ANALYTICAL STUDIES OF OXIDANTS FOR CATALYTIC OXIDATION OF ORGANIC COMPOUNDS

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DEDICATED TO

My Parents and wife Manik

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Certified that the work incorporated in the thesis "ANALYTICAL STUDIES OF OXIDANTS FOR CATALYTIC OXIDATION OF ORGANIC COMPOUNDS" submitted by Mr. Sudhakar Shivram Ramdasi was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

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ABSTRACT

ABSTRACT

Title of the thesis: "Analytical Studies of Oxidants for Catalytic Oxidation of Organic Compounds".

The thesis is presented in three parts. The first part describes a method developed for determination of activities of sample-additive reagents used as oxidants for promoting smooth combustion of difficultly combustible compounds in organic elemental analysis. The second part relates to kinetic studies of combustion of phenanthrene using ten such oxidants and the third part gives an account of a study pertaining to catalytic vapour-phase oxidation of four aliphatic alcohols on silicon carbide supported vanadium pentoxide in a semi-microreactor.

Part 1 - A NOVEL METHOD FOR DETERMINATION OF ACTIVITY OF A SAMPLE-ADDITIVE REAGENT IN ORGANIC ELEMENTAL ANALYSIS

It has been a common experience that certain refractory compounds resist smooth combustion and yield low values in the elemental analysis. Methods reported to overcome this problem describe some modified combustion tube fillings and also the use of suitable sample-additive reagents. Although a number of such additive reagents are reported in the literature, information available to grade them according to their activities is insufficient.

Activity of oxidation catalysts for combustion of organic compounds has been studied by earlier investigators by packing a layer in a combustion tube and correlating the minimum temperature required for complete oxidation of a test-compound with the activity of the catalyst[1]. However, the activity of the same catalyst would be different when it is used as an additive reagent in a sample boat, due to its limited quantity and shorter contact time with the test-compound. Only one method for determination of activities of such additive reagents is reported, which is suitable only for combustions carried out in inert gas systems[2]. No attempts seem to have been made so far to develop a suitable method to study the relative activities of sample-additive reagents in oxygen atmosphere, which is a necessity for the conventional rapid combustion method[3].

This part of the thesis describes development of such a method based on partial oxidation of a test-compound under carefully controlled conditions using various sample-additive reagents in oxygen atmosphere. Behaviour of five structurally different organic test-compounds i.e. acetanilide, phenanthrene, 8-hydroxyquinoline, cholesterol and 1-octadecyl alcohol, has been studied under these conditions and acetanilide has been recommended as the best test-compound due to its combustion characteristics.

Physical properties of these sample-additive reagents have been studied using differential thermal analysis and thermogravimetry. These studies furnished data regarding oxygen availability which has supported the inferences drawn from the partial oxidation studies. Other parameters of these catalysts e.g. mean particle size by scanning electron microscope and surface area also have been determined. Further, the surface properties of the mixed oxides from the catalysts studied (which include some new ones) have been examined using ESCA. Thus, X-ray photoelectron spectra of these oxides have been recorded and the binding energies of electrons for the core levels 2p, 3d etc. of the metals and oxygen (1s) have been discussed in the light of high activities of these mixed oxides, which include thermal decomposition product of $AgMnO_4$, (MnO_2+Ag), (MnO_2+Cu) and (MnO_2+Co).

Part 2 - KINETIC STUDIES OF COMBUSTION OF PHENANTHRENE WITH VARIOUS SAMPLE-ADDITIVE REAGENTS

Information in the literature on the determination of rate of combustion of organic compounds on microscale using different catalysts is very scanty. The only exception is that of Večeřa *et al.*[4] who have carried out systematic study on rate of combustion with a view to developing a rapid method for the microdetermination of carbon and hydrogen.

This part describes the kinetic studies to understand the combustion behaviour of phenanthrene on microscale using ten sample-additive reagents, activities of which have been determined at higher temperatures as described in Part 1. The temperature of oxidation is reduced to 300° for a conveniently measurable rate of combustion. The rate has been studied by estimating at fixed time-intervals the carbon dioxide obtained after combustion of the oxidation products formed. The rate constants of this pseudo-first order reaction have been determined. Equations for the best straight lines for the curves showing relationship of the sample combusted with time have been found out by the method of least squares.

Activities of the catalysts showed a general correlation with intercepts of the best straight lines on Y-axis, but the rate constants and the slopes of the equations could not give any guiding information regarding such a correlation.

The control of combustion of an organic compound on a microscale using a sample-additive reagent thus seemed to be extremely difficult for desired accurate kinetic studies.

Part 3: CATALYTIC VAPOUR-PHASE OXIDATION OF SOME ALIPHATIC ALCOHOLS ON VANADIUM PENTOXIDE IN A SEMI-MICROREACTOR

Aldehydes form a very important class of organic compounds as they are among the most reactive compounds. Although a number of methods are available for their preparation on industrial scale, the well known Oxo process[5a,b] (by formylation of a suitable olefin), dehydrogenation of alcohols over copper chromite catalyst[6] and oxidation of alcohols over silver catalyst[7] seem to be the major processes.

The oxidation of lower aliphatic alcohols has a special industrial significance, for these aldehydes are important intermediates. Catalytic vapour-phase oxidation of ethyl alcohol to acetaldehyde on industrial scale using silver catalyst is a case in point.

Although catalytic vapour-phase oxidation is a domain of chemical engineers, a study of catalytic vapour-phase oxidation of alcohols to obtain the respective aldehydes using silicon carbide supported vanadium pentoxide in a semimicro reactor was undertaken to assess the possibility of getting useful information for its further scaling up. Thus, this part of the thesis presents some attempts for catalytic vapour-phase oxidation of four aliphatic alcohols, 1-butanol, 1-hexanol, 1-octanol and 1-decanol, which has been carried out on V_2O_5/SiC catalyst ($\sim$ 10% w/w) at 250°, 300° and 350° in a specially designed semi-micro reactor. The oxidation products have been studied using gas chromatography. In addition to the expected aldehydes and small quantities of acids, some unidentified product was obtained in each case, the nature of which was decided using GC-MS.

It was observed that the conversion of the oxidised alcohol to aldehyde per pass was excellent (~ 90%) in 1-butanol and appreciably good (~ 70%) in 1-hexanol. The conversion was rather low (~ 40%) in 1-octanol and 1-decanol as the formation of the undesirable product had increased considerably, unlike that in 1-butanol and 1-hexanol.

It was concluded that such a study on semi-microscale could be quite useful for scaling up similar processes.

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PART 1

A NOVEL METHOD FOR DETERMINATION OF ACTIVITY OF A SAMPLE-ADDITIVE REAGENT IN ORGANIC ELEMENTAL ANALYSIS

1.1 Introduction

A problem frequently encountered in the elemental analysis of an organic compound is its incomplete oxidation which results in low values. A number of compounds containing alkali metals, phosphorus, boron, silicon etc. present difficulties in combustion for the determination of carbon, hydrogen and nitrogen. A host of combustion catalysts as combustion tube fillings have been suggested in the literature to achieve complete oxidation of such refractory compounds and their relative activities have been studied under various conditions.

1.1.1 Activity of combustion catalysts

In the past, some investigators have studied the activity of various combustion catalysts by packing a small layer of about 30-40 mm length in a combustion tube and determining the minimum temperature required for complete oxidation of the test compound. The first attempt seems to have been made by Horáček and Körbl[1] who studied the activities of 28 catalysts by employing acetic acid as the test compound, which was mixed in the stream of oxygen in constant amount. It was concluded that the thermal decomposition product of $AgMnO_4$ was most effective among the catalysts studied. Horáček and coworkers[2] also determined the activity of the catalysts using methane as a test compound and determined lowest temperature required in each case for its complete conversion to CO_2 and H_2O. This led to grouping of the catalysts in two groups. The first group, which was considered to be quite active, oxidised methane quantitatively below 500° and the second one, which showed comparatively poor activity, could not bring about quantitative oxidation even at 650°.

Methane as a test compound was also used by Kainz and Horwatisch[3] who in their study pertaining to the factors affecting the oxidising activity of combustion catalysts concluded that the slow decrease in activity was due to partial sintering of oxides. They recommended a mixture of CuO and CO_3O_4 as the best catalyst. The same authors determined the activity of various oxides and metal preparations under comparable conditions in oxygen and in carbon dioxide[4] and grouped the oxidants in three groups.

1. Oxides, which show the same oxidation action in oxygen and in carbon dioxide.
2. Oxides, which are distinctly more active in oxygen than in carbon dioxide, and

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Throughout the work described in this thesis, the temperatures were recorded in degrees celsius.

3. Preparations which have an oxidising action in oxygen and dehydrogenating action in carbon dioxide.

1.1.2 Activity of oxidants as sample-additive reagents

Whereas the studies for the use of the catalysts in the combustion tube filling were quite intense at one time, the introduction and wide acceptance of the empty tube combustion method of Belcher and Ingram[5] shifted the emphasis to the study of their activities as sample additives in the combustion boat. It is argued that when such a combustion catalyst is used as a sample-additive reagent its activity would differ due to limited quantity and its shorter contact time with the sample.

With the advent of automatic CHN-analysers the use of such oxidants has assumed special significance, as the oxidation of the organic compound has to be effected in helium atmosphere and incomplete oxidation of the compound would defeat the very purpose of such analysers.

The role of a wide range of sample-additive reagents used for complete oxidation of organic compounds in the conventional combustion methods and those based on inert carrier gas systems has been discussed by Fildes[6] giving an excellent review of the work carried out by the earlier investigators. Indeed, a variety of such additive reagents have been recommended in the literature.

Thus, a number of metal oxides which include WO_3, V_2O_5, NiO, Co_2O_3, Co_3O_4 and SnO_2, $AgMnO_4$ and its decomposition product, some mixture of oxides and some metals have been recommended as very effective oxidative aids. The refractory compounds which need the use of oxidants cited above are some sulfonamides, compounds containing phosphorus and also some compounds containing elements such as B, Si, Se, Ge, Tl etc.[7].

V_2O_5 which is reported to be a versatile additive oxidant[8,9,10] has been used for oxidation of minute amounts of carbon held by alkaline earth salts[11]. It is also found to be very satisfactory for smooth combustions of organoboron and organosilicon compounds[12]. NiO[13,14] was first used as an additive reagent in Dumas nitrogen analysis by Fukuda[15] and it has been claimed as an oxidant better than CuO, CoO and MnO_2[16]. Co_2O_3[10] and Co_3O_4[14,17,18] also have been recommended as oxygen donors. $AgMnO_4$ and its thermal decomposition product have been studied extensively[19] and recommended as very powerful oxidants by many investigators[8,20,21].

SnO_2[22] and WO_3[23,24] have also been used as effective oxidants; the latter has been described as specially suitable for the analysis of phosphorus containing compounds[24]. In addition to WO_3 many other oxidants e.g. $K_2Cr_2O_7$[25], V_2O_5[9], Pb_3O_4[26] have been used successfully for the analysis of phosphorus containing compounds, but potassium-persulphate recommended earlier for the same purpose was found to be unsuitable[27] for the analysis of such compounds due to evolution of large quantities of SO_3 during combustion.

Use of some metals also has been advocated to achieve satisfactory oxidation of difficultly combustible compounds. Thus, platinum black or sponge[28] and also platinized asbestos[29] seem to have been used earlier. Recently, powdered tin[10] has found use as an additive reagent because it increases the temperature in the immediate vicinity of the sample.

In addition to the above, $AgVO_3$[30], CrO_3[31] on asbestos for organosilicon compounds, Pb_3O_4[32], $KMnO_4$[33,34], $KClO_3$ and $KClO_4$[35,36] have also been tried by some investigators but of all these, the most suitable oxidant seems to be $AgVO_3$ which has also been used for satisfactory oxidation of fluorocarbons[37]. The use of CuO has been suggested since long but its efficiency as an additive reagent has been determined only recently by Childs[8].

A number of mixtures of additive oxidants also have been cited in the literature. Thus, $KMnO_4$ and CuO have been used together for axidation of some samples in nitrogen analysis[34]. $KClO_3$ in 1:19 admixture with the commercial catalyst for the F and M Model 185 Elemental Analyser, was found satisfactory by Ono[38]. Kirsten[39] suggested use of a mixture of WO_3 and Ag_2SO_4 as a combustion additive in the ultramicrodetermination of C, H and N. Another mixture mentioned by Celon[40] contains MnO_2, CrO_3 and WO_3. Kiparenko et al.[41] have recently suggested the use of 1:1 mixture of thermal decomposition product of $AgMnO_4$ and chromium III oxide as an effective sample additive.

1.1.3 Need for development of a suitable method to determine the activity of a sample-additive reagent

From the foregoing account, it will be clear that a number of investigators have investigated suitability of various oxidants for promoting smooth combustion of refractory compounds, both in the conventional combustion methods and also in the automatic analysers based on inert carrier gas systems. It is obvious that no one except Childs[8] seems to have graded the sample oxidants according to their activities. This is because no attempt seems to have been made to determine their relative activities. Such an attempt has been made only by Childs[8], who has tackled the problem elegantly. However, he has based his conclusions essentially on the action of the oxidants on carbon. As the activation energy needed for the oxidation of carbon and that for an organic compound would be much different, it would be more logical to base the gradation of activities of such oxidants by oxidising an organic compound rather than oxidising carbon.

Furthermore, it would be advisable to study the relative activities of such oxidants in oxygen atmosphere for the following two reasons.

1. The activities of such oxidants could be different in oxygen and helium.
2. If the activity of an oxidant is found to be sufficient to convert the nitrogen of the organic compound into nitrogen oxides quantitatively, it would form a basis for the simultaneous determination of carbon, hydrogen and nitrogen in an organic compound using the empty tube combustion method of Belcher and Ingram[*].

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[*] A separate study is being conducted in this laboratory for this purpose and it has been possible to increase the formation of nitrogen oxides in acetanilide from 10% to 50% with the use of such oxidants.

1.1.4 Basic requirements for developing such a method

1. It is obvious that in order to differentiate between the activities of different sample-additive reagents in oxygen atmosphere, complete combustion of the compound must be avoided. As a result, partial oxidation of a suitable compound under carefully controlled conditions should be carried out to throw light on the activity of the sample-additive reagent.

2. It would also be necessary to select a suitable compound which should undergo a clean oxidation in that the residual uncombusted compound should be free from oxidation products.

3. The oxidation products obtained from the organic compound should be volatile, so that they may be swept off for their quantitative determination by complete combustion and further estimation of the end products formed.

1.1.5 Mechanism of catalysis by solid catalysts

Catalysis by solid surfaces invariably involves the adsorption of the reactants on the catalyst surface. There are mainly, two types of adsorption, namely, Van der Waals' adsorption and chemisorption. In Van der Waal's adsorption the reactant molecules are held on the catalyst surface by physical forces which correspond to those involved in Van der Waal's equation of state for gases. The evolved heat in physical adsorption is only a few hundred calories per mole. As a result, the reactivity of the adsorbed molecules is not altered much. This type of adsorption is therefore less important in connection with surface catalysis of reactions of stable molecules.

On the other hand, in chemisorption, the reactive molecules are held on the surface by valence forces similar to those which hold atoms together in molecules. These forces being much stronger than those in Van der Waal's adsorption, the heats evolved during chemisorption are of the same orders as those evolved in chemical reactions, which are usually 10 to 100 kilocalories per mole. Thus, due to the significant energy changes in chemisorption the reactivities of the molecules are markedly enhanced.

A special case of chemisorption involves dissociation of the adsorbed molecule, and the resulting adsorbed atoms which are held by the catalyst surface became considerably more reactive. Adsorption of hydrogen molecule by tungsten results in the dissociation of the hydrogen molecule and the hydrogen atoms held on the surface of tungsten are more reactive than are the free hydrogen molecules. The same process may hold good when oxidation is carried out using metal catalysts in an atmosphere of oxygen.

In addition to the physical processes, namely Van der Waal's adsorption and chemisorption described above, mechanism of oxidation of an organic compound involves loss of electrons by the compound oxidised and gain of electrons by the oxide catalyst, which is reduced. Thus, when CuO is used for oxidation of an organic compound Cu^{2+} from the oxide is reduced to Cu^{+} or Cu^{0} by receiving electrons. A better undefstanding of the reactions such as formation and decomposition of oxides is possible from the theory of ionization and that of atomic and ionic structures. An example of oxidation $FeO \rightarrow Fe_2O_3$ will make the concept clearer. FeO oxidises to Fe_2O_3 with the help of oxygen in air, thus changing Fe^{2+} into Fe^{3+} by losing electrons during combination of Fe^{2+} with oxygen.

In the process of combustion, the term oxidation is used when a substance combines with oxygen, and so far as the metal oxides are concerned the term oxidation would involve the passage of an oxide representing a lower stage of combination with oxygen e.g. Fe^{2+} as shown above, to an oxide equivalent to a higher stage of combination i.e. Fe^{3+}. In short, when the metal oxides are used for the oxidation of an organic compound, they are reduced by gaining electrons and release oxygen to oxidise the organic compound.

1.1.6 Role of transition metal oxides as oxidants

It is well known that the transition metal oxides form an important class of oxidants for catalytic oxidation of organic compounds. These transition elements have partly filled 'd' or 'f' orbitals. They exibit variable valencies by receiving electrons to fill up the orbitals and can be sub-divided into three groups.

i) The main transition elements or d-block elements.

ii) The lanthanide elements, and

iii) The actinide elements.

The transition metals used in this study belong essentially to the d-block elements. These d-block elements comprise three series. The first one begins with Sc which has an electronic configuration 4 S^2 3 d and which is followed by V, Cr, Mn, Fe, Co, Ni and Cu. All these elements have partly filled 3 d orbitals either in the ground state of the free atom (except Cu) or in one or more of their chemically important ions (all except Sc).

The second transition series begins from Y having an electronic configuration 4 S^2 4 d and the next eight elements Zr, Nb, Mo, Tc, Ru, Rh, Pd and Ag all have partially filled 4 d orbitals either in the free element (except Ag) or in one or more of the chemically important ions (except Y).

The third series begins with Hf having a ground state outer electron configuration 6 S^2 5 d^2 and contains the elements Ta, W, Re, Os, Ir, Pt and Au. All these have partly filled 5 d orbitals in one or more chemically important oxidation states as well as (except Au) in the neutral atom.

The oxides of the above elements of these three transition series, being capable of changing their oxidation states, are known to be valuable oxidants. In our study we have included oxides of some of them and also mixtures of these oxides, the only exception being Ce which belongs to the lanthanide series.

1.2 EXPERIMENTAL

A systematic study of relative activities of sample additives was carried out in the atmosphere of oxygen. For this purpose, the conditions for rapid carbon and hydrogen determination essentially by the empty tube combustion method of Belcher and Ingram[5] were simulated to effect partial combustions of variety of compounds with various sample-additive reagents at different temperatures and under carefully controlled conditions. The organic compound was partially oxidised under these conditions to yield some volatile products, which in turn were oxidised completely at 900° to obtain the usual combustion endproducts. Carbon dioxide obtained ultimately was used as a measure of activity of the sample-additive reagent. The experimental details are as under.

1.2.1 Apparatus and Equipment

i) CH-RC type combustion apparatus of Dr. Hösli for rapid determination of C-H, as supplied by M/s.Modern Microchemical Instruments, Holland, with a modified combustion tube[42] to carry out partial combustions of compounds under controlled conditions. Quartz-wool plug in the combustion tube extended about 5 mm beyond the main furnace, towards the gas inlet. A 60 mm long quartz capsule (i.d. 6.5 mm, wall thickness 0.75 mm) with a hook at the closed end was used for the compound and sample-additive reagent mixture.

ii) An automatic unit of Derivatograph obtained from "Mom", Budapest, Hungary and Netzsch STA-409 Thermal Analyser of Geratebau GmbH, were used to obtain TG and DTA of oxidants under the following experimental conditions:

Sample size: 100 mg (for Mom Budapest Derivatograph)
20-50 mg (for Netzsch STA-409 Analyser)
Reference compound: α-Al_2O_3
Sample holder: Platinum crucible
Temperature range: 25-1200°C
Linear heating rate: 10°/min.
Atmosphere: Air

iii) The mean particle size of oxidants was determined using Stereoscan 150-A Scanning Electron Microscope supplied by Cambridge Analysing Instruments Ltd., U.K.

iv) 'Monosorb' surface area analyser of Quantachrome Corporation, USA was used for determination of surface area.

v) ESCA: XPS-spectra were recorded using a VG Scientific ESCA-3 Mk-II spectrometer provided with Al and Mg anodes.

vi) Perkin-Elmer 683 IR spectrophotometer and Specord UV-Vis spectrophotometer of Carl-Zeiss, were used to record IR and UV spectra of the test compounds.

vii) The purity of the residual product obtained after controlled partial combustions was checked using Hewlett-Packard Gas Chromatograph Model 700 equipped with TCD. detector.

1.2.2 Materials

(a) Test-compounds: Following compounds of analytical purity were used for partial combustions under controlled conditions.

(i) Acetanilide, (ii) Phenanthrene, (iii) 8-Hydroxyquinoline, (iv) 1-Octadecyl alcohol, and (v) Cholesterol.

(b) Sample-additive reagents: All the reagents were passed through 100 # sieve.

1) Copper oxide, G.R., E. Merk.
2) Tungsten trioxide, chem. pure Riedel-De Haen
3) Zirconium dioxide, calcined, B.D.H.
4) Ceric oxide, L.R., Thomas Tyrer and Co.
5) Cobaltous oxide, spec. pure
6) Manganese dioxide, spec. pure
7) Nickel oxide, spec. pure.

IR spectra of phenanthrene and its residual product were recorded on Perkin-Elmer 599-B spectrophotometer as the model 683 was out of order for some time.

These were prepared by the method reported in the literature[44].

8) Vanadium pentoxide:

It was prepared by heating ammonium vanadate, Riedel-De Haen make, to 400° for 2 hours.

Cobalto-cobaltic oxide:

This was prepared by three different methods as follows:

9) By heating cobaltous nitrate at 500° for 4 hours.

10) By precipitating from 50 ml of a solution containing 2.91 g of cobaltous nitrate with stirring and dropwise addition of a solution of sodium hypochlorite containing an excess of sodium hydroxide. The precipitate was washed thoroughly to remove the unreacted reagents and dried at 150°. It was heated further to 500° for 2 hours.

11) 1.40 g oxalic acid dissolved in 25 ml water was neutralised with 1N potassium hydroxide. After adding slight excess of alkali, the solution was added dropwise with stirring to 50 ml of a solution containing 2.38 g cobaltous chloride, hexahydrate. The resulting precipitate was washed thoroughly and dried at room temperature. It was heated further to 500° for 2 hours.

12) Silver Oxide, L.R., HPC, New Delhi

13) Silver tungstate:

This was prepared according to Yeh[45]. 3.30 g $Na_2WO_4 \cdot 2\,H_2O$ was dissolved in water and the solution diluted to 1 litre. To this was added slowly a 0.1N aqueous solution of silver nitrate until the precipitation was completed. The mixture was then boiled for 10 minutes, cooled, and the supernatent liquid decanted. The precipitate of silver tungstate was washed twice with hot water and then several times with cold water to remove excess silver nitrate. It was filtered out and dried at 100^{o} for 2 hours. Yield: 4.21 g.

The following mixed oxides were prepared according to the procedure reported by Horáček and Körbl[46].

14) (Fe_2O_3 + Ag): Ag dispersed in Fe_2O_3

50 ml ammoniacal $AgNO_3$ solution containing 1.70 g $AgNO_3$ was added dropwise with stirring to 50 ml aqueous solution of $FeSO_4$ containing 5.56 g $FeSO_4 \cdot 7H_2O$. The resulting precipitate was filtered, washed thoroughly with water to remove the unreacted reagents. The mixed oxide was dried at 100^{o} and heated at 550^{o} for 3 hours. Yield: 1.52 g.

(Analysis: Fe: 46.10%; Ag: 33.70%).

15) (CeO_2 + Ag): Ag dispersed in CeO_2

75 ml ammoniacal $AgNO_3$ solution containing 3.40 g

$AgNO_3$ was added dropwise with stirring to 50 ml aqueous solution of $Ce_2(SO_4)_3$ containing 7.13 g $Ce_2(SO_4)_3.8H_2O$. The resulting precipitate was filtered and washed several times to remove the unreacted reactants. It was then dried in an oven at 100° and finally heated at 550° for 3 hours. Yield: 5.04 g.

(Analysis: Ce: 50.37%; Ag: 37.60%)

16) (MnO_2 + Ag): Ag dispersed in MnO_2: 3.38 g $MnSO_4.H_2O$ was dissolved in 100 ml water. 75 ml ammoniacal $AgNO_3$ solution containing 3.40 g $AgNO_3$ was added to this solution dropwise with stirring. The resulting precipitate of mixed oxides was filtered and washed free of the unreacted reactants. It was then dried at 100° and heated at 550° for 3 hours. Yield: 3.13 g.

(Analysis: Mn: 27.82%; Ag: 43.08%).

17) (Co_2O_3 + Ag): Ag dispersed in Co_2O_3

To 100 ml aqueous solution containing 5.62 g $CoSO_4.7H_2O$ was added 400 ml NaOH solution containing 1.60 g NaOH slowly with stirring. An aqueous solution of $AgNO_3$ containing 1.70 g $AgNO_3$ in 50 ml, was added dropwise to this solution with stirring. The resulting precipitate was washed thoroughly to remove the unreacted reagents and excess alkali. It was then dried at 100° and heated further at 550° for 3 hours. Yield: 2.68 g.

(Analysis: Co: 41.91%; Ag: 36.00%).

18) (MnO_2 + Cu): Cu dispersed in MnO_2

19) (MnO_2 + Co): Co dispersed in MnO_2

These two mixed oxides were also prepared similarly by reacting aqueous solutions of $MnSO_4$ containing 1.69 g $MnSO_4.H_2O$ in 100 ml in each case with 50 ml each ammoniacal solutions of $CuSO_4$ and $Co(NO_3)_2$ prepared by dissolving 2.91 g of $CuSO_4.5H_2O$ and 2.50 g of $Co(NO_3)_2.6\ H_2O$, respectively. Both the catalysts were thoroughly washed and dried as before and heated to 550° for 3 hours. Yields: 1.10 g and 1.07 g respectively.

(Analysis for 18 : Mn: 47.16%; Cu: 7.60% and
Analysis for 19: Mn: 43.60%; Co: 18.36%)

20) Thermal decomposition product of $AgMnO_4$

This was prepared by the method of Körbl[47] as described below:

$AgMnO_4$ was prepared by double decomposition of $KMnO_4$ with $AgNO_3$. 1.94 g $KMnO_4$ was dissolved in 40 ml hot distilled water and the solution treated with 2.04 g $AgNO_3$ dissolved in 15 ml water. The solution yielded crystals of $AgMnO_4$ on standing for about two hours. The product was filtered off with suction on a sintered glass filter and washed with 15 ml water. Since concentrated $AgMnO_4$ solution decomposes slightly at 100°, the product was crystallised from 40 ml preheated water. The solution was then filtered and the separated crystals washed with a small quantity of water. It was then dried in an oven at 60-70° for half an hour. The yield of $AgMnO_4$ was 0.90 g. The product was powdered by crushing in a morter and then heated in small portions on a burner flame in a test tube, shaking it all the time. The decomposition product formed had four times the volume of the original crystals.

(Analysis: Mn: 23.36%; Ag: 51.44%).

1.2.3 Procedure

The temperatures used for partial combustions were 430°, 500°, 570°, 640° and 710°.

After the furnaces attained the usual temperatures (silver-furnace 520°, main furnace 900° * and the movable sample furnace at the desired temperature) the oxygen gas flow was regulated at 50 ml/min. About 3 mg test-compound was weighed accurately in the capsule, to which was added about 35 mg accurately weighed sample-additive reagent to form ~ 3 mm layer. Thorough mixing of the sample and the

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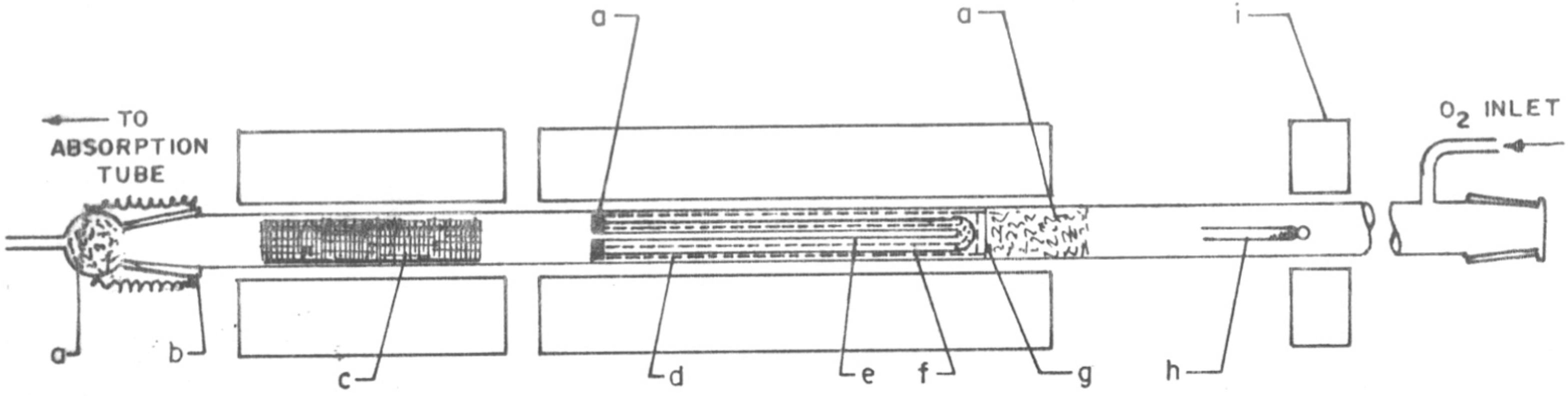
*Partial combustion results of the test-compounds using platinum foil in the hot zone of the combustion tube (900°) were reproduced very satisfactorily when the experiments were repeated without the platinum foil.



a — QUARTZ WOOL
b — B-10 JOINT
c — SILVER GAUZE
d — PLATINUM FOIL (dotted line)
e — SMALL QUARTZ TUBE FUSED TO THE COMBUSTION TUBE
f — QUARTZ TUBE SURROUNDING TUBE 'e'
g — PLATINUM GAUZE DISC
h — QUARTZ CAPSULE CONTAINING SAMPLE WITH OXIDANT
i — SAMPLE FURNACE

FIG. 1. COMBUSTION TUBE FOR ACTIVITY DETERMINATION OF OXIDANTS

reagent was ensured by rotating the capsule for sometime. Weighed CO_2 absorption tube and other absorption tubes were attached and the capsule introduced in the combustion tube with its open end facing the main furnace and at a distance of 40 mm from it as shown in Fig.1. The movable split type sample-furnace was drawn on the combustion tube and the partial combustion started from the closed end of the capsule by advancing the furnace at a rate of 10 mm/min. Combustion was discontinued after five minutes by pushing back the sample-furnace. The CO_2 absorption tube was disconnected and weighed exactly as before. The yield of CO_2 i.e. the percentage of carbon oxidised, was used as a measure of activity of the reagent.

