THERMOANALYTICAL INVESTIGATIONS OF THE CATALYTIC OXIDATION OF ORGANIC POLLUTANTS ADSORBED ON ACTIVATED CARBON

by

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ABSTRACT

Several catalytic carbons have been investigated for in situ oxidation of adsorbed organic pollutants. For styrene, it was found that metal oxide and metal catalysts promoted selective oxidation, while preserving the carbon. CuO, Cr_2O_3, MnO_2, V_2O_5, and various mixed oxides were effective in the temperature range 140°-230°C, but with some accompanying polymerization and/or chemisorption. Pt and Pd effected complete oxidation, with no adverse side reactions, of not only styrene, but also benzene, toluene,and ethylbenzene. The temperature range was 160°-250°C.

Vanadia-impregnated carbon catalyzed the oxidation of methylethyl ketone, methylmethacrylate,ethylacrylate, and n-butylacrylate in the temperature range 100°-250°C. Platinized, palladized, and nickelized activated carbons were effective between 140°-200°C. Measurements of the difference in temperature between oxidation of adsorbates and of adsorbent, gave an average value of 100°C to 150°C.

There was a noticeable decrease of adsorptive capacity of the catalytic carbon after about 10 cycles of oxidation on the same sample, probably because of deposition of chemisorbed matter on active sites. For vanadia-impregnated carbon, a decrease in catalytic activity was observed with increasing numbers of cycles and electron spin resonance studies suggested that this was due to reduction of V_2O_5

to V_2O_4. Formation of charge-transfer complexes on catalytic sites, during oxidation of aromatic hydrocarbons, also was indicated by esr measurements.

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PREFACE

The Problem And Its Significance To Air Pollution Control

The interaction of various factors involving the response of the public to the environmental crisis, new scientific findings on the effects of pollutants and the coincident popularization of ecological concepts lead to a consensus on the need to control the deterioration of our environment. In the field of air pollution, the chief pollutants are nitrogen oxides, carbon monoxides, sulfur dioxide and organic emissions which include hydrocarbons and non-hydrocarbons vapors and particulates.

The gravity of this air pollution menace is indicated by surveys conducted in 1965 which estimated that the amount of organic solvents discharged into the atmosphere (exclusive of motor exhausts) was 550 ton/day for the Los Angeles area and 300 tons/day for the San Francisco Bay area.[1]

Over half of the emissions in Los Angeles came from coating operations where the average concentration of organic vapors emitted ranged from 100 to 200 ppm (vol/vol).[2] Another survey conducted that year estimated organic emission from processing industries in Delaware Valley amounted to be 685 tons/day.

An additional 118 tons/day of organic solvent were emitted from surface coating and dry cleaning operations.[3]

It should be recognized that both mobile and stationary sources contribute to gaseous emissions, and there exists some accepted technology, for the control of both categories.[4-7] The complete destruction of these contaminants, or their reduction to low and acceptable concentrations, is the ultimate objective of any control technology. Among the accepted methods are liquid scrubbing, thermal incineration, catalytic combustion, and adsorption.

Adsorption methods are very useful in air pollution control because gaseous pollutants can be concentrated on the adsorbent. Activated carbon is the most useful medium for the adsorption of organic vapors, especially from moist gas streams, because the carbon is non-polar and it releases water as it adsorbs organic matter.

Disposal of pollutant gases that have been concentrated by adsorption may be effected in any of the following ways:

(1) The adsorbent with its adsorbate may be discarded.

(2) The adsorbate may be desorbed and either recovered, if it is valuable, or discarded.

(3) The adsorbate may be oxidized on the adsorbent surface. If the adsorbent is not simultaneously oxidized, it may be recovered.

The last alternative holds much promise for activated

carbon systems and it has been looked into by Turk in 1955.[8] The present energy crisis makes fuel-intensive processes like thermal incineration unattractive. Both the scarcity of fuel and the cost of available fuel need to be considered when catalytic or thermal incineration methods are being evaluated. This is particularly true for most odor-related emissions, since many of the problems are associated with high volumes of air containing minute amounts of contaminants. There must be an external supply of fuel to heat these large volumes of gas to incineration temperatures.

It follows, therefore, that there is a category of gaseous emissions to the atmosphere, for which existing technology seems inadequate. This category comprises emissions which are harmful or maladorous, which are too dilute to contribute enough thermal energy to make incineration attractive, and yet not dilute enough to make the activated carbon system economical, which cannot effectively be removed by scrubbers even with the aid of chemical agents such as permanganate, and which are not satisfactorily "covered" by masking agents. In spite of all these delimitations, such emissions are far from uncommon. Typical contaminants include styrene, methyl-ethyl ketone, and various mixtures such as lacquer solvents and the like.

Temperature-rise contributed by oxidation

The temperature-rise, contributed by complete oxidation of a contaminant in an air stream at 1000cfm, could be approximately calculated using the equation[9]

$$T_c = \frac{56HG}{Q\left[\frac{530}{460 + T_o}\right]} \qquad (1)$$

where,

T_c = teperature-rise furnished by contaminant oxidation.

H = Heat of combustion of contaminant (BTU/gal)

G = Rate of generation of contaminant into emission (gal./min.)

Q = Total emission (cu.ft./min.)

T = degrees F.

