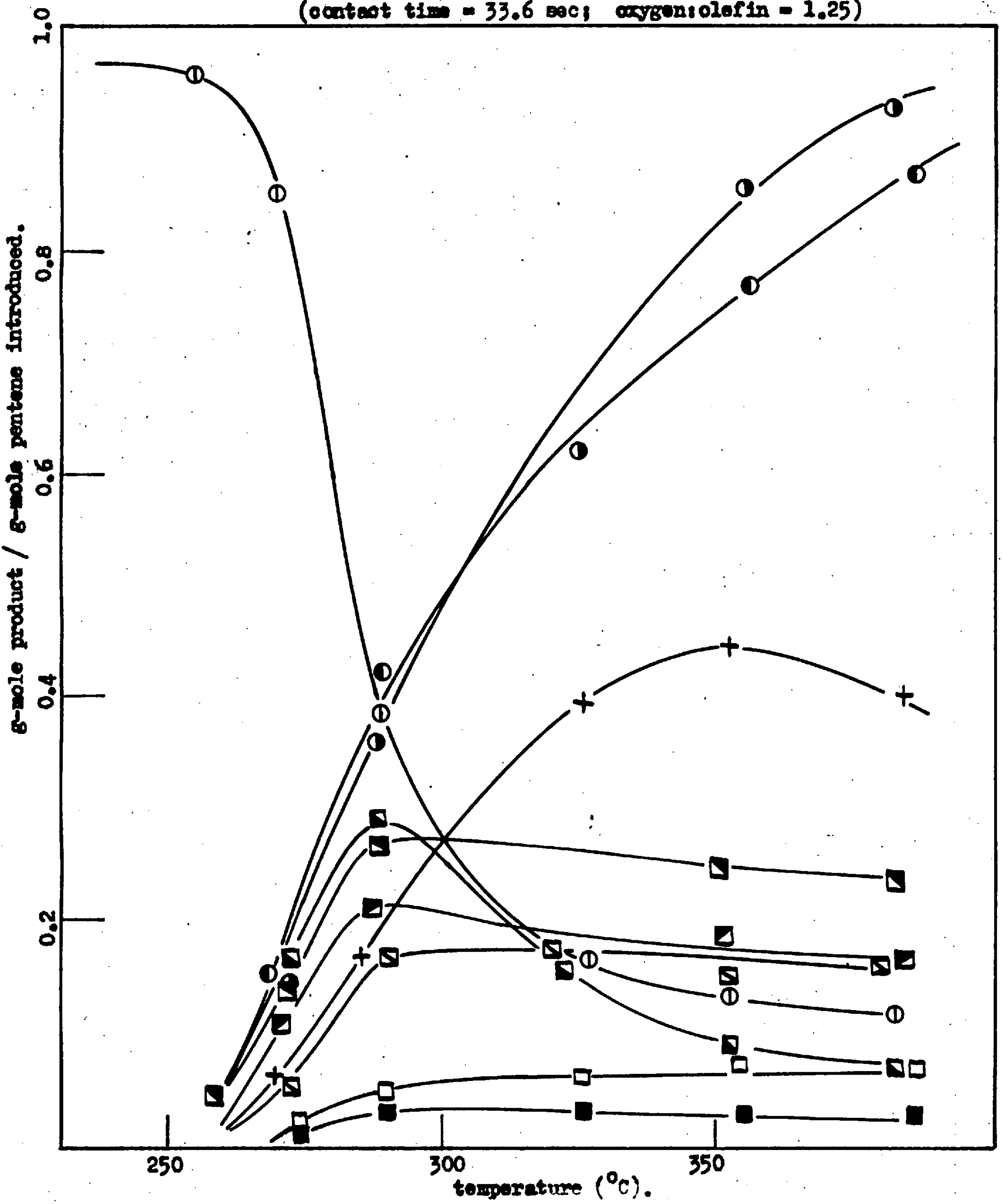


TABLE III. 1. THE OXIDATION OF PENT-1-ENE ON AN "OLD" VANADIUM PENTOXIDE CATALYST.

(oxygen:olefin = 1.25; contact time = 33.6 sec.; temperature = 300°C.)

PRODUCTS	g-mole product/g-mole pentene introduced
ethylene	0.36
propylene	0.15
pent-1-ene + pent-2-ene	0.075
C_{10} hydrocarbons	0.05
acetaldehyde	0.66
propionaldehyde	0.08
n-butyraldehyde	0.06
acetone	0.165
methyl ethyl ketone	0.10
pentanones	0.03
methyl alcohol	0.21
isobutene oxide	0.02
2,3-epoxypentane	0.045

B. CATALYTIC OXIDATION OF BRANCHED-CHAIN PENTENES.

The first branched-chain pentene to be studied was 2-methyl but-2-ene. This fuel has a non-terminal double bond as does pent-2-ene, but it does not on the other hand have a reactive (allylic) methylene group.

1. 2-Methyl but-2-ene.

The 2-methyl but-2-ene used contained 8% of the isomer 2-methyl but-1-ene. The removal of this isomer would be ineffective as isomerization of 2-methyl but-2-ene under the reaction conditions produces 2-methyl but-1-ene in concentrations in excess of 8% (Table III. 10.).

(a) The effect of temperature.

The variation with temperature of product formation during the catalytic oxidation of 2-methyl but-2-ene is shown in Fig. III. 9(a). The products are qualitatively similar over the whole of the temperature range investigated. The major products are acetaldehyde and acetone, the concentration of the former increasing with temperature and reaching a maximum value at 340°C. and subsequently decreasing again. The concentration of acetone produced also increases with temperature, reaching a maximum value at ca. 365°C. but showing no subsequent decrease with further temperature rise. The amounts of each of these two products formed under a given set of conditions are quite different. 2,3-Epoxy-2-methylbutane is also formed in quantities greater than those of the analogous compound derived from pent-2-ene, and its concentration reaches a maximum value at ca. 305°C. The decrease with further increase in temperature in the concentration of these primary products coincides with an increase in concentration of the minor products.

Similar studies were made of the variation with temperature of the products of the homogeneous oxidation of 2-methyl but-2-ene. 50% of the fuel is consumed at ca. 275°C. The chief differences between the uncatalysed and catalysed reactions is the formation of only very small amounts of dimeric (C_{10}) hydrocarbons and of 2,3-epoxy-2-methylbutane. Acetaldehyde now reaches a maximum at ca. 300°C. while acetone increases continuously with temperature. III. 9(b).

(b) The effect of contact time.

The catalytic oxidation of 2-methyl but-2-ene was studied at two temperatures, viz 250°C. and 300°C., on an "old" pumice-supported vanadium pentoxide catalyst. The work at 250°C. was carried out to avoid the occurrence of appreciable gas-phase oxidation, and that at 300°C. was done in order to effect a direct comparison with similar work on pent-2-ene.

(i) 250°C.

The amounts of the major products (acetaldehyde and acetone) increase with contact time (Fig. III. 10.) while the quantity of residual 2-methyl but-2-ene decreases. The amount of 2-methyl but-1-ene present increases with contact time in the region 0-20 sec. and thereafter remains constant and finally decreases slightly. The quantities of the minor products, 2,3-epoxy-2-methylbutane and methyl isopropyl ketone, at first increase with contact time and then remain constant. The lower hydrocarbons ethylene and propylene are present in trace quantities, no other products were detected.

(ii) 300°C.

The variations with contact time of 2-methyl but-2-ene consumption and of product formation at 300°C. (Fig. III. 11.) are much more marked than at 250°C. Acetaldehyde and acetone reach maximum concentrations at 60-70 sec. contact time and then decline. The concentration of carbon dioxide, rises however almost linearly with increasing contact time, even when the major organic products are declining. 2,3-Epoxy-2-methylbutane, methyl isopropyl ketone, propylene and ethylene show the same variation with contact time as do the major organic products. The maximum concentrations of all these compounds are attained at 40-50 sec. contact time.

(c) The effect of oxygen:olefin ratio.

Two sets of results were obtained at temperatures of 250°C. and 300°C. respectively.

(i) 250°C.

Fig. III. 12. shows some of the results obtained at 250°C. The constant concentration of 2-methyl but-1-ene shows that 2-methyl but-2-ene is oxidized preferentially under these conditions. All the oxygenated products show an increased rate of formation with increasing oxygen availibility, the dimeric (C_{10}) hydrocarbons on the other hand, are unaffected by changes of reactant ratio.

(ii) 300°C.

At 300°C. the amounts of products formed are much greater than at 250°C. and the variation of reactant ratio produces a much more pronounced effect on the consumption of the olefin and on the formation of the products at the higher temperature (Fig. III. 13.). Products which are not formed at 250°C. but are detected at 300°C. include methyl ethyl ketone and n-butraldehyde. Throughout the region studied, the consumption of olefin increases with oxygen availability, becoming substantially constant when the molar oxygen:olefin ratio exceeds 1.75. Concurrent increases in the amounts of products formed in the reactant ratio range 0.25-1.25 are followed by subsequent decreases, the rates and extents of which reflect the vulnerabilities of the primary products to further oxidation.

FIG. III.9(a). THE OXIDATION OF 2-METHYL BUT-2-ENE : THE EFFECT OF TEMPERATURE.
("old" catalyst; contact time = 33.6 sec; oxygen:olefin = 1.25)

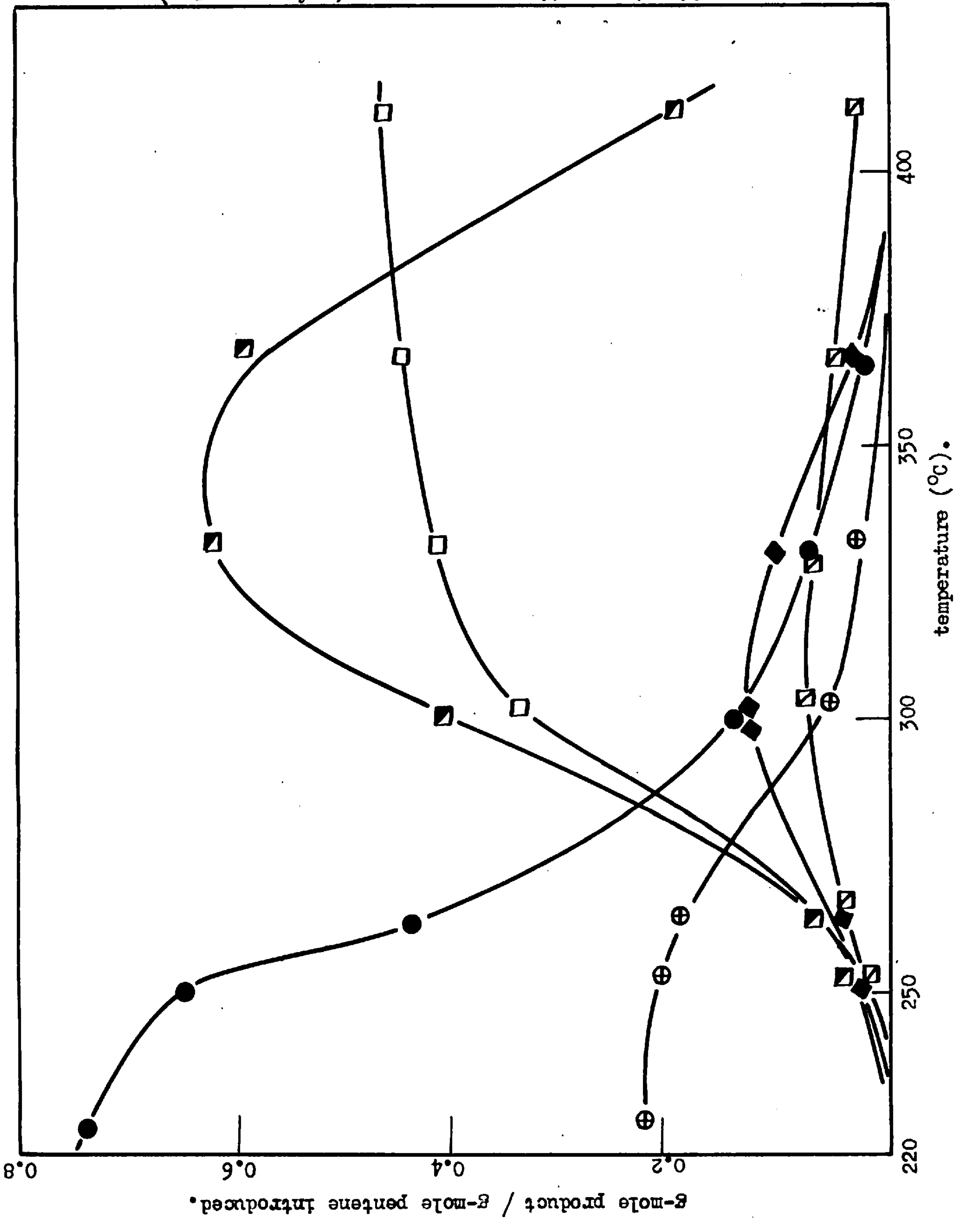


FIG. III.9(b). THE OXIDATION OF 2-METHYL BUT-2-ENE IN THE GAS PHASE: THE EFFECT OF TEMPERATURE.
(contact time = 33.6 sec.; oxygen:olefin = 1.25)

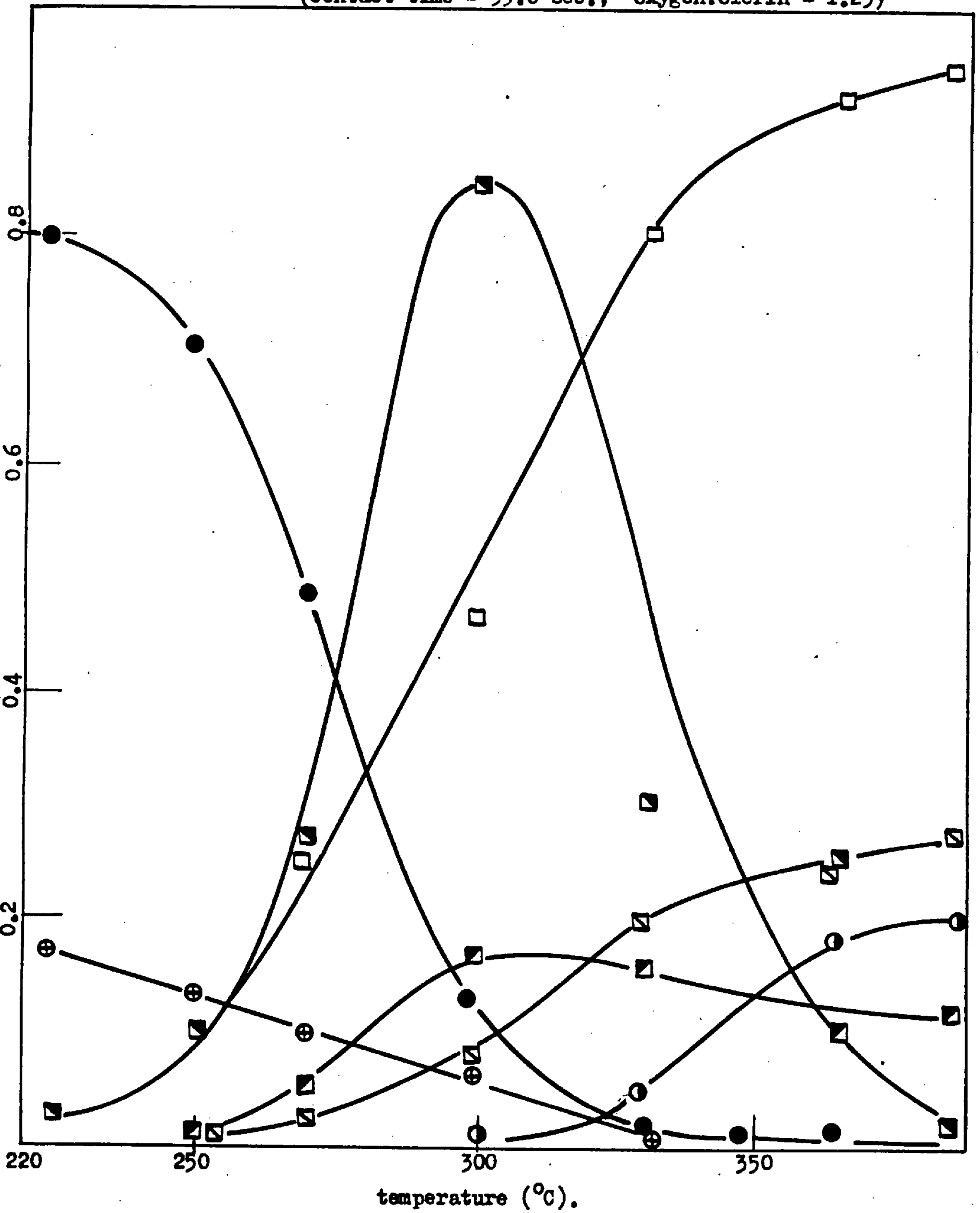


FIG. III.10 THE OXIDATION OF 2-METHYL BUT-2-ENE AT 250°C:
THE EFFECT OF CONTACT TIME ("old" catalyst: oxygen: olefin = 1.25)