1.2.4 Condensed volatile product

Following procedure was adopted to examine if any volatile products from the sample condensed and resided in the part of the combustion tube between the capsule and the main furnace at the end of the partial combustion. The capsule containing the residual sample and reagent was removed and combustion was carried out as usual with the movable sample-furnace at 710°. Increase in the weight of CO_2 absorption tube was checked at the end of the combustion. In all the cases this increase was negligible ($\sim 20\ \mu g$) indicating that the volatile oxidation products formed in the partial combustion were completely combusted and estimated.

1.2.5 Nature of the residual material

The residual material in the capsule obtained after five such partial combustions of a test-compound at 430°, using V_2O_5 as the oxidant, was collected by extraction with ether and the infrared spectrum of the material obtained on evaporation was compared with that of the test-compound. Infrared spectra of the residual products and the test-compounds are shown in Fig.2 to 6. Except in the case of acetanilide, the spectra in each other case indicated that the residual material contained some non-volatile oxidation product, in addition to the test-compound. However, in the case of acetanilide, the spectra of the residual material and the test-compound were identical. UV spectra (Fig.7) and GLC data (Fig.8) also confirmed this observation. Further, the infrared spectra of the residual products of acetanilide obtained on partial combustions at 710° with all the individual reagents showed that the residual products were essentially acetanilide carrying negligible impurities. The purity of the products was found to be >97% from their UV spectra. Acetanilide was thus found to be the most dependable test-compound to study the activity of the sample-additive reagents by the proposed method.

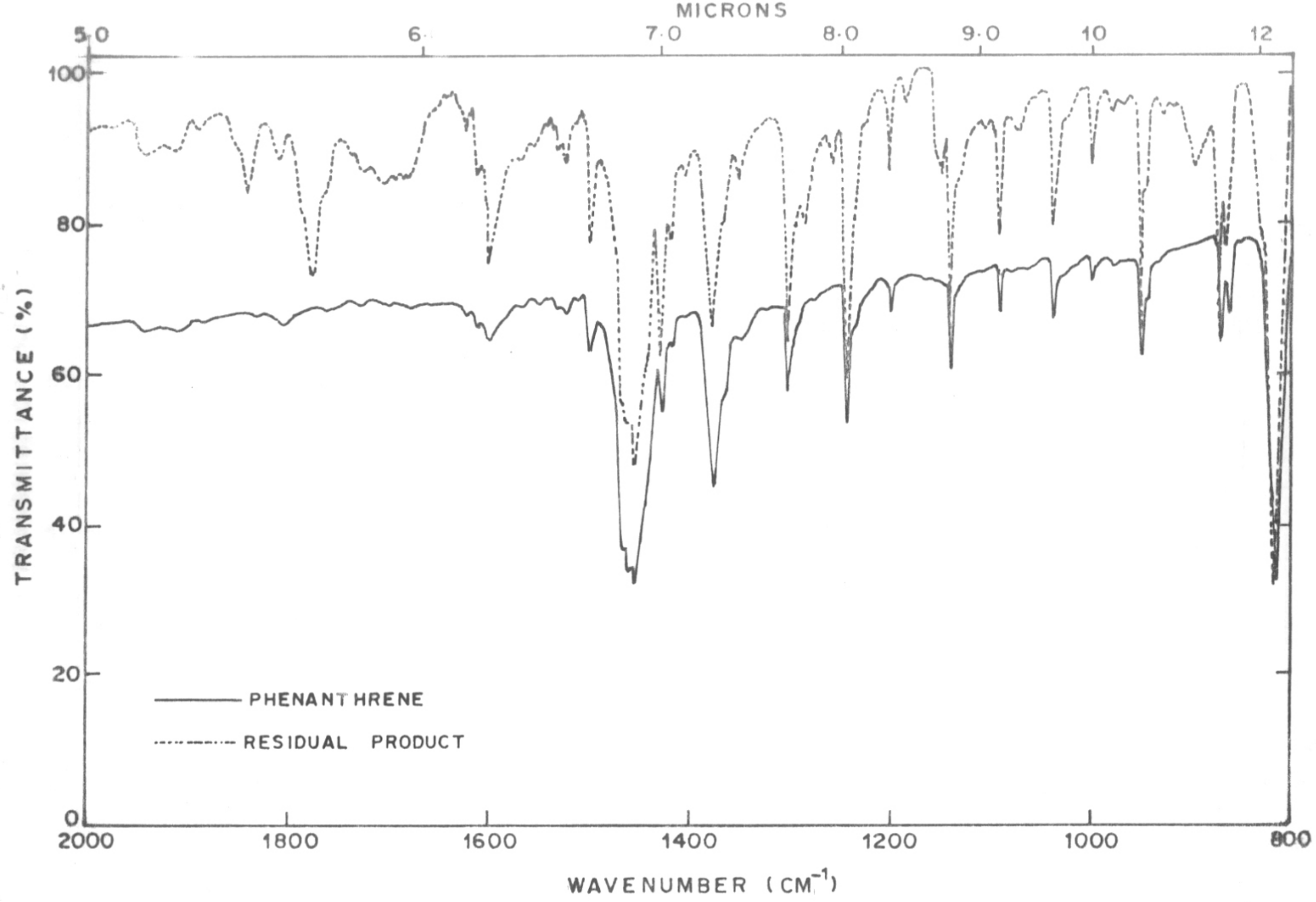


FIG. 2. IR SPECTRA (IN PART) OF PHENANTHRENE AND ITS RESIDUAL PRODUCT AFTER PARTIAL COMBUSTION, IN NUJOL

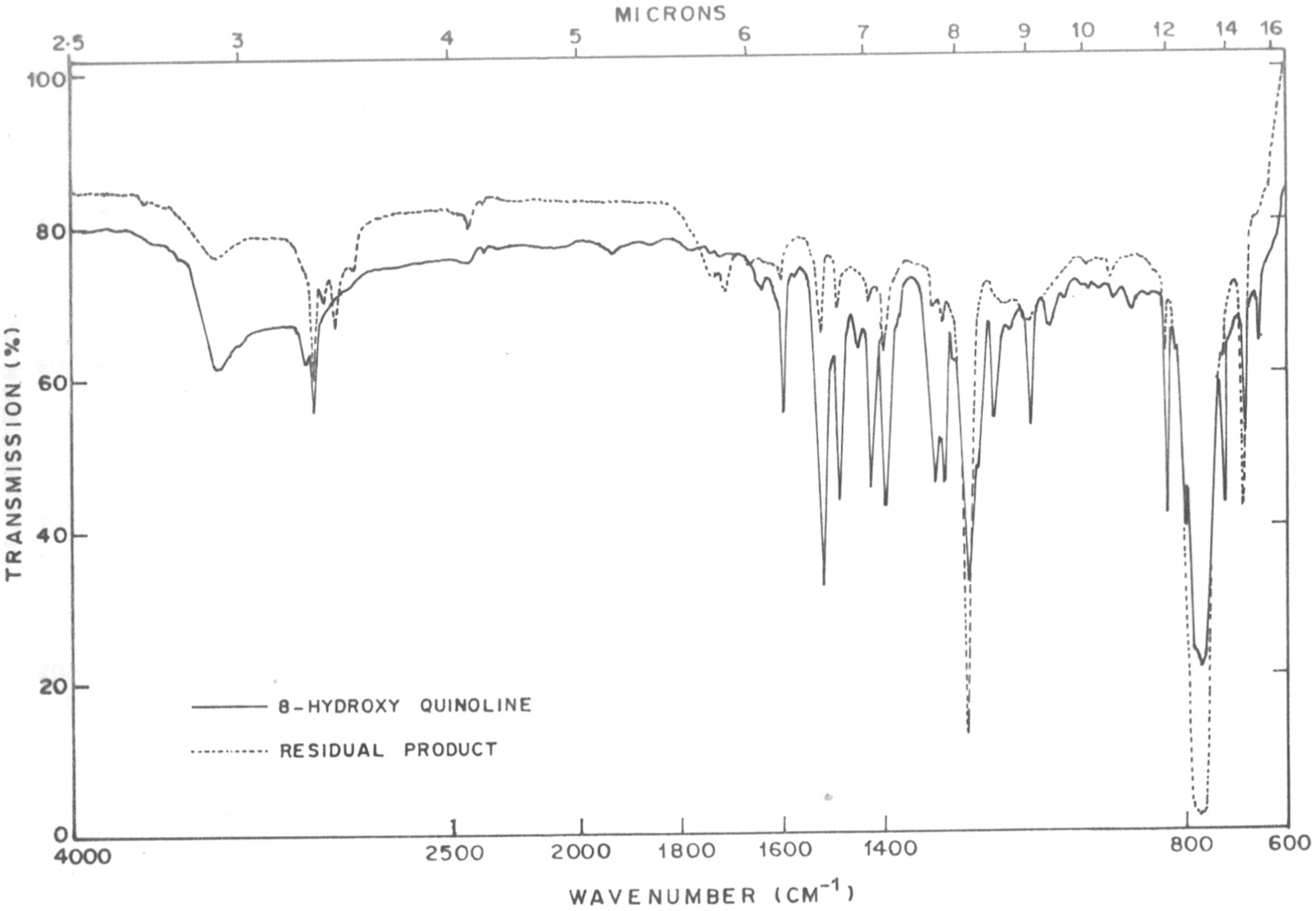


FIG. 3. IR SPECTRA OF 8-HYDROXY QUINOLINE AND ITS RESIDUAL PRODUCT AFTER PARTIAL COMBUSTION, IN $CHCl_3$

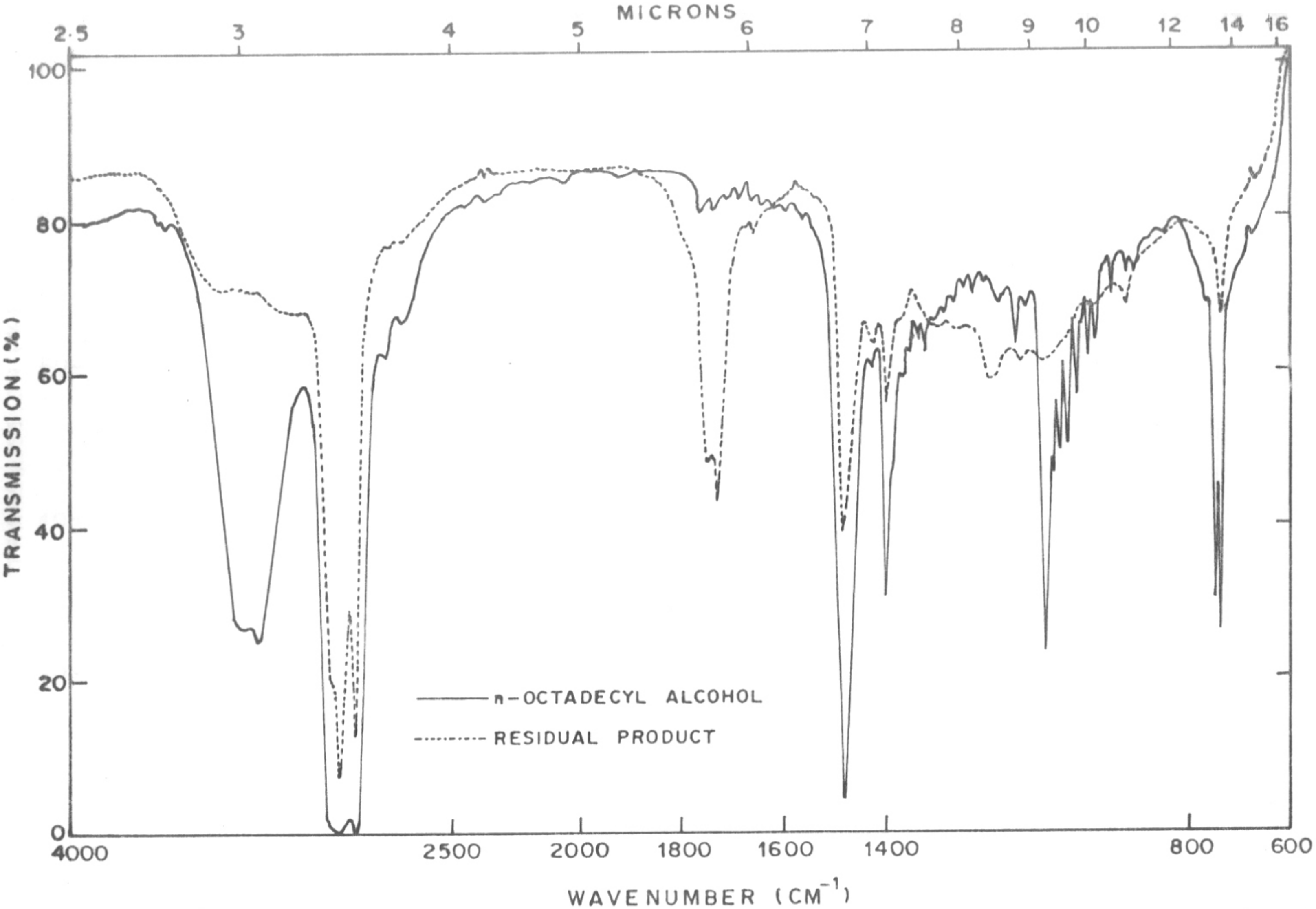


FIG. 4. IR SPECTRA OF 1-OCTADECYL ALCOHOL AND ITS RESIDUAL PRODUCT AFTER PARTIAL COMBUSTION, IN NUJOL

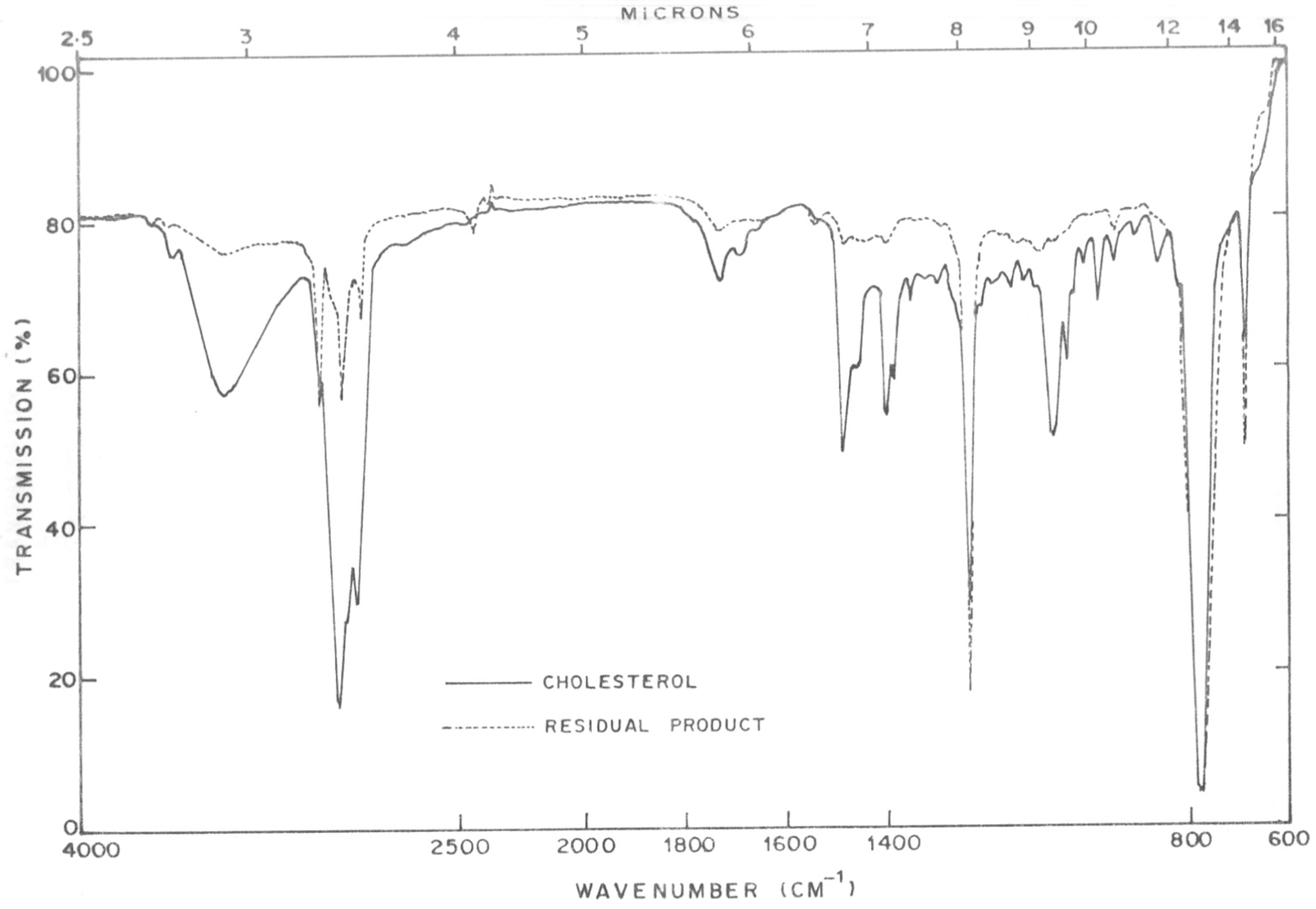


FIG. 5. IR SPECTRA OF CHOLESTEROL AND ITS RESIDUAL PRODUCT AFTER PARTIAL COMBUSTION, IN $CHCl_3$

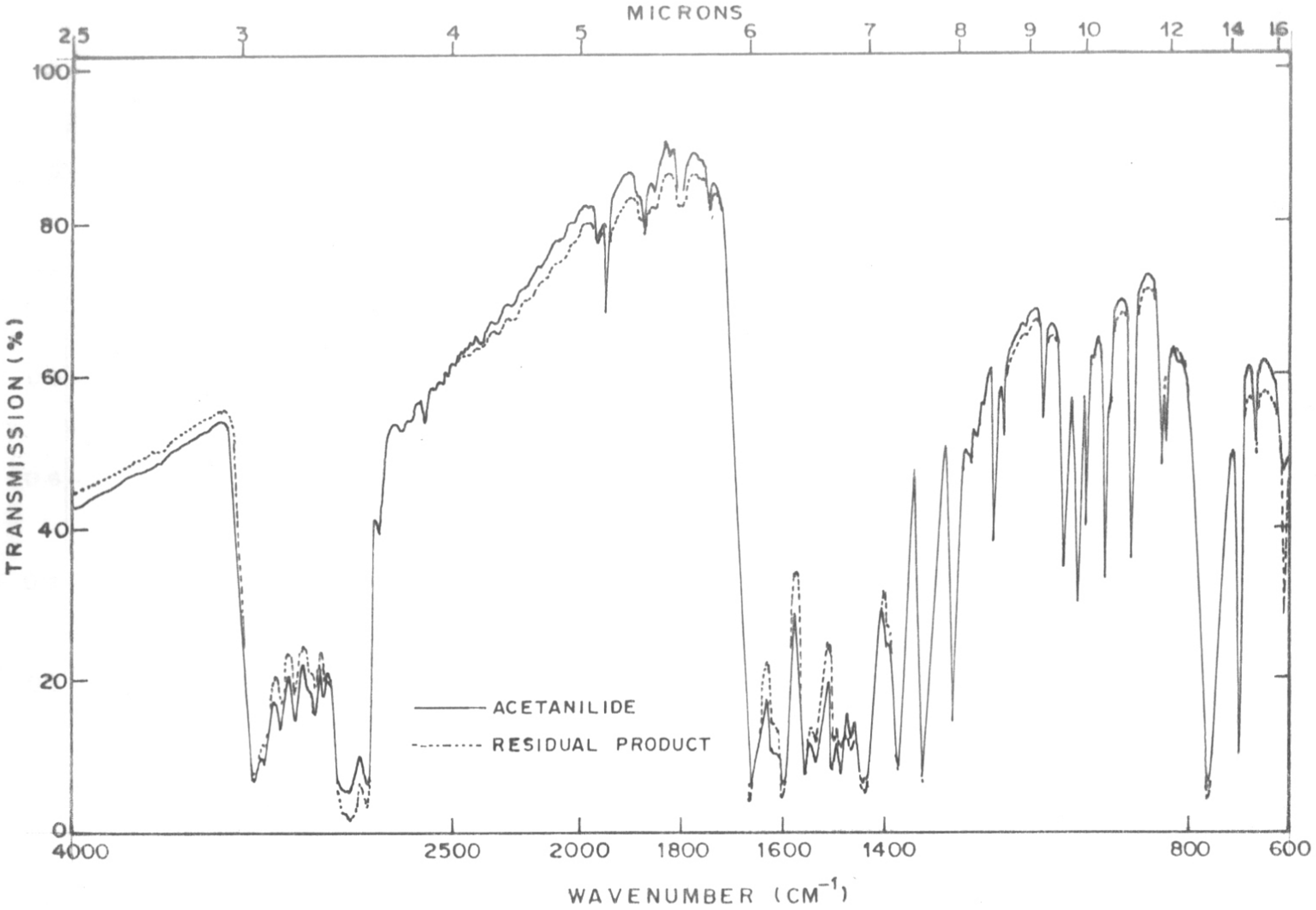


FIG. 6. IR SPECTRA OF ACETANILIDE AND ITS RESIDUAL PRODUCT AFTER PARTIAL COMBUSTION, IN NUJOL

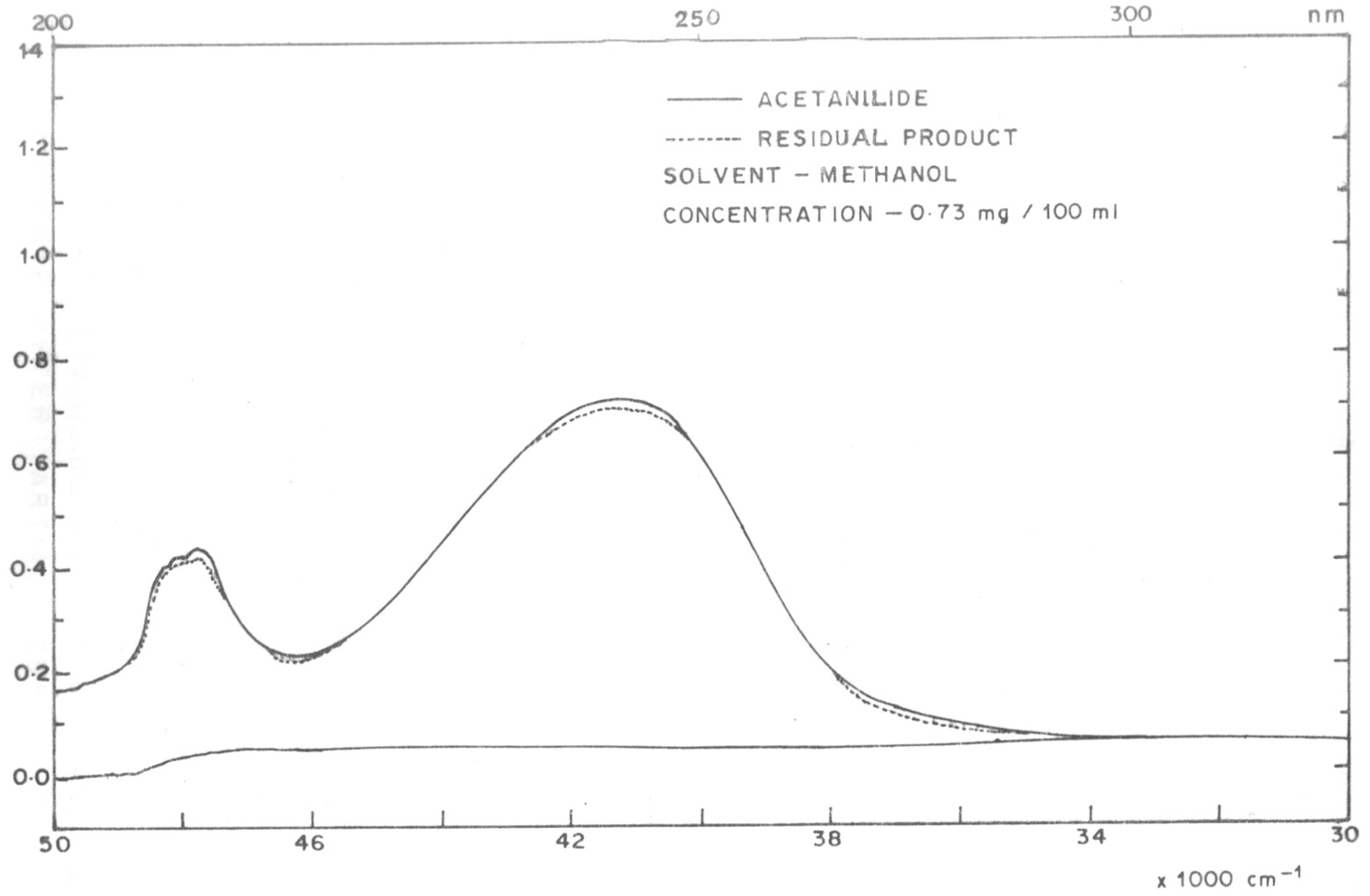
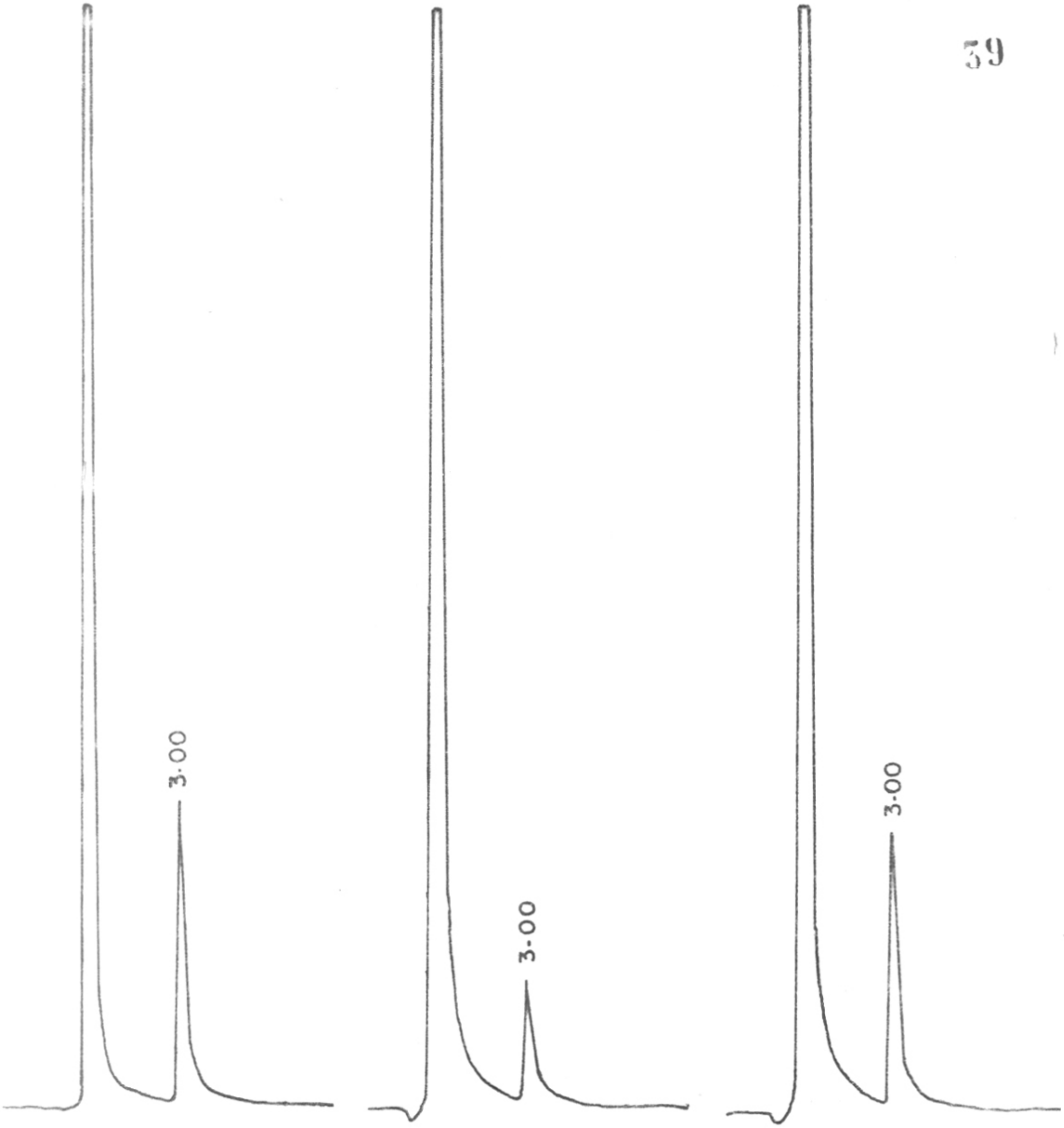


FIG. 7. UV SPECTRA OF ACETANILIDE AND ITS RESIDUAL PRODUCT AFTER PARTIAL COMBUSTION



(a) (b) (c)

Column : 5% OV−17 on Chromosorb WAW DMCS

Column temp. : 180° C , carrier gas (H_2) flow rate : 60 ml / min

Chart speed : 0·6 in / min

FIG. 8. GLC OF ACETANILIDE AND ITS RESIDUAL PRODUCTS AFTER PARTIAL COMBUSTION

(a) ACETANILIDE (b) AND (c) RESIDUAL PRODUCTS

1.2.6 Method of determination of mean particle size[43]

The oxidant was dispersed in amyl acetate containing 1% collodion and sprayed on a clean aluminium foil which was mounted suitably for obtaining a microphotograph in Scanning Electron Microscope. Fig.16 to 18(p.61-63) depict the microphotographs of the oxidants. The particles in the microphotograph were divided in three equal parts and particles of various sizes were counted in each part. The cumulative percentage of each particle size was then calculated from percentage of particle size and the log of size of particles in microns was plotted against the cumulative percentage on a probability graph paper. The mean particle size was obtained from the antilog of the figure indicated against 50 cumulative percentage.

The data and calculation for determining mean particle size of (Co_2O_3 + Ag) is given below as an example and the relevant probability graph is shown in Fig.19.(p.64).

Calculation for mean particle size of the particles of (Co_2O_3+Ag):

Size in μm	log. of μm	Frequency of occurrence	% of each particle size	Cumulative percentage
0.167	-0.7773	30	31.25	31.25
0.333	-0.4776	36	37.50	68.75
0.500	-0.3010	19	19.79	88.54
0.667	-0.1759	3	3.13	91.67
1.000	0.0000	5	5.21	96.88
1.167	0.0671	3	3.13	100.01
	Total	96		

The value against 50 cumulative percentage from the graph = -0.6400

∴ Mean particle size = 0.23 μm

1.2.7 Surface area determination

Surface area of oxidants was determined by the single point BET method by measuring adsorption of nitrogen at liquid nitrogen temperature and at a nitrogen concentration of 0.3 mol % (balance helium), based on dynamic adsorption/desorption technique. Sample size used was 200 - 300 mg.