Units of the constant 56, are F.deg/standard cu.ft., and in arriving at the above equation, the approximate specific heat of dry air, in the temperature range of 70°F to 800°F is assumed to be 0.24 BTU/lb. F at 1 atmosphere pressure. Since one pound of air occupies 13.5 cu.ft.at 70°F, 1 BTU will warm 1 standard cu.ft. (70°F) of air 56 F. degrees. The equation has neglected heat losses, heat capacity of the moisture and other combustion products in the air stream, and changes of specific heat with temperature.

The equation can be reduced to

$$T_c = 29 \times \text{" Percent of L.E.L "} \qquad (II)$$

if it is assumed[53, 54], that the latent heat of a

contaminated air stream (HG/Q), at the lower Explosive Limit (L.E.L.), is roughly a constant, having a value of 52 BTU/standard cu.ft. Combustible gas meters are customarily scaled directly in "Percent of L.E.L.", and we could write

$$\frac{HG}{Q} = 0.52 \times \text{"Percent of L.E.L."} \qquad \text{(III)}$$

Substitution of equation (III), in (I), and taking room temperature as reference ($T_o = 70$), leads to equation (II). If we consider, for example, air containing 100 ppm styrene, the temperature-rise contributed by oxidation can be calculated considering that for this contaminant, the Lower Explosive Limit is 11,000 ppm (vol/vol). A concentration of 100 ppm is 1.1% of L.E.L., and substitution in equation (II) leads to a value 89°F as the temperature-rise.

This concentration, therefore, contributes an insignificant heat content, but produces a significant odor nuisance. The same stream would saturate about 16 lb/hr of activated carbon per 1000 cfm, and would deposit some polymer on the carbon surface. Chemical consumption of potassium permanganate would be about 1.71 lb/hr. per 1000 cfm, but the reaction is slow and the required scrubber detention time would be very high[10].

The Lower Explosive Limits of some other hydrocarbon pollutants of interest are shown in Table I. For a mixture of combustible organic compounds, the L.E.L. can be calculated using the modified Le Chatelier's mixture law[11]

$$\text{L.E.L. (in \% conc.)} = \frac{100}{P_1/N_1 + P_2/N_2 + \ldots . P_n/N_n}$$

where P_1, P_2, ...P_n = volume % of each flammable vapor, and N_1, N_2 .....N_n = volume % of each flammable vapor in air at the Lower Explosive Limit.

Considering the above limitations, it was suggested[8] that a solution to the problem could be realized by adsorbing the contaminant on activated carbon and then oxidizing the adsorbate *in situ*, while preserving the carbon. The preliminary study by Turk[8] showed promise and the present investigation was undertaken to carry out a systematic survey of various catalytic systems, using the novel technique of "temperature-programmed desorption" of the adsorbate in an oxidizing atmosphere. This technique was first employed by Cvetanovic *et al*[12] in the study of chemisorption and surface reactions on metal oxide catalysts. More recently [13], the technique was extended to the study of metal catalysts in polymerization and self-hydrogenation reactions of ethylene on silica-supported platinum. The regions in which reactions occur can be rapidly determined.

TABLE I

Lower Explosive Limit (L.E.L.) Of Some Hydrocarbon Pollutants.

Compound	B.Pt °C	L.E.L. ppm	Odor Threshold ppm
Benzene	80.1	14,000	3-60
Ethylbenzene	136.0	10,000	100
Methylethyl ketone	79.6	20,000	200
Styrene	145-6	11,000	100
Toluene	110.6	14,000	200

Objectives of the Present Study

The initial objective in this study was to carry out a systematic evaluation of the energy, temperature and mass changes that occur during the progress of the catalytic oxidation. Chemical analysis of the effluent would help determine the nature of the intermediate oxidation products, the aim being a complete destruction of the pollutant to CO_2 and H_2O. No attempt was made to determine the percentage conversion of the adsorbate, since the ultimate objective, to be taken up in the second phase of this research, is to develop a cycling adsorption-oxidation system for the control of gaseous effluents. Emphasis was placed on obtaining catalysts that would promote selective oxidation of the adsorbate at a low enough temperature while leaving the carbon intact. In short, what we hoped to achieve is oxidation of pollutant with simultaneous regeneration of the activated carbon.

In view of the wide range of pollutants which are of interest, the study has been divided into three parts:

PART I: CATALYTIC OXIDATION OF AROMATIC HYDROCARBONS-EVALUATION OF CATALYSTS.

PART II: CATALYTIC OXIDATION OF OXYGENATED ORGANIC COMPOUNDS-EVALUATION OF CATALYSTS.

PART III: REGENERATION STUDIES.

It is hoped that the results of this investigation

will provide economically feasible methods for purification of a variety of types of contaminated air streams for which no satisfactory technology now exists.

PART I

CATALYTIC OXIDATION OF AROMATIC HYDROCARBONS

INTRODUCTION

Reactions in Air Atmosphere

The oxidation of hydrocarbons is currently of great interest and voluminous patent and journal literature has accumulated. No attempt will be made here to write a comprehensive review, and it must be emphasized from the start that our interest lies in complete oxidation of hydrocarbons producing CO_2 and H_2O and not in partial or selective oxidation.