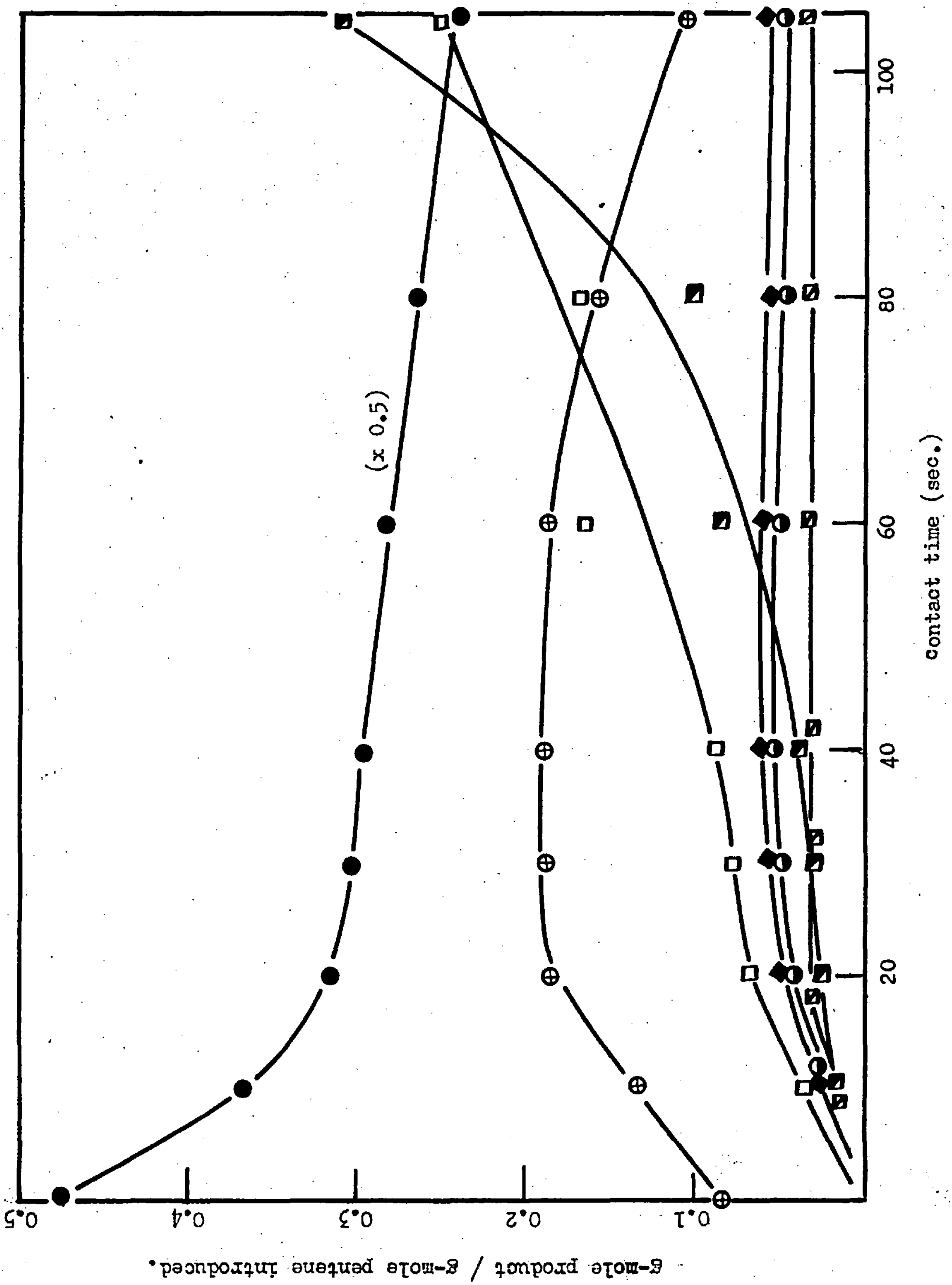


FIG. III.11(a). THE OXIDATION OF 2-METHYL BUT-2-ENE AT 300°C: THE EFFECT OF CONTACT TIME ON MAJOR PRODUCTS. ("old" catalyst; oxygen:olefin = 1.25)

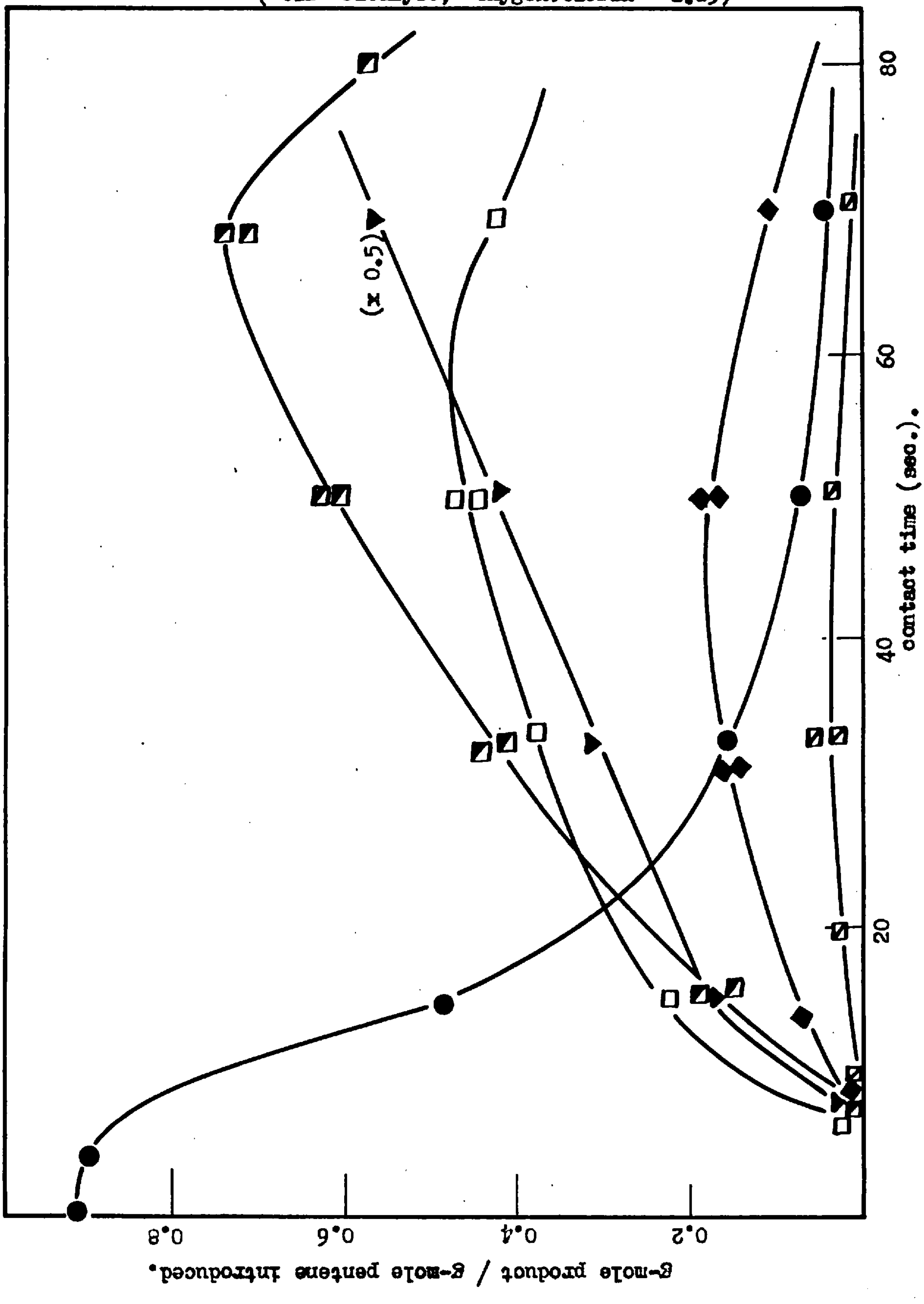


FIG. III.11(b). THE OXIDATION OF 2-METHYL BUT-2-ENE AT 300°C: THE EFFECT OF CONTACT TIME ON MINOR PRODUCTS. ("old" catalyst; oxygen:olefin = 1.25).

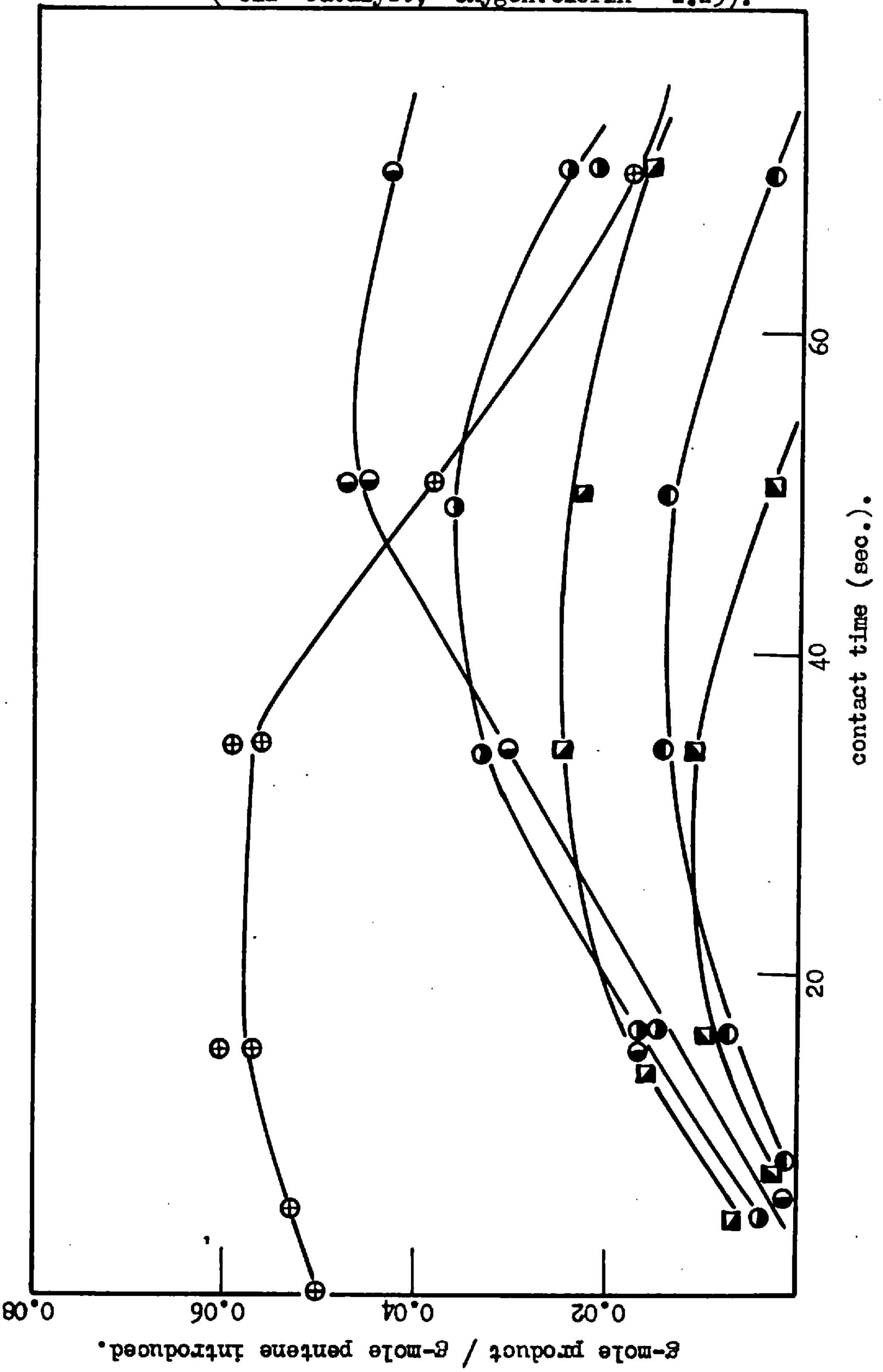


FIG. III.12. THE OXIDATION OF 2-METHYL BUT-2-ENE AT 25°C : THE EFFECT OF OXYGEN:OLEFIN RATIO. ("old" catalyst: contact time = 33.6 sec.)

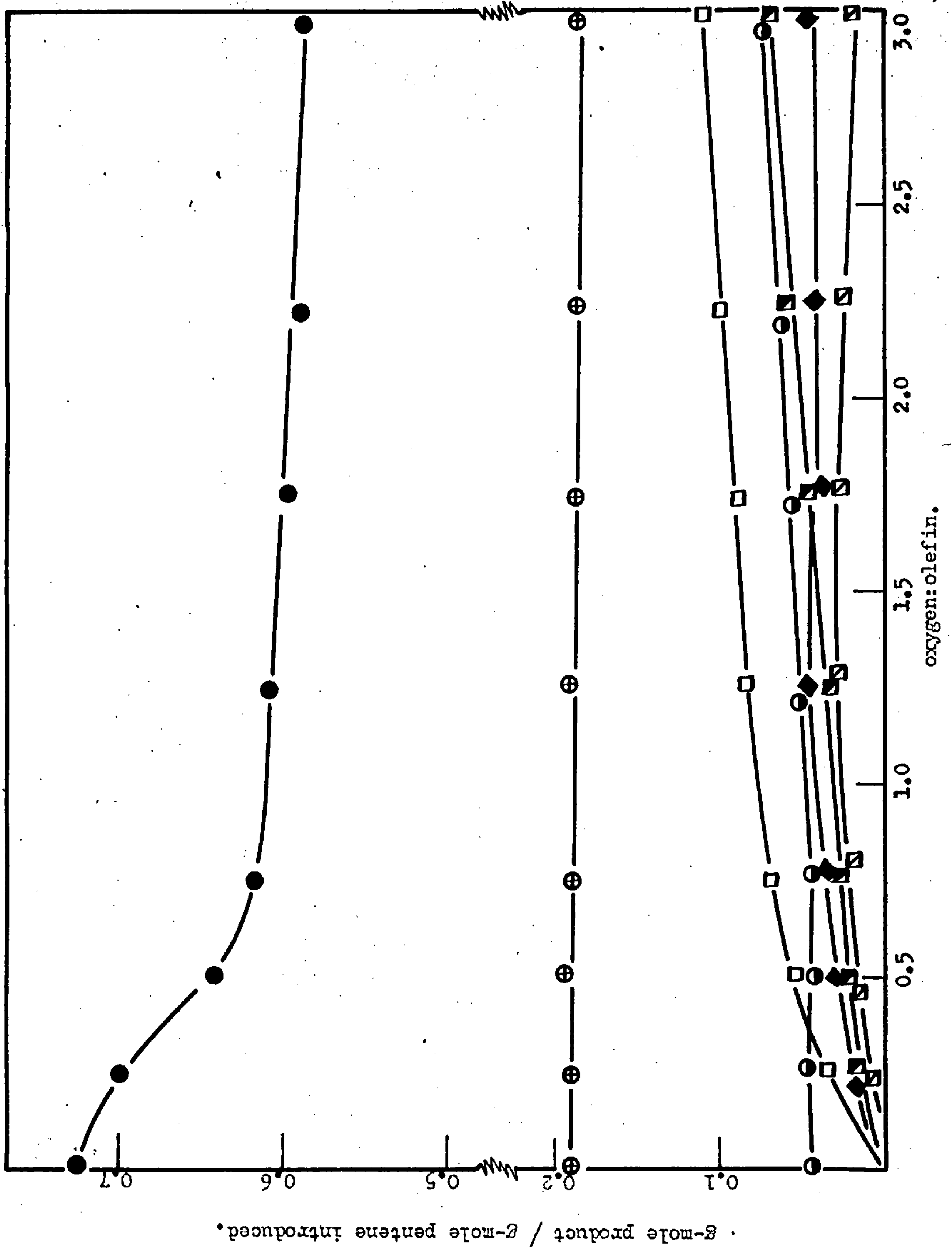


FIG. III.13(a) THE OXIDATION OF 2-METHYL BUT-2-ENE AT 300°C : THE EFFECT OF OXYGEN:OLEFIN ON MAJOR PRODUCTS. ("old" catalyst ; contact time = 33.6 sec.)