1.2.8 XPS of the oxidants

A thin layer of powdered sample was pressed onto a suitable holder to record the photoelectron spectra. MgKα (1253.6 eV) was used for excitation for all the catalysts with the exception of V_2O_5 where AlKα (1486.6 eV) was used. The photoelectron kinetic energy was measured with reference to E_F. All the XPS spectra were recorded under similar conditions (50 eV pass energy, 4 mm entry slit, pressure $< 10^{-9}$ torr). The calibration of the spectrometer was checked by determining the binding energies of Au $4f_{7/2}$ (84.0 eV), C 1s (285.0 eV), Ag $3d_{5/2}$ (368.3 eV) and Cu 2 $p_{3/2}$ (932.4 eV) levels using spectroscopically pure metals (Johnson and Matthey, U.K.). These BE values are in good agreement with the literature values.

The binding energies of the electrons in the oxidants were then determined within ±0.2 eV.

1.3 Results and Discussion

1.3.1 Activity of the sample-additive reagents

Results of partial combustions of acetanilide at 430°, 500°, 570°, 640° and 710° under controlled conditions using the sample-additive reagents are summarized in Table 1, and some of them are depicted in Fig.9. It is obvious from the results that the thermal decomposition product of $AgMnO_4$ has the maximum activity. This was

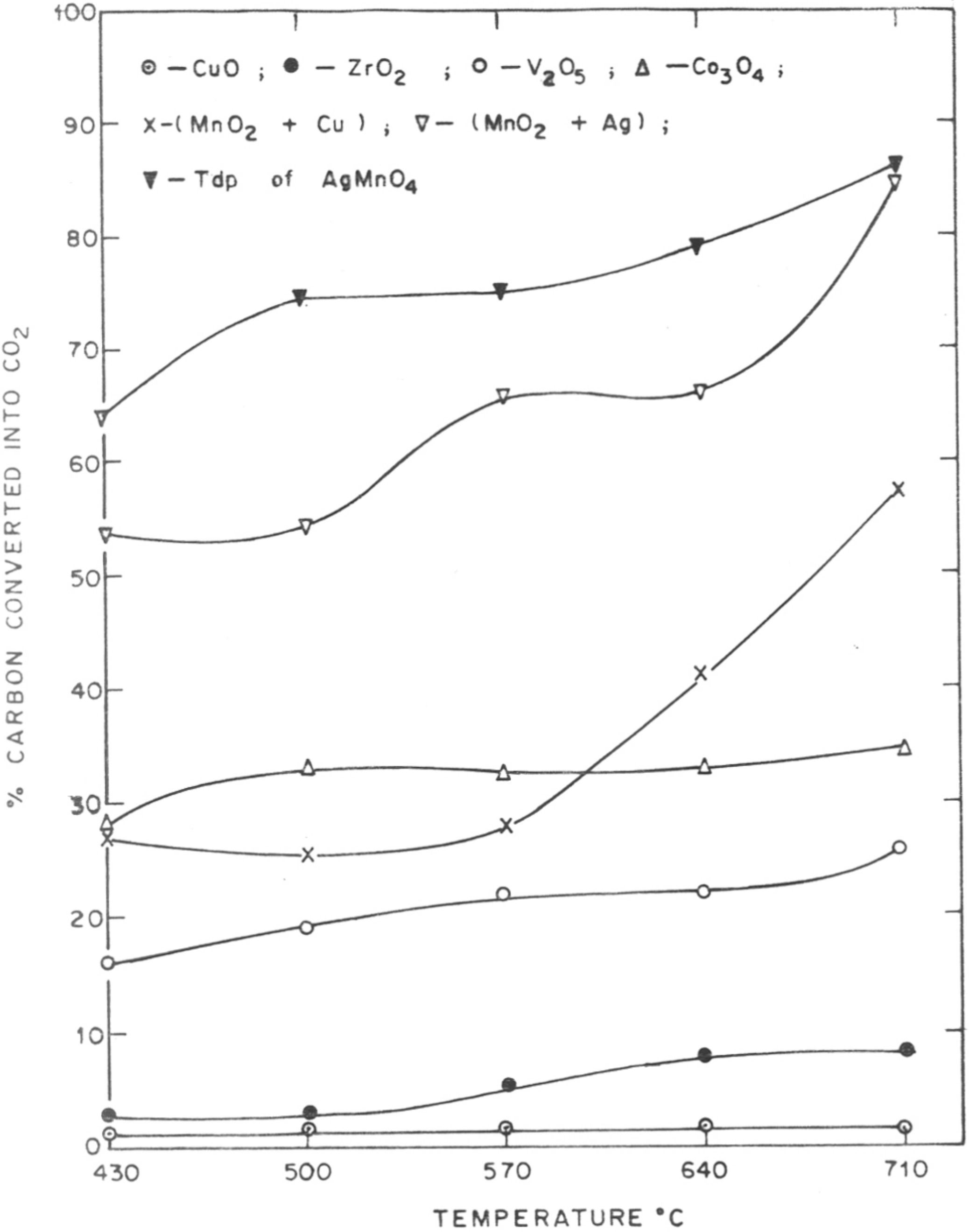


FIG. 9. PARTIAL OXIDATION OF ACETANILIDE WITH DIFFERENT SAMPLE – ADDITIVE REAGENTS

TABLE 1 - PARTIAL OXIDATION OF ACETANILIDE AT VARIOUS TEMPERATURES

Sample-additive reagent	% Carbon converted into CO_2* (i.e. % activity)				
	430°	500°	570°	640°	710°
1 Blank (without reagent)	0.37	1.53	2.20	2.87	3.64
2 CuO	1.21	1.82	1.30	1.72	1.61
3 WO_3	1.70	1.41	3.07	2.14	1.90
4 CoO	2.03	2.86	2.25	1.88	4.51
5 MnO_2+	3.28	4.98	4.92	5.26	4.51
6 NiO	2.70	2.53	2.39	2.45	5.75
7 Ag_2WO_4	1.08	1.47	1.36	2.94	7.02
8 ZrO_2	2.92	3.01	5.22	8.24	8.32
9 V_2O_5	16.02	19.05	22.16	21.56	26.17
10 Co_3O_4[a]	12.15	15.04	15.52	22.23	34.75
11 Co_3O_4[b]	28.17	33.36	32.71	32.82	34.67
12 Co_3O_4[c]	10.48	11.19	16.76	22.96	28.47
13 CeO_2	22.66	28.73	29.15	30.03	36.38
14 (Fe_2O_3+Ag)	8.59	15.53	16.80	18.02	27.39
15 (CeO_2+Ag)	6.85	14.96	25.67	28.93	34.06
16 (Co_2O_3+Ag)	10.49	27.15	45.09	43.35	45.48
17 Ag_2O	15.20	23.50	43.00	43.50	45.73
18 (MnO_2+Cu)	27.13	25.75	27.72	41.54	57.44
19 (MnO_2+Co)	6.48	13.11	21.74	36.92	57.58
20 (MnO_2+Ag)	53.90	54.53	66.15	66.49	85.16
21 T.d.p. of $AgMnO_4$	64.21	74.89	75.21	79.07	85.89

*Values for the reagents calculated after deducting blank.

a: Prepared from cobaltous nitrate.

b: Prepared from cobaltous nitrate and sodium hypochlorite.

c: Prepared from cobaltous oxalate.

+MnO_2 prepared according to Večeřa <u>et al</u>.[62] showed high activity. Vide Table 2 for further information.

observed by Childs[8] also in his work carried out using helium atmosphere. Ag dispersed in MnO_2 also has a remarkably comparable activity.

Further, it can be seen that the entire range of reagents used in this study can be grouped in three distinct groups according to their activities. Thus CuO, WO_3, CoO, MnO_2, NiO, Ag_2WO_4, ZrO_2 exhibit low activity; V_2O_5, Co_3O_4, CeO_2, Ag_2O, (Fe_2O_3+Ag), (CeO_2+Ag), (Co_2O_3+Ag) have medium activity and (MnO_2+Cu), (MnO_2+Co), (MnO_2+Ag) and t.d.p. of $AgMnO_4$ comprise the most active group. A comparison of the order of activity of some of these reagents in the inert atmosphere reported by Childs[8] with the one observed by us in the oxygen atmosphere clearly shows that their orders of activity are different in helium and oxygen atmospheres.

In helium: T.d.p. of $AgMnO_4 > CuO > V_2O_5 > WO_3$
In oxygen: T.d.p. of $AgMnO_4 > V_2O_5 > WO_3 > CuO$

This comparison, therefore, justifies the need of the method for determining the activities of sample-additive reagents in oxygen atmosphere separately although a method has already been reported for the determination of the activities in helium atmosphere.

1.3.2 Dependance of activity on the structure of the test-compound

Table 2 gives the activity data obtained using five test-compounds having sufficient structural variety. Only some oxidants from the three different groups showing low, medium and high activities were selected for this study. It would be clear that although t.d.p. of $AgMnO_4$ shows the maximum activity for all the test-compounds, phenanthrene resists the oxidation (66.41% conversion) as compared to the remaining four compounds and 8-hydroxyquinoline undergoes the oxidation (94.30% conversion) more smoothly than the rest.

Another point which emerges clearly is that the order of activity depends entirely on the structures of the test-compounds as the combustion characteristics of all of them are different. Thus, although t.d.p. of $AgMnO_4$ shows the maximum activity for all of them, (MnO_2+Ag) is the next best for acetanilide (85.16%) and phenanthrene (58.99%). However, the oxidants which are next best to t.d.p. of $AgMnO_4$ in their activities in oxidising 8-hydroxyquinoline, 1-octadecylalcohol and cholesterol are (Co_2O_3+Ag) (84.93%), (MnO_2+Cu) (71.87%) and Co_3O_4 (prepared by the action of sodium hypochlorite on cobaltous nitrate)(78.82%), respectively.

TABLE 2 - PARTIAL OXIDATION OF TEST-COMPOUNDS AT 710°

Sample-additive reagent	% carbon converted into CO_2* (i.e. % activity)				
	Acetanilide	Phenanthrene	8-Hydroxyquinoline	1-Octadecyl alcohol	Cholesterol
1 Blank (without reagent)	3.64	2.50	3.97	2.73	11.32
2 CuO	1.61	0.15	53.33	13.66	40.74
3 MnO_2 +	4.51	2.52	28.17	24.67	31.69
4 V_2O_5	26.17	25.37	77.60	50.80	57.13
5 Co_3O_4 b	34.67	22.56	68.71	52.73	78.82
6 (CeO_2+Ag)	34.06	18.90	41.72	44.13	33.49
7 (Co_2O_3+Ag)	39.59	29.17	84.93	66.26	63.89
8 (MnO_2+Co)	57.58	35.59	65.14	55.20	45.88
9 (MnO_2+Cu)	57.44	34.41	66.14	71.87	60.39
10 (MnO_2+Ag)	85.16	58.99	81.77	68.32	59.09
11 T.d.p. of $AgMnO_4$	85.89	66.41	94.30	91.18	84.02

*Values for the reagents calculated after deducting blank.

b: Prepared from cobaltous nitrate and sodium hypochlorite.

+MnO_2 prepared by reacting $MnSO_4$ and $KMnO_4$ according to Večera *et al.*[62] showed high activity i.e. 81.3% conversion of carbon in acetanilide at 710°. However, it has not been included in this list of sample-additive reagents as the pertinent physical data is not available so far. The reasons for its high activity are being investigated separately.

1.3.3 DTA and TG

Results of thermal analyses of the oxidants used in this study are given in Table 3 and depicted in Fig.10 to 15. As described before all the oxidants are divided into three groups according to their activities. Thus oxidants No.1 to 7 (CuO to ZrO_2) show low activity i.e. less than 10%. The group having medium activity is constituted by oxidants No.8 to 16 (V_2O_5 to Ag_2O), the activities of which are between 25 to 50%. The last group containing four oxidants No.17 to 20 show high activity. One point which emerges clearly is that the oxidants with high activity namely t.d.p. of $AgMnO_4$, (MnO_2+Ag), (MnO_2+Co) and (MnO_2+Cu) show multiple number of peaks indicating appreciable weight loss as compared to the groups of oxidants showing medium and low activity. It can be seen that the oxidants which belong to medium activity group and show weight loss comparable to that in oxidants having high activity, tend to lose the oxygen at comparatively high temperatures i.e. beyond 900°. The cases of Co_3O_4 and (Co_2O_3+Ag) are in point. As against this, in the oxidants

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*The broad curves upto 250° seen in some of the thermograms are believed to be essentially due to difference in the heat capacities of the crucibles and their contents used for recording the thermograms.

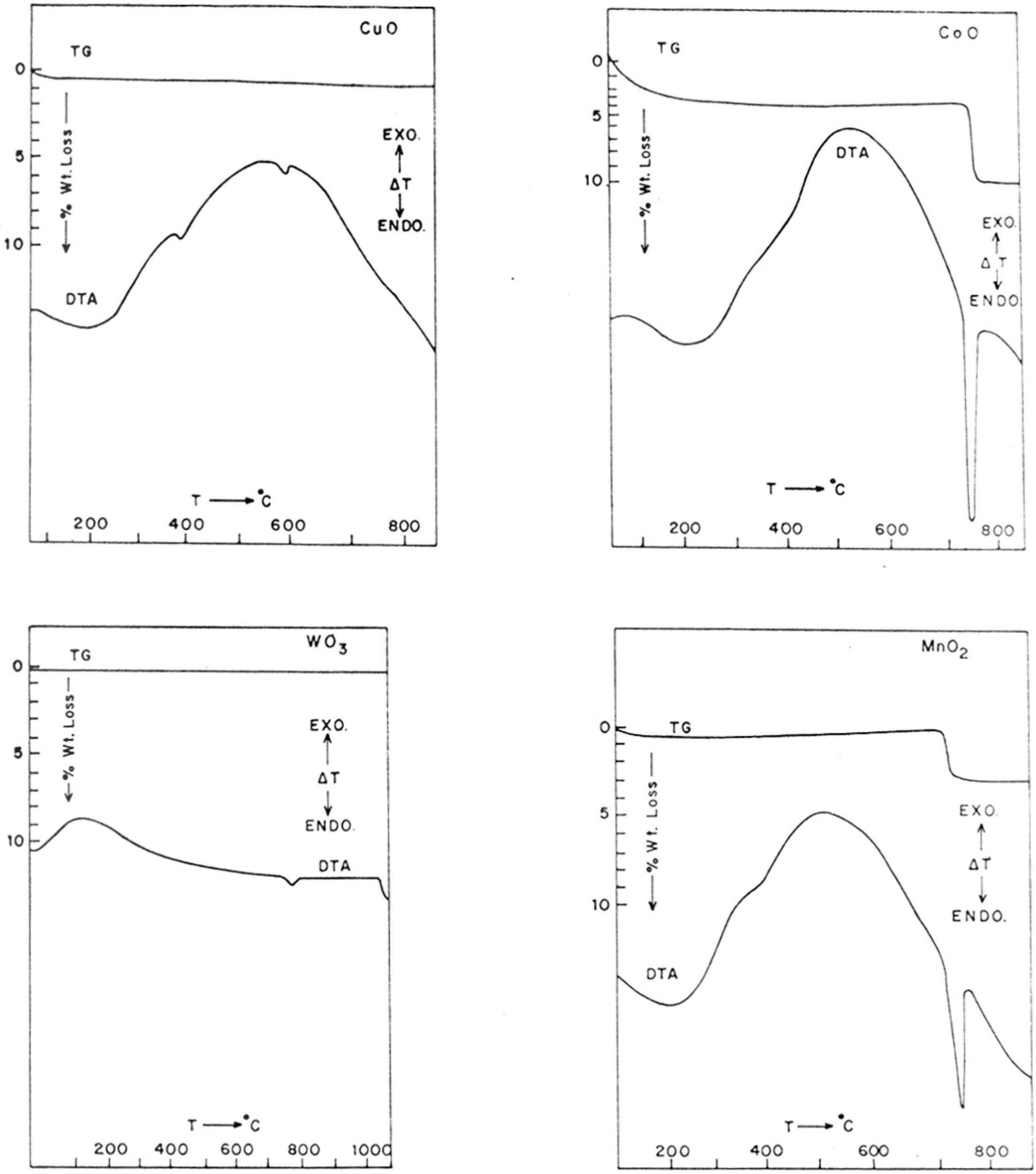


FIG. 10. DTA AND TG CURVES OF OXIDANTS.

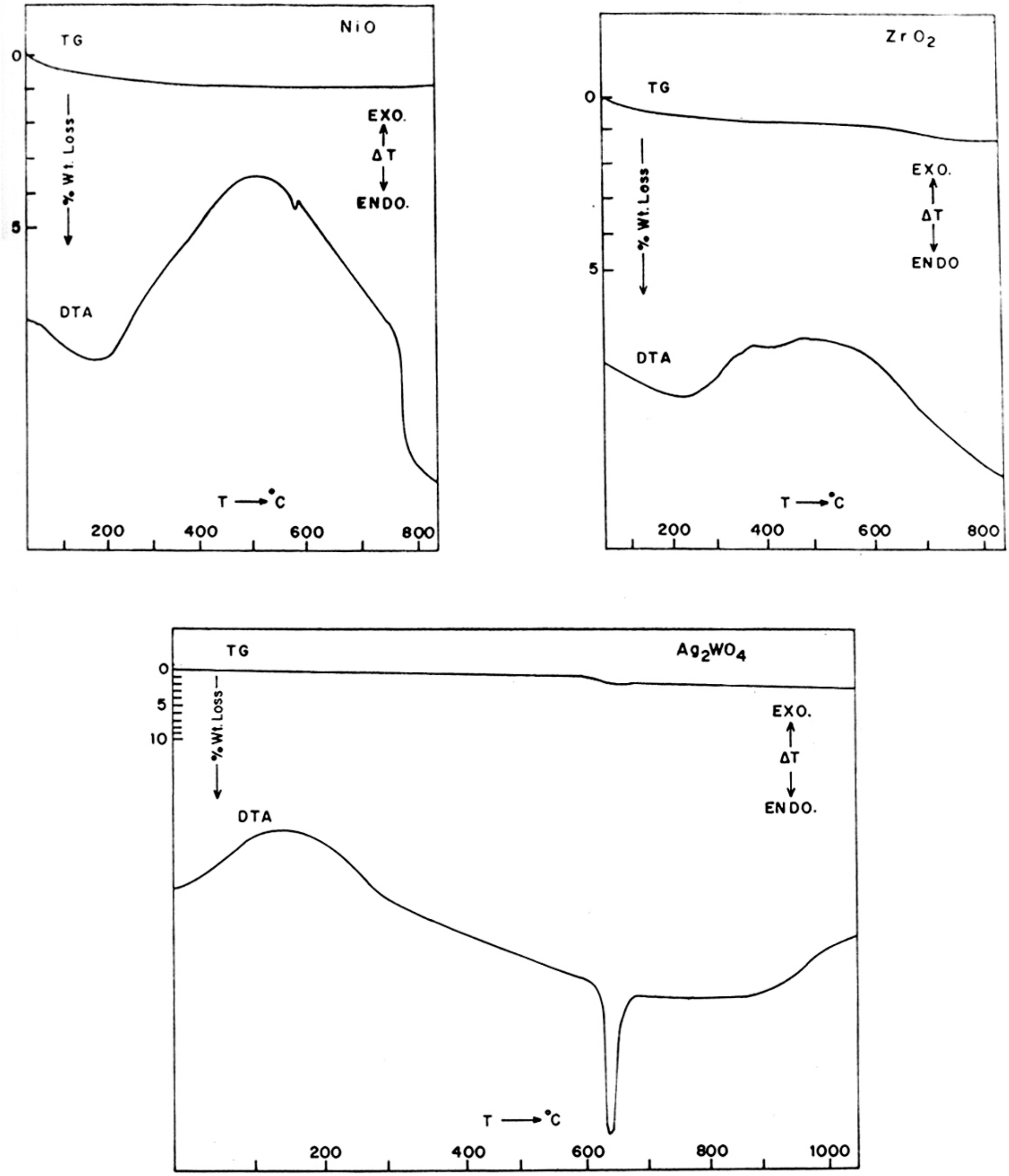


FIG. 11. DTA AND TG CURVES OF OXIDANTS.

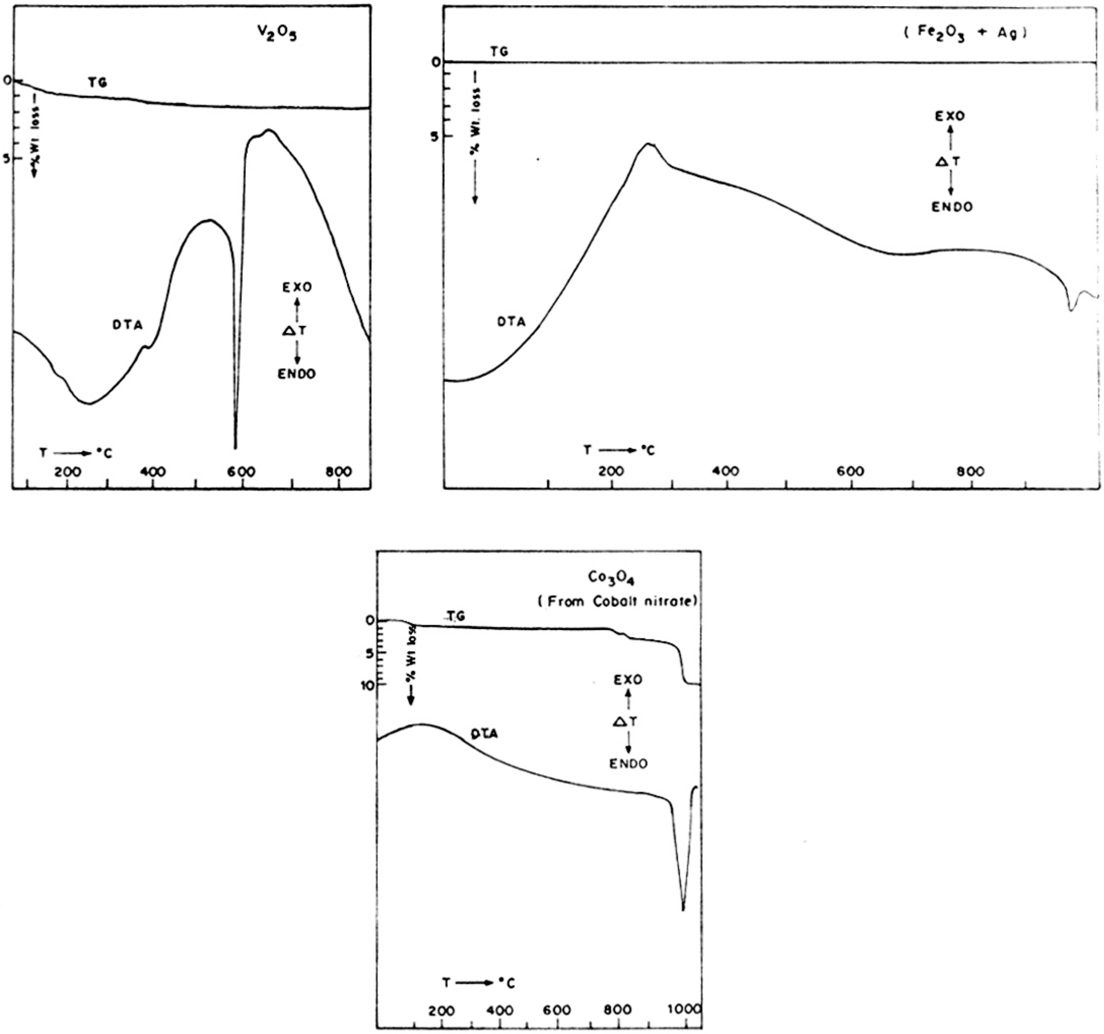


FIG. 12. DTA AND TG CURVES OF OXIDANTS

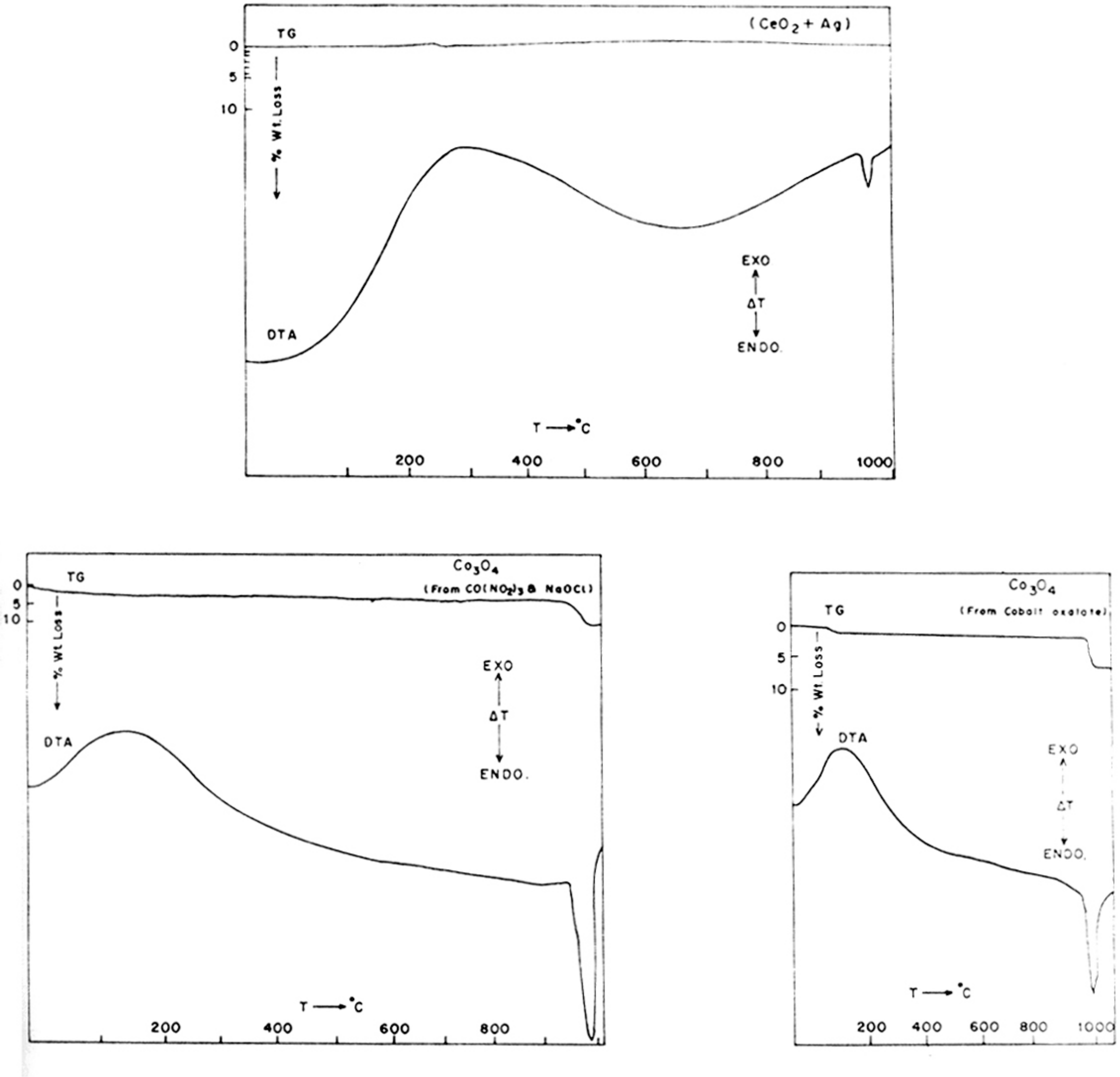


FIG. 13. DTA AND TG CURVES OF OXIDANTS

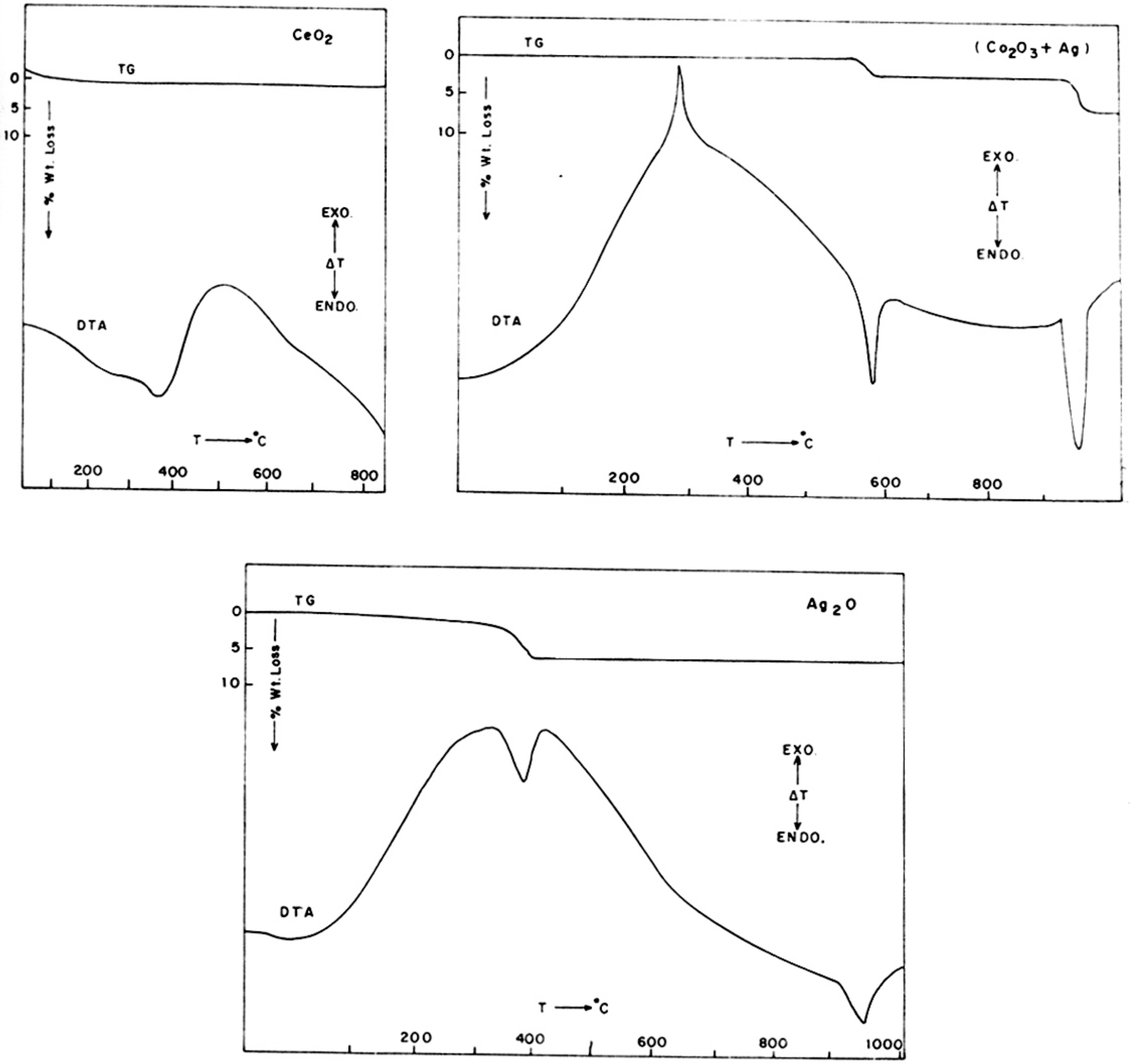


FIG. 14. DTA AND TG CURVES OF OXIDANTS.