The addition of a catalyst to aid the process of oxidation by reducing the ignition temperature to initiate oxidation is a very valuable technique in air pollution abatement. By this method a suitable catalyst will initiate oxidation at a temperature as low as 260°C. When the heat content of the contaminated air is sufficiently high, the process, once started will sustain itself without further addition of heat from external source. This method is therefore most economical when the temperature of the contaminated air is close to 260°C at its source or when the heat of reaction is sufficiently high so that outside addition of heat is unnecessary once the catalytic reaction has started.

Catalytic combustion is feasible when the concentration of organic vapors in the contaminated air is one hundred to several hundred ppm (vol/vol), but safely below the lower explosive limit. When the concentration is between 2 ppm and 100 ppm or more an adsorption-oxidation system employing

activated carbon has been suggested,[8] in which adsorption of the contaminant on the carbon is followed by *in situ* oxidation of the adsorbate. Currently accepted methods make use of adsorption in combination with oxidation in a seperate unit after stream or hot air desorption.[14] Partial oxidation is often a poor solution because intermediate products of organic vapors may be as odorous or more odorous than unoxidized material. Lunche[15] notes that in a number of cases the odor and eye irritation index have actually increased across a catalytic combustor due to the formation of partial oxidation products.

The use of catalytic oxidation for solvent vapors[16-18] and for fume and odor control[19,20] has been discussed and the selective oxidation over metal oxide catalysts of aromatic hydrocarbons is well known.[21-23] Vapor-phase catalytic oxidation is effective in oxidizing organic compounds and most investigators have used metals or metal oxides either unsupported or supported on non-reactive materials such as alumina, silica gel and asbestos.

A recent study by Fazekas *et al*[23] involved complete oxidation over Cr_2O_3-MnO_2 supported on γ-alumina. The minimum temperature was 500°C at a maximum pressure of 60 atm. Residual hydrocarbons after catalytic oxidation with the above parameters amount to 300 ppm for C_1-C_4 hydrocarbons and 20 ppm for C_{5+} hydrocarbons. Although they reported no

odor nuisance when this level of impurities is mixed with gaseous CO_2, a concentration of 300 ppm may be lethal to the human population. A more efficient method for its removal is therefore desirable.

Stein et al[24] used a micro-catalytic chromatographic technique to study complete oxidation of hydrocarbons on unsupported simple oxide catalysts. Stone[25] has also studied oxidation over metal oxide catalysts. The results of these investigations and those of several others led to the following observations.

(1) Oxides with high activity towards hydrocarbon oxidation are generally p-type semi-conductors (Mn_2O_3, CoO, NiO, Cr_2O_3 and Cu_2O). They exhibit little selectivity by themselves.

(2) Oxides of representative elements show little activity in hydrocarbon oxidation.

(3) Transition metal oxides of moderate activity are n-type semi-conductors (WO_3, MoO_3, V_2O_5 and Fe_2O_3).

(4) Some metals such as Pt, Pd, Ag, V, Co, Ni, Mo, Mn and Cu are effective oxidation catalysts.

(5) Mixed oxides and bimetallic mixtures can function as oxidation catalysts.

The oxidation of some hydrocarbons over the noble metal catalysts Pt and Pd, has been investigated by Barnard and Mitchell[26] and Margolis[27] has written a review on catalytic oxidation of hydrocarbons. More recently Popovskii[28] wrote a review on the intense or complete

oxidation of hydrocarbons in the presence of solid oxide catalysts.

It was therefore logical to resort to the literature on catalytic oxidations as a guideline for our investigations. The innovation we have tried to introduce relies on the use of activated carbon as the support for catalysts. This would therefore impose the following limitations:

(a) A highly active oxidation catalyst would tend to make the carbon pyrophoric.

(b) If the catalyst activity is low, only easily oxidizable pollutants would be converted.

(c) An excess of the impregnant might reduce the adsorption capacity of the carbon.

Because of the above limitations on the support, the intricacies of this problem can be readily appreciated. Catalytic oxidations on non-oxidizable carriers as noted above, are generally conducted at elevated temperatures. At ambient temperature the impregnated carbon itself is stable towards oxidation, but its kindling temperature is significantly lowered, as will be shown in the experimental section (fig. 1).

The role of carbon as a support is even further complicated by the fact that it can function as a conductor, semi-conductor and insulator depending on its electronic properties and hence it encompasses all regions of catalysts classification.[29] Unimpregnated activated carbons have

been used for vapor-phase oxidations of compounds like CO_2 SO_2 and H_2S.[30-32] The oxidation of gases such as H_2S on activated carbon can also be accomplished by deposition of metals and oxidants on the carbon surface. A copper-chromite -impregnated carbon will oxidize H_2S in air streams or in natural gas streams where little or no oxygen is present.[33] Rao and Houger[34] have oxidized NO to NO_2 over activated carbon.

Although some investigators have reported[35,36] on the rapid reaction, sometimes leading to ignition taking place at low temperatures (50-100°C), when air or oxygen is passed over carbon beds on which the vapors of organic compounds are desorbed, a fuller understanding of this phenomenon is lacking. In study conducted by Fish et al,[37] no evidence of heterogenous catalysis by carbon was observed and they concluded that gaseous reactions which take place between oxygen and organic compounds in the presence of carbon are homogeneously catalyzed. The reactions were initiated by the temperature rise provided by oxidation of the carbon. Nevertheless, the work that provided the impetus for the present research was done by Turk,[8] who reported on chromite-impregnated activated carbon as an adsorbent-oxidation catalyst. He provided some data on the temperature of the effluent stream after it had passed through a bed of the impregnated carbon, but no data were given on the optimum oxidation conditions,nor were chemical analysis of the effluent made to determine any intermediate products. The work we now report has tried to cover these gaps. Many other catalysts have been evaluated and an apparatus is described which is generally

useful for rapid evaluation of other systems.