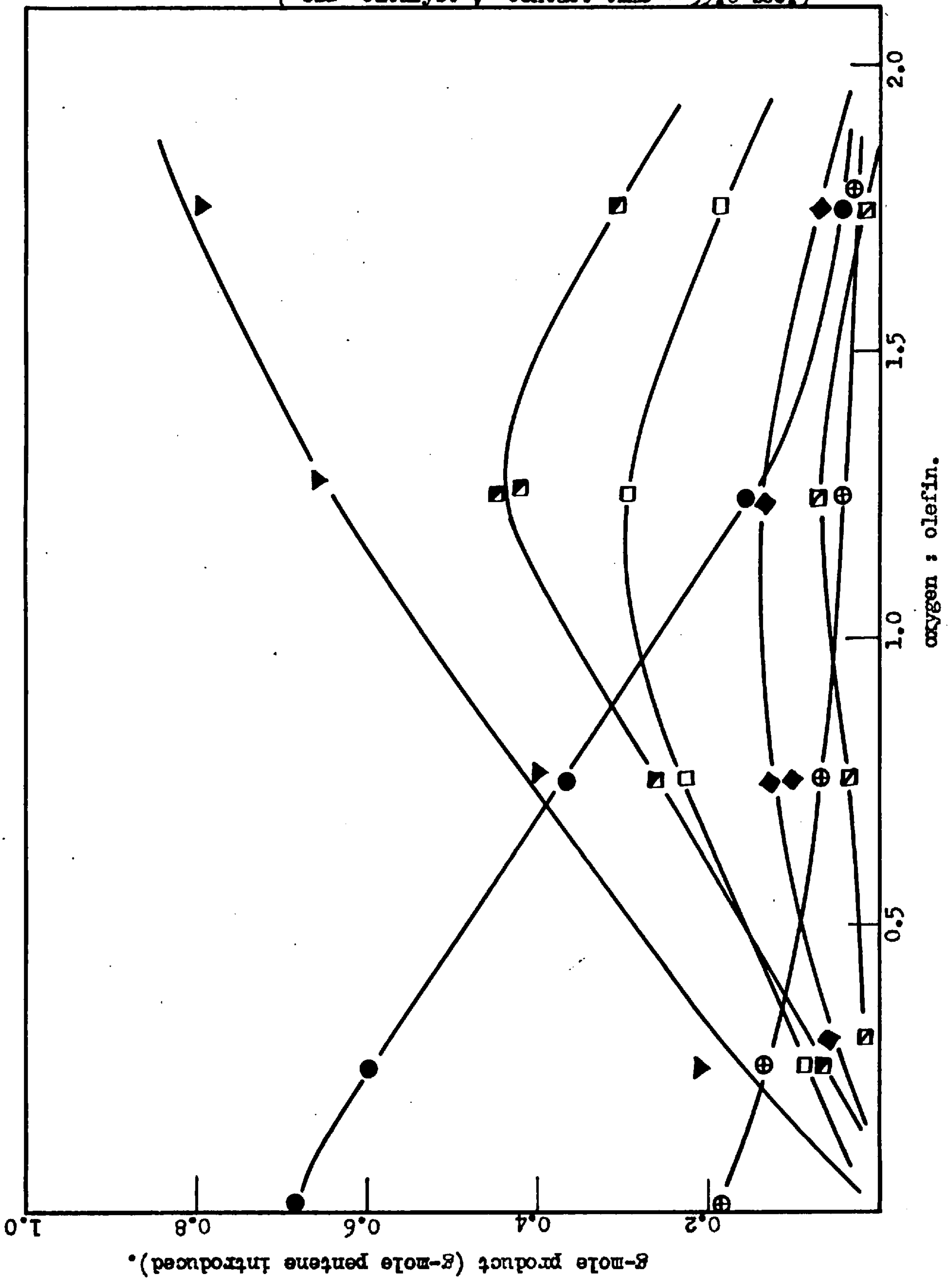
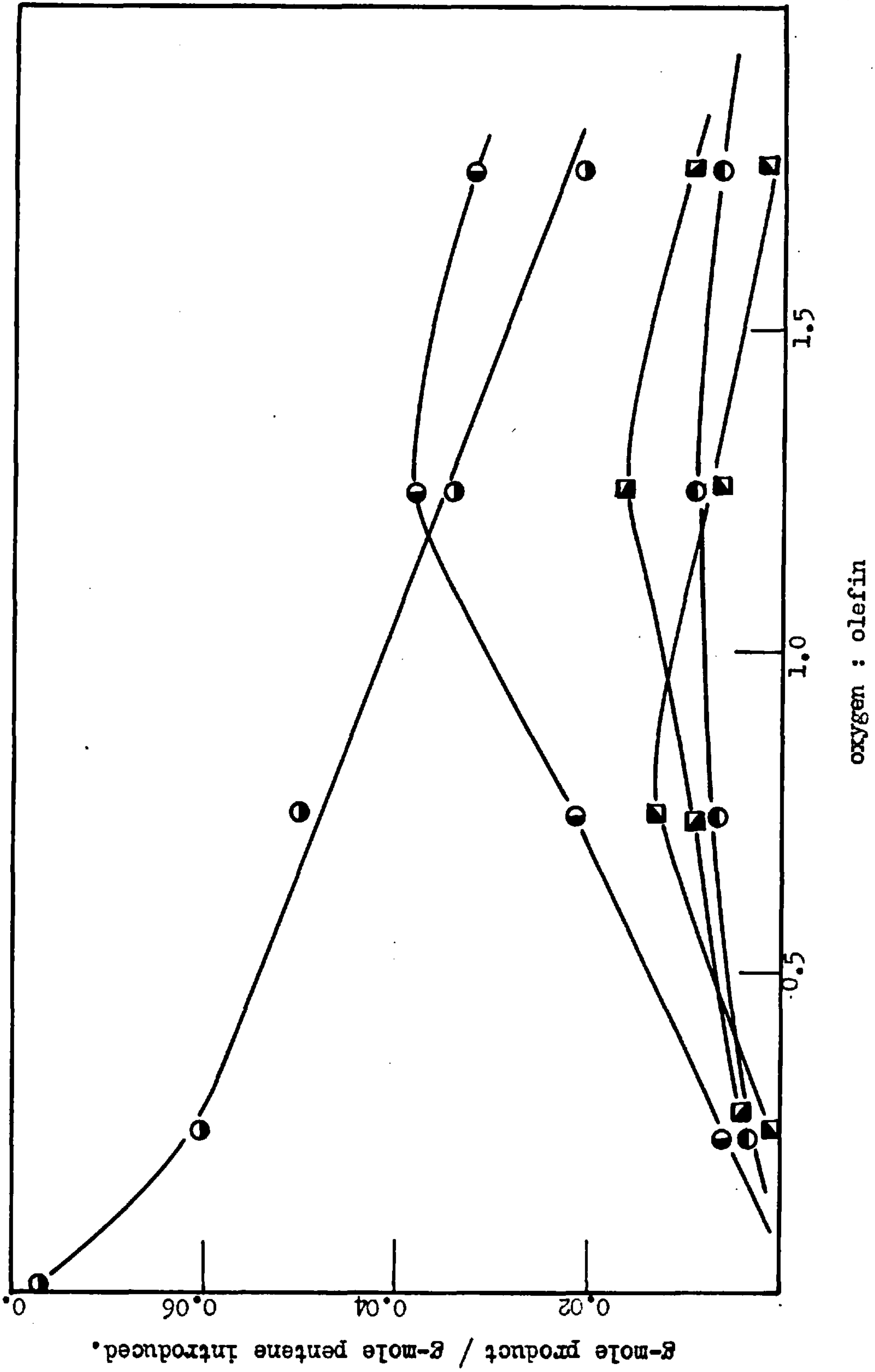


FIG. III.13(b). THE OXIDATION OF 2-METHYL BUT-2-ENE AT 300°C: THE EFFECT OF OXYGEN:OLEFIN ON MINOR PRODUCTS. ("old" catalyst; contact time = 33.6 sec.)



2. 2-Methyl but-1-ene.

2-Methyl but-1-ene was studied in less detail and only for comparative purposes. The variation with temperature of the amounts of products formed in the homogeneous reaction are given in Fig. III. 14. 50% of the olefin is oxidized at a temperature of 350°C. and methyl ethyl ketone and formaldehyde are the main oxygenated products.

The products formed during the heterogeneous catalytic oxidation of 2-methyl but-1-ene on an "old" pumice-supported vanadium pentoxide catalyst (Table III. 2.) are qualitatively the same as those formed under similar conditions from 2-methyl but-2-ene. The presence of a large proportion of 2-methyl but-2-ene in the effluent gases indicates the occurrence of extensive isomerization of 2-methyl but-1-ene to 2-methyl but-2-ene.

FIG. III.14. THE OXIDATION OF 2-METHYL BUT-1-ENE IN THE GAS PHASE: THE EFFECT OF TEMPERATURE.
(contact time = 33.6 sec; oxygen:olefin = 1.25).

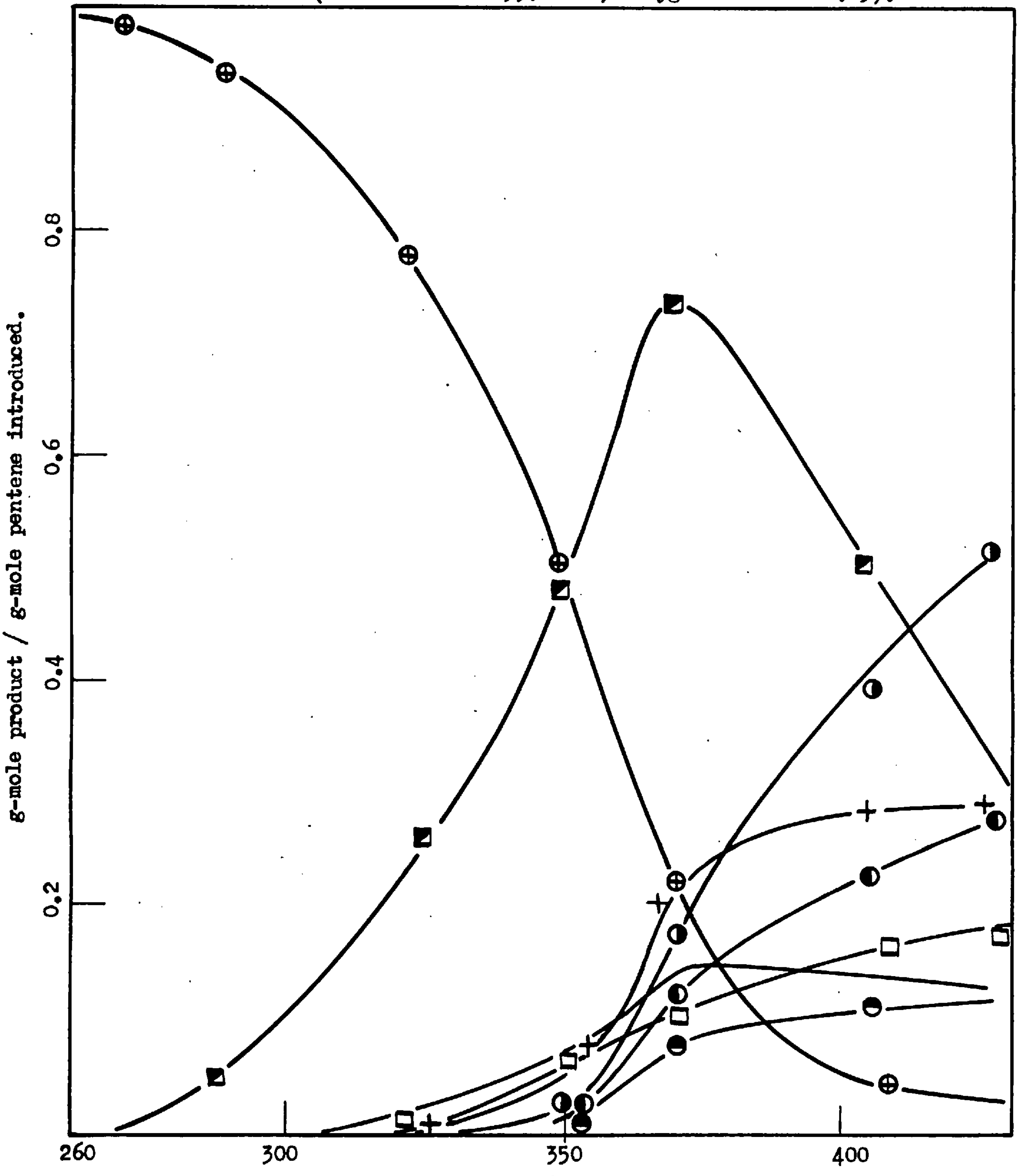


TABLE III. 2. THE OXIDATION OF 2-METHYL BUT-1-ENE ON AN "OLD" VANADIUM PENTOXIDE CATALYST.

(oxygen:olefin = 1.25; contact time = 33.6 sec.; temperature = 300°C.)

PRODUCTS	g-mole product/g-mole pentene introduced
ethylene	traces
propylene	traces
2-methyl but-1-ene	0.024
2-methyl but-2-ene	0.053
C_{10} hydrocarbons	0.10
acetaldehyde	0.57
acetone	0.44
methyl ethyl ketone	0.08
methyl isopropyl ketone	traces
2,3-epoxy-2-methylbutane	0.08

3. 3-Methyl but-1-ene.

Studies similar to those described for 2-methyl but-1-ene were carried out using 3-methyl but-1-ene. The variations with temperature of the amounts of products formed in the gas-phase are shown in Fig III. 15. 50% of the olefin is oxidized at a temperature of 330°C. and the main oxygenated products are isobutyraldehyde and formaldehyde.

The catalytic oxidation of 3-methyl but-1-ene on an "old" pumice-supported catalyst gives products which are qualitatively the same as those formed from 2-methyl but-2-ene under similar conditions. The amounts formed are shown in Table III. 3.

FIG. III.15. THE OXIDATION OF 3-METHYL BUT-1-ENE IN THE GAS PHASE: THE EFFECT OF TEMPERATURE.
(contact time = 33.6 sec; oxygen:olefin = 1.25)

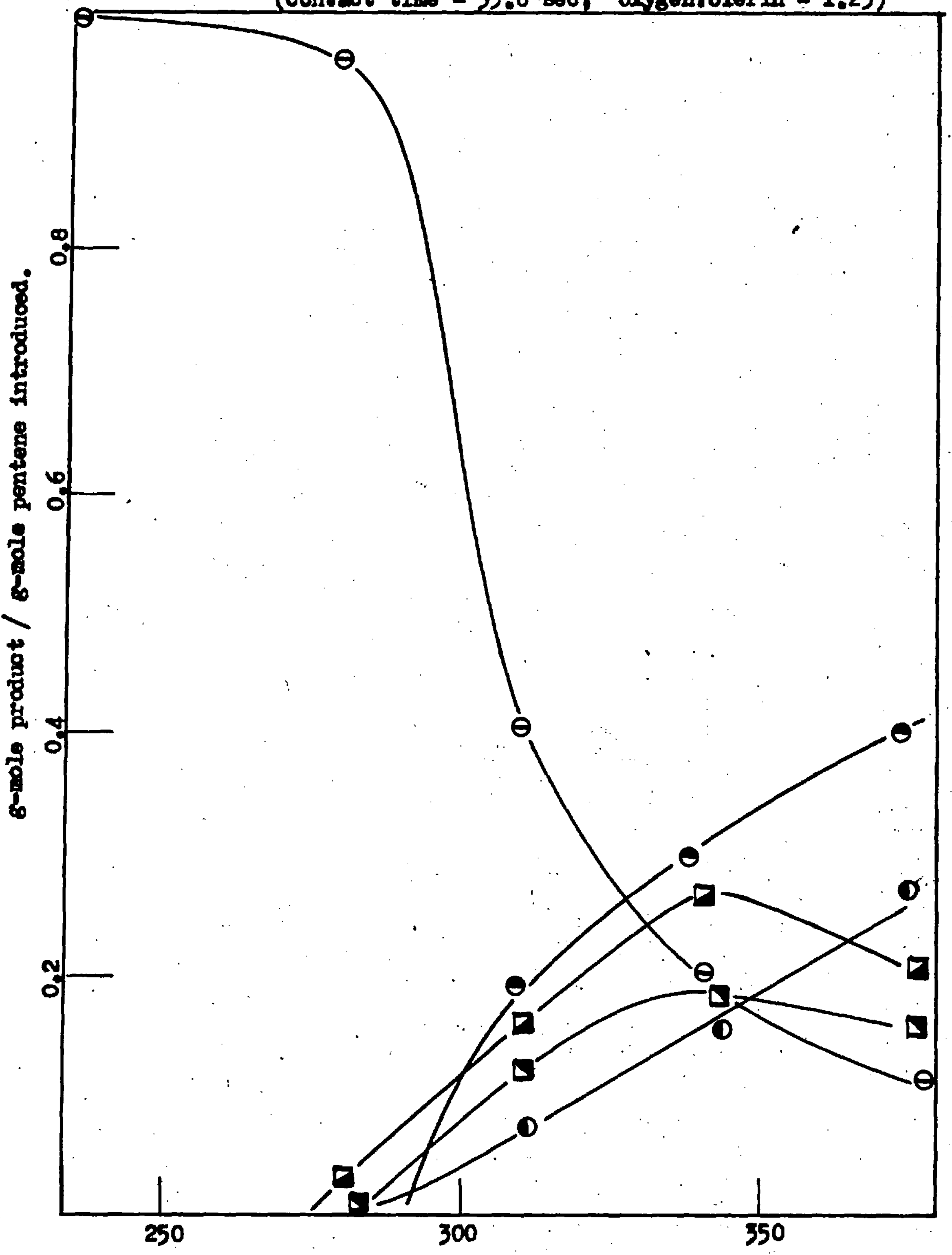


TABLE III. 3. THE OXIDATION OF 3-METHYL BUT-1-ENE ON AN 'OLD' VANADIUM PENTOXIDE CATALYST.

(Oxygen:olefin = 1.25; contact time = 33.6 sec; temperature = 300°C.)

PRODUCTS	g-mole product/g. mole pentene introduced
ethylene	traces
propylene	traces
3-methyl but-1-ene + 2-methyl but-1-ene	0.640
2-methyl but-2-ene	0.069
C_{10} hydrocarbons	0.018
acetaldehyde	0.027
acetone	0.040
methyl ethyl ketone	0.010
methyl isopropyl ketone	0.003
isobutene oxide	traces
2,3-epoxy-2-methylbutane	0.005

C. THE CARBON BALANCE FOR THE HETEROGENEOUS CATALYTIC OXIDATIONS.

The carbon balances for the heterogeneous catalytic oxidation of pent-2-ene (Table III. 4. and III. 5.) and 2-methyl but-2-ene (Table III. 6.) were calculated at various contact times and reactant ratios at 300°C. Similar calculations were also carried out for 2-methyl but-2-ene at 250°C. (Table III. 7.). In all cases the carbon balance approaches 100% except under combinations of high contact times and high oxygen availability under which conditions further oxidation of products to oxides of carbon doubtless explains the deficiency.

TABLE III. 4. CARBON BALANCE: PENT-2-ENE ON A "NEW" CATALYST.