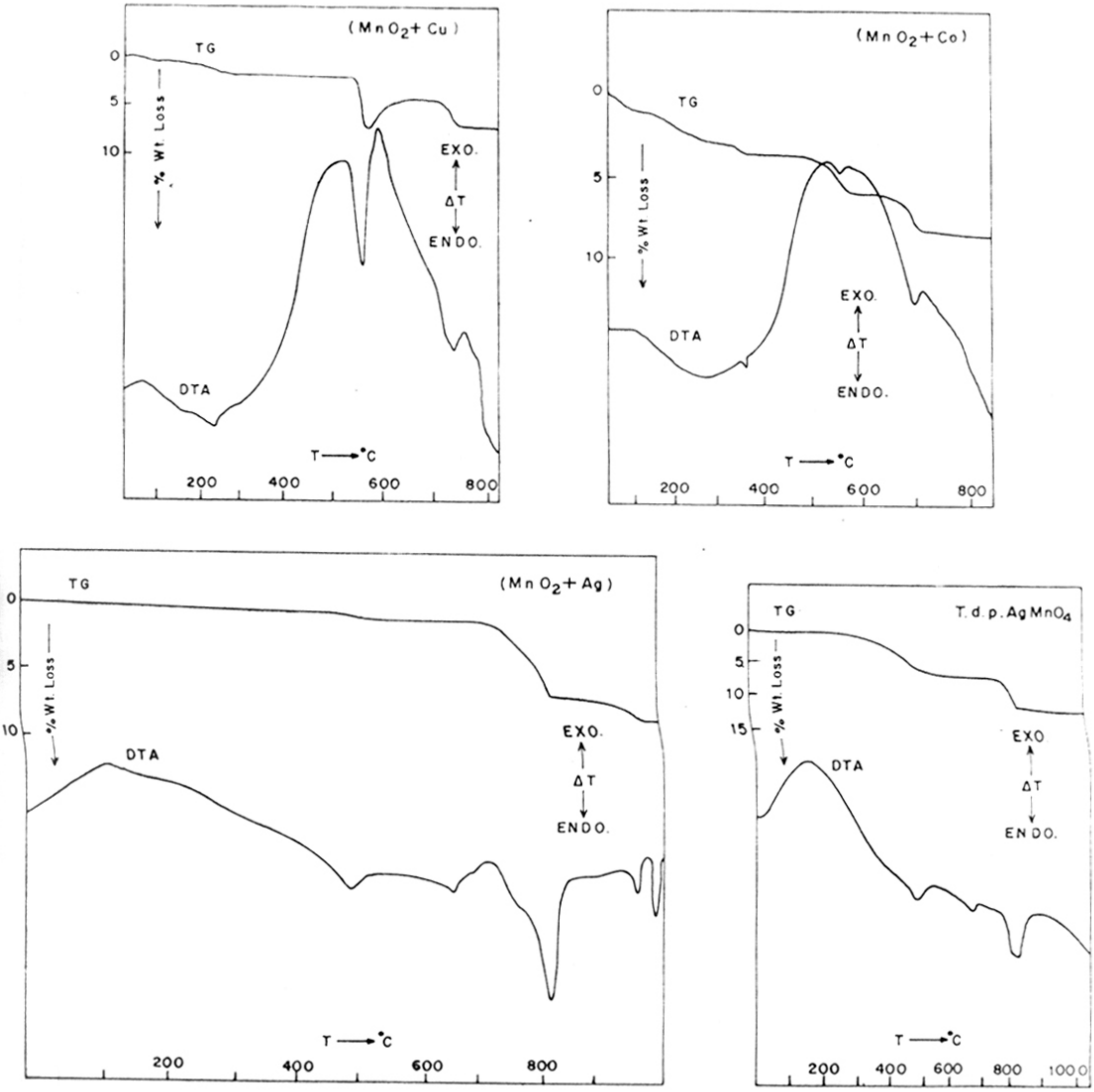


FIG. 15. DTA AND TG CURVES OF OXIDANTS.

TABLE 3 - RESULTS OF THERMAL ANALYSIS OF OXIDANTS

S.No.	Oxidant (with % activity)	Peak No.	DTA	TG	% Wt. loss	Type of change	Peak characteristic
1	CuO (1.61)	1	400°	-	-	Physical	endotherm
		2	590°	-	-	Physical	endotherm
2	WO_3 (1.90)	1	800°	-	-	Physical	endotherm
3	CoO (4.51)	1	740°	740°	6.00	Chemical	sharp endotherm.
4	MnO_2 (4.51)	-	400°	-	-	Physical	-
		1	740°	740°	2.90	Chemical	sharp endotherm
5	NiO (5.75)	1	590°	-	-	Physical	endotherm
6	Ag_2WO_4 (7.02)	1	635°	635°	1.00	Chemical	sharp endotherm
7	ZrO_2 (8.32)	1	-	770°	0.60	Chemical	-
8	V_2O_5 (26.17)	1	250°	250°	0.90	Chemical	endotherm
		2	380°	380°	1.20	Chemical	exotherm
		3	590°	-	-	Physical	sharp endotherm.
9	(Fe_2O_3+Ag) (27.39)	1	250°	-	-	Physical	exotherm
		2	962°	-	-	Physical	endotherm
10[a]	Co_3O_4 (28.4)	1	-	760°	0.50	Chemical	-
		2	-	800°	0.50	Chemical	-
		3	990°	990°	7.00	Chemical	sharp endotherm.

.....contd.

TABLE 3 (Contd.)

S.No.	Oxidant (with % activity)	Peak No	DTA	TG	% Wt loss	Type of change	Peak characteristic
11	(CeO_2+Ag)	1	246°	246°	0.75	Chemical	broad exotherm
	(34.06)	2	951°	-	-	Physical	endotherm
12[b]	Co_3O_4 (34.67)	1	980°	980°	7.00	Chemical	sharp endotherm
13[c]	Co_3O_4 (34.75)	1	1010°	1010°	6.50	Chemical	endotherm
14	CeO_2 (36.38)	1	375°	-	-	Physical	endotherm
15	(Co_2O_3+Ag) (39.59)	1	260°	-	-	Physical	sharp endotherm
		2	593°	593°	2.50	Chemical	sharp endotherm
		3	944°	944°	3.40	Chemical	sharp endotherm
16	Ag_2O	1	390°	390°	5.50	Chemical	endotherm
	(45.73)	2	951°	-	-	Physical	endotherm
17	(MnO_2+Cu) (57.44)	1	240°	240°	0.40	Chemical	endotherm
		2	560°	560°	4.20	Chemical	sharp endotherm
		3	740°	740°	2.20	Chemical	sharp endotherm
18	(MnO_2+Co) (57.58)	1	200°	200°	2.00	Chemical	endotherm (shoulder)
		2	360°	360°	0.60	Chemical	endotherm (shoulder)
		3	550°	550°	2.20	Chemical	endotherm
		4	700°	700°	2.20	Chemical	endotherm.

...contd.

TABLE 3 (Contd.)

S.No.	Oxidant (with % activity)	Peak No.	DTA	TG	% Wt loss	Type of change	Peak characteristic
19	(MnO_2+Ag) (85.16)	1	95°	95°	0.50	Chemical	exotherm
		2	480°	480°	1.00	Chemical	endotherm
		3	640°	-	-	Physical	endotherm
		4	750°	750°	2.00	Chemical	endotherm (shoulder)
		5	810°	810°	4.00	Chemical	endotherm
		6	960°	960°	1.00	Chemical	endotherm
20	T.d.p. of $AgMnO_4$ (85.89)	1	490°	490°	7.50	Chemical	endotherm
		2	665°	-	-	Physical	endotherm
		3	810°	810°	5.00	Chemical	endotherm

a: Prepared from cobaltous nitrate.

b: Prepared from cobaltous nitrate and sodium hypochlorite.

c: Prepared from cobaltous oxalate.

showing high activity, most of the oxygen is made available upto 810°. It may be added that the stages of weight loss are much less in oxidants having medium and low activities than in those showing high activity.

The oxidants which do not show any weight loss and yet show medium activities are CeO_2 and (Fe_2O_3+Ag) which undergo only physical changes. This cannot be explained unless the physical changes also contribute to the activities of the oxidants. Similar behaviour in CuO, WO_3 and NiO may be ignored due to their poor activities.

In (MnO_2+Cu) a weight gain of 1.90% was observed between 560° to 630°, which may be due to absorption of oxygen by the oxidant.

1.3.4 Mean particle size data

The activity of the catalyst is known to depend on the particle size. As the same material carrying particles of smaller size would have larger surface area as compared to the one having bigger particle size, it is generally known that the material containing smaller particles would have more activity.

In our study although the materials handled were different it was thought worthwhile to compare the activity of two materials having a comparable particle size. With this view particle size determination of all the oxidants

TABLE 4 - MEAN PARTICLE SIZE AND SURFACE AREA DATA OF OXIDANTS

S.No.	Oxidant	Mean particle size µm	Surface area m^2/g
1	CuO	0.38	0.06
2	WO_3	0.43	1.69
3	CoO	0.13	0.03
4	MnO_2	0.40	0.03
5	NiO	0.11	0.76
6	Ag_2WO_4	0.16	0.52
7	ZrO_2	0.82	2.23
8	V_2O_5	1.02	2.99
9	$(Fe_2O_3 + Ag)$	0.15	5.50
10[a]	Co_3O_4	0.17	3.53
11	(CeO_2+Ag)	0.15	6.01
12[b]	Co_3O_4	0.06	9.86
13[c]	Co_3O_4	(Agglomerates)	1.77
14	CeO_2	0.28	18.56
15	(Co_2O_3+Ag)	0.23	10.10
16	Ag_2O	(Agglomerates)	0.92
17	(MnO_2+Cu)	0.18	14.99
18	(MnO_2+Co)	0.17	15.45
19	(MnO_2+Ag)	0.13	9.82
20	T.d.p. of $AgMnO_4$	0.20	1.95

a: Prepared from cobaltous nitrate

b: Prepared from cobaltous nitrate and sodium hypochlorite.

c: Prepared from cobaltous oxalate.

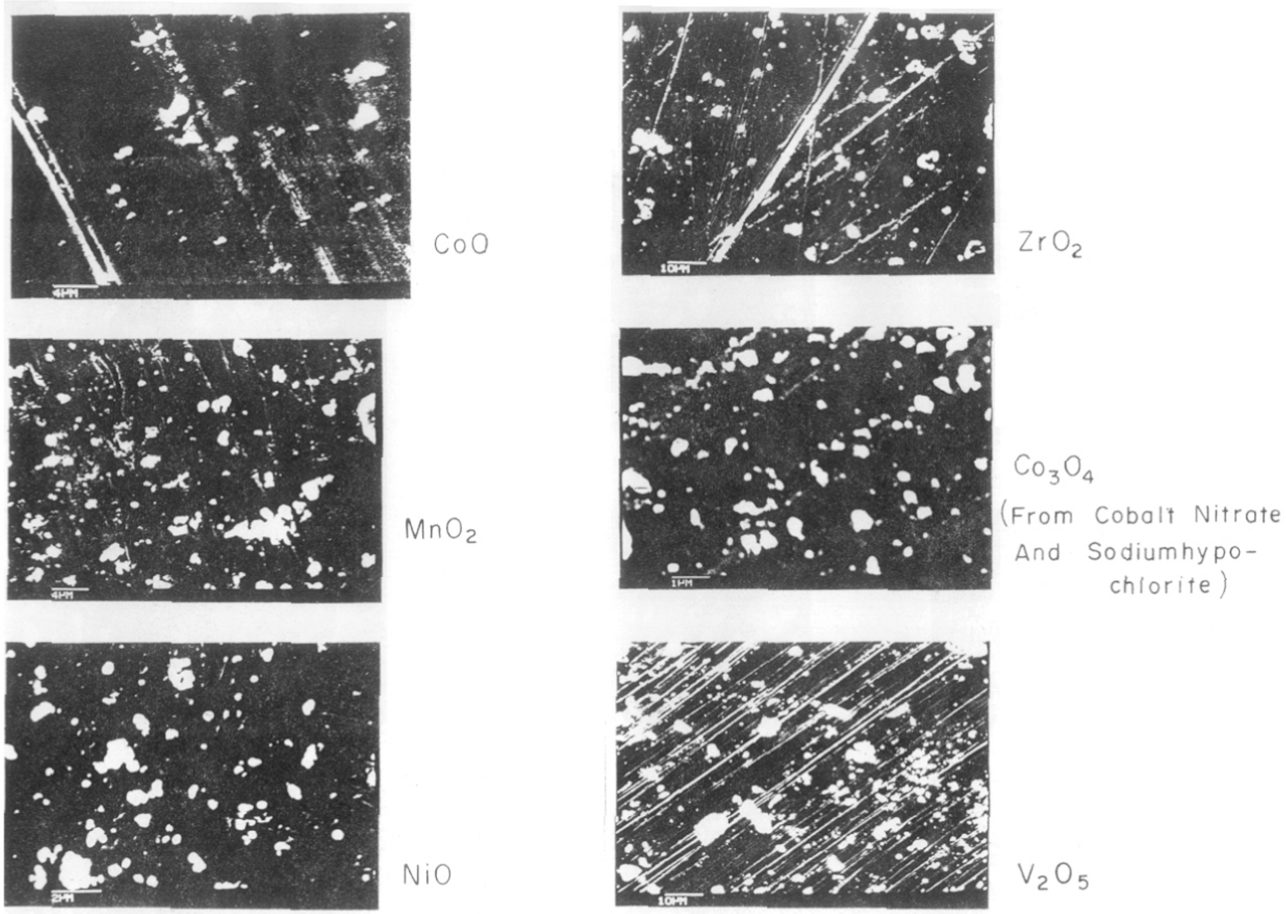
used was carried out as described before and the results are given in Table 4.

1.3.5 Surface area data

The data collected is given in Table 4. It can be seen that (MnO_2+Cu) and (MnO_2+Co) have comparable activities at 710° (57.44% and 57.58%). Their mean particle size (0.18 and 0.17 μm) and surface area (14.99 and 15.45 m^2/g) are also comparable. However, t.d.p. of $AgMnO_4$ and (MnO_2+Ag) which have similar activities (85.89% and 85.16%) have different particle size (0.20 and 0.13 μm) and very much different surface area (1.95 and 9.82 m^2/g). The activity of the catalysts studied, therefore, seems to be a characteristic of the individual catalysts and thus it cannot be correlated with these parameters. Perhaps sintering of the particles at high temperature may be one of the reasons for this anomaly.

1.3.6 X-ray photoelectron spectroscopy (XPS)

As the particle size and surface area determinations were not of much avail for correlating them with the activities, it was argued that the surface properties of the oxidants, if studied using X-ray photoelectron spectroscopy, might provide some explanation regarding their order of activities. It was believed that such a study might be specially useful in the oxidants having mixed oxides as the oxidation states of the elements involved would be revealed by their respective binding



CoO

ZrO_2

MnO_2

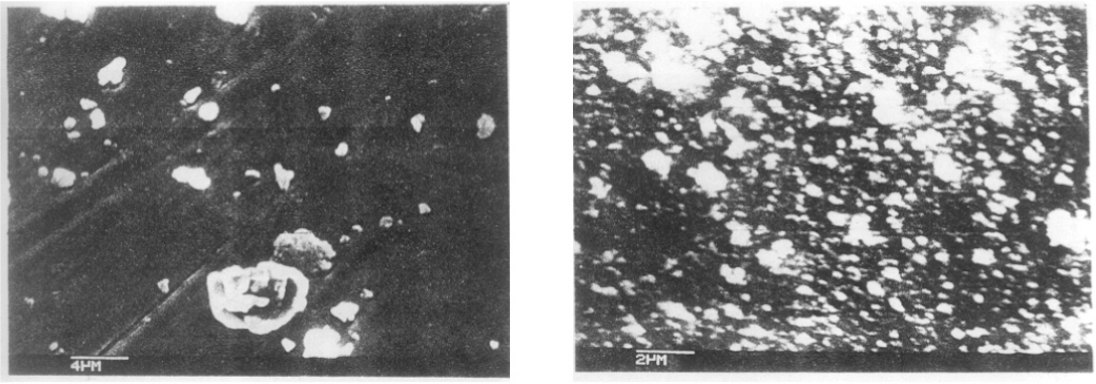
Co_3O_4 (From Cobalt Nitrate And Sodiumhypochlorite)

NiO

V_2O_5

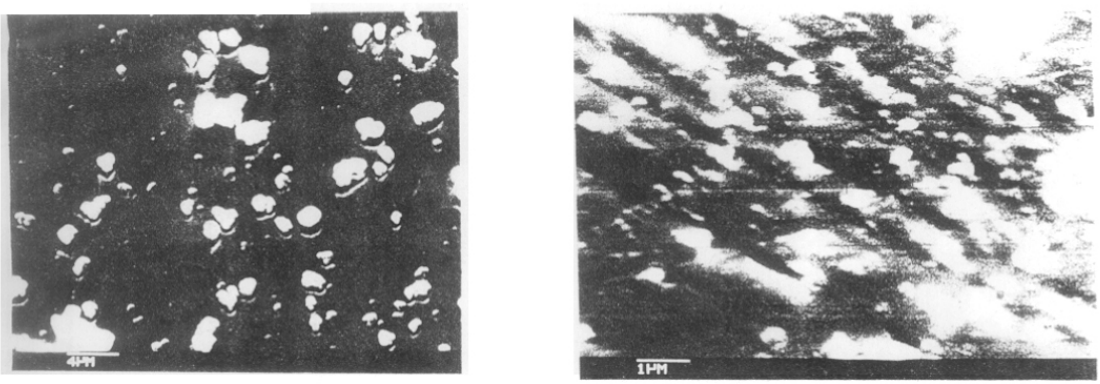
FIG. 16. SCANNING ELECTRON MICROPHOTOGRAPHS OF OXIDANTS

(Method given on p. 40)



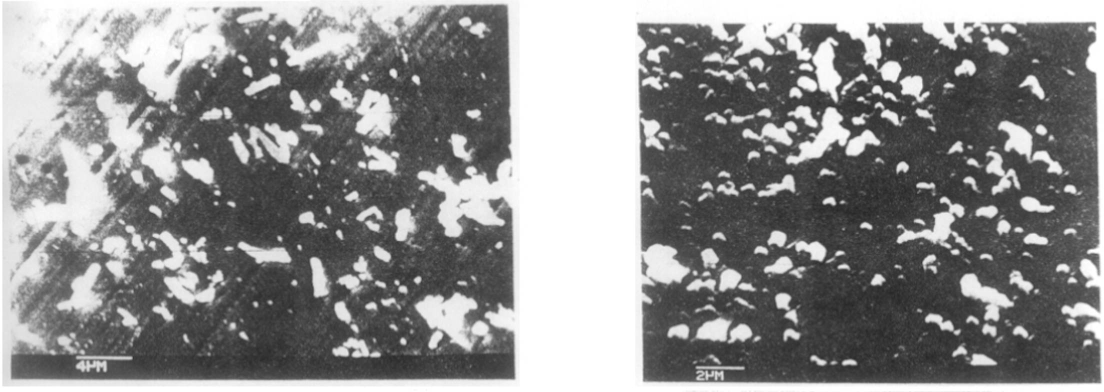
CuO

(Fe_2O_3 + Ag)



WO_3

Co_3O_4
(From Cobalt Nitrate)

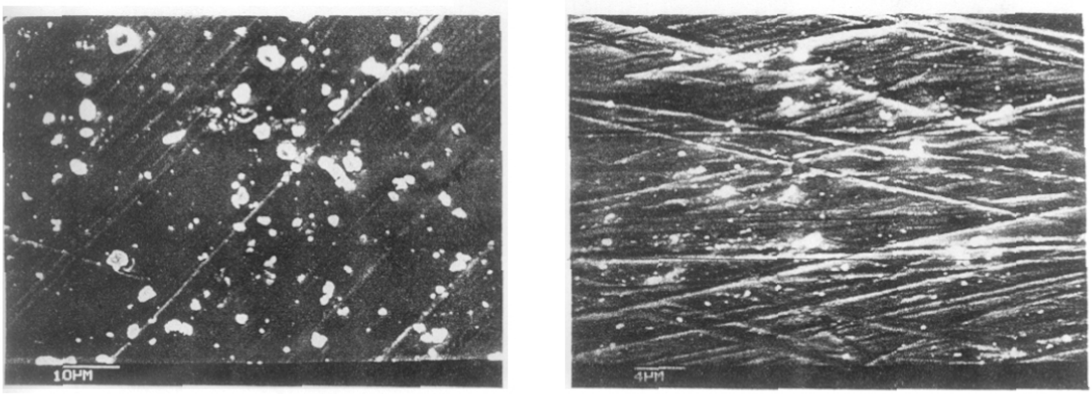


Ag_2WO_4

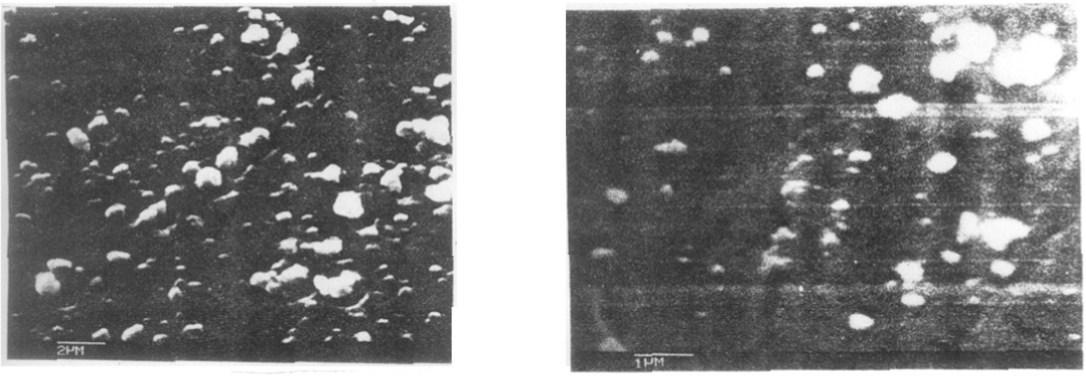
(CeO_2 + Ag)

FIG. 17. SCANNING ELECTRON MICROPHOTOGRAPHS OF OXIDANTS

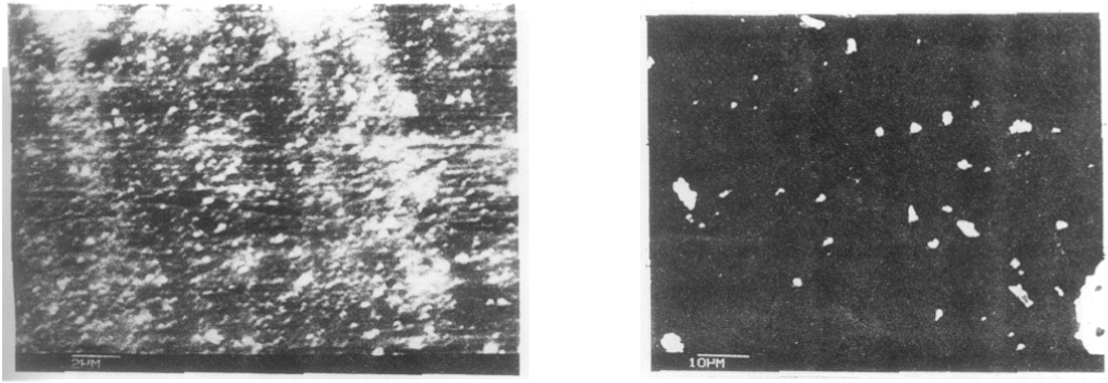
(Method given on p. 40)



CeO_2 $(MnO_2 + Co)$



$(Co_2O_3 + Ag)$ $(MnO_2 + Ag)$



$(MnO_2 + Cu)$ T. d. p. $AgMnO_4$

FIG. 18. SCANNING ELECTRON MICROPHOTOGRAPHS OF OXIDANTS

(Method given on p. 40)

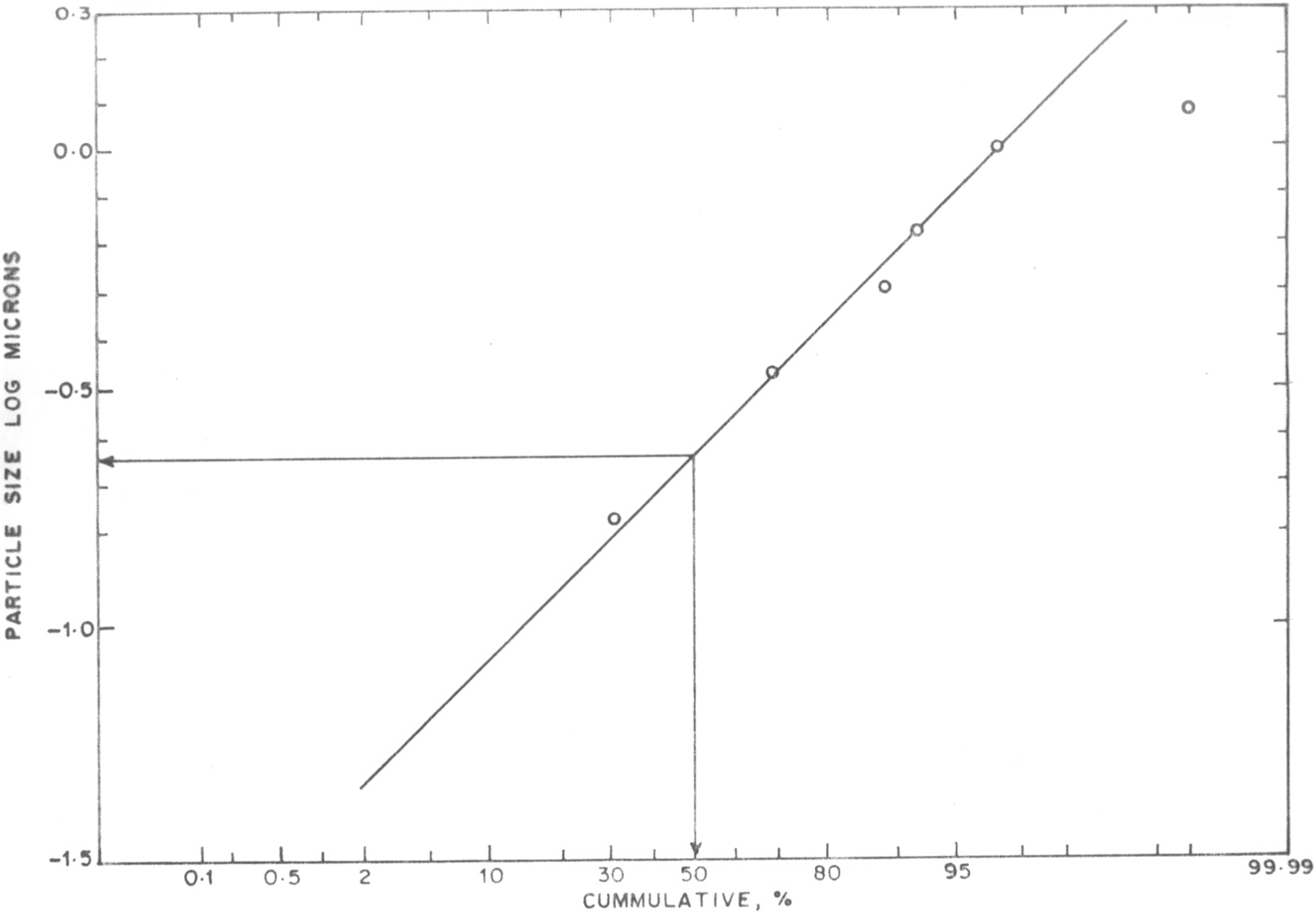


FIG. 19. PROBABILITY GRAPH FOR PARTICLE SIZE OF (Co_2O_3 + Ag)
(Method given on p. 40)

energies, multiplet splittings and the associated satellites.

The x-ray photoelectron spectra of the mixed oxides were therefore recorded and the binding energies for the core levels 2p, 3d, etc. of the respective elements and oxygen (1s) are given in Tables 5 to 8.