Reactions in Ozone Atmosphere.

Whereas the reactive atmosphere in this study is air, Deitz and Bitner[38] have carried out reactions on activated carbon using ozone and their results strongly indicate that foreign adsorbates could be selectively oxidized at ambient temperatures. They pointed out that some fundamental knowledge of this type of reaction as well as those with oxygen-containing gases is singularly lacking. The ozone study revealed that there was progressive etching of the carbon resulting in the following reactions:

$$C_xO_y\ (\text{solid}) + O_3 \longrightarrow C_{x-1}O_{y+1}\ (\text{solid}) + CO_2 \qquad (1)$$

$$C_xO_y\ (\text{solid}) + O_3 \longrightarrow C_{x-2}O_y\ (\text{solid}) + CO_2 + CO \qquad (2)$$

One could therefore anticipate that reactions (1) and (2) could occur preferentially with an adsorbate. Micropore plugging could be expected from chemisorption of oxygen atom by the reaction:

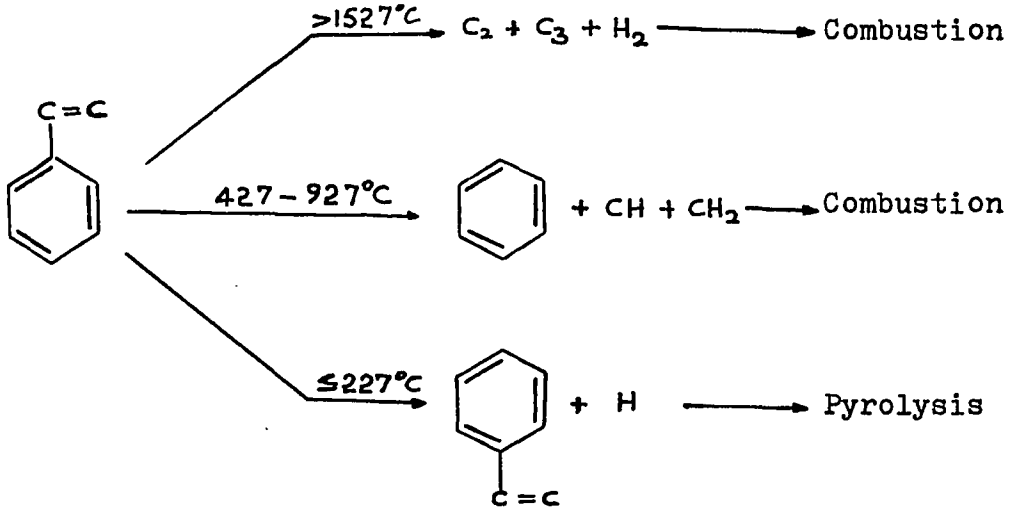
$$C_xO_y\ (\text{solid}) + O_3 \longrightarrow C_xO_{y+1}\ (\text{solid}) + O_2 \qquad (3)$$

These reactions would lead to a change in the adsorptive capacity of the carbon, as has been in fact observed by Coughlin and Ezra[39] who worked on the adsorption of Phenol and nitrobenzene on pre-oxidized and pre-reduced carbon. A decrease in adsorption was found for oxidized carbon and the ozone reaction resulted in the decrease of nitrogen adsorption. However the economy and safety in ozone applications are questionable.

Oxidation of Styrene

The oxidative removal of styrene whose adverse effects on workers have been demonstrated constituted the major area of this study in the field of aromatic hydrocarbons. Styrene presents a problem of being liable to polymerization as well as cracking and hydrogenation reactions to give benzene, toluene, ethylbenzene and ethylene. Because of these possible by-products the work was extended to include these materials.

The only reported work in the literature on the oxidation of styrene in the vapor phase is that of Petrella and Sellers.[40] They used the technique of kinetic spectroscopy to study the combustion of styrene monomer under a variety of oxygen-to-fuel ratios and initiation temperatures. The proposed pyrolysis and combustion modes of styrene in oxygen at the different initiation temperatures can be written as follows:



Only between 427 and 927°C was combustion to CO and CO_2 observed. Thermal cracking was found to preceed combustion within this temperature range. Cracking was minimal between 97°C and 230°C. At temperatures approaching 1527°C the monomer dissociates with loss of hydrogen atoms to form C_2, C_3, and possibly larger carbon fragments which condense into soot, and H_2 burns to H_2O.

We were interested in finding an activated carbon with a high ignition temperature, a carbon that also has good adsorptive capacity for organic pollutants of interest.

It should be noted that while many catalysts have been reported to be effective for the complete oxidation of hydrocarbons when such catalysts are supported on inert materials, there is no certainty as to their oxidative ability when carbon is the support material, especially as it is sometimes necessary to calcine these catalysts in air at elevated temperatures in order to activate them. Moreover, the usual configuration is passage of the contaminated stream through a catalyst bed held at a temperature that would normally initiate oxidation of carbon. In this work, we have initially adsorbed the pollutant on the carbon at ambient temperatures and then subsequently desorbing the material by controlled temperature-programming in a reactive atmosphere. No attempt has been made at isothermal regeneration (oxidation), although this could be invoked in practice once the conditions have been optimized.