Carbon input 1.02 x 10^{-3} g-atoms/minute

oxygen:olefin = 1.25; temperature = 300°C.

contact time (sec)	15.0	33.6	60.0
Carbon output (% of carbon input)			
pent-2-ene	94.2	53.0	41.7
acetaldehyde	2.8	19.9	9.2
acetone	0.4	2.2	3.7
propionaldehyde	1.1	7.5	4.5
C_2 hydrocarbons	1.5	9.0	10.4
C_3 hydrocarbons	0.5	2.0	3.2
C_4 hydrocarbons	0.3	0.7	1.5
C_5 epoxide	0.5	7.7	7.6
TOTAL	101	102	83

TABLE III. 5. CARBON BALANCE: PENT-2-ENE ON AN "OLD" CATALYST.

Carbon input: 1.02 x 10^{-3} g-atoms/minute.

oxygen:olefin = 1.25. temperature = 300°C.

contact time	15.0	33.6	60.0
Carbon output (% of carbon input)			
pent-2-ene	84.0	21.0	7.8
acetaldehyde	3.6	19.2	8.9
propionaldehyde	1.2	7.2	4.0
acetone	0.4	1.6	3.3
methyl alcohol		1.2	21.0
crotonaldehyde		0.3	1.4
butanone		2.2	2.8
sec butyl alcohol		0.8	1.4
C_5 epoxide	0.33	5.2	1.7
C_4 epoxides	0.16	0.2	0.4
C_3 oxide		0.6	0.9
C_2 oxide		2.0	2.9
ethyl alcohol		0.2	2.3
C_5 ketones		6.4	6.6
C_4 hydrocarbons	0.3	0.6	0.8
C_3 hydrocarbons	0.7	1.8	3.0
C_2 hydrocarbons	1.3	8.8	9.1
CO_2	7.1	9.4	13.9
acids + anhydrides	0.1	12.8	16.4
TOTAL	97	100	106

TABLE III. 6. CARBON BALANCE: 2-METHYL BUT-2-ENE AT 300°C.

Carbon input: 9.7 x 10^{-4} g-atoms/minute.

oxygen:olefin	1.25	1.25*	1.25	0	0.25	0.75	1.25*	2.0
contact time (sec)	15	33.6	60	33.6	33.6	33.6	33.6	33.6
Carbon output (% of carbon input)								
2-Me-but-2-ene	51.3	14.7	5.6	67	60	36	15.7	2.4
2-Me-but-1-ene	6.0	5.0	2.7	19	12.7	7.3	4.3	2.0
C_{10} hydrocarbons	6.7	6.6	6.0	16	13.3	9.2	6.7	2.0
C_2 hydrocarbons	0.7	1.2	1.8		0.23	0.8	1.5	1.3
C_3 hydrocarbons	0.4	0.9	0.8		0.13	0.4	0.5	0.1
acetaldehyde	7.0	17.4	28.0		2.7	10.2	17.3	7.5
acetone	12.2	22.0	27.2		4.4	13.0	17.6	7.0
CO_2	3.4	6.5	10.0		1.5	4.1	6.3	9.1
C_5 epoxide	7.3	16.0	14.0		6.8	12.7	13.3	3.7
C_5 ketone	5.4	3.5	2.3		1.4	3.7	6.7	0.7
n-butyraldhyde	0.3	0.9	1.7		0.3	0.6	1.9	0.5
butanone	0.5	0.5				0.9	0.5	
TOTAL	101	95	100	102	103	99	92	37

*From two different series of runs.

TABLE III. 7. CARBON BALANCE: 2-METHYL-BUT-2-ENE AT 250°C.

Carbon input: 9.7×10^{-4} g-atoms/minute

oxygen:olefin	1.25	1.25	1.25	0.0	0.5	1.5	2.5
Contact time (sec)	20	60	90	30	30	30	30
Carbon output (% of carbon input							
2-Me-but-2-ene	64.0	57.0	49.5	72.2	64.0	60.3	58.6
2-Me-but-1-ene	18.2	18.8	13.4	18.8	18.5	18.3	18.3
C_{10} hydrocarbons	8.0	10.6	9.2	9.0	9.0	9.0	9.0
acetaldehyde	0.8	2.5	6.9		0.7	1.8	2.0
acetone	3.8	6.9	11.8		3.8	4.5	6.3
C_5 epoxide	5.0	5.3	5.6		2.4	3.3	5.6
C_5 ketone	2.6	3.3	3.0		1.7	2.6	2.3
n-butyraldehyde		0.4	0.5				
butanone			0.2				
TOTAL	102	105	100	100	100	100	102

D. AUXILIARY STUDIES ON THE SUPPORT AND ON THE CATALYST.

1. Catalyst.

Further work was carried out in order to study in more detail the changes in activity and selectivity which take place during the use of pumice-supported vanadium pentoxide as a catalyst for the oxidation of pentenes. These changes are particularly marked when pent-2-ene is used as fuel. In order to attempt to relate these changes with the physicochemical properties of the catalyst itself, pent-2-ene was allowed to pass through a bed of initially fresh catalyst (8-10 mesh (B.S.)) at 300°C., with a contact time of 33.6 sec. and an oxygen:olefin ratio of 1.25 and the effluent gases were periodically analysed. The extents of consumption of the fuel and of formation of major oxygenated products were taken as a measure of the activity of the catalyst. These quantities (expressed as g-mole/g-mole pentene introduced) were plotted against the "age" of the catalyst (Fig. III.16.). In the first sixty minutes of the life of a new catalyst the rate of consumption of pent-2-ene falls at first and then gradually increases until ca. 260 min. have elapsed. At this point there follows a sharp and sudden increase in pentene consumption, accompanied by a simultaneous increase in the amounts of the products already present and the appearance of several new products. These changes are indicative of a sudden increase in the activity and decrease in the selectivity of the catalyst. In the life period of 310-500 min. the rate of consumption of pentene is high and constant. After 500 min. the consumption of the fuel falls very sharply suggesting a sudden lowering of activity. The concentrations of the main products, acetaldehyde and propionaldehyde, decrease simultaneously, and it is clear that the catalyst is deactivated at this stage. Small samples of the catalyst at various stages of its activity were removed and their surface areas were determined by the B.E.T. gas adsorption method (Section II. E. 1.). The results, shown in Table III. 8. and Fig. III. 16. indicate the existence of a well-defined relationship between surface area and catalytic activity.

Samples of the surface of the catalyst were removed by abrasion at various stages and were subjected to analysis by X-ray crystallography (Section II. E. 2.). The resulting diffractions (by the Guinier method) are shown in Fig. III. 17. The diffraction patterns obtained by the Debye-Scherrer method show analagous features. Analysis of these patterns by comparison with known line spectra has enabled the phases present to be identified.

The active "new" catalyst consisted of pure vanadium pentoxide, which was identified by comparison with the reference pattern of this compound (103).

A catalyst in which the specificity change has just occurred consisted of a mixture of sodium vanadyl vanadate ($Na_2O.V_2O_4.5V_2O_5$) and a small amount of vanadium pentoxide.

The diffraction pattern of the former compound has been described by Hood and Sorum (104).

The "old" deactivated catalyst gave a pattern identical with that of the catalyst removed just after the specificity change.

The pumice-support gave a pattern consisting of two very broad bands only and can be said to be amorphous and as such would not have contributed to the line patterns from the catalysts.

2. Supports.

Pumice was used as support for vanadium pentoxide, throughout the studies described in the above sections. In view of the results of the measurements of surface area, however, it was considered important to investigate the effect of surface area alone on catalytic activity. Alumina was therefore also used as a support for vanadium pentoxide and the resulting catalyst was employed in studies of the oxidation of pent-2-ene. The consumption of pent-2-ene and the formation of products at 300°C. are shown in Table III. 9. The pumice-supported catalyst which has a surface area 100 times lower than that of alumina-supported catalyst, nevertheless has a higher activity per unit volume although the selectivity in each case is similar.

FIG. III.16. THE OXIDATION OF PENT-2-ENE:
AGEING OF THE CATALYST.
(contact time = 33.6 sec; oxygen:olefin = 1.25; temperature = 300°

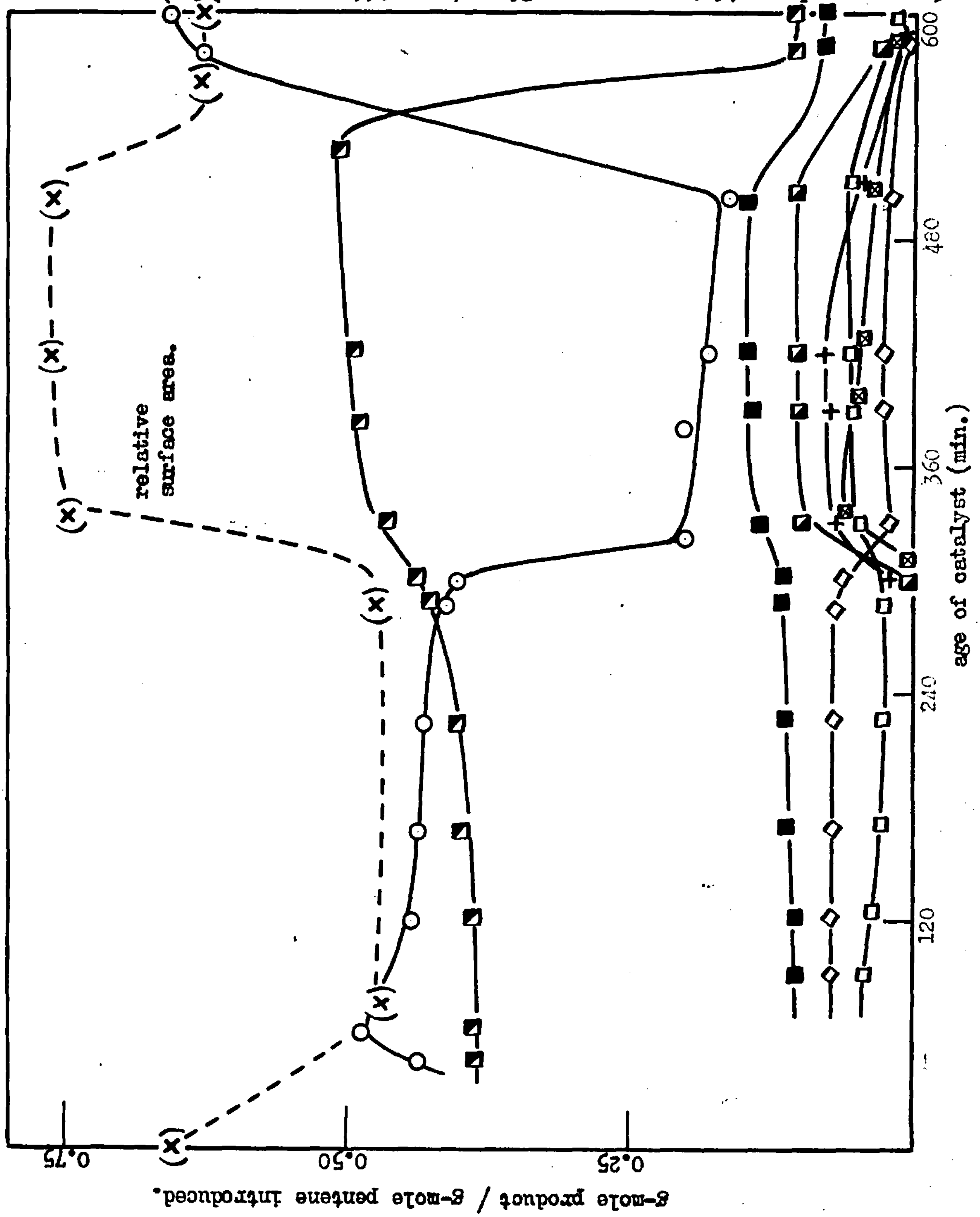


TABLE III. 8. THE SURFACE AREAS OF VANADIUM PENTOXIDE/PUMICE CATALYSTS: THE EFFECT OF CATALYST AGE.

catalyst age (minutes)	0	70	290	324	420	495	555	610
colour of catalyst	A	B	B	C	D	D	E	E
Area (m^2/g) (degassed at 350°C.)	0.66	0.46	0.47	0.75	0.76	0.77	0.64	0.64
Area (m^2/g) (degassed at 500°C.)	0.76	0.76	0.76	0.75	0.75	0.77	0.76	0.77

A = yellow-grey.

B = dark brown-grey.

C = dark blue-grey.

D = very dark blue-grey.

E = dark grey.

Key to FIG. III. 17.

THE DIFFRACTION OF X-RAYS BY VANADIUM PENTOXIDE-ON-PUMICE CATALYSTS WHICH HAVE BEEN USED IN STUDIES OF THE OXIDATION OF PENT-2-ENE.

(Guinier camera; Cu target; 50kV; 10mA)

A. Active unspecific catalyst (used for 6 hours)

B. Deactivated old catalyst (used for 13 hours)

C. Active specific new catalyst (used for 0-4½ hours)

D. Pumice support.

(The exposure to X-rays of films A, B and C was 360 minutes and of film D was 480 minutes).

FIG. III.17.

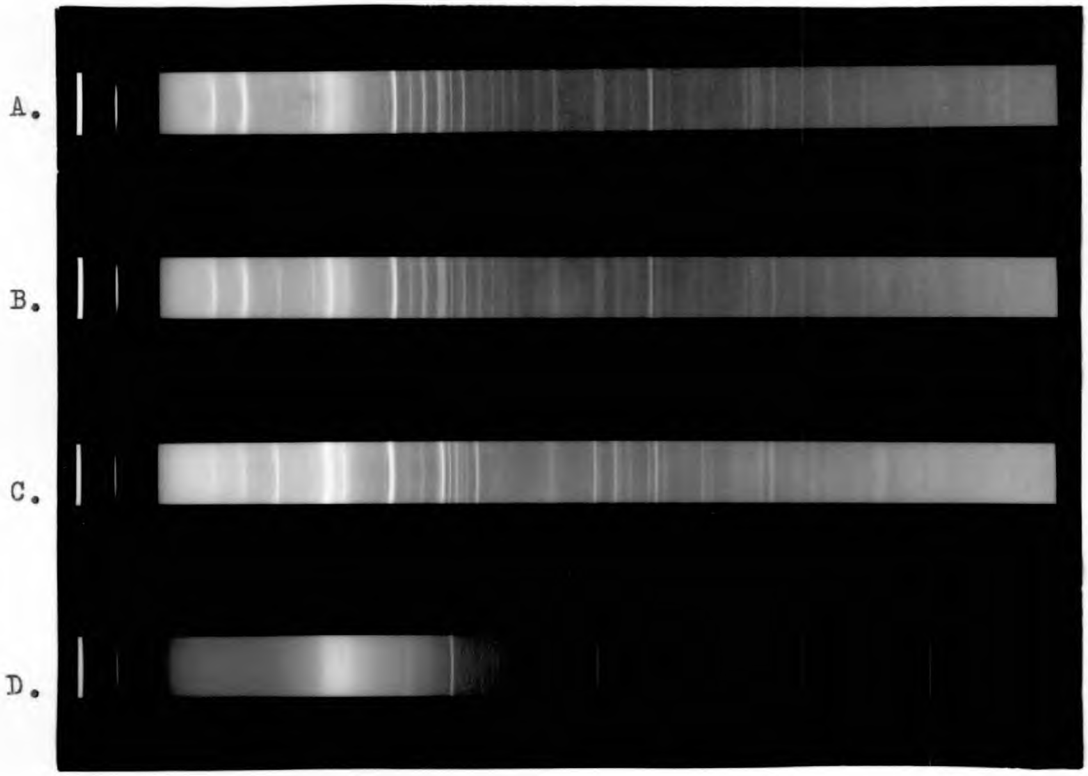


TABLE III. 9. THE OXIDATION OF PENT-2-ENE ON A VANADIUM PENTOXIDE CATALYST SUPPORTED ON ALUMINA.

(Oxygen:olefin = 1.25; Contact time = 33.6 sec.; Temperature = 300°C.)

PRODUCTS	g-mole product/g-mole pentene introduced
ethylene	0.066
propylene	0.012
pent-1-ene	0.006
pent-2-ene	0.308
C_{10} hydrocarbons	0.06
acetladehyde	0.021
acetone	0.045
isobutene oxide	traces
2,3-epoxypentane	0.003
methyl alcohol	0.105

(plus large quantities of carbon dioxide)

E. THE ISOMERIZATION OF PENTENES.

The isomerization of each of the pentenes, both during the homogeneous reaction and on a "new" pumice-supported vanadium pentoxide catalyst, was studied at 300°C. with a contact time of 33.6 sec. These investigations were of course, carried out in the absence of oxygen to avoid oxidation of the olefin. A given mixture of pentene and nitrogen was passed through the reaction vessel, which contained either the catalyst or glass balls of approximately the same mesh size as the catalyst. The emerging gases were analysed and it was possible from a knowledge of the purity of the pentene to calculate the extent of isomerization taking place in each case. The results (Tables III. 10. and III. 11.) show that the pentenes undergo extensive isomerization under the conditions of temperature and contact time used for oxidation studies. Isomerization, therefore, is mechanistically important with reference to this mechanism of oxidation. It is noteworthy that minute amounts of the mormal oxygenated products of oxidation were detected during studies of the isomerization over the catalyst despite the apparent absence of oxygen in the reactant gases.

TABLE III. 10. ISOMERIZATION OF PENTENES ON VANADIUM PENTOXIDE ON PUMICE.

temperature = $300^{\circ}C$; contact time = 33.6 sec.