Measurements for oxygen

Table 5 gives the binding energies of oxygen for 1s core level in different mixed oxides. It would be seen that there is a positive shift in the oxides which contain Mn when the values are compared with those reported for MnO_2 by Rao et al.[48]. An additional peak is seen on a slightly higher side in each of the four mixed oxides of Ag i.e. T.d.p. of $AgMnO_4$, (MnO_2+Ag), (Co_2O_3+Ag) and (Fe_2O_3+Ag). It is also seen in the spectra of $(MnO_2 + Cu)$ and (MnO_2+Co). Moyes and Roberts[49] in their study of Co_3O_4 have reported such an additional peak for oxygen and have attributed it to the presence of hydroxide or adsorbed moisture at the surface. However, the additional peak reported above for the mixed oxides seems to be due to chemisorbed oxygen as the IR spectra of the materials showed absence of a band in the hydroxyl group region. The peaks for lattice oxygen and chemisorbed oxygen are depicted in Fig.20. The values obtained for binding energies of oxygen indicate

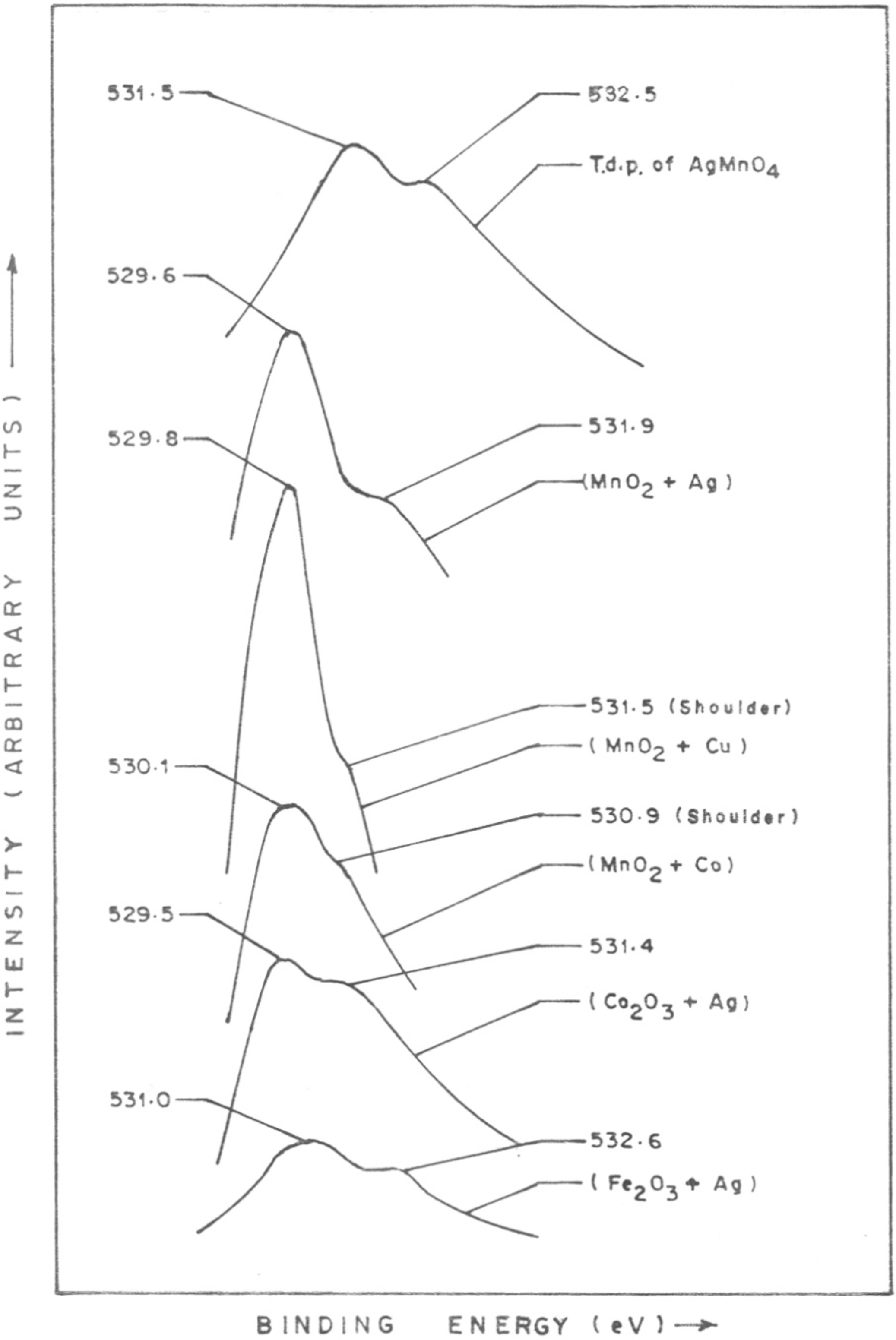


FIG. 20. XPS OF 1s CORE LEVEL OF OXYGEN IN MIXED OXIDES

TABLE 5 - BINDING ENERGIES OF 1s CORE LEVEL OF OXYGEN IN MIXED OXIDES

Mixed oxide	1s (eV)			
	Observed	Reported	△ eV	Ref.
1. T.d.p. of $AgMnO_4$	531.5 532.5	529.2 (MnO_2)	+2.3 +3.3	48,49
2. (MnO_2 + Ag)	529.6 531.9	529.2 (MnO_2)	+0.4 +2.7	48,49
3. (MnO_2 + Cu)	529.8 531.5 (Shoulder)	529.2 (MnO_2)	+0.6 +2.3	48,49
4. (MnO_2 + Co)	530.1 530.9 (Shoulder)	529.2 (MnO_2)	+0.9 +1.7	48,49
5. (Co_2O_3 + Ag)	529.5 531.4	529.5 531.5 (Co_3O_4)	0.0 -0.1	48,49
6. (Fe_2O_3 + Ag)	531.0 532.6	529.3 (Fe_2O_3)	+1.7 +3.3	48,49

TABLE 6 - BINDING ENERGIES OF 2p CORE LEVELS OF MANGANESE IN MIXED OXIDES

Mixed oxide	$2p_{3/2}$ (eV)			$2p_{1/2}$ (eV)			Reference
	Observed	Reported (MnO_2)	Δ(eV)	Observed	Reported (MnO_2)	Δ(eV)	
1. T.d.p. of $AgMnO_4$	642.6	641.9	+0.7	653.3	653.5	-0.2	48
2. (MnO_2 + Ag)	642.0	641.9	+0.1	653.9	653.5	+0.4	48
3. (MnO_2 + Cu)	642.0	641.9	+0.1	653.6	653.5	+0.1	48
4. (MnO_2 + Co)	642.1	641.9	+0.2	653.7	653.5	+0.2	49

TABLE 7 - BINDING ENERGIES OF 2p CORE LEVELS OF IRON, COBALT AND COPPER IN MIXED OXIDES

Mixed oxide	$2p_{3/2}$ (eV)			$2p_{1/2}$			Reference
	Observed	Reported	ΔeV	Observed	Reported	ΔeV	
Fe in (Fe_2O_3+Ag)	712.4	710.3 (Fe_2O_3)	+2.1	726.5	723.6 (Fe_2O_3)	+2.9	48
Co in (Co_2O_3+Ag)	779.7	780.0 (Co^{+3})	-0.3	795.0	795.5 (Co^{+3})	-0.5	48
Co in (MnO_2+Co)	781.3	781.5 (CoO)	-0.2	796.2	797.0 (CoO)	-0.8	48
Cu in (MnO_2+Cu)	933.3	933.2 (CuO)	+0.1	not recorded.	953.4 (CuO)	-	48

TABLE 8 - BINDING ENERGIES OF 3d CORE LEVELS OF SILVER IN MIXED OXIDES

Mixed Oxide	$3d_{5/2}$ (eV)			$3d_{3/2}$			Reference
	Observed	Reported (Ag_2O)	Δ(eV)	Observed	Reported (Ag_2O)	Δ(eV)	
1. T.d.p. of $AgMnO_4$	368.4	368.6	-0.2	374.4	374.6	-0.2	50,51
2. (MnO_2+Ag)	367.5	368.6	-1.1	373.6	374.6	-1.0	50,51
3. (Co_2O_3+Ag)	368.1	368.6	-0.5	374.0	374.6	-0.6	50,51
4. (Fe_2O_3+Ag)	368.8	368.6	+0.2	374.9	374.6	+0.3	50,51

the tendency to transfer electrons (covalent bonding) in a mixed system as compared to those in the individual metal oxides.

Measurements for Manganese:

Table 6 gives binding energies of 2p core levels of Mn in the mixed oxides. In all these mixed oxides, the observed peaks for $2p_{3/2}$ and $2p_{1/2}$ are shifted to the positive side except in the $2p_{1/2}$ level in the t.d.p. of $AgMnO_4$ where the binding energy indicates a slight reduction. Thus, Mn in these mixed oxides shows a tendency to transfer its outer electrons for formation of a bond with the other metal.

The Mn 2p XPS-spectra recorded here are for the qualitative purpose only to indicate the complex bond formation.

Measurements for Iron, Cobalt and Copper:

Table 7 gives some data obtained for the mixed oxides containing oxides of Ag with those of Fe, Co and Cu, respectively. The binding energy measurements show shifts in all the cases which indicate tendencies for transfering outer electrons for formation of a bond with the other metal in each case.

Measurementsfof silver:

Binding energies at the 3d core levels of Ag in the mixed oxides are given in Table 8. Here also there is a shift at both $3d_{5/2}$ and $3d_{3/2}$ levels indicating the bonding of Ag with the other metal.

It may therefore be concluded that the metals in the mixed oxides seem to have entered into a complex bond formation, and that a more detailed study at other core levels only might provide some additional information regarding the exact nature of the complex bond formation. The indication of such a bond formation in the mixed oxides together with the evidence obtained for the chemisorbed oxygen in them might be the reason for their higher activities.

1.4 Conclusion

From the foregoing discussion it would be clear that the method described for determining the relative activities of the sample-additive reagents in this part of the thesis has several advantages which are detailed below.

1. Unlike the earlier methods for the determination of activities of the combustion catalysts this method is rapid. The apparatus needed is the usual one for the rapid microdetermination of carbon and hydrogen and can be used advantageously without disturbing the arrangement for routine analytical work.

2. The quantity of the catalyst (sample-additive) needed is only a few milligrams.

3. This method has a unique advantage in that the catalysts can be graded according to their activities, which has not been possible by the method of Childs[8] due to the number of oxidation products formed in his method. Although Horáček[2] et al. have been able to group the catalysts in various groups a distinction between two catalysts having similar activities has been possible only by the method described here.

The dependability of the method is also substantiated by the trend of oxygen availability revealed in thermal analysis studies. Although the particle size and the surface area data have not been useful for correlating them with the activities the XPS data furnishes some favourable points to explain the high activity of some of the sample-additive reagents.

PART 2

KINETIC STUDIES OF COMBUSTION OF PHENANTHRENE WITH VARIOUS SAMPLE-ADDITIVE REAGENTS

2.1 Introduction

The method described for determining the activities of sample-additive reagents in Part 1 is based on the ability of the oxidant to oxidise the test compound and studying, essentially, the quantity of the compound oxidised. In this part of the thesis the efforts described are aimed at gathering information about the rate of combustion with a view to correlating it with the activity of the sample-additive reagent.

2.1.1 Methods to study the mechanism of catalytic oxidation

Sachtler[52] has discussed mechanism of the catalytic oxidation of some organic molecules in detail by considering the evidence based on isotopic, chemical evidence and other physical methods including electron diffraction, paramagnetic methods, infra-red spectroscopy etc. It has been pointed out that the transition metal oxide activates the gaseous oxygen and this has been established by tagging a transition metal oxide with ^{18}O and carrying out oxidation with normal $^{16}O_2$. It has been found that the ^{18}O content of the oxide remains constant.

An organic molecule can undergo conversion in different directions giving a variety of products on the surface of a catalyst. Development and studies of theories for catalyst selection, therefore, became important[53]. Selectivity in heterogeneous catalytic oxidation of hydrocarbons has been discussed by Haber[54] in terms of the type of intermediate complex formed. It has been stated that activation of oxygen leads to total oxidation through electrophilic attack on the double bond and formation of the complex of the peroxide or epoxide type. However, partial oxidation requires activation of the hydrocarbon molecule resulting in the formation of the allyl species bonded as ligand in the intermediate complex.

Chemical kinetics study has always been an important tool in understanding the mechanism of oxidation. Its application to the study of combustion behaviour of organic compounds seems to be far more complex[55]. Although there is some information available in literature on the effect of additives in heterogeneous systems on combustion of hydrocarbons, most of this information is in Russian and it is only cited in chemical abstracts[56-58]. Fortunately an excellent review by Ruckenstein et al.[59] has been very useful for this purpose.

In this recent review by Ruckenstein et al. the use of catalytic combustion for a variety of applications mainly gas turbines and aircraft afterburners, etc. have been mentioned. Recent developments in various aspects of catalytic combustion are also summarized. In discussion on heterogeneous reactions in kinetics of fuel oxidation it has been pointed out that the details of the reaction mechanisms for the oxidation on catalysts are not well known for most catalysts, and that they are expected to differ from catalyst to catalyst depending on the intermediates formed and the active sites involved.

Ruckenstein *et al.*[60] and Yu Yao[61] have studied the kinetics for the oxidation of CO and some simple hydrocarbons by oxygen over various transition metal oxides. In pure oxides the rate of oxidation is inhibited by water vapour, which is due to strong chemisorption of water on surfaces. The rate of oxidation is not greatly influenced by the oxygen partial pressure.

2.1.2 Study of combustion kinetics on microscale

Information in the literature on the determination of rate of combustion of organic compounds on *microscale* using different catalysts is very scanty. The only exception is that of Večeřa *et al.*[62] who have carried out systematic study on rate of combustion with a view to developing a rapid method for the microdetermination of carbon and hydrogen. By studying the progress of combustion with different flow rates of oxygen, they arrived at the optimum conditions for rapid combustion analysis of organic compounds. They have reported also on the activities of different catalysts using them in the form of a layer in the combustion tube and have inferred that the thermal decomposition product of $AgMnO_4$ loses its activity when used continuously. They have recommended Co_3O_4 as the best catalyst for smooth combustion of organic compounds. However, the present work deals with the use of such catalysts as sample-additive reagents and for the reason explained in Part 1, namely the use of limited quantity of the catalyst their behaviour was expected to differ from what was observed by Vecera and coworkers. The results reported in Part 1, indicate that the reasoning is borne out since the t.d.p. of $AgMnO_4$ has emerged as the best sample-additive reagent among those studied.

2.1.3 Limitations in the measurements

Unlike most of the other reactions in solutions, the heterogeneous reaction which is studied here would naturally have certain limitations. The first one is the accurate temperature control which is rather difficult. The second one is the accuracy in the determination of the end products of combustion at fixed time intervals. This is mainly because our experience shows that the combustion, when carried out at a low temperature for a conveniently measurable rate, yields the end products in pulses. On the other hand, at a slightly higher temperature the combustion proceeds rapidly to make the measurements inconvenient and unmeaningful. This is the main reason for postponing the determination of activation energies of the systems studied. Attempts are in progress for a suitable improvisation of the apparatus to enable the determinations of the activation energies.

2.1.4 Present Work

The work presented in this part of the thesis describes the determination of gross rates of combustion of phenanthrene using ten different sample-additive reagents. Unlike in Part 1, where acetanilide has been used as the test-compound, phenanthrene had to be used for the study in this part because the end products of combustion are only CO_2 and H_2O in phenanthrene and the measurement of CO_2 is straightforward without any hindrance. The end products of combustion in the case of acetanilide would contain nitrogen oxides (NO and NO_2) as additional products and the conversion of NO to NO_2 necessitates inclusion of an additional absorption tube containing MnO_2 having enough blank space for conversion of NO to NO_2. As the absorption of CO_2 can be effected only after the removal of nitrogen oxides admixed with it, the measurement of CO_2 in this particular study would be unsatisfactory if acetanilide is used as the test-compound for determining the rates of combustion, because CO_2 has to be weighed at fixed time intervals.

2.1.5 Kinetic study

Kinetic studies in the system described here are rather complex due to many shortcomings inherent to such systems. As the entire study is carried out on microscale the sample used for oxidation, (phenanthrene in this case) has necessarily to be less than 10 mg. The catalyst used for kinetic studies is usually a small fraction of the weight of the sample to be oxidised. However, for the work described here the catalyst had to be used in large proportions to affect the rate of combustion of phenanthrene. Although the combustion under these conditions is expected to be a pseudo-first order reaction due to the large excess of the sample-additive reagent (catalyst) and oxygen, the measurement might not lead to precise data as expected for a first order reaction in solutions. Thus the values of the rate constants and the equations for the best straight lines would grossly give some idea about the relative progress of combustion when different sample-additive reagents are used for combustion of phenanthrene.

2.2 EXPERIMENTAL

2.2.1 Apparatus

The apparatus described in Part 1 on page 22 and in Fig.1 was used for carrying out combustion, with the only exception of the MnO_2 absorption tube which was dropped for the reasons explained above. The sample furnace was maintained at 300 ± 5^0 all through.

2.2.2 Materials

i) Phenanthrene A.R.

ii) "Dehydrite" brand granular magnesium perchlorate, anhydrous, for absorption of water. Arthur H. Thomas Co., USA.

iii) "Ascarite" brand sodium hydroxide on asbestos 8-20 mesh for absorption of CO_2. Arthur H. Thomas Co., USA.

iv) The following sample-additive reagents were used, the details of which are already given in Part 1.
a) MnO_2 (b) NiO (c) Co_3O_4[a] (d) V_2O_5 (e) (CeO_2+Ag)
(f) (Co_2O_3+Ag) (g) (MnO_2+Cu) (h) (MnO_2+Co) (i) (MnO_2+Ag)
(j) T.d.p. of $AgMnO_4$.

2.2.3 Procedure

About 3 mg phenanthrene was weighed accurately in the quartz capsule, to which was added accurately weighed

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[a]: Co_3O_4 was prepared from cobaltous nitrate.

sample-additive reagent in the range 30-35 mg. The sample and the oxidant were mixed thoroughly by rotating the capsule. It was then placed in the combustion tube as described in Part 1. The rate of oxygen was regulated to 50 ml/min. A spare preweighed CO_2 absorption tube, through which oxygen was passed continuously at a rate of 5 ml/min separately, was kept ready for replacement at the required time interval.

After ascertaining that the silver-furnace and the main furnace attained the usual temperatures i.e. 520^{o} and 900^{o}, respectively, the movable sample furnace maintained at 300^{o} was drawn over the combustion tube so that the central zone of the furnace covered the sample and oxidant mixture in the capsule. At a suitable fixed time interval after the combustion was started, the CO_2 absorption tube, the weight of which was recorded before starting the combustion, was removed for weighing and the spare preweighed absorption tube was attached quickly in its place. The CO_2 absorption tubes, were thus used alternately for studying the progress of combustion. These absorption tubes were weighed exactly two minutes after their removal from the assembly and flow of oxygen was maintained through them after weighing as described above.

The rate constant k_1 was determined using the usual first-order rate equation $k_1 = \frac{2.303}{t} \log (\frac{a}{a-c})$. The calculations for finding equation for the best straightline were carried out using the method of least squares.

2.3 Results and Discussion

2.3.1 Stages of combustion

The sample-additive reagents studied in this part of the thesis represent all the three groups showing different activities. Thus MnO_2 and NiO which have low activity, Co_3O_4, V_2O_5, (CeO_2+Ag) and (Co_2O_3+Ag) which show medium activity and (MnO_2+Cu), (MnO_2+Co), (MnO_2+Ag) and t.d.p. of $AgMnO_4$ possessing high activity, were selected for studying the rates of combustion of phenanthrene.

In most of the cases, the rate of combustion was rapid in the initial stages and it became steady after the initial stage was over. Only exception to this was (MnO_2+Co) where the initial rate was slow and the combustion was rapid in the second stage (Fig.21c).

2.3.2 Data of combustions

Data obtained during the combustion of phenanthrene with (MnO_2+Ag) as the oxidant is given in Table 9 as an example. Calculations to find the rate constant k_1 and the method of finding the equation for the best straight line are also illustrated. Rate constants and equations obtained

TABLE 9- COMBUSTION DATA OF PHENANTHRENE WITH (MnO_2+Ag) at 300 ± 5°

Phenanthrene: 3.120 mg (MnO_2+Ag): 30.600 mg

Time (min.)	-CO_2 collected (mg)	Sample combusted* (mg)	Total sample combusted (mg)
5	1.520	0.4394	0.4394
10	0.870	0.2515	0.6909
15	0.100	0.0289	0.7198
20	0.095	0.0275	0.7473
25	0.080	0.0231	0.7704
30	0.090	0.0260	0.7964
35	0.055	0.0159	0.8123
40	0.015	0.0043	0.8166
45	0.030	0.0087	0.8253
50	0.045	0.0130	0.8383

*Phenanthrene contains 94.34% carbon

$\therefore$ Wt. of the sample combusted = mg CO_2 X $\frac{12}{(44 x 0.9434)}$

= mg CO_2 X 0.2891

Calculations for the first-order rate constant k_1:

First-order rate equation is

$$k_1 = \frac{2.303}{t} \log \left(\frac{a}{a-c}\right) \qquad (A)$$

Where k_1 = first-order rate constant.

a = initial concentration of the sample in m mol

c = total quantity of the sample combusted at time 't'.

k_1 between 10 min. to 35 min.:

As the combustion proceeds very rapidly in the initial 10 min. (Fig.21c), the data obtained after 10 min. only is considered for calculations.

The quantity of the sample available for combustion at the 10th min. is given by

the initial weight of the sample - total weight of the sample combusted in 10 min.

i.e. 3.1200 mg - 0.6909 mg = 2.4291 mg i.e. 0.013647 m mol.

t (min.)	a (m mol)	c (m mol)	a - c (m mol)	$\frac{a}{a-c}$	$\log \left(\frac{a}{a-c}\right)$
5	0.013647	0.000162	0.013485	1.0120	0.0052
10	0.013647	0.000317	0.013330	1.0238	0.0103
15	0.013647	0.000447	0.013200	1.0338	0.0145
20	0.013647	0.000593	0.013054	1.0454	0.0191
25	0.013647	0.000682	0.012965	1.0526	0.0224

Substituting these values in equation (A)

$$k_1 = \frac{2.303}{5} \times 0.0052 = 0.0024$$

$$= \frac{2.303}{10} \times 0.0103 = 0.0024$$

$$= \frac{2.303}{15} \times 0.0145 = 0.0022$$

$$= \frac{2.303}{20} \times 0.0191 = 0.0022$$

$$= \frac{2.303}{25} \times 0.0224 = 0.0021$$

$\therefore$ Average $k_1 = (2.3 \pm 0.2) \times 10^{-3}$ min^{-1}

i.e. $= (3.83 \pm 0.33) \times 10^{-5}$ sec.$^{-1}$

<u>Finding an equation for the best straight line between the points on the curve of the sample combusted versus time for (MnO_2+Ag) (vide Fig.21b)</u>

Equation of the straight line is in the form $y = a + bx$, where x and y represent the time of combustion in minutes and the quantity of the sample combusted in milligrams, respectively. 'a' indicates the intercept on y-axis and 'b' gives the slope of the straight line.

Equation of the best straight line between the points 10t and 35t:

6 points on the graph are:

(10, 0.6909), (15, 0.7198), (20, 0.7473), (25, 0.7704), (30, 0.7964), (35, 0.8123).

	x	y	xy	x^2
1	10	0.6909	6.9090	100
2	15	0.7198	10.7970	225
3	20	0.7473	14.9460	400
4	25	0.7704	19.2600	625
5	30	0.7964	23.8920	900
6	35	0.8123	28.4305	1225
6	135	4.5371	104.2345	3475
n	$\sum X_j$	$\sum Y_j$	$\sum X_j Y_j$	$\sum X^2_j$

According to least squares method, the normal simultaneous equations are:

$$a\,n + b \sum X_j = \sum Y_j \qquad \text{(i)}$$

$$a \sum X_j + b \sum X^2_j = \sum X_j\, Y_j \qquad \text{(ii)}$$

where n is the number of points on the graph and a and b are constants. Therefore, substituting the above values in the simultaneous equations we get

$$6a + 135b = 4.5371 \text{ (A)} \times 45$$

$$135a + 3475b = 104.2345 \text{ (B)} \times 2$$

On solving them we obtain

$a = 0.646$ (intercept) and $b = 0.005$ (slope)

$\therefore$ The equation for the best straight line between 10t and 35t would be: $y = 0.646 + 0.005x$

by this method for various oxidants have been shown in Table 10 which also includes the percentage activities of the oxidants determined by the method described in Part 1. Fig.21a, 21b and 21c depict the graphical representation of progress of combustion of phenanthrene using various oxidants. The extent of reaction in each case has been shown in Fig.22a, 22b and 22c. Further, the first-order reaction plots showing linear relationship of log $(\frac{a}{a-c})$ with time, are also given inFig.23a, 23b and 23c.

It would be clear from these Figures i.e. Fig.23a, 23b and 23c, that some of them obey the first-order rate law throughout after the initial stage of rapid combustion is over. The plots for (MnO_2+Cu) and T.d.p. of $AgMnO_4$ are in point. The remaining ones, however, show a deviation after sometime which might be due to a change in the order of reaction or some other unknown cause. All these plots in Fig.23a, 23b and 23c indicate the respective times (which can be regarded as the respective origins) at which the systems start obeying the first-order rate law after completion of the initial fast reactions. The range upto which this rate law is obeyed is indicated by the deviation in most of the cases as explained before.

TABLE 10 - RATE CONSTANTS AND BEST STRAIGHT LINE EQUATIONS FOR COMBUSTION OF PHENANTHRENE WITH VARIOUS OXIDANTS

Sl. No.	Oxidant	% activity	Stage of combustion (min.)	Rate constant k_1 X 10^{-5} sec^{-1}	Equation of best straight line
1	MnO_2	2.52	1(0-18)Rapid 2(18-39) 3(39-45)	1.80 ± 0.20	y=0.052 + 0.004x
2	NiO	3.72	1(0-10)Rapid 2(10-60)	- 2.70 ± 0.50	- y=0.042 + 0.005x
3	(CeO_2+Ag)	18.90	1(0-15)Rapid 2(15-40)	1.50 ± 0.17	y=0.257 + 0.003x
4	(Co_2O_3+Ag)	29.17	1(0-12)Rapid 2(12-33)	2.80 ± 0.50	y=0.383 + 0.004x
5	Co_3O_4	30.00	1(0-18)Rapid 2(18-39) 3(39-60)	3.70 ± 0.70	y=0.239 + 0.006x
6	V_2O_5	25.37	1(0-35)Rapid 2(35-50) 3(50-65)	5.17 ± 0.33	y=0.732 + 0.006x
7	(MnO_2+Co)	35.59	1(0-30) 2(30-55)Rapid 3(55-80)	3.50 ± 0.33	y=0.663 + 0.004x
8	(MnO_2+Cu)	34.41	1(0-15)Rapid 2(15-75)	5.70 ± 0.30	y=0.684 + 0.007x
9	(MnO_2+Ag)	58.99	1(0-10)Rapid 2(10-35) 3(35-50)	3.83 ± 0.33	y=0.646 + 0.005x
10	T.d.p. of $AgMnO_4$	66.41	1(0-15)Rapid 2(15-70)	2.33 ± 0.50	y=0.793 + 0.003x