EXPERIMENTAL

There are four sections to be described:

A. DETERMINATION OF IGNITION TEMPERATURE.

B. DETERMINATION OF ADSORPTIVE CAPACITY.

C. IMPREGNATION OF ACTIVATED CARBON WITH CATALYSTS.

D. SATURATION AND OXIDATION OF ADSORBATE.

A. Determination of Ignition Temperature.

Method:

Five commercially available activated aarbons were selected for this determination. An active carbon with a high ignition temperature and good adsorptive capacity would be an ideal material for the adsorption-oxidation system.

The activated carbons were those of Pittsburgh Activated Carbon Division, Calgon Corp. and four other companies as shown in Table II.

TABLE II. Types of Activated Carbon and Their Sources.

Manufacturer	Designation	Mesh Size; U.S. Sieve Series.	Source
Pittsburgh Calgon Corp.	BPL 6/16	6-16	Bituminous Coal
Columbia, Union Carbide Corp.	JxC 6/8	6-8	Bituminous Coal
Witco Chemical Company	256 6/8	6-8	Petroleum Coke
American-Norit Company	6/8	6-8	Bituminous Coal
Barnebey-Cheney Company	6/14	6-14	Coconut Shell

Ignition temperatures were determined using Du Ponts Modular Thermal Analysis System, consisting of a 900 Thermal Analyzer, which is a plug-in module for a 950 Thermogravimetric Analyzer (TGA), and a Differential Scanning Calorimeter Cell (DSC). The DSC was used for ignition temperature measurements.

Between 30 and 40 mg of active carbon, the mesh size of which is as indicated above, was weighed into an aluminum sample pan which was then placed on the sample platform in the DSC Cell. The reference was an empty aluminum pan of the same size. The temperature program was set at 15°C/min and air was passed over the sample at a rate of 300 ml/min; cell volume was 5 ml. Air flowrate was indicated by a Flowmeter which is an integral part of the 900 console. The recorder plots change in sample temperature (T) against furnace temperature, and any reaction is shown as an exothermic peak or an endothermic peak. A typical DSC run is shown in Fig. (1) for both the unimpregnated carbon and carbon impregnated with 1% $(NH_4)_2\ Cr_2O_7$ solution. The results for five different types of carbon obtained under identical conditions are shown in Table 3. Samples were dried at 120°C and cooled to room temperature in a dessicator before each run.

TABLE III

Ignition Temperatures of Five Commercially Available Carbons.

Type	Ignition Temp. (°C)	Method
Pittsburgh BPL 6/16	493	DSC
Columbia JxC 6/8	470	"
Witco 256 6/8	475	"
American Norit	370	"
Barnebey Cheney Co 6/14	280	"