Feedstock of pentene and nitrogen, no oxygen.

	INPUT					
	P1	P2t	P2c	2MB1	3MB1	2MB2*
OUTPUT						
pent-1-ene	91.0	1.6	1.6	0.1		
pent-2-ene (t)	2.6	58.8	58.8	0.1		
pent-2-ene (c)	2.7	37.9	37.9	0.1		0.8
2-Me-but-1-ene	0.1			57.3	1.8	19.6
3-Me-but-1-ene	2.2	0.1	0.1	0.3	91.2	
2-Me-but-2-ene	1.9			40.3	4.1	66.5
C_{10} hydrocarbons		1.6	1.6	2.4	2.9	13.3
TOTAL	100.3	100.0	100.0	100.3	100.0	100.2

*92% 2-Methyl but-2-ene + 8% 2-methyl but-1-ene

Key.	
P1	pent-1-ene
P2t	*trans*-pent-2-ene
P2c	*cis*-pent-2-ene
2MB1	2-methyl but-1-ene
3MB1	3-methyl but-1-ene
2MB2	2-methyl but-2-ene

TABLE III. 11. ISOMERIZATION OF PENTENES IN THE GAS PHASE.

temperature = 300°C.: contact time (reactor filled with glass balls) = 33.6 sec.

Feedstock of pentene and nitrogen, no oxygen.

	INPUT					
	P1	P2t	P2c	2MB1	3MB1	2MB2*
OUTPUT						
pent-1-ene	97.5	0.1	0.1	0.2		
pent-2-ene (t)		57.3	57.3			0.1
pent-2-ene (c)		42.2	42.2			0.2
2-Me-but-1-ene	0.1			99.4		9.0
3-Me-but-1-ene	2.3	0.3	0.3	0.4	100.0	0.6
2-Me-but-2-ene						90.0
C_{10} hydrocarbons						0.2
TOTAL	99.8	99.8	99.8	100.0	100.0	100.0
T_{c10}(°C.)	269	306	306	302	280	245
T_{c50}(°C.)	285	322	322	350	305	270

*92% 2-Me-but-2-ene + 8% 2-Me-but-1-ene

T_{c10} and T_{c50}: the temperatures at which 10% and 50% respectively of the fuel are consumed during gas phase oxidation (oxygen:olefin = 1.25; contact time = 33.6 sec.

Key.	P1	pent-1-ene	2MB1	2-methyl but-1-ene
	P2t	*trans*-pent-2-ene	3MB1	3-methyl but-1-ene
	P2c	*cis*-pent-2-ene	2MB2	2-methyl but-2-ene

SECTION IV.

DISCUSSION.

SECTION IV.

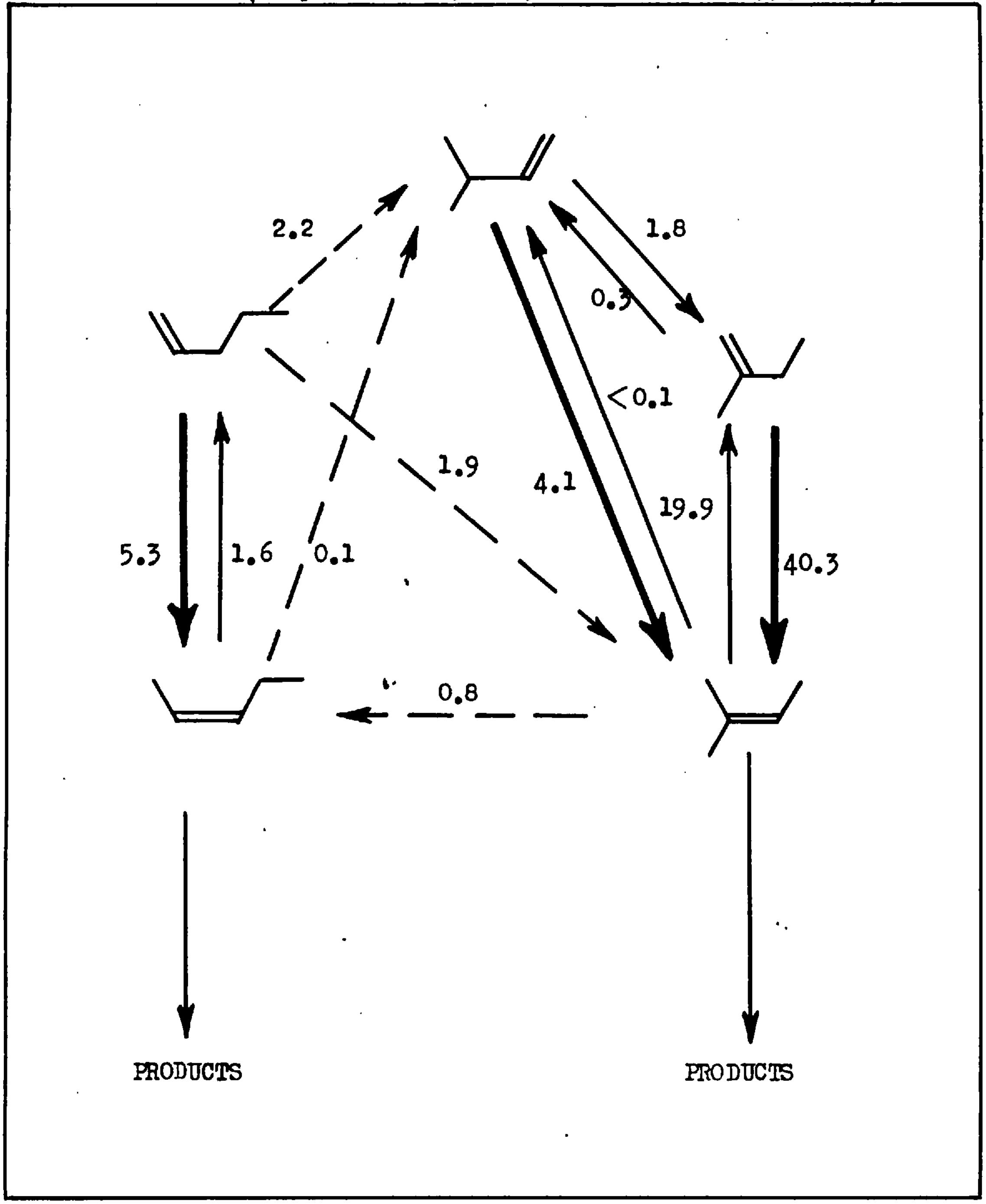
A. THE NATURE OF THE PRODUCTS FORMED.

The main products formed during the heterogeneous catalytic oxidation of pent-2-ene on pumice-supported vanadium pentoxide are acetaldehyde, propionaldehyde, pentanones, 2,3-epoxy pentane, ethylene and propylene. Similarly in the case of 2-methyl but-2-ene under analogous conditions the products obtained are acetaldehyde, acetone, methyl isopropyl ketone, 2,3,epoxy-2-methylbutane, ethylene and propylene. These products are characteristic of addition of oxygen at the double bond of each pentene and, in the case of carbonyl scission compounds, subsequent rupture at the position of the double bond. The other member of the straight-chain series of C_5 acyclic olefins, pent-1-ene, gives substantially the same products as pent-2-ene and similarly the other branched-chain pentenes, 2-methyl but-1-ene and 3-methyl but-1-ene, give the same products as 2-methyl but-2-ene.

This strongly suggests that isomerization of terminal pentenes into non-terminal pentenes of the straight chain and branched-chain series respectively occurs before oxidation takes place. Furthermore, the products obtained by the uncatalysed gaseous oxidation, under similar experimental conditions, of the five acyclic pentenes are characteristic of the carbon skeleton of the initial hydrocarbon indicating that such isomerization is a surface phenomenon.

The isomerization studies which were carried out on the catalyst show that in fact this is so. The double bond tends to shift from the terminal to the non-terminal position. This pattern of isomerization is shown in Fig. IV. 1. On the basis of these isomerization studies, coupled with the pattern of products formed during heterogeneous catalytic oxidation of pentenes, it can be concluded that isomerization precedes oxidation and that the heterogeneous catalytic oxidation of pent-2-ene and 2-methyl but-2-ene are representative of the oxidation of straight- and branched-chain pentenes respectively. This conclusion is further supported by consideration of the temperatures (T_{c50}) at which 50% of each pentene is consumed under similar conditions of gas-phase reaction. In the case of branched-chain pentenes it is significant that 2-methyl but-2-ene has a lower T_{c50} than do its isomers, 2-methyl but-1-ene and 3-methyl but-1-ene. This argument does not hold, however for the two straight-chain pentenes, since pent-1-ene has a lower T_{c50} than does pent-2-ene. In this case, therefore, the effects on the product spectrum of the predominant direction of isomerization and of the relative ease of oxidation of the two isomers are opposed. As the products are largely characteristic of pent-2-ene, the former effect predominates. It is noteworthy however, that the oxidation of straight-chain pentenes is less easily described in terms of pent-2-ene alone than is that of branched chain pentenes in terms of 2-methyl but-2-ene alone. To summarise, it is established that isomerization of terminal pentenes to non-terminal pentenes precedes oxidation

FIG. IV.1 THE PATTERN OF ISOMERIZATION OF PENTENES ON AN "OLD" VANADIUM PENTOXIDE CATALYST.
(temperature = 300°C, contact time = 33.6 sec)



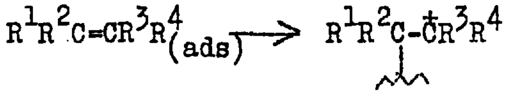
on the catalyst.

B. A PROPOSED MECHANISM FOR THE HETEROGENEOUS CATALYTIC OXIDATION OF BRANCHED-CHAIN PENTENES.

It has already been pointed out that the catalytic oxidation of 2-methyl but-2-ene may be considered as representing the oxidation of all the C_5 acyclic branched-chain pentenes.

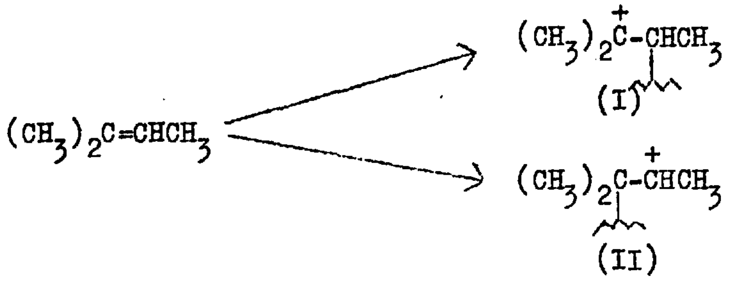
The adsorption of the reactant species as surface-bonded ions on catalytic oxide surface has been widely proposed (Section I. C. 2.). Olefins are known to exist on the surface of the oxide catalysts as cations, adsorption being followed by electron transfer to the surface.

In the present system, it is proposed that the adsorption of pentenes on vanadium pentoxide takes place by the donation of an electron from the opened π-bond to the vanadium pentoxide catalyst, the olefin itself thereby forming cations or positively charged π-bonded complexes adsorbed on the surface:



$$R^1R^2C{=}CR^3R^4{}_{(ads)} \longrightarrow R^1R^2C{-}\overset{+}{C}R^3R^4$$

In the case of 2-methyl but-2-ene, such an electron transfer process would result in the formation of two kinds of surface-bonded cations;



$$(CH_3)_2C{=}CHCH_3 \longrightarrow (CH_3)_2\overset{+}{C}{-}CHCH_3 \quad (I)$$

$$(CH_3)_2C{=}CHCH_3 \longrightarrow (CH_3)_2C{-}\overset{+}{C}HCH_3 \quad (II)$$

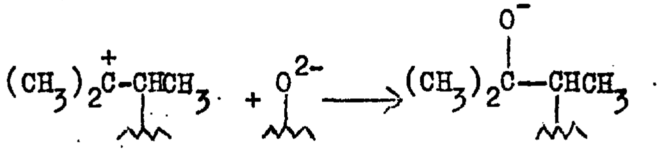
Similarly the existence of negatively charged species resulting from the adsorption of oxygen on the catalyst surface is widely proposed (Section I. C. 2.), and involves the donation of electrons from the catalyst to oxygen.

$$O_{2(ads)} + e \longrightarrow O_2^{2-},\ O^-,\ O_2^-$$

The products of heterogeneous catalytic oxidation of 2-methyl but-2-ene (Section III. B.) can be accounted for by the interaction of the cationic species (I and II) with each of the oxygen anions.

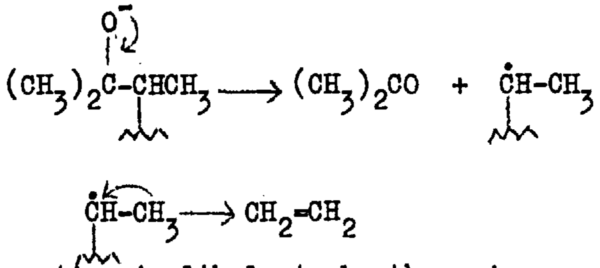
1. <u>The interactions of olefinic cations with oxygen anions</u>.

(a) <u>Cation I with O^{2-}</u>.



$$(CH_3)_2\overset{+}{C}\text{-}CHCH_3 + O^{2-} \longrightarrow (CH_3)_2\overset{O^-}{C}\text{—}CHCH_3$$

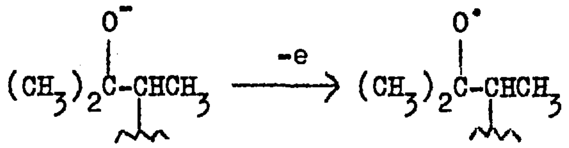
This adsorbed anion will readily undergo electron transfer and scission of a C-C bond to give acetone and ethylene:



$$(CH_3)_2\overset{O^-}{C}\text{-}CHCH_3 \longrightarrow (CH_3)_2CO + \dot{C}H\text{-}CH_3$$

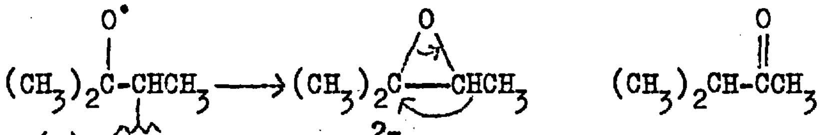
$$\dot{C}H\text{-}CH_3 \longrightarrow CH_2{=}CH_2$$

This reaction is likely to be the major route by which the interaction of I and O^{2-} leads to products. However, if the adsorbed anion has lost an electron to the surface before the C-C bond breaks, an adsorbed alkoxy radical will result:



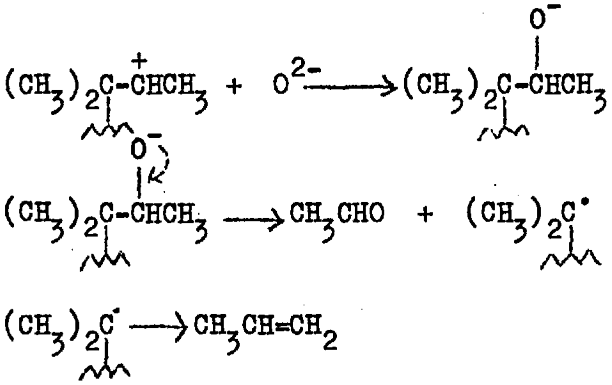
$$(CH_3)_2\overset{O^-}{\underset{\sim}{C}}\text{-}CHCH_3 \xrightarrow{-e} (CH_3)_2\overset{O^\bullet}{\underset{\sim}{C}}\text{-}CHCH_3$$

which can rearrange to give 2,3-epoxy-2-methylbutane which may in turn isomerize to methyl isopropyl ketone:



(b) Cation II with O^{2-}

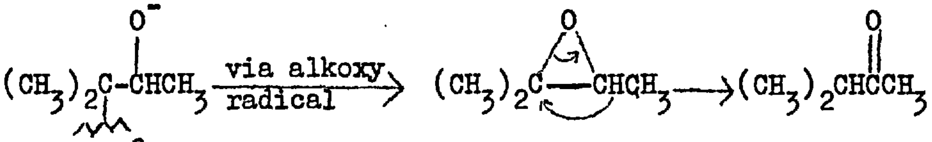
Similarly, the interaction of cation II with O^{2-} results in the formation of acetaldehyde and propylene, together with smaller quantities of, 2,3-epoxy-2-methylbutane and methyl isopropyl ketone:



$$(CH_3)_2\underset{\sim}{C}\text{-}\overset{+}{C}HCH_3 + O^{2-} \longrightarrow (CH_3)_2\underset{\sim}{C}\text{-}\overset{O^-}{C}HCH_3$$

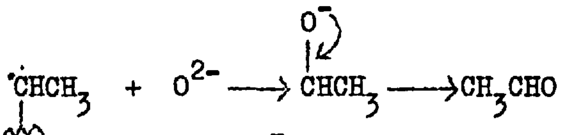
$$(CH_3)_2\underset{\sim}{C}\text{-}\overset{O^-}{C}HCH_3 \longrightarrow CH_3CHO + (CH_3)_2\underset{\sim}{C}^\bullet$$

$$(CH_3)_2\underset{\sim}{C}^\bullet \longrightarrow CH_3CH{=}CH_2$$



As O^{2-} will be the predominant anionic species present, being the anion of the V_2O_5 lattice itself, reactions of this kind are likely to be responsible for the formation of the major products. This conclusion is consistent with the mechanism suggested. The plausibility of the above reactions is strongly supported by the fact that, in the absence of oxygen, the fuel will react with the oxygen in the vanadium pentoxide lattice to form small quantities of acetone, acetaldehyde and lower olefins; under these conditions, O^{2-} will almost certainly be the active oxidant.