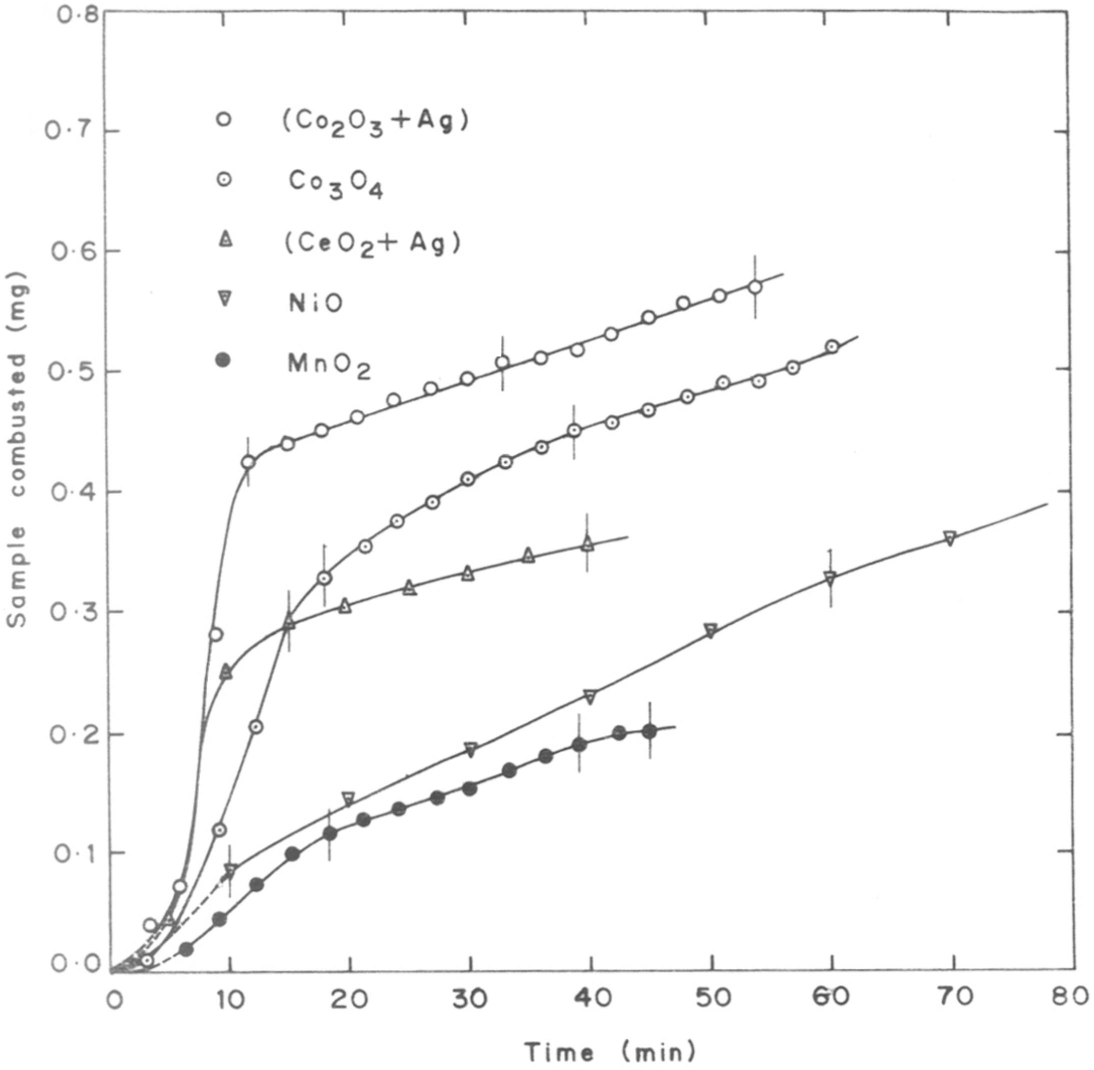


FIG. 21a PROGRESS OF COMBUSTION OF PHENANTHRENE WITH VARIOUS OXIDANTS

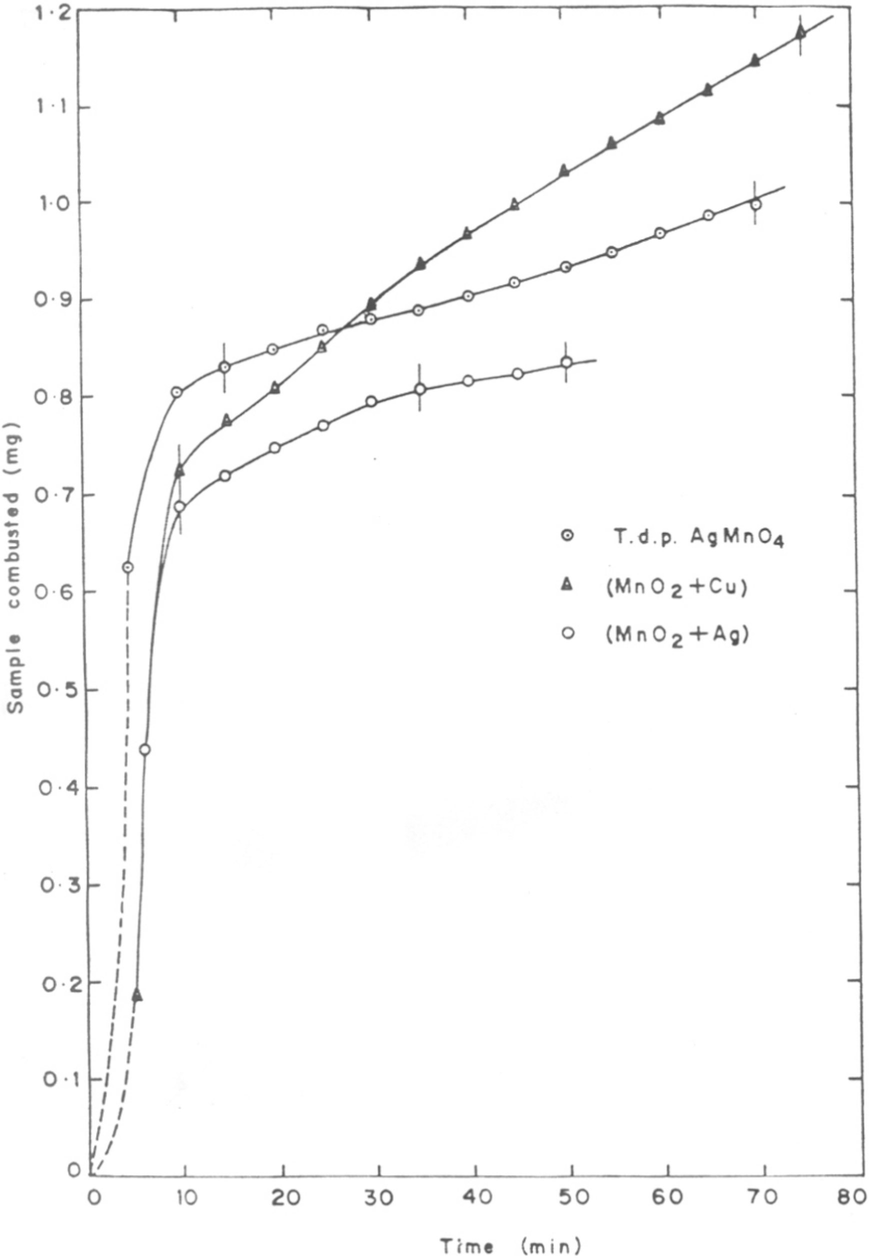


FIG. 21b PROGRESS OF COMBUSTION OF PHENANTHRENE WITH OXIDANTS HAVING HIGH ACTIVITY

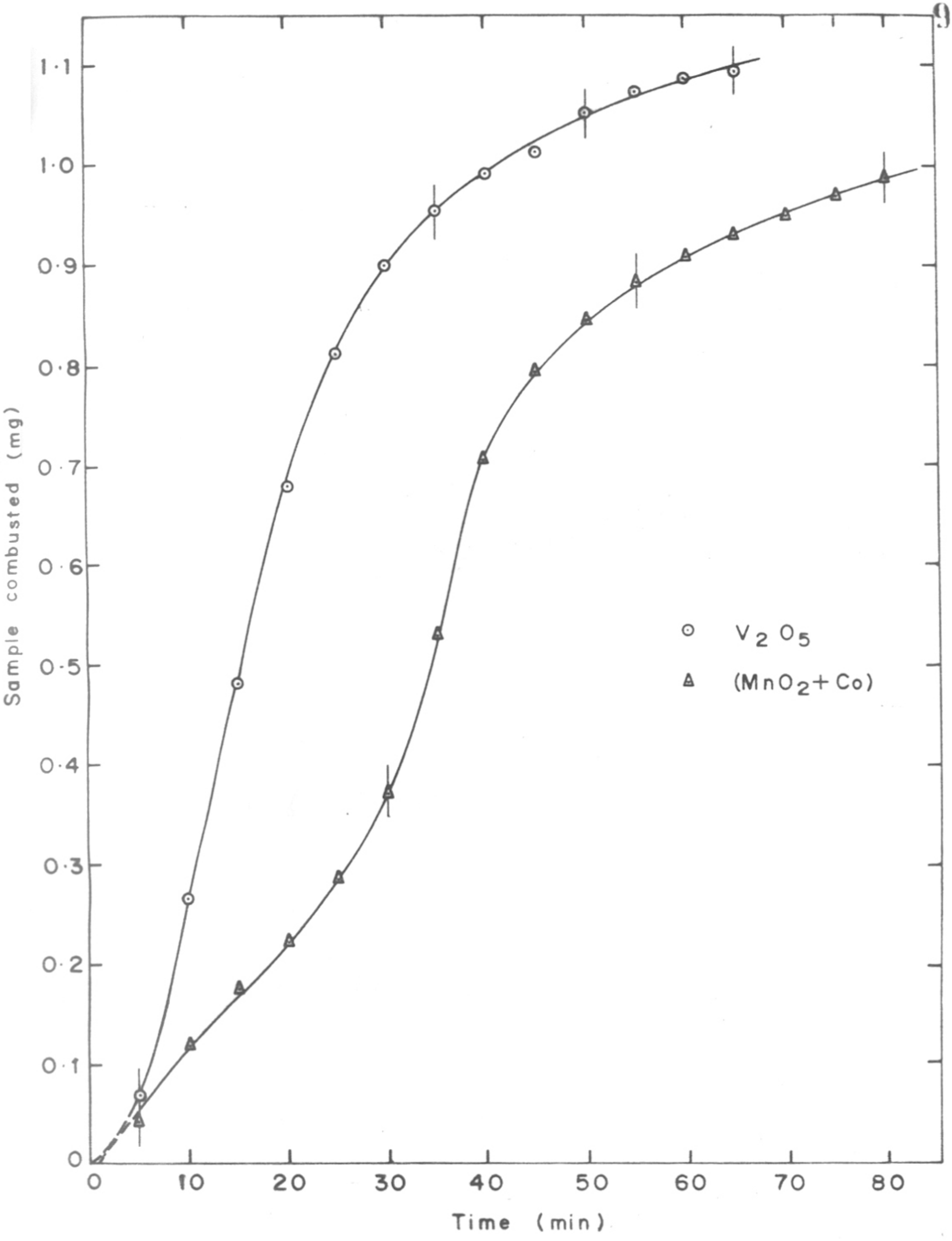


FIG. 21c PROGRESS OF COMBUSTION OF PHENANTHRENE WITH V_2O_5 AND (MnO_2+Co)

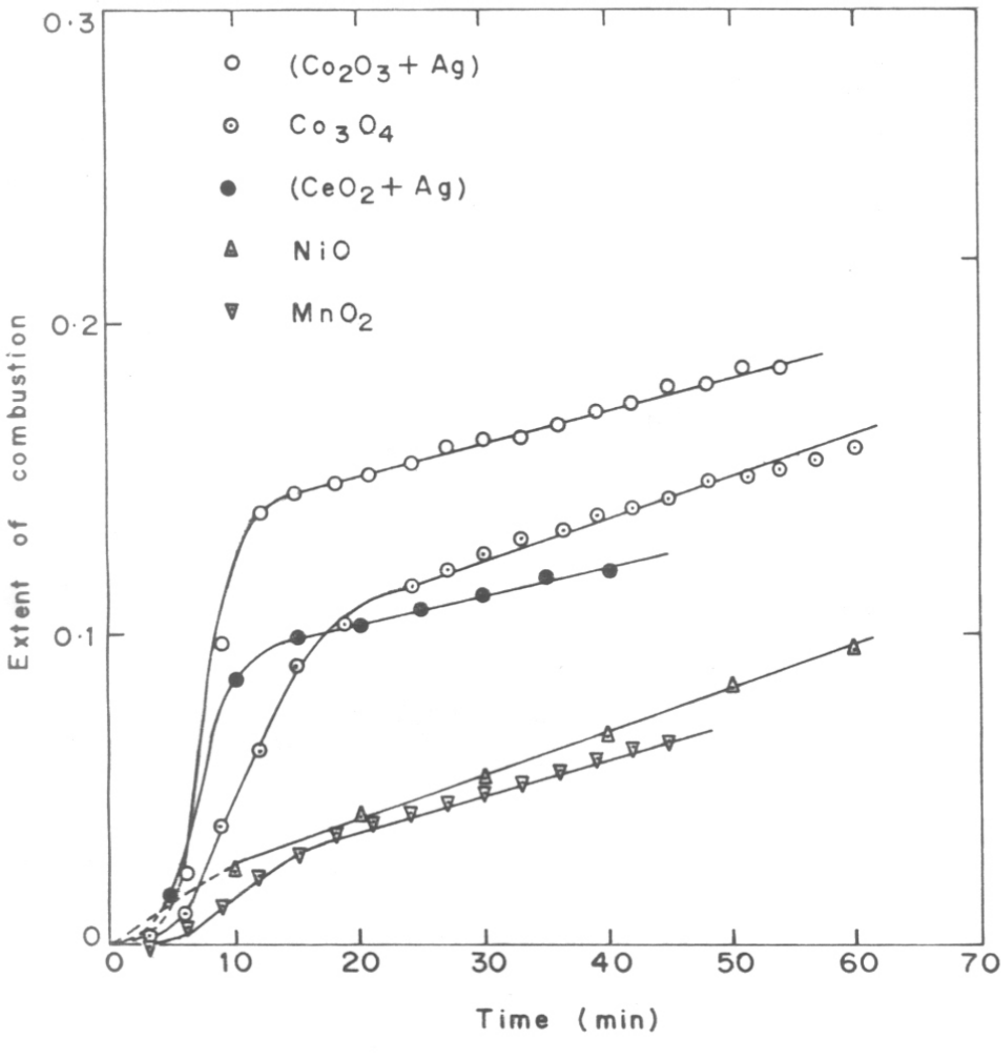


FIG. 22a EXTENT OF COMBUSTION OF PHENANTHRENE WITH VARIOUS OXIDANTS

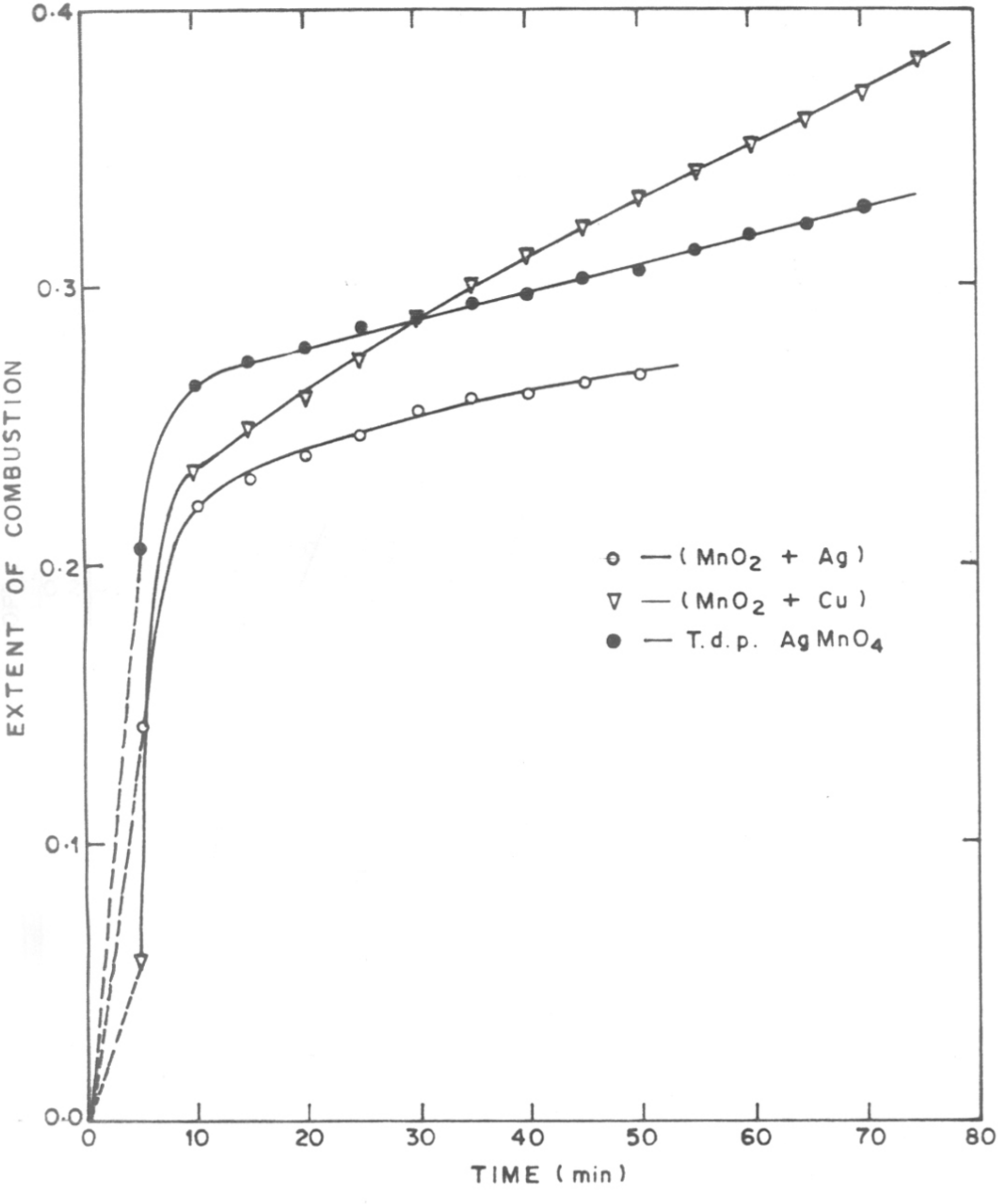


FIG. 22 b . EXTENT OF COMBUSTION OF PHENANTHRENE WITH OXIDANTS HAVING HIGH ACTIVITY

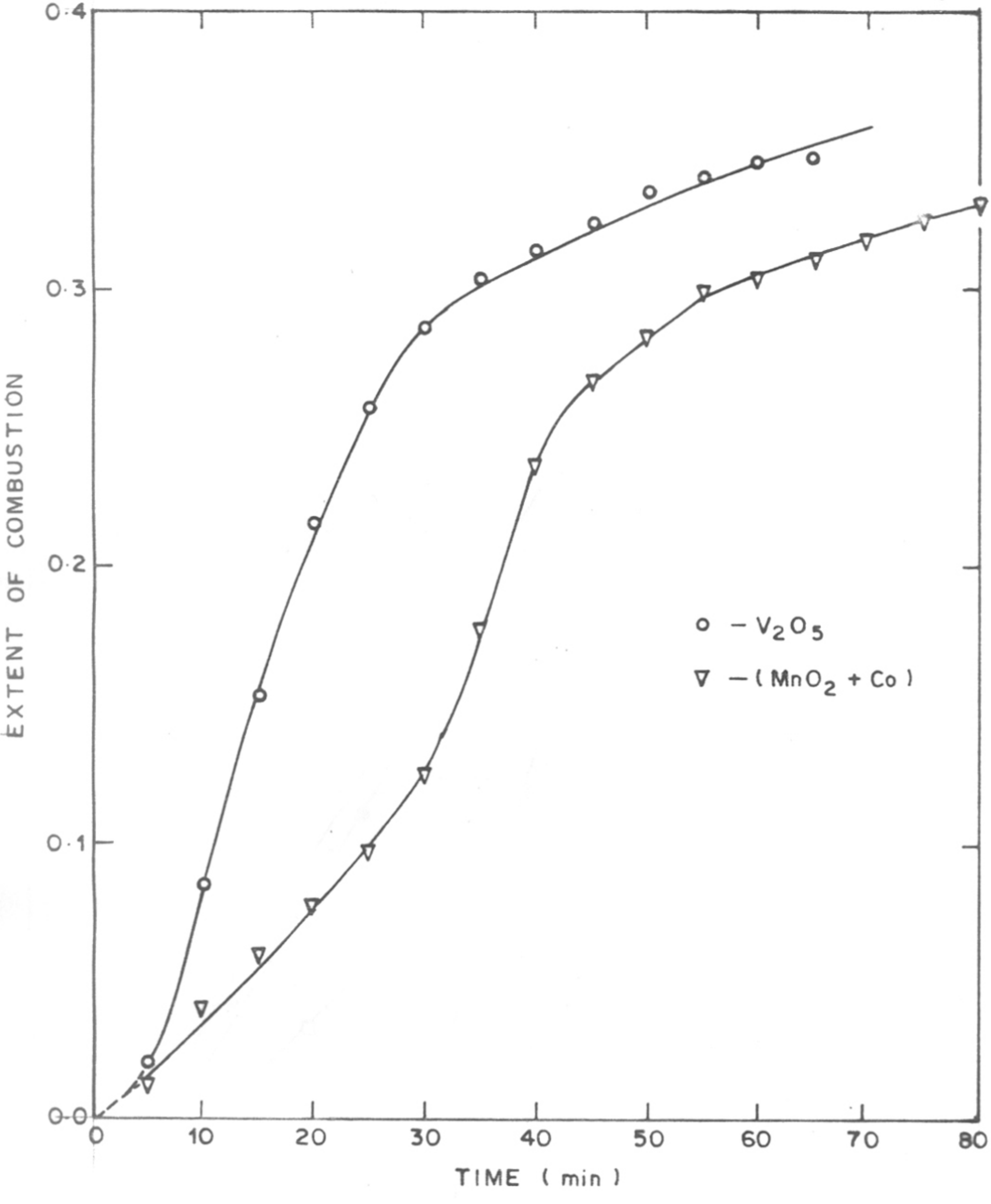


FIG. 22c. EXTENT OF COMBUSTION OF PHENANTHRENE WITH V_2O_5 AND (MnO_2 + Co)

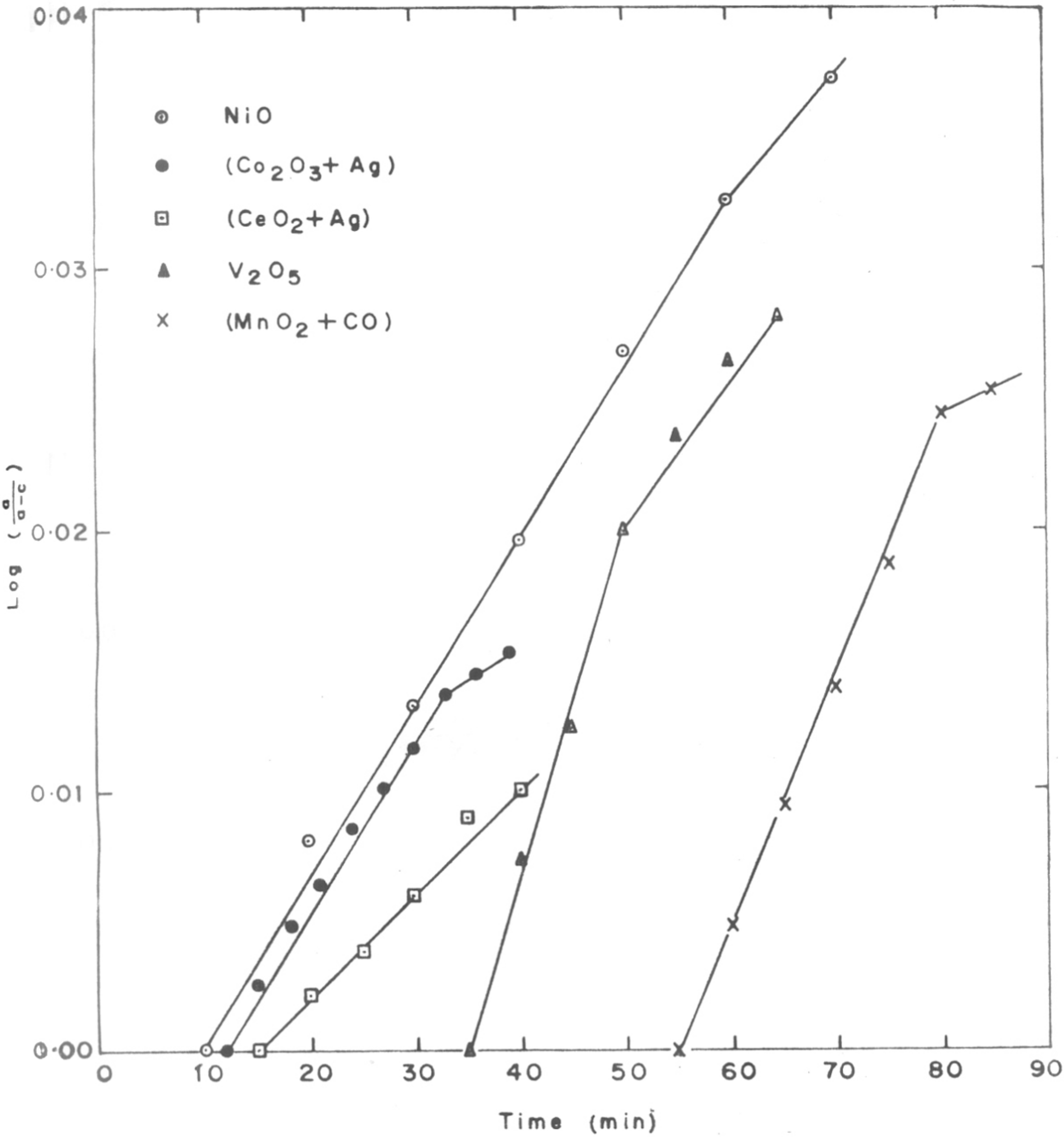


FIG. 23a FIRST ORDER PLOTS FOR COMBUSTION OF PHENANTHRENE WITH VARIOUS OXIDANTS.

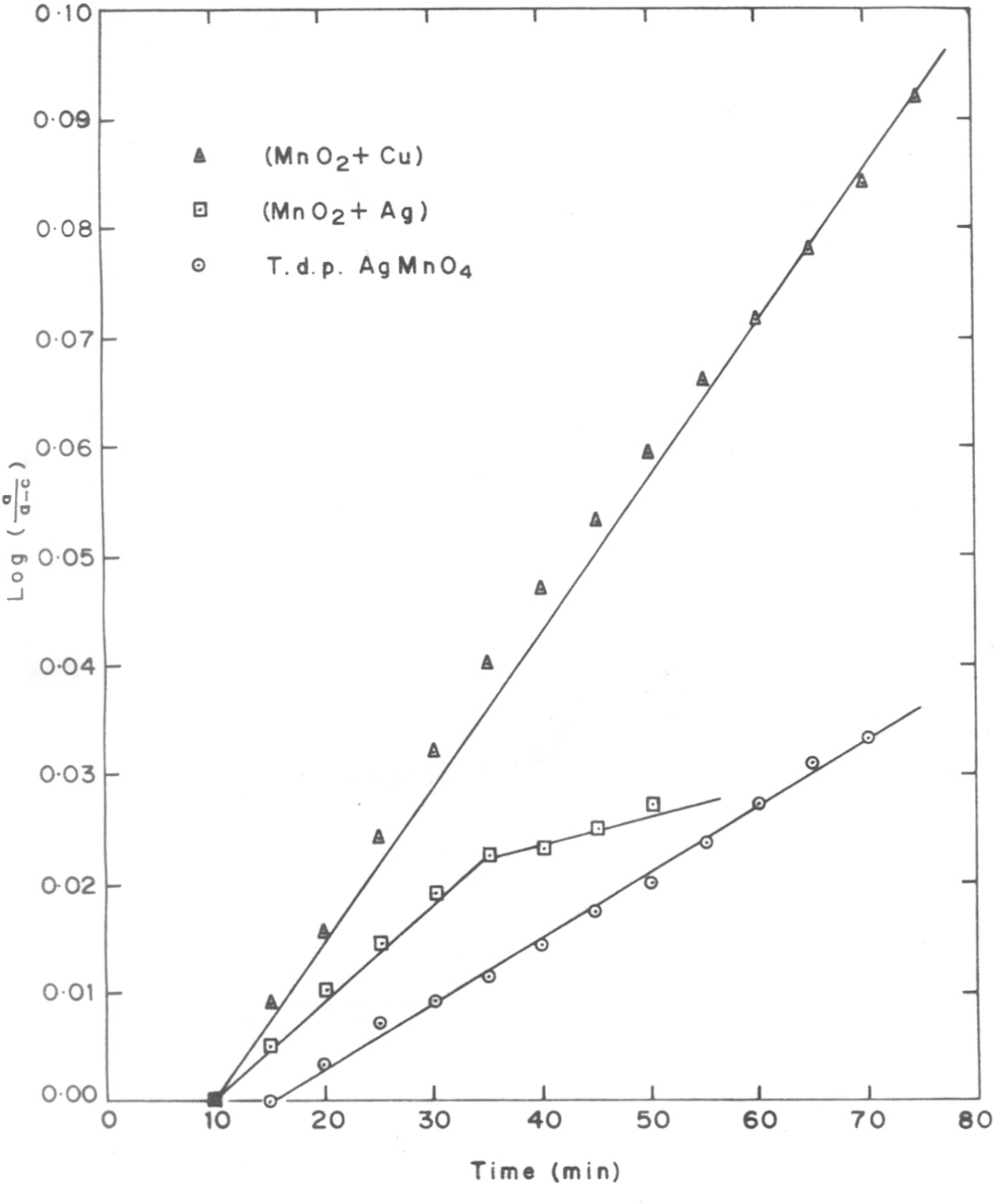


FIG. 23b FIRST ORDER PLOTS FOR COMBUSTION OF PHENANTHRENE WITH VARIOUS OXIDANTS.

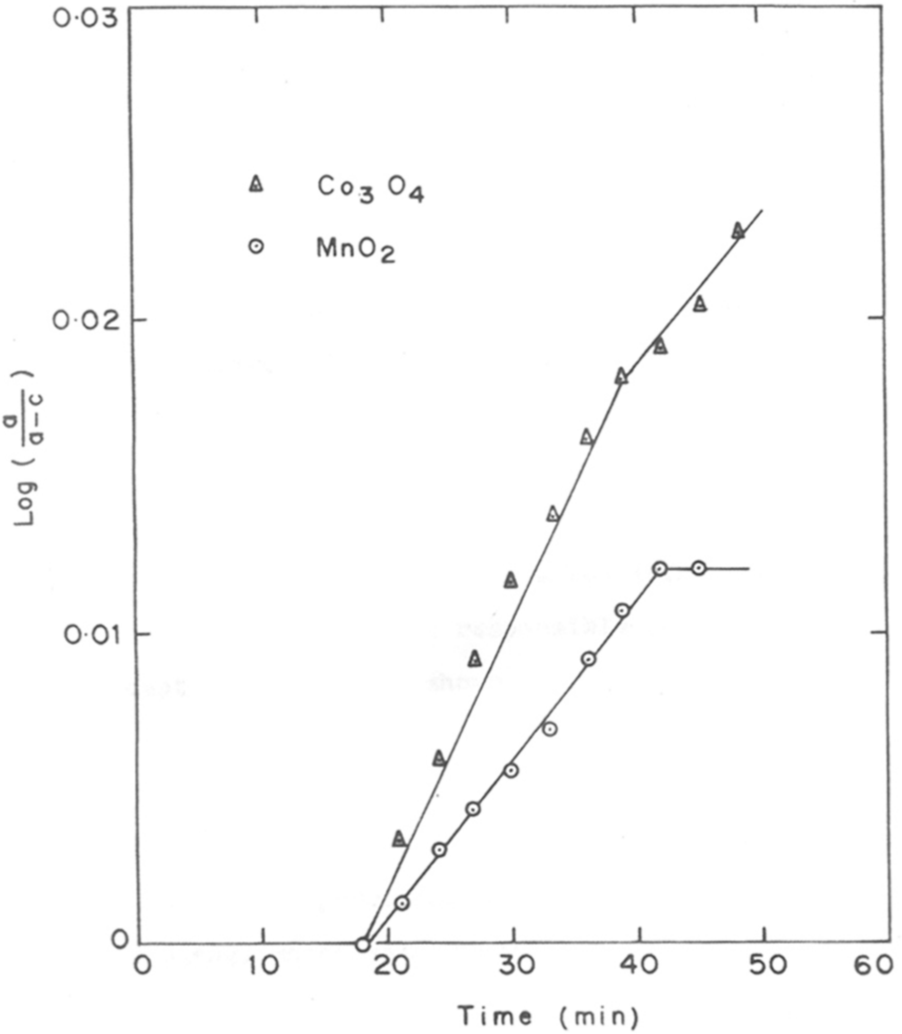


FIG. 23c FIRST ORDER PLOTS FOR COMBUSTION OF PHENANTHRENE WITH VARIOUS OXIDANTS

2.3.3 Relation of activity with the combustion data

It is obvious that neither the rate constants nor the slopes of various equations can be satisfactorily correlated with the activities of the sample-additive reagents. The only point which seems to be hopeful for this purpose is the intercept on y-axis (vide Table 10) in the equation describing the second stage of the combustion in each case except in (MnO_2+Co) where the equation was found for the third stage for the reasons explained above. The trend of this intercept value is upwards with the increasing activity of the oxidants. A deviation in this trend is noticed in V_2O_5 and Co_3O_4. A fast rate of combustion of phenanthrene with V_2O_5 in the initial stage of 0-35 min. which influences the value of intercept on y-axis is responsible for the high intercept value (0.732) shown by V_2O_5 as compared to those shown by others having medium activity similar to V_2O_5. On the otherhand, Co_3O_4 gives a low value of the intercept on y-axis (0.239) which is due to the initial slow rate of combustion of phenanthrene with it as compared to that in (Co_2O_3+Ag) which has an activity comparable to that of Co_3O_4. The intercept-activity correlation seems to hold good in the remaining oxidants which possess high activity and also in those which possess low activity.

2.4 Conclusion

From the above discussion it is clear that the rate constants and slopes of the equations do not give any guiding information regarding the activity of the oxidant. However, the intercept on y-axis indicated by the equations does show a general correlation with the activity. Slight deviation in this general correlation may be due to the different initial rates of combustion in some isolated cases e.g. V_2O_5 and Co_3O_4. The empirical observations described here lead to gross inferences as the heterogeneous catalysis system used is quite complex and the refined treatment for rate expressions etc. would need a deep study by chemical engineers with deeper theoretical considerations for deriving a more meaningful and accurate information.

PART 3

CATALYTIC VAPOUR-PHASE OXIDATION OF SOME ALIPHATIC ALCOHOLS ON VANADIUM PENTOXIDE IN A SEMI-MICROREACTOR

3.1 Introduction

Aldehydes form a very important class of organic compounds as they are among the most reactive compounds. They easily undergo a number of reactions such as oxidation, reduction, addition reactions, condensation reactions, disproportionation, reaction with Grignard reagents etc. Some aldehydes are available from natural resources e.g. acetaldehyde in apples and also as a by-product of alcohol fermentation, citral in lemongrass oil, benzaldehyde in bitter almonds, cinnamaldehyde in cinnamon and vanillin in vanilla bean. They also occur as aldoses in the carbohydrates group.

3.1.1 General methods for the preparation of aldehydes[63]

Following are some of the methods of preparation of aldehydes.

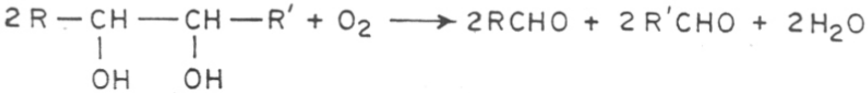
1) Aldehydes are prepared by the oxidation of primary alcohols.

$$R\cdot CH_2OH + O \xrightarrow{\text{Pyridinium chlorochromate}} R\cdot CHO + H_2O$$

2) They are also prepared by catalytic dehydrogenation of primary alcohols.

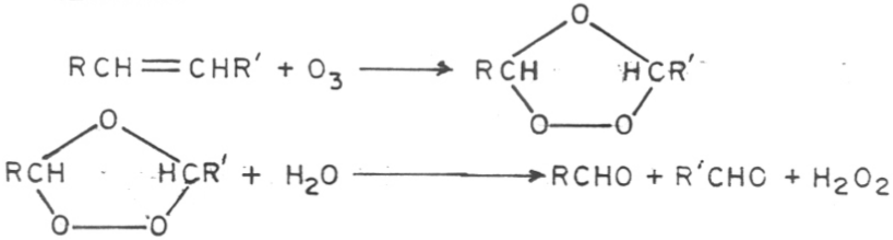
$$R\cdot CH_2OH \xrightarrow{Cu} RCHO + H_2$$

3) Oxidation of glycols also leads to formation of aldehydes.