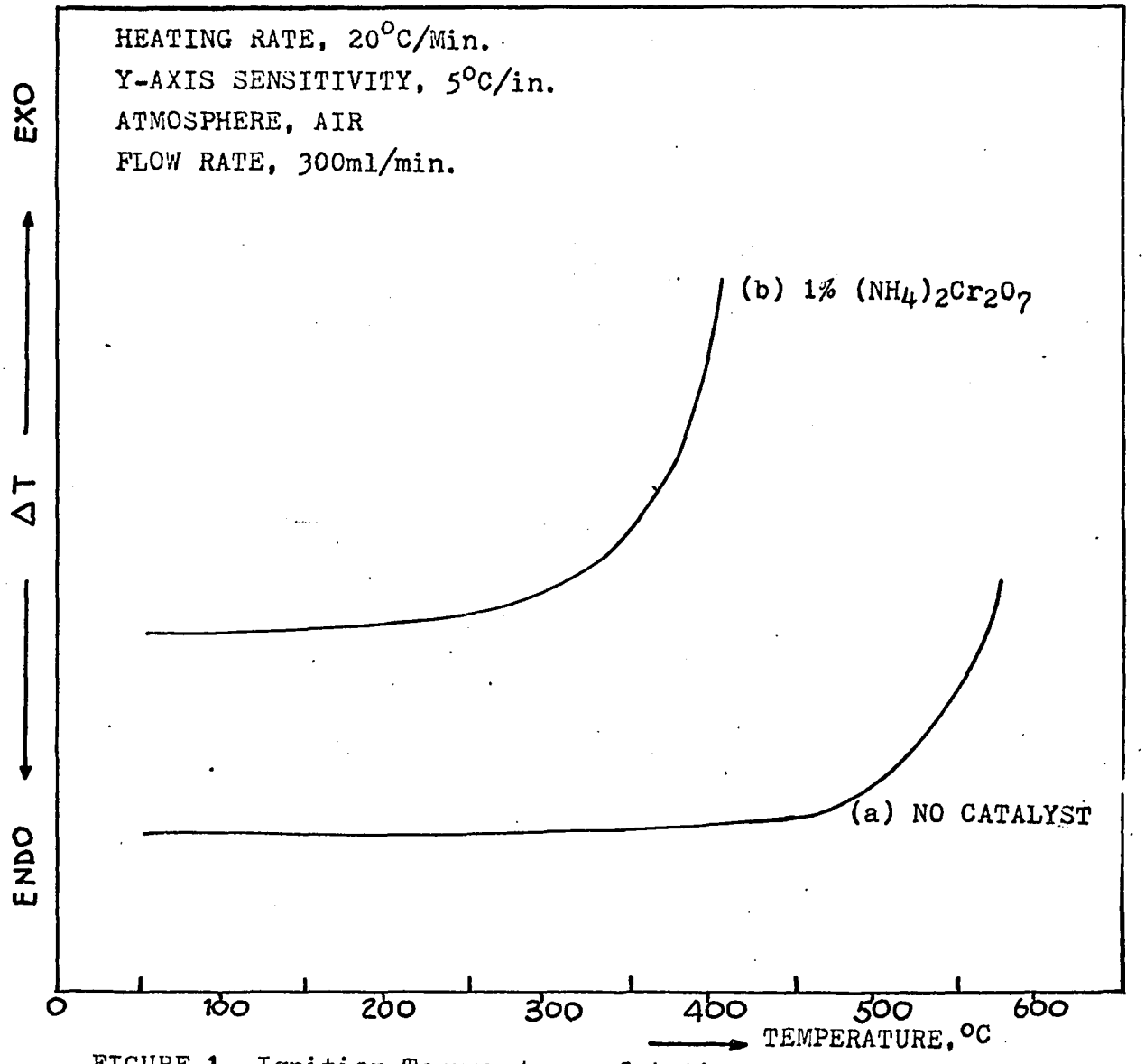


FIGURE 1. Ignition Temperature of Activated Carbon Using DSC. (a) No Catalyst (b) Impregnated with 1% $(NH_4)_2Cr_2O_7$.

B. Determination of Adsorptive Capacity

Method:

A modified version of the TGA was used in order to avoid contamination of the control end of the balance. This modification was originated by Ruth et al.[41], and the saturation train in this work is shown in Fig. 2.

A nitrogen purge flows through the balance housing, and a modified Pyrex furnace tube and a baffle provide a separation between balance and adsorption zone. Reaction gas, consisting of nitrogen flowing through a bubbler where it is saturated with the compound of interest enters the inner tube of the concentric furnace tube shown in Fig. 2 and passes over the activated carbon. The reaction gas leaves the inner tube through slots in the circular platinum baffle held in place at the end of the inner tube by means of a side-arm attached to the balance housing. Reaction gas and nitrogen purge gas pass together through the annular space between inner and outer tubes and are discharged together through an opening near the end of the outer tube.

For the study of comparative adsorption capacity of the carbons, the pollutant chosen was styrene of fixed volume (10ml) kept at 25°C in the saturator. Nitrogen flow-rate through the saturator was kept constant at 300 ml/min. giving a concentration of 6,870 ppm (vol/vol) styrene in the stream. The counter flow of nitrogen through the balance housing was at the rate of 450 ml/min.[41].