The concentrations of acetaldehyde and acetone produced are not equimolar, in marked contrast to the gas-phase reaction (49)(50). This can be accounted for by the predominant formation of one of the cationic species. The formation of cation I would appear to be favoured for steric reasons and would lead to amounts of acetone larger than those of acetaldehyde. This is consistent with the results obtained at 250°C., but at 300°C. acetaldehyde predominates particularly at higher contact times and oxygen:olefin ratios, possibily due to its additional formation by further oxidation of lower olefins or their surface precursors:

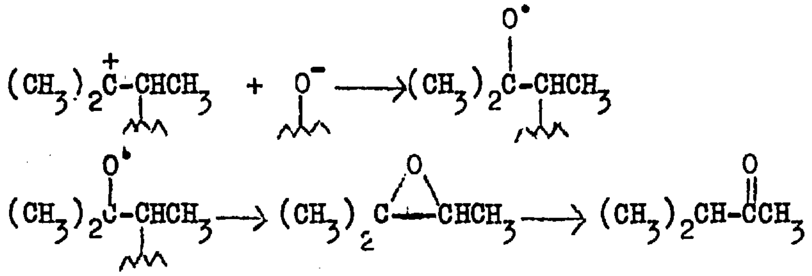
e.g. 

$$\dot{C}HCH_3 + O^{2-} \longrightarrow \overset{O^-}{\overset{|}{C}}HCH_3 \longrightarrow CH_3CHO$$

(c) Cation I with O^-.

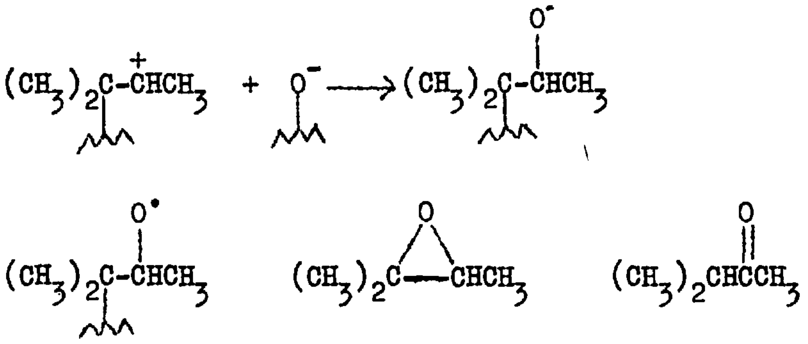
Although the common surface anion is O^{2-}, the formation of this species from molecular oxygen involves the rupture of the O=O bond and the transfer of four electrons per oxygen molecule. It is unlikely that this will be a one-stage process, hence the reaction of the olefin cation with the intermediate anion O^- and with O_2^- needs to be considered.

The interaction of cation I with O^- gives an adsorbed alkoxy radical (instead of the corresponding anion formed from O^{2-}) and will produce 2,3-epoxy-2-methylbutane: and, by isomerization, methyl isopropyl ketone:



(d) Cation II with O^-.

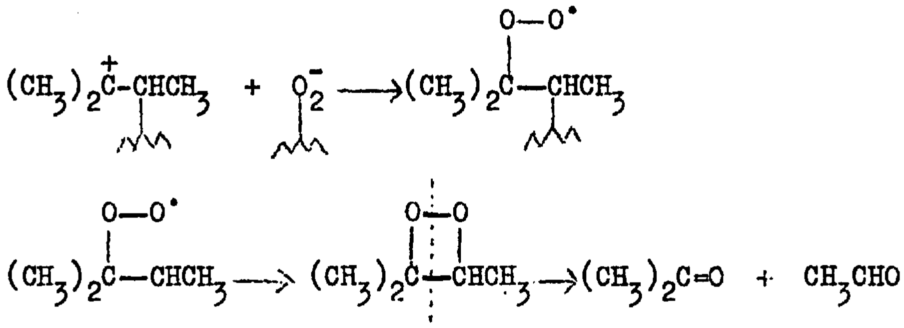
The products obtained will in this case be the same as those resulting from interaction (c):



(e) Cation I with O_2^-.

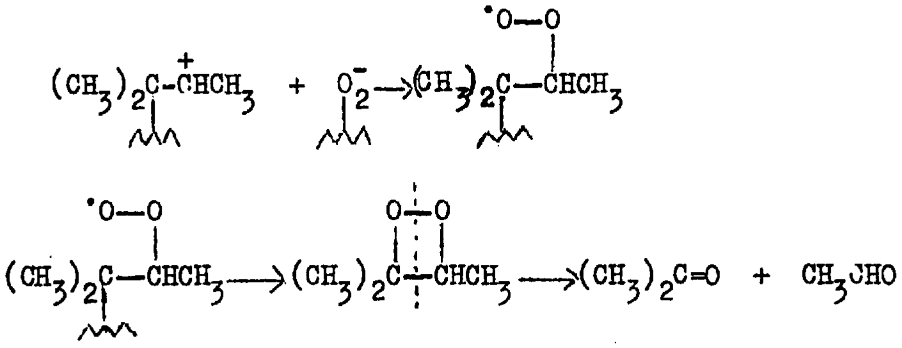
The diatomic anion O_2^- is less well substantiated as a surface species than O^- and O^{2-} (61) but its possible reactions will be considered for the sake of completeness.

The interaction of olefin cations with O_2^- would probably give equimolar quantities of acetaldehyde and acetone, via the intermediate formation of a surface-bound alkylperoxy radical.



(f) <u>Cation II with O_2^-</u>.

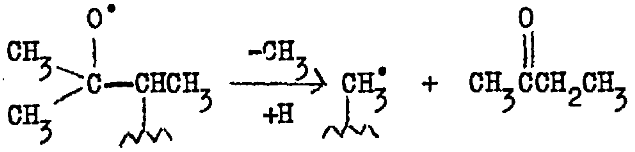
Similarly the interaction of this anionic oxygen species O_2^- with cation II would again result in the formation of acetaldehyde and acetone.



It is unlikely, however, that these reactions compete significantly with the reactions of the well-substantiated species O^{2-} in forming acetone and acetaldehyde.

(g) <u>Other reactions</u>.

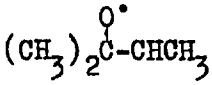
The other products, which are formed during heterogeneous catalytic oxidation of 2-methyl but-2-ene but are not accounted for by the interactions discussed above, are dimeric (C_{10}) hydrocarbons, methyl ethyl ketone and n-butyraldehyde. 2-Methyl but-1-ene can be formed by the surface isomerization of 2-methyl but-2-ene (Fig. IV. 1.); C_{10} hydrocarbons are obviously products of dimerization (again probably on the surface), while methyl ethyl ketone and n-butyraldyhyde can be formed by the interaction of O^{2-} with small amounts of 2-methyl but-1-ene and pent-1-ene respectively, formed by isomerization. Alternatively, methyl ethyl ketone could arise by loss of a methyl group in the adsorbed tert-alkoxy radical.



$$(CH_3)_2C(O^\bullet)\text{—}CHCH_3 \xrightarrow[+H]{-CH_3} CH_3^\bullet + CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$$

The type of mechanism postulated is therefore generally consistent with the results obtained. Further support for the mechanism is provided by the measured effects of temperature, contact time and oxygen:olefin ratio, which cause variations in the formation of the products. It would be expected that these variables would affect the formation of the different oxygen anions and the effects to be expected theoretically should correlate with the experimental results obtained.

2. The effect of temperature.

Many workers (60)(61) have visualized the presence of O_2^- and O^- at lower temperatures and of O^{2-} only at higher temperatures due to substantial activation energy for the transfer of the second electron to the uninegative oxygen ion. In the present studies, products like 2,3-epoxy-2-methylbutane and methyl isopropyl ketone rise to maximum concentrations at somewhat lower temperatures than acetone, acetaldehyde, ethylene and propylene. If the former products are formed from the interaction of olefinic cations with O^-, it can be safely concluded that the results are consistent with the proposed mechanism. Conversion of the adsorbed alkoxy radical  $(CH_3)_2\overset{O^\bullet}{\overset{|}{C}}-CHCH_3$ to 2,3-epoxy-2-methylbutane does not involve either electron transfer or atomic migration and this process is thus likely to require only a small activation energy which may be available at low temperatures. On the other hand the concentrations of acetone and acetaldehyde which are formed by the interactions of olefinic cations and O^{2-}, pass through maxima at higher temperatures. Moreover the amounts of acetone and acetaldehyde formed are greater than those of 2,3-epoxy-2-methylbutane and methyl isopropyl ketone and this quantitative difference increases with temperature, in agreement with the postulation that O^{2-} predominates at high temperatures.

3. The effect of contact time.

Methyl isopropyl ketone and 2,3-epoxy-2-methylbutane reach their maximum concentrations at a lower contact time than do acetaldehyde and acetone. This is in qualitative agreement with the probable effect of increasing contact time on the stability of surface species i.e. facilitation of electron transfer processes. This would mean that O^- would be the predominant species at lower and O^{2-} at higher contact times.

At very high contact times, however the concentrations of the major products formed at 300°C. begin to fall off rapidly despite the small increase in pentene consumption. This can be ascribed to the occurrence of side reactions converting, by further oxidation, the primary products to carbon dioxide, the concentration of which continues to rise even at very high contact times.

4. The effect of oxygen:olefin ratio.

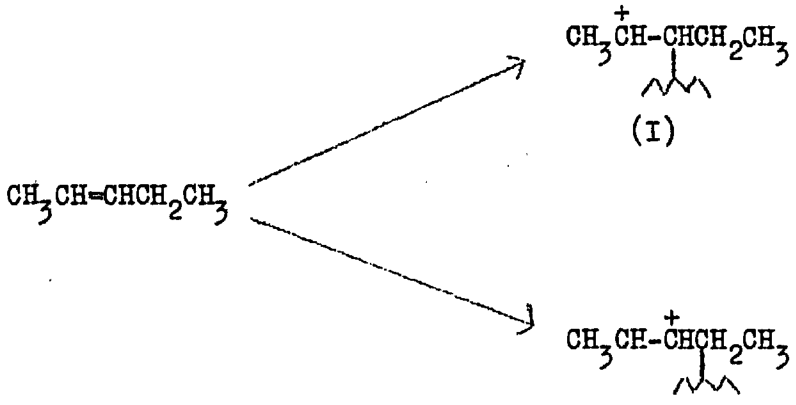
In terms of surface species, it would be expected that an increase in oxygen:olefin ratio would result in an increase in the amount of O^- relative to O^{2-}, with a consequent increase in the production of methyl isopropyl ketone and 2,3-epoxy-2-methylbutane relative to that of acetaldehyde and acetone. Any such effect is, however, complicated by two factors. Firstly, by the same argument, the less important oxygen species, O_2^-, would become significant at higher oxygen: olefin ratios, giving acetaldehyde and acetone and, secondly, the fuel-rich mixtures the absolute rate of formation of products increases with the oxygen:olefin ratio due to the greater absolute concentration of all oxygen species. Despite these drawbacks, the study of changes in this particular variable serves to show clearly that the isomerization of pentenes is independent of oxygen:olefin ratio. At 250°C., for example, where there is least likelihood of further reaction of the 2-methyl but-1-ene formed, the amount of this isomer remains constant with changing reactant ratio.

C. A PROPOSED MECHANISM FOR THE HETEROGENEOUS CATALYTIC OXIDATION OF STRAIGHT-CHAIN PENTENES.

The heterogeneous catalytic oxidation of pent-2-ene is representative of the oxidation of straight-chain pentenes, as is clear from the isomerization and oxidation studies of pent-1-ene.

The major products of the heterogeneous catalytic oxidation of pent-2-ene over pumice-supported vanadium pentoxide are acetaldehyde, propionaldehyde, acetone, 2,3-epoxy-pentane, ethylene, propylene and pent-1-ene. These products are formed when the catalyst is "new" and other products, the most abundant of which are methyl alcohol, methyl ethyl ketone, pentanones and crotonaldehyde, are produced when the catalyst becomes "old". The products formed on both "new" and "old" catalysts can be largely be accounted for on the basis of mechanisms similar to those proposed for the oxidation of 2-methyl but-2-ene.

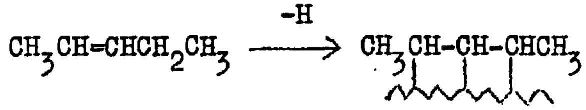
The anionic species present during the oxidation of pent-2-ene would be the same as those in the case of 2-methyl but-2-ene i.e. O^{2-}, O^{-}, and O_2^{-}, in this probable order of importance. The cationic species likely to be formed by the electron transfer processes already discussed are as follows:-



$CH_3CH{=}CHCH_2CH_3 \rightarrow CH_3\overset{+}{C}H-CHCH_2CH_3$ (I)

$CH_3CH{=}CHCH_2CH_3 \rightarrow CH_3CH-\overset{+}{C}HCH_2CH_3$ (II)

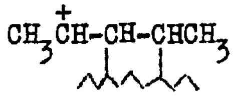
In the case of this olefin, however, the presence of secondary hydrogen in the allylic position (the C-H bond strength of which is considerably less than that of primary hydrogen) may lead to the formation also of a tribonded surface complex by abstraction of this hydrogen.



$CH_3CH{=}CHCH_2CH_3 \xrightarrow{-H} CH_3CH-CH-CHCH_3$

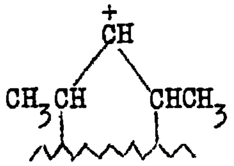
(III)

The corresponding cations, resulting from electron transfer,



$CH_3\overset{+}{C}H-CH-CHCH_3$

and

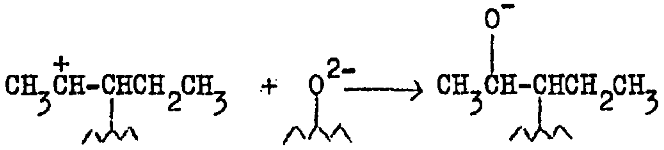


(IV) (V).

must therefore be considered, and the first of these (IV) is likely to predominate.

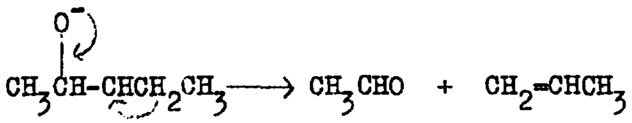
1. The interactions of olefinic cations with oxygen anions.

(a) Cation I with O^{2-}



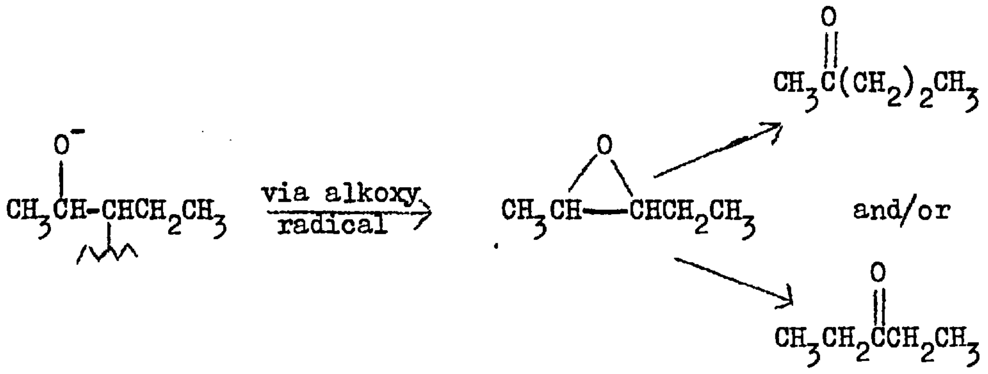
$$CH_3\overset{+}{C}H\text{-}CHCH_2CH_3 + O^{2-} \longrightarrow CH_3\overset{O^-}{C}H\text{-}CHCH_2CH_3$$

This adsorbed alkoxy anion undergoes electron transfer and scission of the adjacent C-C bond to give acetaldehyde and propylene.



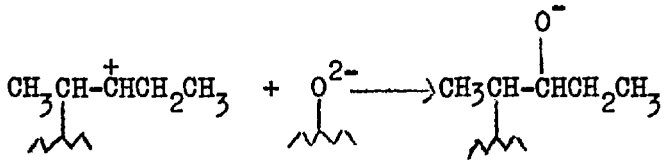
$$CH_3\overset{O^-}{C}H\text{-}CHCH_2CH_3 \longrightarrow CH_3CHO + CH_2{=}CHCH_3$$

The adsorbed alkoxy anion may also produce 2,3-epoxypentane and straight-chain pentanones by donation of electrons from the electron-rich oxygen atom to the electron-deficient carbon atom.