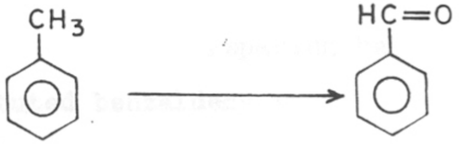


$$2R-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-R' + O_2 \longrightarrow 2RCHO + 2R'CHO + 2H_2O$$

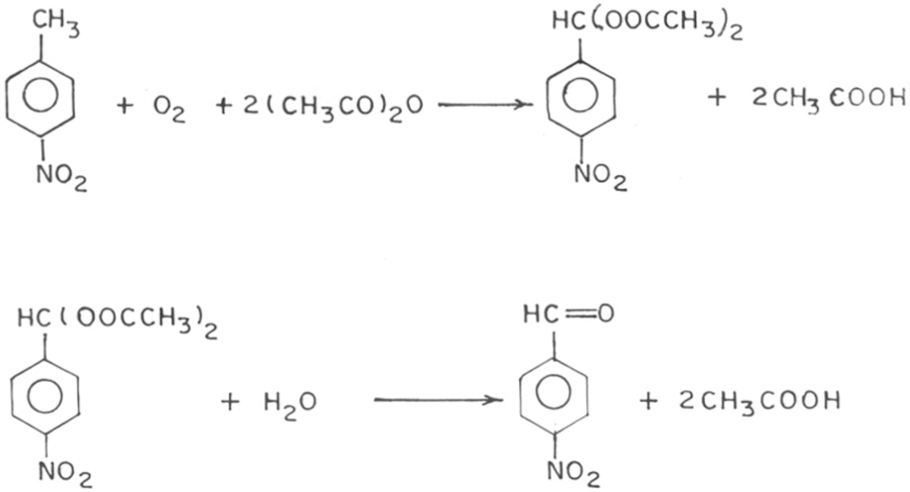
4) They are also obtained through ozonisation of olefins.



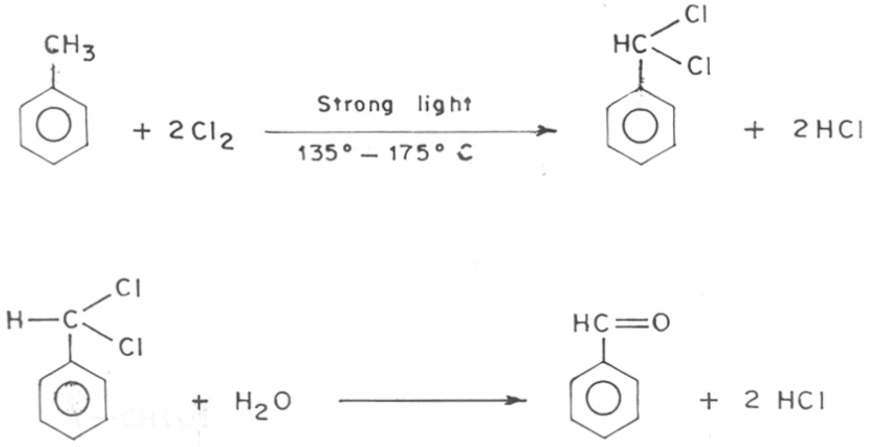
5) Oxidation of methyl group attached to a benzene ring.



A benzal diacetate is formed in the presence of acetic acid and acetic anhydride. It is then hydrolysed by dilute acid to aldehyde. This reaction is valuable in preparing some substituted benzaldehydes e.g. p-nitrobenzaldehyde as shown below.



6) Introduction of two chlorine or bromine atoms into the methyl group attached to the aromatic ring and subsequent hydrolysis of the halogenated compound also yields aldehydes. This is a very useful method for preparing benzaldehyde and substituted benzaldehydes in the laboratory as well as on industrial scale.



7) Pyrolysis of metallic salts of carboxylic acids. Although this method is used for preparing ketones, it is used for the preparation of an aldehyde also by pyrolysis of a mixture of salt of an appropriate acid with the salt of formic acid. Very often calcium salts are used. Salts of rare earths are used to advantage.

$$(RCOO)_2Ca + (HCOO)_2Ca \longrightarrow 2RCHO + 2CaCO_3$$

8) Controlled reduction of acid chlorides (Rosenmund reaction).

This is particularly useful for preparing unsaturated aldehydes. Poisoned catalysts are used to avoid further reduction of the aldehyde to the corresponding alcohol.

$$R-COCl + H_2 \xrightarrow{\text{Poisoned Pd catalyst}} R-CHO + HCl$$

9) Reduction of one mole of a Grignard reagent with orthoformic acid. The intermediate acetal is easily hydrolysed in dilute acid to yield the aldehyde.

$$HC(OC_2H_5)_3 + RMgX \xrightarrow{H_2O} RCH(OC_2H_5)_2 + MgOHX + C_2H_5OH$$

$$R-CH(OC_2H_5)_2 + H_2O \xrightarrow{H_3O^+} R\cdot CHO + 2\ C_2H_5OH$$

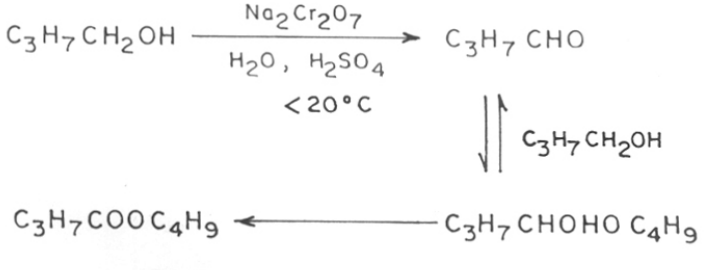
3.1.2 Liquid-phase oxidation of alcohols

A variety of reagents reported in the literature for oxidation of alcohols to corresponding carbonyl compounds include the following. They are commonly used on laboratory scale to obtain aldehydes from primary alcohols and ketones from secondary alcohols.

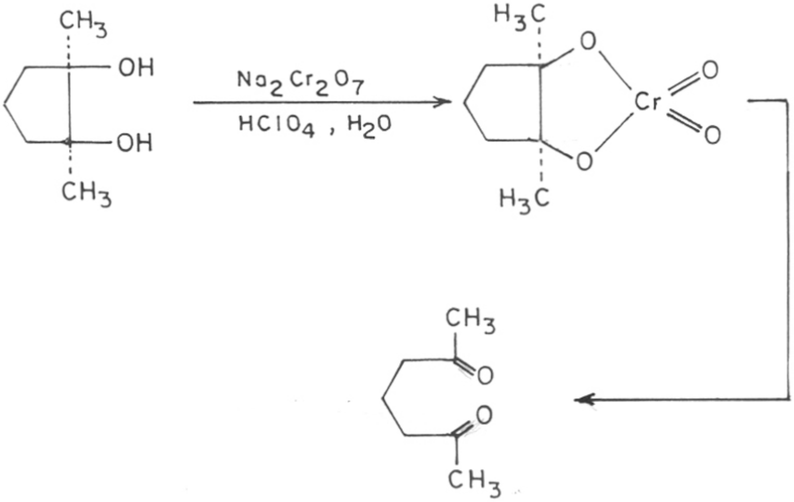
1. Chromic acid

This reagent is particularly useful in the oxidation of secondary alcohols to ketones. The reaction is usually carried out in acetic acid medium, using aqueous acidic chromic acid[64a]. If there are no complicating structural features, the ketone is obtained in high yield.

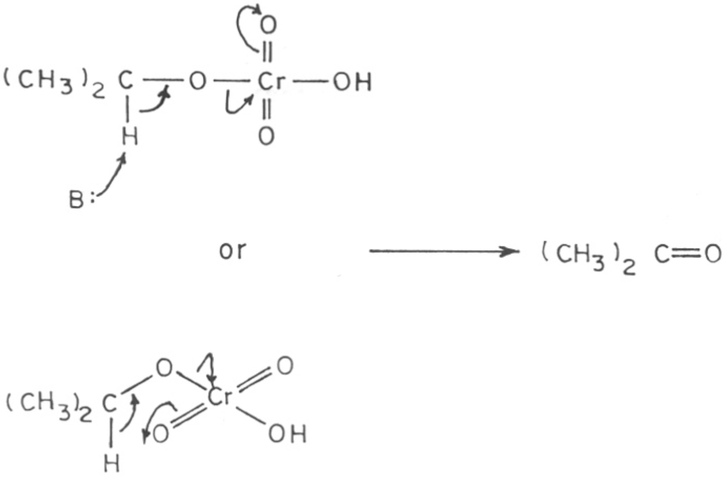
However, oxidation of primary alcohols to the corresponding aldehydes is usually not quite satisfactory when this reagent is used. This is because the aldehyde is oxidised further to the carboxylic acid. Also sometimes the aldehyde reacts with the unchanged alcohol under the acidic conditions to form a hemiacetal which is oxidised further to an ester.



Tertiary alcohols, in general, are not affected by chromic acid, but tertiary 1,2-diols are rapidly cleaved if they are sterically capable of forming cyclic chromate esters. e.g. cis-1,2-Dimethylcyclopentandiol is oxidised 17 X 10^3 times faster than the trans isomer.

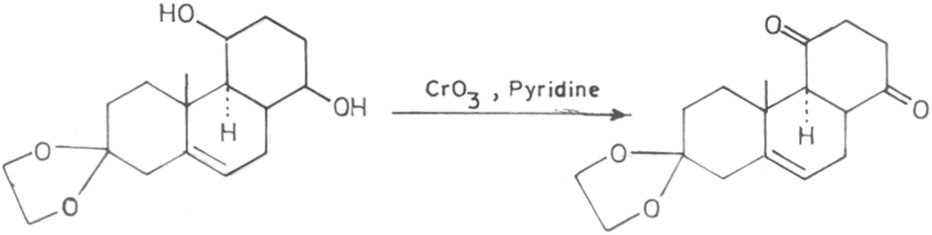


Oxidation of alcohols by chromic acid takes place by formation of a chromate ester first, which is followed by breakdown of the ester, shown below for oxidation of isopropanol. Whether proton abstraction from the ester takes place by an intermolecular or intramolecular process is still uncertain.



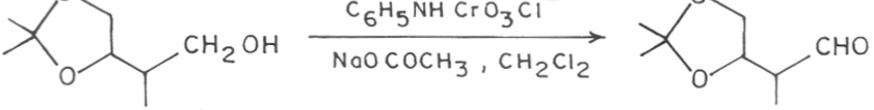
2. <u>Chromium trioxide-pyridine complex</u>

This reagent prepared by adding a concentrated aqueous solution of chromium trioxide to pyridine is particularly useful for oxidation of alcohols which contain acid-sensitive functional groups[64a,b,65]. Here also the secondary alcohols are converted into ketones in good yield.



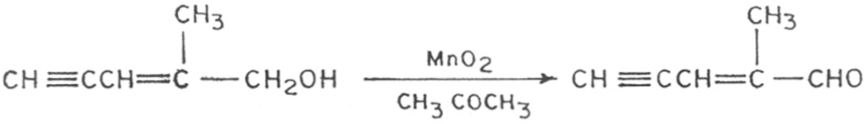
In primary alcohols, allylic and benzylic alcohols could be easily converted but, the yields of aldehydes from non-allylic alcohols were not satisfactory initially. However, the yields were improved after some modifications were introduced in the procedure. The complex $CrO_3.2C_6H_5N$ was isolated and the oxidation carried out using methylene chloride under anhydrous conditions[66]. Good yields were also obtained by adding the alcohol to a solution of chromium trioxide in a mixtufe of pyridine and methylene chloride.

A disadvantage of the method was that a considerable excess of the reagent is usually required. It was overcome by Corey and Fleet[67] who oxidised a wide range of alcohols in methylene chloride with the complex of chromium trioxide and 3,5-dimethyl pyrazole. Pyridinium chloro-chromate, $C_6H_5\overset{+}{N}HCrO_3Cl^-$ used by Corey and Suggs[68] is easily prepared by adding pyridine to a solution of chromium trioxide in hydrochloric acid. In order to carry out oxidation of compounds containing acid-sensitive protecting groups the slightly acidic nature of the reagent is covered by addition of powdered sodium acetate.



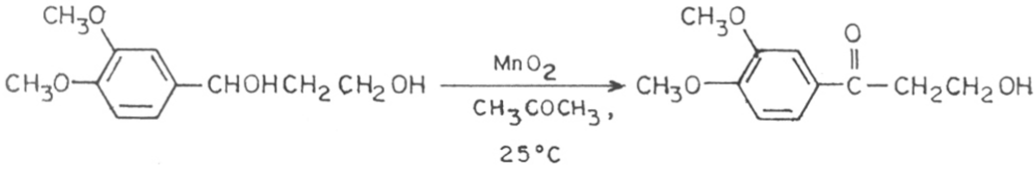
3. Manganese dioxide

This is a mild reagent for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds[69]. It is specific for allylic and benzylic hydroxyl groups. The manganese dioxide for this purpose is prepared by the reaction of manganous sulphate with potassium permanganate in alkaline solution. The hydrated manganese dioxide is highly active but whether the active reagent is manganese dioxide or some other manganese compound adsorbed on its surface is not known as yet. Olefinic and acetylenic bonds are unaffected. Hydroxyl groups adjacent to the acetylenic bonds are easily oxidised.



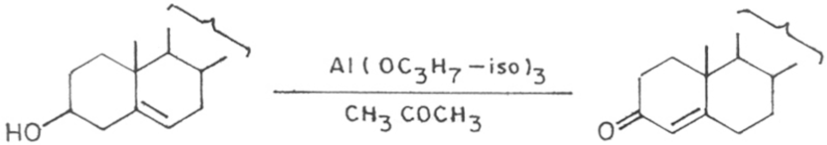
$$\mathrm{CH{\equiv}CCH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_2OH} \xrightarrow[\mathrm{CH_3COCH_3}]{\mathrm{MnO_2}} \mathrm{CH{\equiv}CCH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-CHO}$$

However, under ordinary conditions saturated alcohols are not affected and selective oxidation of activated hydroxyl groups is achieved.

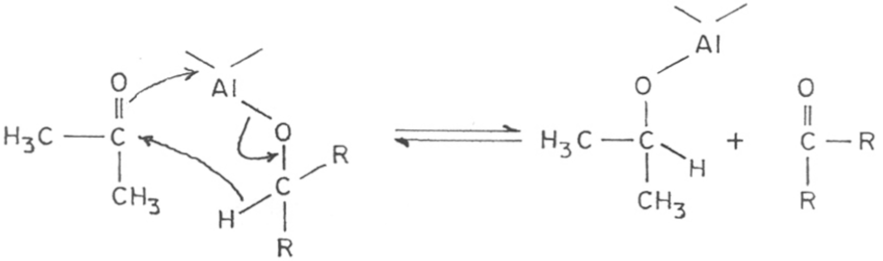


4. Oppenauer oxidation

Oppenauer oxidation is carried out using aluminium alkoxides in acetone[70]. It is widely used in steroids for the oxidation of allylic secondary hydroxyl groups to αβ-unsaturated ketones.



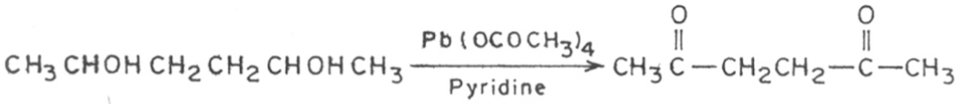
βγ-Double bonds generally migrate into conjugation with the carbonyl group under the conditions of the reaction. The mechanism involves formation of the aluminium alkoxide of the alcohol, which is oxidised through a cyclic transition state shown below where acetone also participates.



5. Lead tetra-acetate

This is also a good reagent for oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, respectively. Pyridine is the solvent of choice as other solvents i.e. benzene, hexane or chloroform give high yields of tetrahydrofuran derivatives i.e. cyclised products, if a δ C-H group is present in the molecule. However, if pyridine is used as a solvent the carbonyl compound is obtained in good yield irrespective of whether the alcohol undergoing oxidation contains a δ C-H group or not. Allylic and saturated alcohols are thus oxidised without cyclisation[71].

$$CH_3(CH_2)_3CH_2OH \xrightarrow[\text{Pyridine}]{Pb(OCOCH_3)_4} CH_3(CH_2)_3CHO$$



$$CH_3CHOHCH_2CH_2CHOHCH_3 \xrightarrow[\text{Pyridine}]{Pb(OCOCH_3)_4} CH_3\overset{\overset{O}{\|}}{C}-CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

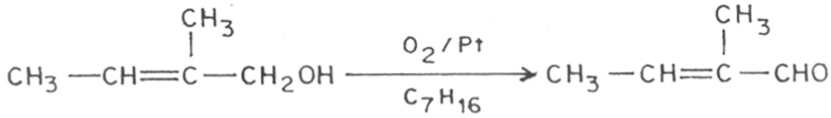
$$C_6H_5CH{=}CHCH_2OH \xrightarrow[\text{Pyridine}]{Pb(OCOCH_3)_4} C_6H_5CH{=}CH-CHO$$

6. Catalytic oxidation with oxygen and platinum

An additional useful method for oxidation of primary and secondary alcohols under mild conditions makes use of platinum catalyst and molecular oxygen. The reaction can be controlled suitably to give either aldehydes or acids from primary alcohols. Double bonds are not affected and unsaturated alcohols can therefore be oxidised to unsaturated aldehydes[72].

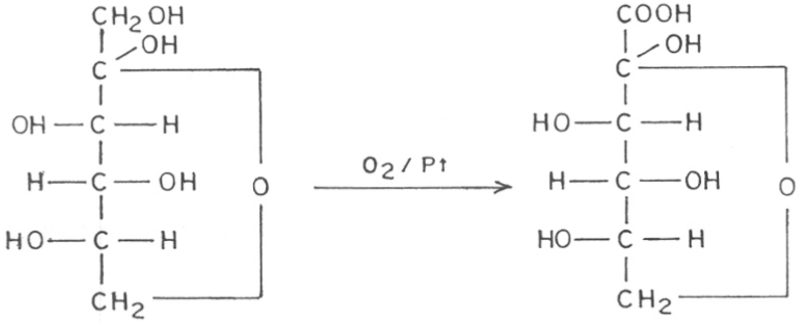
$$CH_3(CH_2)_{10}CH_2OH \xrightarrow[C_7H_{16}\quad ^1/_2\ hr]{O_2/Pt} CH_3(CH_2)_{10}CHO$$

$$\xrightarrow{2\ hr} CH_3(CH_2)_{10}COOH$$



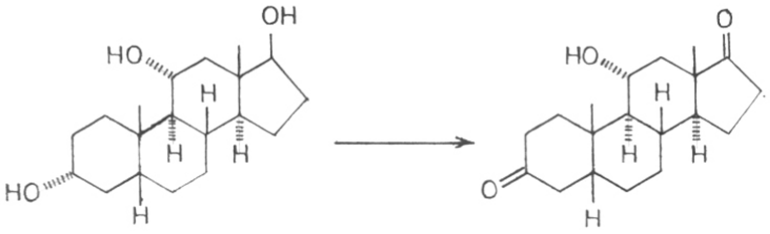
$$CH_3-CH{=}\overset{\overset{CH_3}{|}}{C}-CH_2OH \xrightarrow[C_7H_{16}]{O_2/Pt} CH_3-CH{=}\overset{\overset{CH_3}{|}}{C}-CHO$$

Generally, the primary alcohols are attacked before secondary alcohols, and in cyclic alcohols axial groups react before equatorial[73]. The method has been widely used in carbohydrates[74] to effect selective oxidation of specific hydroxyl groups e.g. L-sorbose is oxidised at 30°C to 2-keto-L-gulonic acid, an intermediate in a synthesis of ascorbic acid.



7. N-halo-imides

Other useful reagents for oxidation of primary and secondary alcohols are the N-halo-imides[75]. N-bromo-succinimide and N-bromo and N-chloro-acetamide readily oxidise the primary alcohols and secondary alcohols to aldehydes and ketones, respectively. Secondary alcohols are generally oxidised more rapidly than primary alcohols. In cyclic secondary alcohols, axial hydroxyl groups are oxidised more easily than equatorial ones. The solvents used are aqueous dioxan or acetone. The reagent has found application for selective oxidation in nuclear hydroxyl groups in steroid series. Oxidation of aetiocholan-3α,11α,17β-triol to aetiocholan-11α-ol 3,17-dione with N-bromo-acetamide in aqueous acetone is an example.



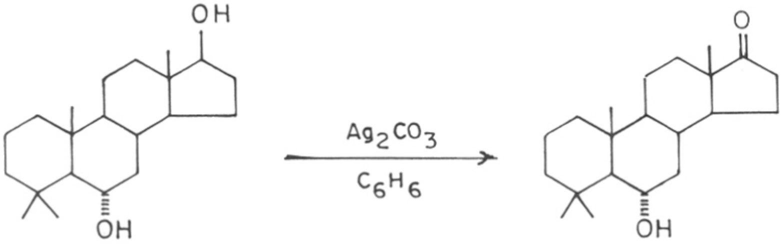
1-Chlorobenzotriazole, 4-phenyl-1,2,4-triazoline -3,5-dione, and 2,3-dichloro-5,6-dicyanobenzoquinone are among the other organic oxidising agents.

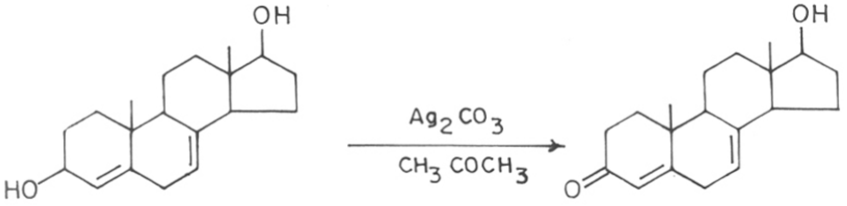
8. Reagents supported on inert supports

As described above, many useful procedures have been reported for oxidation of alcohols to the corresponding carbonyl compounds. However, these have been associated with some drawbacks such as relative difficulties in the preparation of the reagents and in the working-up of the reaction mixture after oxidation. A new approach in heterogeneous oxidation procedure makes use of reagents supported on inorganic materials and also some insoluble polymers. A brief account of work on the use of such reagents by some investigators is given below.

(i) Silver carbonate precipitated on celite[76]: This is an excellent reagent for oxidising primary and secondary alcohols to aldehydes and ketones in high yields under neutral mild conditions. Benzylic and allylic alcohols are oxidised more readily than secondary alcohols, which undergo oxidation more easily than primary alcohols.

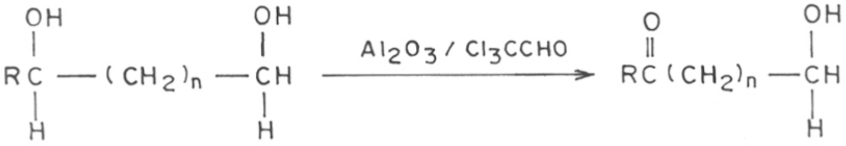
Highly hindered hydroxyl groups are not attacked, thus allowing selectivity in oxidation. The reaction is carried out in boiling benzene and the product is obtained by filtering off the spent reagent and evaporating off the solvent.





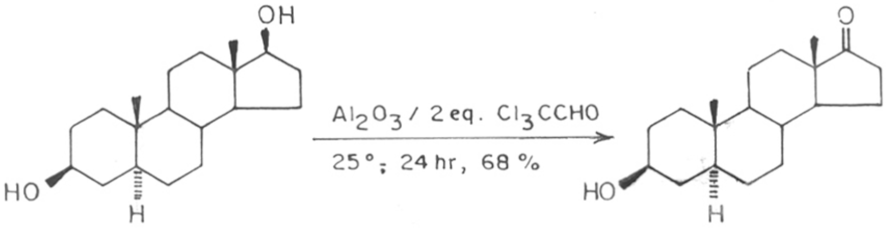
(ii) Trichloroacetaldehyde on alumina:

Posner et al. have reported oxidation of secondary alcohols to the corresponding carbonyl compounds with trichloroacetaldehyde on alumina[77].



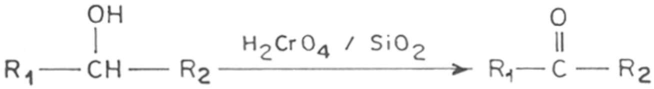
$$\underset{H}{\overset{OH}{RC}} - (CH_2)_n - \underset{H}{\overset{OH}{CH}} \xrightarrow{Al_2O_3\,/\,Cl_3CCHO} \overset{\overset{O}{\|}}{RC}(CH_2)_n - \underset{H}{\overset{OH}{CH}}$$

It was observed that in some cases benzaldehyde also could be used as the oxidant. The primary alcohols are not easily oxidised by trichloroacetaldehyde or benzaldehyde. Also the selectivity in certain cases is much better than that in silver carbonate.



(iii) Chromic acid on silica gel:

Chromic acid adsorbed on silica gel has been used as an effective oxidant for the oxidation of compounds containing primary and secondary hydroxyl groups[78]. The activity of the reagent lasts for one week if stored properly. Several examples have been cited and the ease in oxidation and further work up of the reaction mixture is stressed.

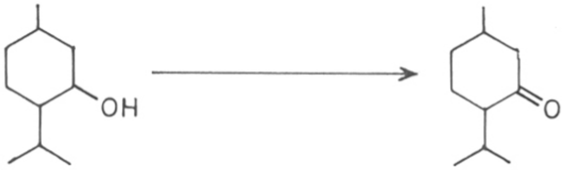


$$R_1-\overset{OH}{\overset{|}{CH}}-R_2 \xrightarrow{H_2CrO_4\ /\ SiO_2} R_1-\overset{O}{\overset{\|}{C}}-R_2$$

(iv) Silica-gel supported chromic acid reagents:

Pyridinium chromate on silica-gel and chromic acid on silica-gel have been used successfully by Sukh Dev *et al.*[79] for efficient oxidation of a variety of secondary and primary alcohols. Pyridinium chromate on silica-gel has been found to be quite safe for the oxidation of alcohols containing acid-labile functions such as a cyclopropane ring. It was shown to be effective for the oxidation of allylic and benzylic alcohols also.

As described above, Santaniello et al.[78] also reported oxidations with chromic acid absorbed on silica gel but their reagent remained active only for a week whereas Sukh Dev et al.[79] prepared the reagent by using sodium dichromate-aqueous sulphuric acid on silica-gel which was active even after one year's storage. Oxidation of (-)menthol to menthone was carried out successfully using this reagent.



(v) Polymer supported reagents:

Recently, the reagents supported on insoluble polymers have been found to be particularly convenient for solving many problems in organic synthesis. The polymeric support provides a particular reaction environment which can enhance the reactivity of many reagents. This technique has also been used for carrying out oxidation of alcohols. Accordingly, a polymeric thioanisole[80] has been reported to be effective for the Corey oxidation of alcohols[81].

A simple method of obtaining a polymer supported reagent has been reported by Cainelli et al.[82]. They displaced chloride ions of chloride form of Amberlyst A-26, an anion exchange resin containing quaternary ammonium groups by stirring it in aqueous solution of chromium trioxide. The CrO_4H^- form of the resin is very effective in oxidising primary and secondary alcohols to the corresponding carbonyl compounds. This reagent, unlike some of the earlier ones, has not been evaluated for alcohols containing acid-sensitive substituents.

A comprehensive review in two parts[83,84] on organic synthesis using supported reagents by McKillop and Young gives a detailed account of various reagents supported on alumina, silica gel, graphite, montmorillonite K-10, girdler KSF, molecular sieves and kieselguhr. It also includes some more supported reagents e.g. chromyl chloride, potassium permanganate, etc. for the oxidation of alcohols to aldehydes and ketones.

3.1.3 Catalytic vapour-phase oxidation of alcohols

The reagents described so far are used conveniently for conversion of alcohols to the respective carbonyl compounds on laboratory scale. They are very useful for handling reactions involving small quantities of costly products where selective methods of oxidation are desirable, though some of them do find applications on industrial scale. In the processes of oxidation of organic compounds on industrial scale, vapour-phase oxidation using a suitable catalyst on an inert support, which constitutes a part of heterogeneous oxidation methods, has several advantages over the other methods of oxidation where liquid-phase is used. Some of them are enumerated below.

1) In liquid-phase oxidation, separation and recovery of the catalysts pose certain problems which are not encountered in vapour-phase oxidation.

2) The separation of intermediate products is more inconvenient in liquid-phase oxidation.

3) Usually liquid-phase oxidation involves pressure reactions.

4) Corrosion problems are encountered frequently in liquid-phase oxidation due to acidic or basic nature of the medium.

5) Liquid-phase oxidations are suitable for batch processes but vapour-phase oxidations are preferred for continuous operations needed for large scale production in industry.

Catalytic vapour-phase oxidation has been used for converting hydrocarbons to aldehydes[85-91] and also for oxidising primary alcohols to aldehydes[92-96]. The method has also been studied extensively for oxidation of benzene to maleic anhydride, ethylene to ethylene oxide and methanol to formaldehyde[97] which clearly shows its important role in industry.

Although catalytic vapour-phase oxidation is a domain of chemical engineers, it was believed that some attempts to carry out catalytic vapour-phase oxidation of simple alcohols on a semi-micro scale would give some idea as to whether the data so collected could be of any significant value for scaling up such processes. Oxidation of some aliphatic alcohols to corresponding aldehydes on vanadium pentoxide was therefore initiated with a view to studying the selectivity of formation of aldehydes. Vanadium pentoxide was selected as a catalyst for this study due to its importance in industry and also because sufficient information on its mode of activity is available in the literature. For example, the behaviour of vanadium oxide catalysts has been discussed in detail in connection with selectivity of oxidation of O-xylene to phthalic anhydride[98]. Various species of oxygen adsorbed at the surface of transition metal oxides have also been identified by Bielánski and Haber[99] in their study.

It appears from a literature survey of the past ten years that there has been an emphasis on the study of oxidation of o-xylene to phthalic anhydride[87,88] and methanol to formaldehyde[93-95] using V_2O_5 and some other metal oxides as catalysts in admixture with it. Thus, V_2O_5 has been used along with TiO_2 for the oxidation of O-xylene[87] and methanol[95]. It has also been used along with NiO, Fe_2O_3 and Co_3O_4 in various proportions for the oxidation of methanol to formaldehyde[93]. It was observed that highest yields of formaldehyde were obtained with atomic ratio V/Me = 1. Oxidation of methanol has also been studied with V_2O_5 supported on γ-Al_2O_3, CeO_2, TiO_2 and ZrO_2[95]. A silica-gel supported mixture containing V_2O_5-K_2SO_4 and silica-gel in the proportion 10:20:70 has been used in a kinetic study of oxidation of methanol[94]. Similarly, Tin-Vanadate has been used to study the rates of oxidation of p-xylene in the temperature range 320° to 420°C in an isothermal differential flow reactor[100].