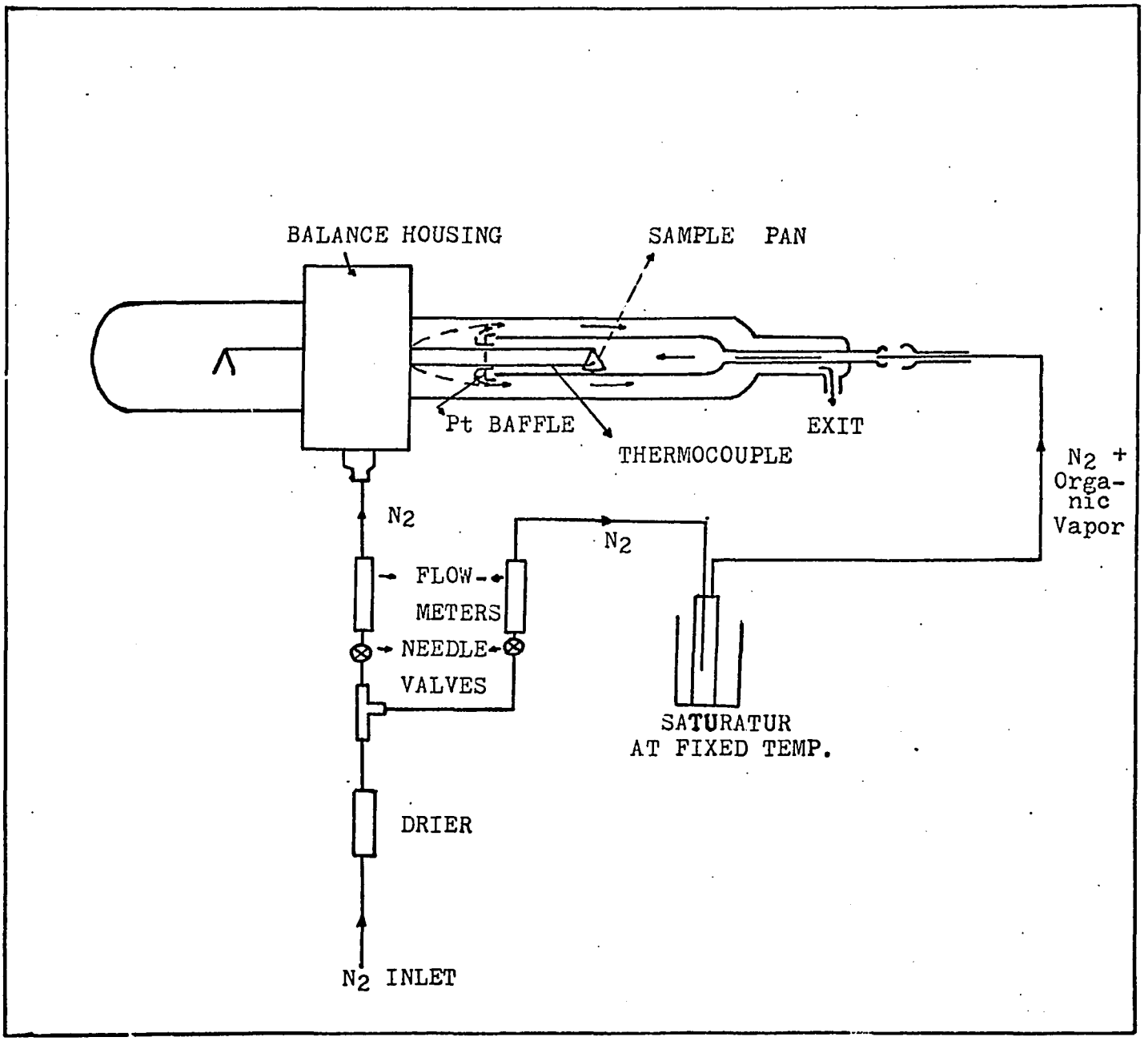


FIGURE 2. SATURATION TRAIN WITH MODIFIED DuPONT TGA.

A known weight (30-40 mg) of the carbon, was saturated with styrene, the weight increase at saturation having been automatically monitored by the thermobalance. Each run was made isothermally at an average ambient temperature of 25°C. A typical saturation run is given in Fig. 3. Results are given in Table IV for unimpregnated Activated carbon and for the carbon impregnated with 1% $(NH_4)_2\ Cr_2O_7$ solution. The instrument sensitivity was set at 4 mg./in.

TABLE IV

Saturation Capacity of Four Commercially Available Activated Carbons.

Sorbate - Styrene

Concentration = 6,870 ppm (vol./vol.)

Temperature = Ambient (25°C).

Source	Saturation Capacity mg/mg Activated carbon unimpregnated	Sat. Capacity mg/mg AC impregnated with $(NH_4)_2\ Cr_2O_7$
Pittsburgh BPL 6/16	0.404	0.399
Columbia JxC 6/8	0.405	0.372
Witco 256 6/8	0.374	0.331
Barnebey-Cheney 6/14	0.347	0.317