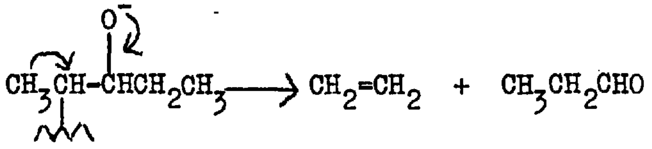
(b) Cation II with O^{2-}

The interaction of cation II with the oxygen anion, O^{2-}, can account similarly for the formation of propionaldehyde, pentanones, 2,3-epoxy-pentane and ethylene:



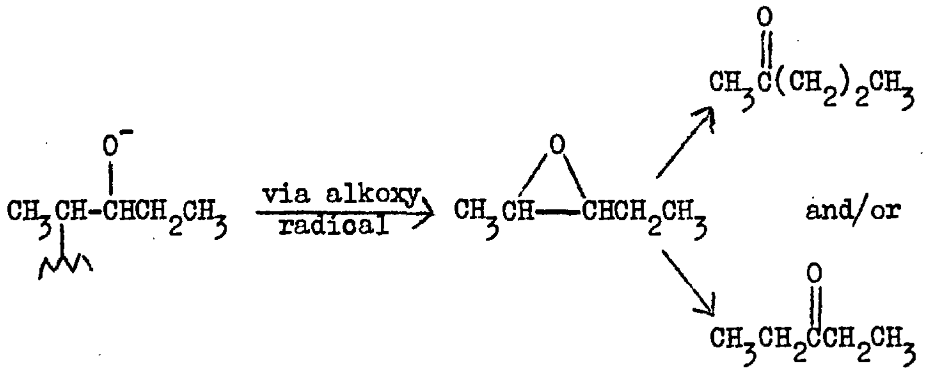
$$CH_3CH\text{-}\overset{+}{C}HCH_2CH_3 + O^{2-} \longrightarrow CH_3CH\text{-}\overset{O^-}{\overset{|}{C}}HCH_2CH_3$$

Electron transfer with C-C scission and H-shift leads to the formation of propionaldehyde and ethylene,



$$CH_3CH\text{-}\overset{O^-}{\overset{|}{C}}HCH_2CH_3 \longrightarrow CH_2{=}CH_2 + CH_3CH_2CHO$$

while electron transfer from the oxygen atom to the electron-deficient carbon atom leads to production of 2,3-epoxy-pentane which may subsequently isomerize giving pentanones.

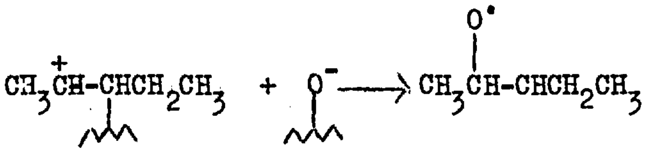


$$CH_3CH\text{-}\overset{O^-}{\overset{|}{C}}HCH_2CH_3 \xrightarrow[\text{radical}]{\text{via alkoxy}} CH_3\underset{\ }{CH}\overset{O}{\text{—}}CHCH_2CH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}(CH_2)_2CH_3 \text{ and/or } CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$$

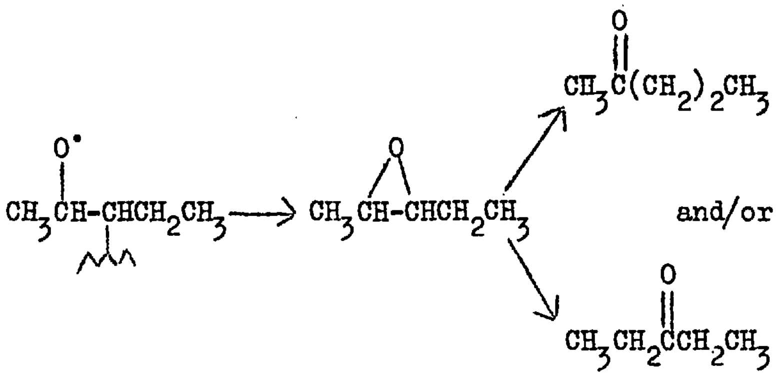
As in the case of 2-methyl but-2-ene, the amounts of acetaldehyde and propionaldehyde formed are not equivalent, acetaldehyde predominating. As less propylene is formed than ethylene, however, this may be of little significance. It may well be therefore that considerable amounts of acetaldehyde result from multibonded cationic species such as IV (Section IV. C. 1.).

(c) Cation I with O^-.

The adsorbed alkoxy radical is formed by the interaction of cation I with O^- and will rearrange to give 2,3-epoxy-pentane which subsequently isomerizes, giving pentanones.



$$CH_3\overset{+}{C}H\text{-}CHCH_2CH_3 + O^- \longrightarrow CH_3\overset{O^{\cdot}}{\overset{|}{C}}H\text{-}CHCH_2CH_3$$



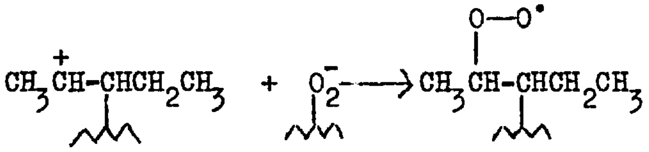
$$CH_3\overset{O^{\cdot}}{\overset{|}{C}}H\text{-}CHCH_2CH_3 \longrightarrow CH_3CH\text{-}CHCH_2CH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}(CH_2)_2CH_3 \text{ and/or } CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$$

(d) Cation II with O^-.

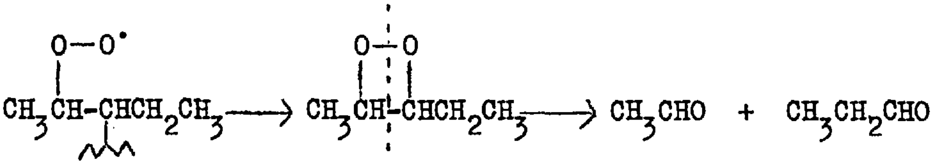
This interaction will produce the same products as (c).

(e) Cation I with O_2^-.

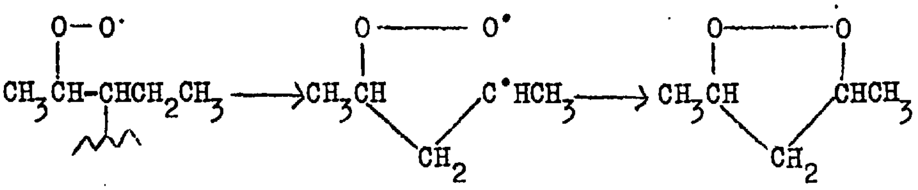
The interaction of cation I with O_2^- would result in the formation of cyclic peroxides which would undergo fission giving acetaldehyde and propionaldehyde:



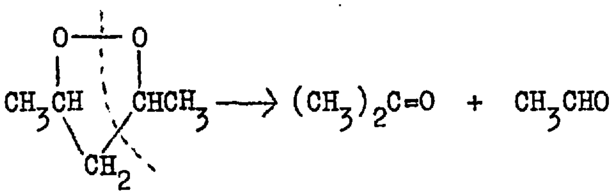
$$CH_3\overset{+}{C}H\text{-}CHCH_2CH_3 + O_2^- \longrightarrow CH_3\overset{O-O^{\cdot}}{\overset{|}{C}}H\text{-}CHCH_2CH_3$$



On the other hand, the intermediate peroxy radical may undergo rearrangement by shifting of the hydrogen atom of the reactive α-methylene group to the adjacent carbon atom to give a peroxy-biradical capable of forming a cyclic peroxide with a five-membered ring (105).



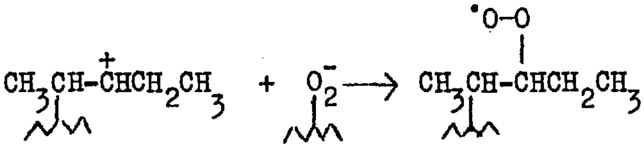
Fission of this particular cyclic peroxide followed by hydrogen transfer would result in the formation of acetone and acetaldehyde:

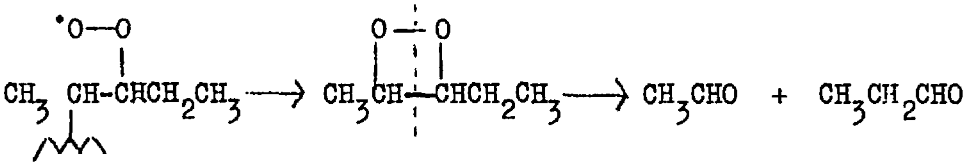


thus explaining the small quantities of acetone produced.

(f) Cation II with O_2^-.

Acetaldehyde and propionaldehyde are produced by a mechanism analogous to that in (e).



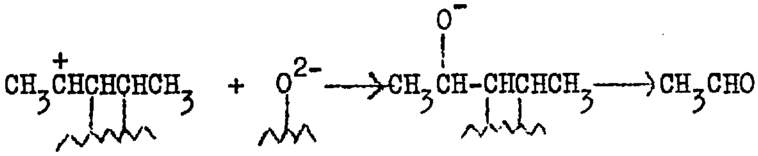


In this case, ring expansion is less likely as the reactive α-methylene group is not adjacent to the electron deficient carbon atom.

According to the work of Stone (61) the anionic species, O_2^-, is of relatively little importance and the very small amounts of acetone found in the products is consistent with this conclusion.

(g) The reactions of cation IV.

The reaction of cation IV with the predominant anion, O^{2-}, produces acetaldehyde by a mechanism similar to those already discussed:

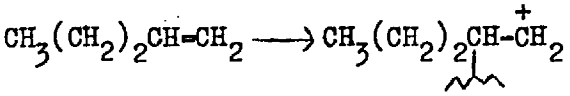


$$CH_3\overset{+}{C}HCHCHCH_3 + O^{2-} \longrightarrow CH_3\overset{O^-}{CH}-CHCHCH_3 \longrightarrow CH_3CHO$$

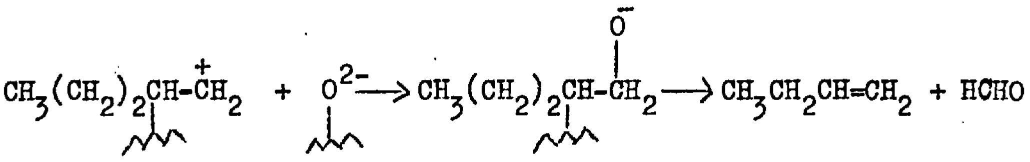
The formation of this species, which is formally analogous to α-H abstraction in the gaseous oxidation or autoxidation of olefins, may thus afford an explanation of the formation of quantities of acetaldehyde which are large compared with those of any other product.

(h) Other reactions.

The major products obtained from the heterogeneous catalytic oxidation of pent-2-ene can be accounted for on the basis of the above mechanism. Other minor products are formed, however, which require further explanation. These are pent-1-ene, ethylene oxide, propylene oxide, 2,3-epoxy-butane, isobutene oxide, crotonaldehyde, n-butyraldehyde, methyl alcohol, ethyl alcohol, sec-butyl alcohol, maleic acid . and crotonic acid. Pent-1-ene is the isomerization product of pent-2-ene and n-butyraldehyde is a subsequent major oxidation product of pent-1-ene. Ethylene oxide and propylene oxide can be accounted for by the further oxidation of the ethylene and propylene produced by their reactions with O^{2-}. The formation of 2,3-epoxy-butane and isobutene oxide is difficult to explain. It is possible that these products arise from degradation reactions consequent upon the oxidation of pent-1-ene.



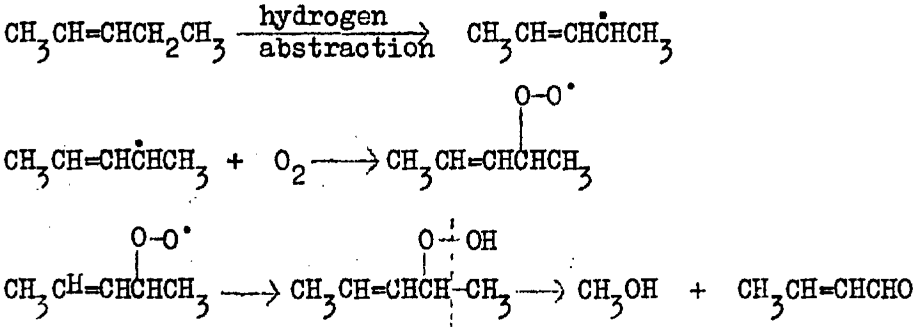
$$CH_3(CH_2)_2CH{=}CH_2 \longrightarrow CH_3(CH_2)_2CH-\overset{+}{C}H_2$$



$$CH_3(CH_2)_2CH-\overset{+}{C}H_2 + O^{2-} \longrightarrow CH_3(CH_2)_2CH-\overset{O^-}{\overset{|}{C}}H_2 \longrightarrow CH_3CH_2CH{=}CH_2 + HCHO$$

The but-1-ene formed can isomerize to but-2-ene and isobutene and the olefins may then be oxidized to their respective epoxy compounds.

A very important product which is formed when the catalyst is unselective is methyl alcohol , the production of which is accompanied by the formation of a small amount of crotonaldehyde. A possible mechanism for the formation of these two compounds is hydrogen abstraction at the reactive α-methylene group followed by addition of molecular oxygen to give a radical, $RO_2^{\bullet}$; this last species, as a result of further hydrogen abstraction, produces hydroperoxide which undergoes isomerization with simultaneous C-C bond fission to give methyl alcohol, and crotonaldehyde.

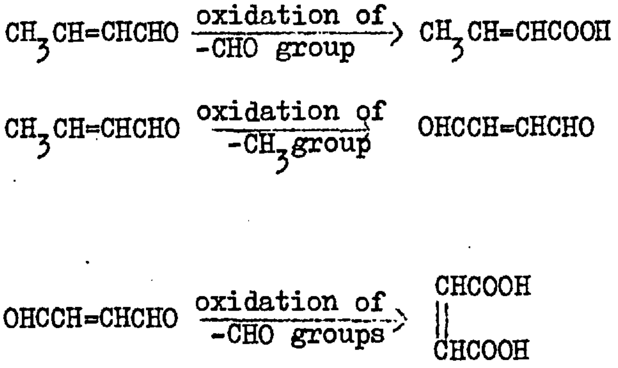


$$CH_3CH{=}CHCH_2CH_3 \xrightarrow[\text{abstraction}]{\text{hydrogen}} CH_3CH{=}CH\dot{C}HCH_3$$

$$CH_3CH{=}CH\dot{C}HCH_3 + O_2 \longrightarrow CH_3CH{=}CH\overset{O-O^{\bullet}}{\overset{|}{C}}HCH_3$$

$$CH_3CH{=}CH\overset{O-O^{\bullet}}{\overset{|}{C}}HCH_3 \longrightarrow CH_3CH{=}CH\overset{O\,\vdots\,OH}{\overset{|}{C}}H\vdots CH_3 \longrightarrow CH_3OH + CH_3CH{=}CHCHO$$

This is not consistent, however, with the small amount of crotonaldehyde formed as compared to the quantity of methyl alcohol formed, unless it is assumed that crotonaldehyde, being the more susceptible to further oxidation, is readily consumed. This would then account for the formation of crotonic acid and maleic acid.



$$CH_3CH{=}CHCHO \xrightarrow[\text{-CHO group}]{\text{oxidation of}} CH_3CH{=}CHCOOH$$

$$CH_3CH{=}CHCHO \xrightarrow[\text{-}CH_3\text{group}]{\text{oxidation of}} OHCCH{=}CHCHO$$

$$OHCCH{=}CHCHO \xrightarrow[\text{-CHO groups}]{\text{oxidation of}} \begin{array}{l} CHCOOH \\ \| \\ CHCOOH \end{array}$$

Any attempt at explanation of the minor products formed on "old", unselective catalysts is, however, of necessity highly speculative.

D. CHANGES IN THE ACTIVITY AND SELECTIVITY OF THE CATALYST.

The changes occurring in the activity and the selectivity of pumice-supported vanadium pentoxide during its use as an oxidation catalyst are best discussed with reference to pent-2-ene as it is with this compound that the changes are most marked. The studies of catalyst properties carried out help to establish a relationship between activity and selectivity and the surface area and phase composition (i.e. crystallographic structure) of the catalyst.

It is clear (Section III. D., Fig. III. 9) that vanadium pentoxide undergoes a series of sudden changes of activity and selectivity during its life as an active catalyst. The activity is low and the selectivity is high in the first 300 minutes of its use, which is characterised by formation of small amounts of a few specific products. After this time, the activity suddenly increases considerably and the selectivity drops sharply as is shown by the formation of an increased number of products in greater total quantity and an increase in the consumption of pentene.

1. Changes in surface area, activity and selectivity.

An increase in surface area results generally in increased catalytic activity and although this relationship is not without exception (Section I. B. 2.), it was found in the present studies that surface area is definitely closely and systematically related to the activity and the selectivity of the catalyst.

(a) Increase in activity after 300 minutes.

After the first 300 minutes of the life of the catalyst i.e. simultaneously with the increase in activity and the decrease in selectivity, an increase in surface area occurs from 0.46 m^2/g to 0.76 m^2/g. Increases of surface area exactly similar to those observed after 300 minutes' use of the catalyst are caused by heating a fresh unused sample of the catalyst to 500°C. This indicates that a structural change may take place both on heating to 500°C. and on using the oxide as a catalyst at ca. 300°C. and this could well account for the observed variations in activity and selectivity.

(b) Decrease in activity after 490 minutes.

After ca. 490 minutes, the activity drops very sharply and this is accompanied by a sharp decrease in surface area from 0.76 m^2/g to 0.64 m^2/g. It is likely that this involves no structural change but merely surface 'blocking', e.g. by carbon deposition.

(c) Pseudo-changes in activity in the first 60 minutes.

In the first 60 minutes the catalyst appears to suffer a small decrease in activity but no change in surface area was detected. It is likely that this change in activity is not real since during the very early life of the catalyst pentene is being adsorbed. Indeed, as the surface becomes progressively saturated, greater amounts of pentene can be found in the effluent gases. Therefore, this change in pentene 'consumption' is not due to oxidation but to adsorption thus providing a psuedo-change in activity. Furthermore the lack of quantitative variation in the formation of the products during this period is indicative of the above conclusion.