Reactors for catalytic vapour-phase oxidation:

In an excellent review on laboratory catalytic reactors Doraiswamy and Tajbl[101] have described packed bed integral and differential reactors, external recycle reactors, agitated reactors, tubular reactors etc. They have also described microreactor which can be used to advantage by connecting it further to a gas chromatograph. A more recent review on reactos by Christoffel[102] also includes some information on micropulse reactors.

The attempts described in this part of the thesis were essentially aimed at the study on conversion of some aliphatic alcohols to the corresponding aldehydes at various temperatures on vanadium pentoxide supported on silicon carbide using a packed bead steady-state flow-type semi-microreactor. A semi-microreactor was used because a microreactor with an on-line gas chromatograph was not available. The details of this empirical approach are described in the following experimental section.

3.2 EXPERIMENTAL

Vapour-phase oxidation of four aliphatic alcohols was carried out over silicon carbide supported vanadium pentoxide catalyst (~10% w/w) in a semi-microreactor at 250°, 300° and 350°. The oxidation products collected in a receiver were analysed quantitatively by gas chromatography. Small quantities of gaseous products which could not be trapped were ignored.

3.2.1 Apparatus and Equipment

The experimental set-up is shown schematically in Fig.24.

a) A specially fabricated semi-microreactor of corning glass i.d. 11 mm and 330 mm long was provided with a B-10 g.g. joint at the outlet and a side-arm near the inlet as shown in the Fig. The reactor was connected to a receiver of 5 ml capacity and its outlet was joined to an aspirator. A guard tube containing $MgClO_4$ was attached to the side-arm and the inlet was covered with a rubber septum.

b) A micro-furnace 110 mm long and having 13 mm i.d. preheater type 5676-A, as supplied by Arthur H. Thomas Co., USA, was used for heating the reactor and the desired temperature was controlled within ±5°C using 'Aplab' temperature controller, Model 9601, equipped with Chromel-Alumel thermocouple.

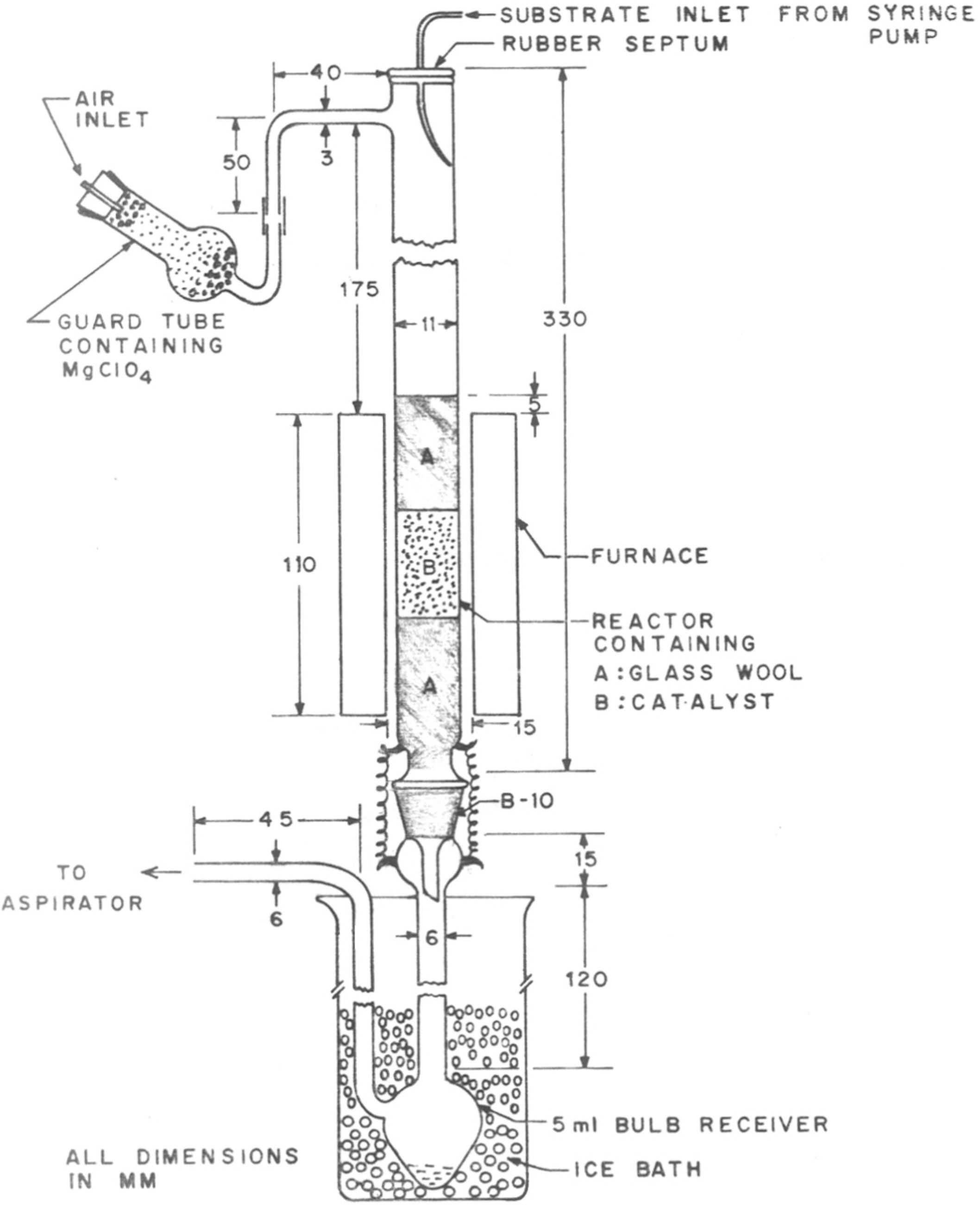


FIG. 24: EXPERIMENTAL SET-UP FOR THE CATALYTIC VAPOUR-PHASE OXIDATION OF ALIPHATIC ALCOHOLS.

c) A syringe pump of Sage Instruments, Model 351, Division of Orion Research, Inc., Cambridge, Mass., USA, was used for regulating the feed rate of the substrate.

d) Hewlett-Packard Gas Chromatograph Model 5840A equipped with FID, 5840A data terminal and a 5% carbowax 20M on chromosorb W AW column (1.22 m x 6.4 mm i.d.) was used for gas chromatography.

e) GC-MS: Mass spectra were recorded at 30 eV electron energy on AEI GC-MS-30 Unit. Carrier-gas used was helium (30 ml/min.) and a 5% carbowax 20M on chromosorb W AW was used in a glass column (1.80 m x 4 mm i.d.) maintained at suitable temperatures.

3.2.2 Materials

Ammonium metavanadate, C.P., Riedel-De Haen make
Silicon carbide, SC 5232 Pure, Norton, USA
Oxalic acid, A.R., S.D's Lab.Chem. Industry
1-Butanol, A.R., Glaxo Laboratories
1-Hexanol, L.R., B.D.H.
1-Octanol, L.R., B.D.H.
1-Decanol, L.R., B.D.H.

Preparation of the catalyst:

V_2O_5 catalyst supported on SiC was prepared as follows.

The granular SiC support, 6-8 mesh (50 g) was impregnated by covering it with a solution of ammonium metavanadate (6.43 g) in 10% aqueous solution of oxalic acid (100 ml). It was placed on a waterbath after 30 min for evaporation. The coated SiC granules were dried in an oven at 100° for an hour and finally calcined in a muffle furnace at 400° for two hours. The SiC supported V_2O_5 catalyst was then cooled and sifted to remove the powder. It was stored in a desiccator. Final weight of the catalyst was 54.72 g, which indicated that V_2O_5 supported on SiC was 8.62%.

3.2.3 Procedure

3.30 g catalyst was packed in the reactor tube in the form of a 35 mm long bed after introducing a glass wool plug of 40 mm length. This was followed by another 40 mm long plug of glass wool. The reactor tube was then positioned vertically in the furnace in such a way that the catalyst bed was covered by the central zone of the furnace. The receiver was attached and the inlet of the reactor was covered with a rubber septum through which the needle of the syringe containing the substrate was introduced. The thermocouple was introduced in between the reactor tube and the furnace taking care that the temperature near the centre of the catalyst-bed was recorded. After the furnace attained the desired temperature a flow of dry air at a rate of 15 ml/min. was regulated through the system with the help of an aspirator. The addition of the substrate was started and its feed rate was maintained at 0.016 ml/min. throughout using the syringe pump. The vaporised substrate passed over the catalyst and the oxidation products along with the unreacted material condensed in the receiver. The feeding was discontinued after 60 min. but the flow of dry air was maintained further for 30 min. to ensure the maximum transfer of the reaction products to the receiver. The furnace was switched off and raised to the cooler part of the reactor. The receiver was removed after ensuring that the catalyst bed had cooled to almost room temperature and its contents were analysed by gas chromatography. As the reaction mixture contained some unidentified product, it was analysed further by GC-MS.

Determination of acid content in the oxidation products:

The reaction products were taken in 25 ml of 50% ethanol and titrated against 0.01N NaOH solution using phenolphthalein indicator.

Regeneration of the catalyst:

The catalyst was regenerated by heating it in a muffle furnace at 400^o for two hours.

Preparation of decanal

This was prepared according to the method described by Corey and Suggs[68].

To a suspension of pyridinium chlorochromate (3.23 g, 15 m.mol) in 20 ml of anhydrous methylene chloride was added 1-decanol (1.58 g, 10 m mol) in 5 ml of methylene chloride in one portion with stirring. After two hours, 50 ml of dry ether was added and the supernatent liquid was decanted from the black gum. The insoluble residue was washed thoroughly three times with 10 ml portions of ether. The combined organic layer was passed through a 1" pad of silica gel and the solvent removed by distillation. Distillation of the residue gave 1.12 g (70% yield) decanal. (b.p. 80°/7 mm). GLC analysis showed 82% purity.

Other aldehydes except butanal were prepared similarly. Pure butanal was already available in this laboratory in connection with some other work.

3.3 Results and Discussion

The data obtained in the oxidation experiments of the alcohols are presented in Tables 11 to 15. The GLC of their oxidation products are depicted in Fig.25 to 28 and the analytical data collected in Tables 16 to 20.

3.3.1 Recoveries of the total oxidation product

The smooth flow of air through the reactor seemed to be interrupted occasionally in some cases due to accumulation of the condensed reaction products at the outlet of the reactor. However, this was not a serious problem and the product distribution error was ~ ± 3% as evidenced by some repetition experiments. Although the recoveries of the total oxidation products were generally good (between 85-90%), they were found to be somewhat less satisfactory in some cases (between 80-85%). This may be attributed to the retention of a part of total oxidation product in the glass wool plug at the outlet of the reactor as explained above. Attempts were made to increase the recoveries by ether extraction of the reactor-filling but the evaporation of the solvent resulted in a loss of a part of oxidation products, which was clear from a change in the product distribution. Only the material collected in the receiver was, therefore, used for analysis and inferences drawn regarding product distribution.

TABLE 11 - CATALYTIC VAPOUR-PHASE OXIDATION OF 1-BUTANOL

Reactor temperature	Air flow rate ml/min.	Feed rate ml/min.	Total feed time min.	Quantity passed over the catalyst	Oxidation product (g)	% Recovery (w/w)
250°	15	0.016	60	0.96 ml (0.78 g)	0.69	88.46
300°	15	0.016	60	0.96 ml (0.78 g)	0.62	80.00
350°	15	0.016	60	0.96 ml (0.78 g)	0.63	81.00

TABLE 12 - CATALYTIC VAPOUR-PHASE OXIDATION OF 1-HEXANOL

Reactor temperature	Air flow rate ml/min.	Feed rate ml/min.	Total feed time (min.)	Quantity passed over the catalyst	Oxidation product (g)	% Recovery (w/w)
250°	15	0.016	50	0.80 ml (0.65 g)	0.52	80.00
300°	15	0.016	40	0.64 ml (0.52 g)	0.42	80.77
350°	15	0.016	60	0.96 ml (0.79 g)	0.75	94.94

TABLE 13 - CATALYTIC VAPOUR-PHASE OXIDATION OF 1-OCTANOL

Reactor temperature	Air flow rate ml/min.	Feed rate ml/min.	Total feed time (min.)	Quantity passed over the catalyst	Oxidation product (g)	% Recovery (w/w)
250°	15	0.016	60	0.96 ml (0.79 g)	0.66	83.54
300°	15	0.016	60	0.96 ml (0.79 g)	0.65	82.28
350°	15	0.016	60	0.96 ml (0.79 g)	0.72	91.14

TABLE 14 - CATALYTIC VAPOUR-PHASE OXIDATION OF 1-DECANOL

Reactor temperature	Air flow rate ml/min.	Feed rate ml/min.	Total feed time (min.)	Quantity passed over the catalyst	Oxidation product (g)	% Recovery (w/w)
250°	15	0.016	60	0.96 ml (0.80 g)	0.69	86.25
300°	15	0.016	60	0.96 ml (0.80 g)	0.72	90.00
350°	15	0.016	60	0.96 ml (0.80 g)	0.64	80.00

TABLE 15 - CATALYTIC VAPOUR-PHASE OXIDATION OF 1-OCTANOL OVER FRESH AND REGENERATED V_2O_5/SiC CATALYST AT 350°C

	Air flow rate ml/min.	Feed rate ml/min.	Total feed time (min.)	Quantity passed over the catalyst	Oxidation product (g)	% Recovery (w/w)
Fresh catalyst	15	0.016	60	0.96 ml (0.79 g)	0.72	91.14
Once used catalyst	15	0.016	60	0.96 ml (0.79 g)	0.71	89.87
Twice used catalyst	15	0.016	60	0.96 ml (0.79 g)	0.72	91.14

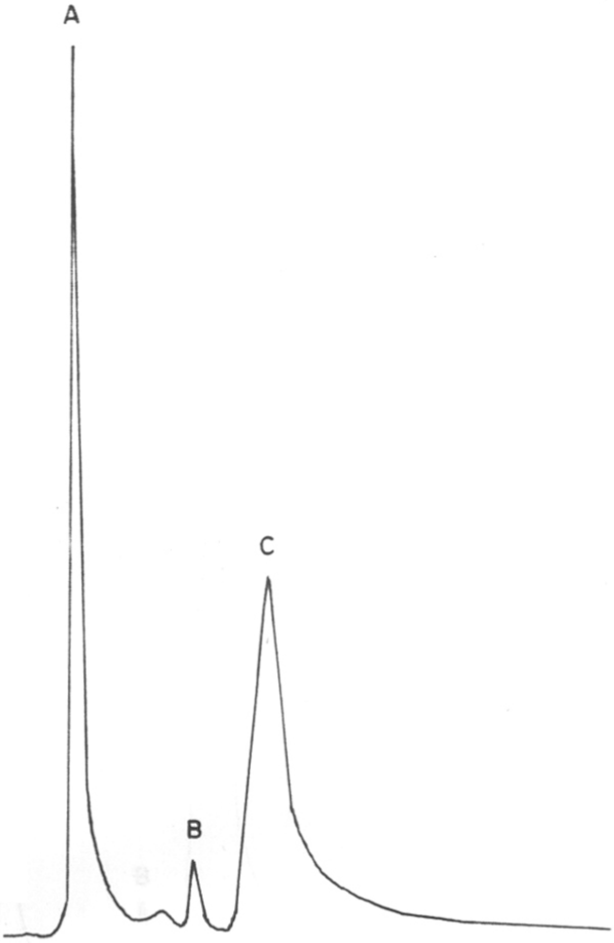


FIG. 25. GLC OF OXIDATION PRODUCT OF 1-BUTANOL
A: BUTANAL, B: UNIDENTIFIED PRODUCT,
C: 1-BUTANOL
CONDITIONS: COLUMN 5% CARBOWAX 20 M ON CHROMOSORB W AW 1·22 m x 6·4 mm (id) AT 50 °C, CARRIER GAS (N_2) FLOW RATE – 20 ml / min, CHART SPEED – 1cm / min, DETECTOR – FID.

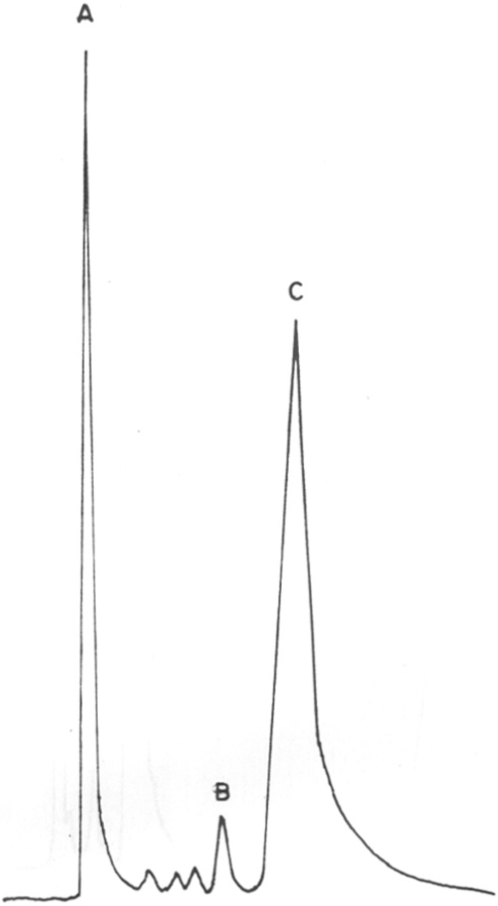


FIG. 26. GLC OF OXIDATION PRODUCT OF 1-HEXANOL

A : HEXANAL ; B : UNIDENTIFIED PRODUCT
C : 1-HEXANOL
CONDITIONS : COLUMN – 5% CARBOWAX 20 M ON
CHROMOSORB W AW, 1·22 m x 6·4 mm (id) AT 75°C,
CARRIER GAS (N_2) FLOW RATE – 20 ml / min,
CHART SPEED – 1 cm / min, DETECTER – FID.

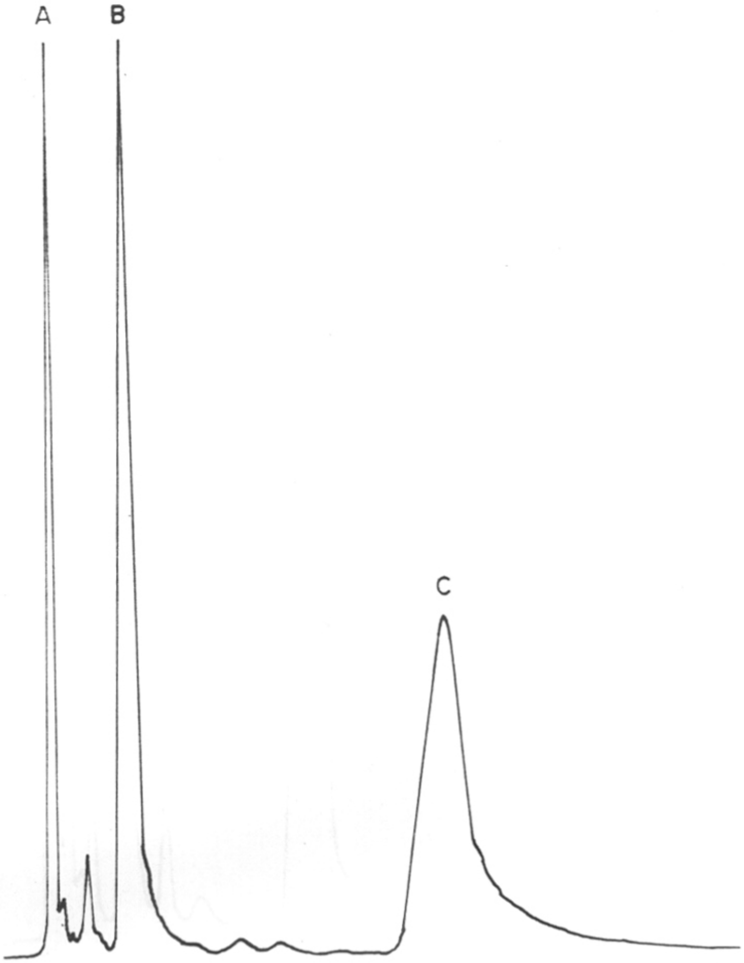


FIG. 27 GLC OF OXIDATION PRODUCT OF 1-OCTANOL

A : UNIDENTIFIED PRODUCT, B : OCTANAL,

C : 1-OCTANOL

CONDITIONS : COLUMN – 5 % CARBOWAX 20 M ON CHROMOSORB W AW, 1·22 m x 6·4 mm (id) AT 90°C, CARRIER GAS (N_2) FLOW RATE – 20 ml / min, CHART SPEED – 1 cm / min, DETECTOR – FID.

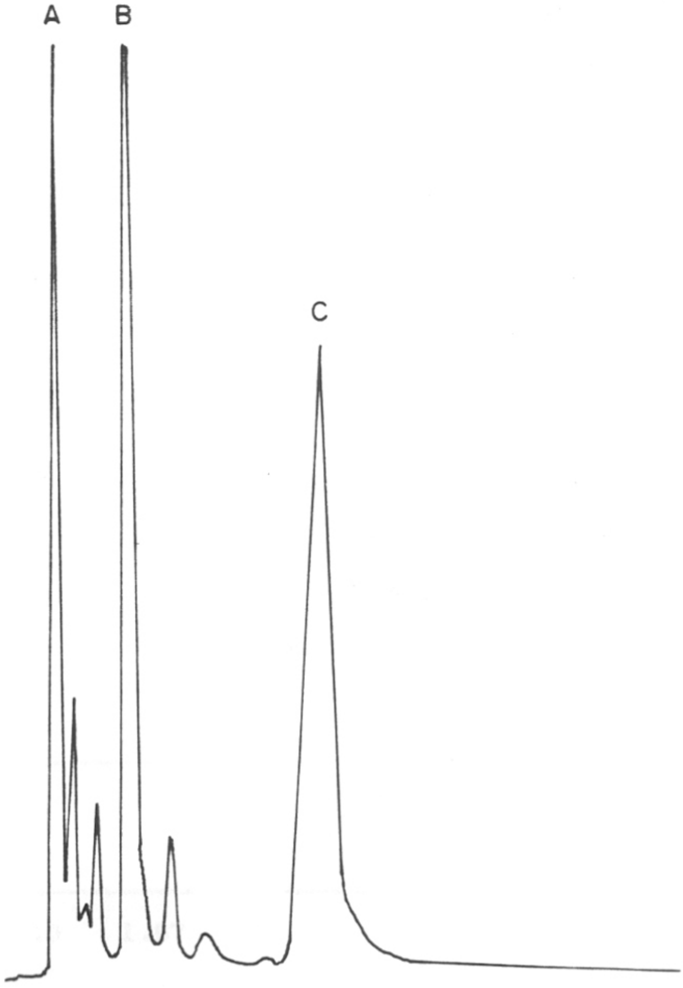


FIG. 28. GLC OF OXIDATION PRODUCT OF 1-DECANOL

A : UNIDENTIFIED PRODUCT, B : DECANAL

C : 1-DECANOL

CONDITIONS : COLUMN 5% CARBOWAX 20 M ON CHROMOSORB W AW, 1·22 m x 6·4 mm (id) AT 120°C, CARRIER GAS (N_2) FLOW RATE – 20 ml / min, CHART SPEED – 1 cm / min, DETECTOR – FID.

TABLE 16 - GLC ANALYTICAL DATA OF OXIDATION PRODUCTS OF 1-BUTANOL (EXCLUDING ACID CONTENT)

Column temperature: 50°C, Carrier gas (N_2) flow rate: 20 ml/min.

Compound	Temp. of reactor			Retention times of standards
	250°	300°	350°	
	%	%	%	
Alcohol	85.40	63.00	43.60	1-butanol: 4.37 min.
Aldehyde	7.51	32.75	50.00	butanal: 1.09 min.
Unidentified	3.98	2.82	3.58	-
Impurities	3.10	1.41	2.82	-
*Conversion to aldehyde	52.92	90.62	90.14	-
Acid content (determined titrimetrically)	1.10	1.67	2.50	-

*Calculations based on the quantity of total alcohol oxidised inclusive of that oxidised to acid. Percentage purity of the starting material was also considered.

TABLE 17 - GLC ANALYTICAL DATA OF OXIDATION PRODUCTS OF 1-HEXANOL (EXCLUDING ACID CONTENT)

Column temperature: 75°C, Carrier gas (N_2) flow rate: 20 ml/min.

Compound	Temp. of reactor			Retention times of standards
	250°	300°	350°	
	%	%	%	
Alcohol	82.50	65.50	45.75	1-hexanol: 4.92 min.
Aldehyde	9.50	24.64	37.82	hexanal: 1.30 min.
Unidentified	0.88	1.02	1.38	-
Impurities	7.10	5.39	15.04	-
*Conversion to aldehyde	57.34	74.00	71.58	-
Acid content (determined titrimetrically).	1.86	4.10	5.21	-

*Calculations based on the quantity of total alcohol oxidised inclusive of that oxidised to acid. Percentage purity of the starting material was also considered.

TABLE 18 - GLC ANALYTICAL DATA OF OXIDATION PRODUCTS OF 1-OCTANOL (EXCLUDING ACID CONTENT)

Column temperature: 90°C, Carrier gas (N_2) flow rate: 20 ml/min.

Compound	Temp. of reactor			Retention times of standards
	250°	300°	350°	
	%	%	%	
Alcohol	68.12	37.88	21.75	1-octanol: 7.98 min.
Aldehyde	18.57	26.98	30.83	octanal: 2.08 min.
Unidentified	10.18	32.17	45.68	-
Impurities	3.14	2.97	1.57	-
*Conversion to aldehyde	59.57	44.37	39.73	-
Acid content (determined titrimetrically)	1.46	1.60	3.03	-

*Calculations based on the quantity of total alcohol oxidised inclusive of that oxidised to acid. Percentage purity of the starting material was also considered.

TABLE 19 - GLC ANALYTICAL DATA OF OXIDATION PRODUCTS OF 1-DECANOL (EXCLUDING ACID CONTENT)

Column temperature: 120°C, Carrier gas (N_2) flow rate: 20 ml/min.

Compound	Temp. of reactor			Retention times of standards
	250°	300°	350°	
	%	%	%	
Alcohol	71.02	33.26	18.37	1-decanol: 5.39 min.
Aldehyde	14.87	22.99	29.02	decanal: 2.13 min.
Unidentified	7.57	36.96	45.52	-
Impurities	7.10	6.79	7.00	-
[*]Conversion to aldehyde	53.64	35.97	36.96	-
Acid content (determined titrimetrically)	2.17	2.26	2.74	-

[*] Calculations based on the quantity of total alcohol oxidised inclusive of that oxidised to acid. Percentage purity of the starting material was also considered.

TABLE 20 - GLC ANALYTICAL DATA OF OXIDATION OF 1-OCTANOL OVER FRESH AND REGENERATED V_2O_5/SiC CATALYST AT 350°C

Column temperature: 90°C, Carrier gas (N_2) flow rate: 20 ml/min.

Compound	With fresh catalyst	With regenerated catalyst (once used)	With regenerated catalyst (twice used)
	%	%	%
1-Octanol	21.75	63.69	68.93
Octanal	30.83	15.42	13.98
Unidentified	45.68	15.03	9.23
Impurities	1.57	5.86	7.86
*Conversion to aldehyde	39.73	42.64	44.86
Acid content (determined titrimetrically).	3.03	3.56	4.38

*Calculations based on the quantity of total alcohol oxidised inclusive of that oxidised to acid. Percentage purity of the starting material was also considered.

3.3.2 Conversion of alcohols to aldehydes

It is obvious that the yields of the aldehydes increase with increasing reactor temperatures in all the cases. In accordance with it, the percentage of the unreacted recovered alcohols falls as the reactor temperature is changed from 250° to 300° and 350°. Furthermore, the data given in Tables 16 and 17 for the lower alcohols gives the vital part of information regarding conversion of the total quantities of the alcohols undergoing oxidation to the respective aldehydes, which show a marked increase when the reactor temperature is 300° or 350°. In sharp contrast to this observation, the conversion of the higher alcohols to the respective aldehydes (Tables 18 and 19) is reduced at higher temperatures, which is understandable as the yields of the respective unidentified products show an increase under these conditions.

3.3.3 Impurities

The total quantities of various impurities obtained in each case are given in Tables 16 to 20, which describe the GLC analytical data. The impurities shown in these tables could be due to formation of aldols, esters, ethers, isomerization products etc.

3.3.4 Unidentified products

It will be seen from the same tables that in all these experiments an unidentified product is obtained along with the aldehydes in the oxidation of each alcohol. The formation of such a product is much less in lower alcohols i.e. 1-butanol and 1-hexanol, but similar unidentified products occur in high proportions in the oxidation products of higher alcohols i.e. 1-octanol and 1-decanol. The information sought for their identification was gathered by recording GC-MS of the oxidation product of each alcohol. The mass spectra of the unidentified products of 1-octanol and 1-decanol revealed that they have molecular weights two units lower (molecular ions at m/e 126 and at m/e 154 respectively) than that of the respective aldehydes. It might therefore be inferred that the occurrence of these products could be due to dehydrogenation of these aldehydes. However, the unidentified product obtained in the oxidation of 1-butanol showed a molecular ion at m/e 104 indicating that it might be some condensation product obtained during oxidation. A similar unidentified product found in the oxidation product of 1-hexanol could be either an isomerization product or a hexene as the molecular ion, in its spectrum has appeared at m/e 84. However, in this spectrum, absence of peaks at m/e 31, m/e 45 and m/e 59 which are characteristic of primary, secondary and tertiary alcohols[103], indirectly favour the olefin structure.

3.3.5 Activity of the regenerated catalyst

The results of oxidation of 1-octanol over fresh, once regenerated and twice regenerated V_2O_5/SiC catalyst at 350° are summarized in Table 20. The quantities of unreacted alcohol recovered on using the regenerated catalyst is approximately three times that in the case of fresh catalyst, which clearly indicates that the activity of the regenerated catalyst is much less as compared to that of the fresh one, although the extent of apparent conversion remains almost unaltered in all the three experiments.

3.4 Conclusion

From the foregoing discussion it would be clear that the method studied above is appreciably effective for the oxidation of low molecular weight alcohols to the respective aldehydes.

Aldehydes, especially those of lower molecular weight are important industrial intermediates in the synthesis of alcohols, acids etc. The well known Oxo process used for the manufacture of aldehydes[104a,b] makes use of a mixture of an olefin, carbon monoxide and hydrogen, which is heated under pressure in the presence of a suitable catalyst. However, the catalytic vapour-phase oxidation method employed for the commercial production of acetaldehyde involves use of silver catalyst at 480°C[105]. In this method the oxidation of ethyl alcohol is carried out by passing its vapours and preheated air over the catalyst and the conversion to acetaldehyde per pass ranged from 30-50%. The conversion per pass has been further improved to 74-82% with a multitubular reactor[96b]. This method has replaced the old method of manufacturing acetaldehyde from ethyl alcohol by its catalytic dehydrogenation at 260-290° over a copper chromite catalyst[96a].

In view of the above, the method described in this part of the thesis can be regarded as very valuable and further studies regarding conversion of 1-butanol and other lower alcohols in a single pass would be undertaken shortly.

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