2. Changes in phase composition, activity and selectivity.

(a) Increase in activity after 300 minutes.

X-ray diffraction studies on samples of catalyst possessing different activities and selectivities, i.e. taken from the reaction vessel after different 'lifetimes', show that a phase change accompanies the sharp transition in catalyst properties observed after ca. 300 minutes. Analysis of the Debye-Scherrer results establishes that the fresh unused catalyst is pure vanadium pentoxide (V_2O_5), so that the phase changes taking place must be due to the use of the catalyst.

A new phase is formed when the catalyst undergoes the sharp transition to the more highly active state. X-ray analysis has shown that this is sodium vanadyl vanadate ($Na_2O.V_2O_4.5V_2O_5$). This compound contains vanadium in two valency states, V^{4+} and V^{5+}, and it is evident that its formation must involve reduction of part of the V^{5+} originally present followed by reaction of the resulting V^{4+} with the sodium ions present in the support (pumice). As this change of activity is so sudden, it is likely that the interaction to form sodium vanadyl vanadate takes place when the V^{4+} reaches a critical concentration.

This critical concentration may well be slightly less than 1/6th of the total vanadium, as suggested by the formula $Na_2O.V_2O_4.5V_2O_5$ and by the fact that some (but only little) of the V_2O_5 remains as a separate phase. The fact that sodium vanadyl vanadate is known to be formed by interaction of sodium with vanadium pentoxide at temperatures greater than 400°C. (106), supports strongly the view that the surface area increases at the point of activity increase in a manner analogous to the changes noted on heating to 500°C.

The present work establishes, then, that the change of activity is due to the formation of V^{4+} and its subsequent reaction with the support; this reaction is attended by an increase of surface are a quantitatively consistent with that attendant upon the same reaction under other conditions. The formation of V^{4+} from V^{5+} leaves the catalyst with a 'positive hole'.

$$V^{5+} \longrightarrow V^{4+} + \oplus$$

Accepted theories of the catalytic activity of semiconductors predict that this would cause a change in the activity of the catalyst as is indeed found experimentally. In its 'unselective' state, the catalyst is analogous to a mixed oxide catalyst (Section I. B. 2.).

(b) Decrease in activity after 490 minutes.

The decrease in activity of the catalyst after 490 minutes is not accompanied by any change in phase composition, as shown by the X-ray diffraction studies. It would appear that the decreases in activity and in surface area result from physical pore-blockage, perhaps by carbon, although it is difficult to see why such a phenomenon should occur quite suddenly.

(c) The relationship of phase changes to general catalytic oxidation mechanism.

The postulated mechanism to explain the changes in the activity and the selectivity of the catalyst is consistent with the work of Mars and Van Krevelen (32) and Simard et. al.(35). The former authors have postulated that the mechanism of oxidation of hydrocarbons on vanadium pentoxide can be written:

$$\text{RH} + \text{oxidized catalyst} \xrightarrow{(1)} \text{products} + \text{reduced catalyst}$$

$$\text{Reduced catalyst} + O_2 \xrightarrow{(2)} \text{oxidized catalyst}$$

In this scheme, step (2) is rate-determining (due perhaps to the high activation energy involved in transferring the second electron to O^- to form O^{2-}) so that the process is not kinetically cyclic and the catalyst becomes reduced with resulting changes in activity and selectivity.

These changes can be represented in terms of electron-transfer processes, on the basis of which mechanisms have been postulated (in the present studies) to explain the reaction products formed during heterogeneous catalytic oxidation of pentenes. The fresh unused catalyst may conveniently be represented by the formula $V^{5+}_{2n}O^{2-}_{5n}$. In terms of electron-transfer, step (1) in the mechanism of Mars and Van Krevelen may be written as:

$$mRH + mO^{2-} \xrightarrow{(1)} \text{products} + 2me$$

$$(\text{i.e. } mRH + V^{5+}_{2n}O^{2-}_{5n} \longrightarrow \text{products} + V^{5+}_{2n}O^{2-}_{5n-m} + 2me)$$

and step (2) as:

$$2me + \frac{m}{2}O_2 + V^{5+}_{2n}O^{2-}_{5n-m} \xrightarrow{(2)} V^{5+}_{2n}O^{2-}_{5n}$$

If, as stated by Mars and Van Krevelen, step (2) is rate-determining a catalyst results containing some $V^{5+}_{2n}O^{2-}_{5n-m}$, i.e. a partially reduced catalyst. When the average value of m is equal to n/6, the composition of the catalyst corresponds to $V_2O_4 \cdot 5V_2O_5$ and it is likely that this is the critical condition of reduction which causes reaction with the sodium present in the support to give sodium vanadyl vanadate.

E. CONCLUSIONS.

The present studies have established the patterns of isomerization and of oxidation of the five isomeric pentenes on pumice-supported vanadium pentoxide. Elucidation of the accompanying changes in the structure of the catalyst itself has shown that the general mechanism of Mars and Van Krevelen operates during the oxidations and that, in this scheme, re-oxidation of the reduced catalyst is the rate-determining step. Gradual reduction of the catalyst results and eventually causes a phase change which produces a catalyst of higher activity but lower selectivity. This general mechanism may be written in terms of electron-transfer reactions in which electrons are transferred from the adsorbed olefin to the catalyst and from the catalyst to the adsorbed oxygen. Suggestions have been made as to the nature of the surface species so formed, based upon established theories of chemisorption on semiconducting oxides and of their modes of interaction. These theories, although somewhat speculative in detail, enable probable routes to the major products to be elucidated. Further studies of this nature may eventually enable the formation of a particular product to be associated unambiguously with interactions involving given surface species.

REFERENCES.

REFERENCES.

1. Hüttig, G.F.,
   J. Chim. Phys. (1939), 36, 84.

2. Elovich, S. Ya., Zhabrova, G.M., Margolis, L.Ya, and Roginskii, S.Z.,
   Compt. Rend. Acad. Sci., U.R.S.S., (1946), 52, 421.

3. Magneli A and Blomberg, B.
   Acta. Chem. Scand. (1951), 5, 585.

4. Hedvall, J.A.,
   Kinetika i Kataliz (1962), 3, 3.

5. Dickey, F.H.,
   Proc. Natl. Acad. Sci. (1949), 35, 227.

6. Forestier, H.,
   Proc. International Symposium Reactivity of Solids, Gøtenberg (1953), 181.

7. Boudart, M.,
   Chem. Eng. Progr. (1961), 57, 33.

8. Roginskii, S. and Schulz, E.,
   Z. Phys. Chem., (1928), 138, 21.

9. Langmuir, I.,
   J. Amer. Chem. Soc., (1916), 38, 2221.

10. Lennard-Jones, J.E.,
    Trans. Faraday Soc., (1932), 28, 333.

11. Taylor, H.S.,
    Proc. Roy. Soc., (1925), A.108, 105.

12. Fensham, P.J.,
    Quart. Rev., (1957), 11, 227.

13. Wilson, A.H.,
    "Semiconductors and Metals; an Introduction to the Electron Theory of Metals". Cambridge University Press, London, (1939).

14. Raschig, F.,
    Z. Angew Chem. (1906), 19, 1748.

15. Sosnovsky, H.M.C.,
    J. Chem. Phys., (1955), 23, 1486.

16. Wagner, J.B., and Gwathmey, A.T.,
J. Amer. Chem. Soc., (1954), 76, 390.

17. Owen, J.R.,
J. Amer. Chem. Soc., (1947), 69, 2559.

18. Thiele, E.W.,
Ind. Eng. Chem., (1939), 31, 916.

19. De. Boer, J.H.,
Proc. of the First International Congress on Catalysis,
Philadelphia, Pennsylvania (1956), 138.

20. Dowden, D.A.,
J. Chem. Soc., (1950), 242.

21. Rideal, E.K.,
Chem. Ind., (1943), 62, 335.

22. Balandin, A.A.,
Usp. Khim., (1962), 31, 589.

23. Burk, R.E.,
J. Phys. Chem., (1926), 30, 1134.

24. Balandin, A.A.,
Z. physik. Chem., (1929), B2, 289.

25. Trapnell, B.M.W.,
"Advances in Catalysis", Academic Press, New York,
(1951), 3, 17.

26. Maxted, E.B. and Evans, H.C.,
J. Chem. Soc., (1937), 1004.

27. Maxted, E.B.,
Symposium, "Catalysis: Problems of Theoretical and
Metallurgical Research"., Inostr. Lit., Moscow, (1960),100

28. Wolkenstein, Th.,
"Advances in Catalysis", Academic Press, New York (1960),
12, 259.

29. Parravano, G.,
J. Amer. Chem. Soc., (1953), 75, 1448.

30. Karpacheva, S.M., and Rozen, A.M.,
Zh. Fiz. Khim. (1953), 27, 146.

31. Ushakova, V.P., Korneichuk, G.P., Roiter, V.A. and Zhigailo, Ya. V.,
Ukrain. Khim. Zhur. (1957), 23, 191.

32. Mars, J. and Van Krevelen, D.W.,
Chem. Eng. Sci. (1954), 3 (Special Supplement), 41.

33. Maxted, E.B.,
Chem. Ind. (1928), 47, 101.

34. Byström, A., Wilhelmi, K. and Brotzen, O.,
Acta. Chem., Scand (1950), 4, 1126.

35. Simard, G.L., Steger, J.F., Arnott, R.J. and Siegel, L.A.,
Ind. Eng. Chem. (1955), 47, 1424.

36. Clark, H. and Berets, D.J.,
Proc. of the First International Congress on Catalysis, Philadelphia, Pennsylvania (1956), 204.

37. Korneichuk, G.P., Ushakova, V.P. and Skorbilina, T.G.,
Kinetika i Kataliz (1961), 2, 931.

38. Ioffe, I.I., Ezhkova, Z.I. and Lyubarskii, A.G.,
Kinetika i Kataliz (1962), 3, 194.

39. Tipper, C.F.H.,
Quart. Rev. (1957), 11, 313.

40. Mulcahy, M.F.R. and Ridge, M.J.,
Trans. Faraday Soc., (1953), 49, 906, 1297.

41. Batten, J.J., and Ridge, M.J.,
Australian J. Chem. (1955), 8, 370.

42. Mullen, J.D., and Skirrow, G.,
Proc. Roy. Soc., (1958), A.244, 312.

43. Blundell, A., and Skirrow, G.,
Proc. Roy. Soc., (1958), A.244, 331.

44. Skirrow, G.,
Proc. Roy. Soc., (1958), A.244, 345.

45. Lenher, S.,
J. Amer. Chem. Soc., (1931), 53, 3737, 3752.

46. Lenher, S.,
J. Amer. Chem. Soc., (1932), 54, 1830.

47. Lucas, H. J., Prater, A.N. and Morris, R.E.,
J. Amer. Chem. Soc., (1935), 57, 723.

48. Dobrinskaya, A.A. and Neiman, M.B.,
Dokl. Akad. Nauk, S.S.S.R., (1947), 58, 1919.

49. Cullis, C. F., Fish, A. and Turner, D.W.,
Proc. Roy. Soc., (1961), A.262, 318.

50. Cullis, C.F., Fish, A. and Turner, D.W.,
Proc. Roy. Soc., (1962), A.267, ~~1962~~. 433

51. Miller, A.A., Mayo, F.R. and Russel, G.A.,
J. Amer. Chem. Soc., (1956), 78, 1017 - 41.
J. Amer. Chem. Soc., (1958), 80, 2465 - 2507.

52. Margolis, L.Ya.,
Advances in Catalysis, Academic Press, New York, (1963), 14, 444.

53. Benton, A.F. and Drake, L.C.,
J. Amer. Chem., Soc., (1934), 56, 255.

54. Armbruster, M.H.,
J. Amer. Chem. Soc., (1942), 64, 2545.

55. Twigg, G.H.,
Proc. Roy. Soc., (1946), A.188, 92-123.

56. Garner, W.E., Stone, F.S. and Tiley, P.F.,
Proc. Roy. Soc., (1952), A.211, 472.

57. Keier, N.P. and Kitzeva, L.N.,
Dokl. Akad. Nauk., S.S.S.R., (1957), 117, 259.

58. Weisz, P.B.,
J. Chem. Phys., (1953), 21, 1531.

59. Wagner, C.,
J. Chem. Phys., (1950), 18, 69.

60. Nagarjunan, T.S. and Calvert, T.S.,
J. Phys. Chem., (1964), 68, 17.

61. Barry, J.I. and Stone, F.S.,
Proc. Roy. Soc., (1960), A.255, 124.

62. Steacie, E.W.R. and Stovel, H.V.,
J. Chem. Phys., (1934), 2, 581.

63. Twigg, G.H. and Rideal, E.K.,
Proc. Roy. Soc., (1939), A.171, 55.

64. Garner, W.E. and Veal, J.F.,
J. Chem. Soc., (1935), 1487.

65. Thomas, W.J.,
Trans. Faraday Soc., (1957), 53, 1124.

66. Wolkenstein, Th.,
"Advances in Catalysis", Academic Press, New York (1960), 12, 189.

67. Margolis, L.Ya.,
Izvest. Akad. Nauk., S.S.S.R., Otdel Khim. Nauk. (1958), 1175.

68. Rooney, J. J. and Webb, G.,
J. Catalysis (1964), 3, 488.

69. Ioffe, I. I. and Margolis, L.Ya.,
Proc. of the Third International Congress on Catalysis, Amsterdam, Holland, (1964).

70. McBee, E.T., Hass, H.B. and Wiseman, P. A.,
Ind. Eng. Chem., (1945), 37, 432.

71. Murray, K.E.,
Australian J. Sci. Research (1950), 3A, 433.

72. Margolis, L.Ya.,
"Advances in Catalysis", Academic Press, New York, (1963), 14, 465.

73. Milas, N.A. and Walsh, W.L.,
J. Amer. Chem. Soc., (1939), 61, 633.

74. Hadley, D.J., Hall, R.H., Heap, R. and Jacobs, D.I.H.,
J. Chem. Soc., (1954), 1416.

75. Bretton, R.H., Wan, S.U., and Dodge, B.F.,
Ind. Eng. Chem. (1952), 44, 594.

76. Sachtler, W.M.H. and DeBoer, N.H.,
Proc. of the Third International Congress on Catalysis, Amsterdam, Holland, (1964).

77. Ipatiev, V.,
Ber. (1903), 36, 2000.

78. Kyriakides, L.P.,
J. Amer. Chem. Soc., (1914), 36, 1002.

79. Hibbert, H.,
J. Amer. Chem. Soc., (1915), 37, 1753.

80. Norris, J.F., and Reuter, R.,
J. Amer. Chem. Soc., (1927), 49, 2630.

81. Bawn, C.E.H., Pennington, A.A. and Tipper, C.F.H.,
Disc. Faraday Soc., (1951), 10, 282.

82. Kuhlmann, A.G.,
Fr. Pat., (1927), 646263.

83. Milas, N.A. and Walsh, W.L.,
J. Amer. Chem. Soc., (1935), 57, 1389.

84. Foster, H.B.,
U. S. Pat., 2081272.

85. Parks, W.G. and Yula, R.W.,
Ind. Eng. Chem., (1941), 33, 891.

86. Fiegl, F.,
"Spot Tests in Organic Analysis", Elsevier Publishing
Co., Amsterdam, (1960), 369.

87. Bricker, C.E. and Johnson, H.R.,
Ind. Eng. Chem., (1945), 17, 400.

88. Fiegl, F.,
"Spot Tests in Organic Analysis", Elsevier Publishing
Co., Amsterdam, (1960), 352.

89. Jones, I.R. and Riddick, T.R.,
Anal. Chem., (1954), 26, 1035.

90. Warwicker, E.A.,
Ph.D. Thesis, University of London (1959).

91. Scott, R.P.W.,
First Symposium on Vapour Phase Chromatography,
(1956), 131.

92. Keulemans, A.I.M., Kwantes, A., and Zaal, P.,
Anal. Chim. Acta. (1955), 13, 357.

93. Brooks, V.T., and Collins, G.A.,
Chem. Ind. (1956), 921.

94. Adlard, E.R. in D. H. Desty, ed.,
"Vapour Phase Chromatography", Academic Press, New York, (1957), 98.

95. Kyryacos, G., Menapace, H.R. and Boord, C.E.,
Anal. Chem., (1959), 31, 222.

96. Tenney, H. M.,
Anal. Chem. (1958), 30, 2.

97. Farrington P.S., Pecsok, R.T., Meeker, R.L., and Olson, T.J.,
Anal. Chem., (1959), 31, 1512.

98. Pines, H. and Pillia, C.N.,
J. Amer. Chem. Soc., (1959), 81, 3629.

99. Cullis, C.F., Fish, A., Hardy, F.R.F. and Warwicker, E.A.,
Chem. Ind., (1961), 1158.

100. Smith, E.D. and Radford, R.D.,
Anal. Chem. (1961), 33, 1160.

101. Stimson, M.M. and O'Donnell, M.J.,
J. Amer. Chem. Soc., (1952), 74, 1805.

102. Romijn's Method (Standardisation of formaldehyde).
"Analytical Chemistry", 2, Quantitative, 9th edition, 622.

103. National Bureau Standards Circular.
(1958), 8, 539: A.S.T.M. Powder Diffraction Index Card 9-387.

104. Mood, H. and Sprum, H.,
Tidsskr. Kjemi, Bergvesen Met. (1943), 5, 55.

105. Fish, A.,
Quart. Rev., (1964), 18, 243.

106. Toft, R.B.,
Private Communication.