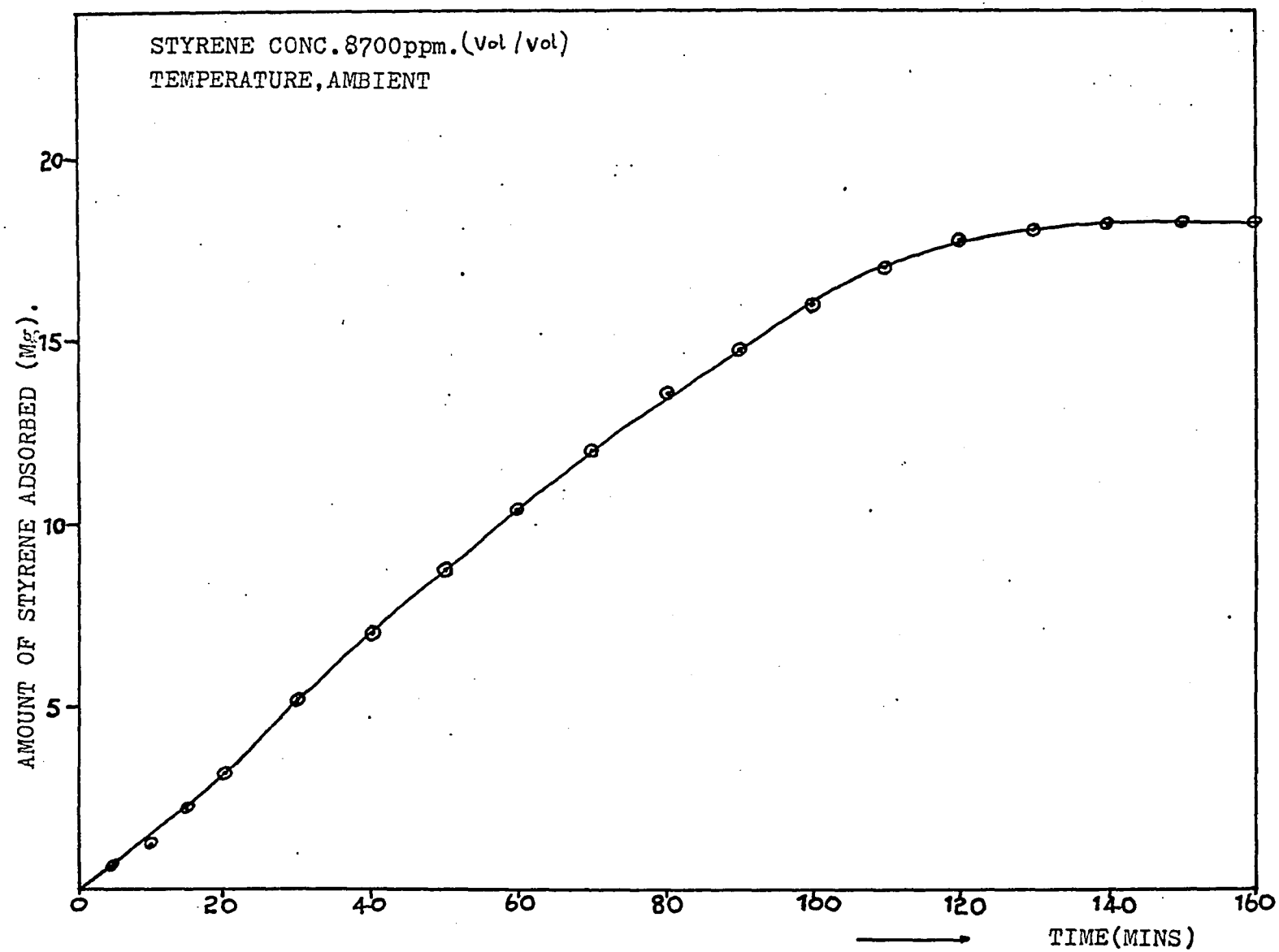


FIGURE 3. Typical Saturation Run(TGA)--Adsorption Of Styrene On Unimpregnated Activated Carbon.

C. Impregnation of Activated Carbon with Catalysts.

Method:

On the basis of ignition temperature and saturation capacity, Pittsburgh Activated Carbon BPL 6/16 mesh, was chosen for all investigations in this research.

There are two methods of impregnation: (I) Vapor-phase impregnation[42] and (II) Solution impregnation[43,8]. The latter method was chosen because of it simplicity and speed. Metallic oxide catalysts chosen from metals of Groups IB, V, VI-B, VII-B and VIII of the Periodic Table were first considered. The oxides were chosen on the basis of their proven activity for oxidation of hydrocarbons. It was assumed that catalytic agents generally used to promote low temperature oxidation at a carbon surface, would be unsuitable because they would render the carbon pyrophoric. Such are metallic catalysts like Pt, Pd, Cu, and Ag. It was however, latter shown that our assumption was erroneous.

The metallic oxides were deposited on the activated carbon according to the method of Turk[8]. For some metals like Cu, Ni, Co, and Mn, it was necessary to use 2% solution of the nitrates instead of the ammonium salts of the oxyanions, such as the 1% solution of $(NH_4)_2Cr_2O_7$ used by Turk[8]. For each impregnation 2 gm of activated carbon were covered with 3 ml of metallic salt solution, usually the nitrates. Decomposition of these nitrates then deposited the oxides on the carbon.

Activation

It was necessary to activate the catalysts after impregnation. A small sample of the carbon impregnated as above was dried at 110°C for 1 hour. Then 40 mg of the dried sample was analyzed in the DSC with temperature program in order to establish the point at which oxidation of carbon is appreciable. A temperature about 50°C below this point was chosen for air activation. For example, in the case of carbon impregnated with 1% solution of $Cr(NO_3)_{3.aq}$ (2 gm/3 ml solution), the carbon oxidation take-off point was 350°C. Consequently the bulk sample was heated in air at 250-300°C for 6 hours in order to activate the catalyst. The various metallic oxides studied and their corresponding activation temperatures are shown in Table V.

TABLE V

Metallic Oxide Catalysts And Their Activation Conditions In Air.

Catalyst	Activation Temperature (^{o}C)	Duration of Activation (hrs.)	Metallic Salt decomposed.
Cr_2O_3	300	3	$(NH_4)_2Cr_2O_7$
Cr_2O_3	300	3	$Cr(NO_3)(H_2O)_9$
CuO	340	6	$Cu(NO_3)_2(H_2O)_3$
Co_3O_4	340	6	$Co(NO_3)_2(H_2O)_6$
NiO	350	8	$Ni(NO_3)_2(H_2O)_6$
MnO_2	320	6	$Mn(NO_3)_2(H_2O)_9$
V_2O_5	230	3	NH_4VO_3
V_2O_5	230	12	NH_4VO_3
MO_3	340	6	$(NH_4)_6Mo_7O_{24}(H_2O)_4$
La_2O_3	350	4	$La(NO_3)_3(H_2O)_6$
WO_3	340	6	$(NH_4)_2W_4O_{13}(H_2O)_8$

Metal Catalysts

Palladium-impregnated carbon was purchased from Engelhard Industries and it contained 0.2% Pd by weight. The activated carbon was made from coconut shell.

Platinum-impregnated carbon was prepared as follows: Platinum foil weighing 92.2 mg was digested with 5 ml of aqua regia in a fume cupboard to a syrupy reddish-brown residue. This was rinsed out with 10 ml of distilled water into a 50 ml volumetric flask and then made up to 50 ml with distilled water. The undissolved platinum was dried at 120°C for one hour and weighed. The difference in weight gave the amount of platinum dissolved and the concentration of the greenish-yellow platinum complex solution was calculated. This was 0.142 mg Pt/ml of solution.

2 mg of Pittsburgh Activated Carbon was then covered with 2 ml of the above solution and was allowed to soak at room temperature until completely dry. The sample was then dried at 120°C for one hour and was decomposed in H_2 at 350°C for one hour to give an impregnated carbon containing 0.284% Pt by weight.

Another sample of carbon was similarly impregnated but was decomposed in air at 350°C for one hour instead of in H_2. There was noticeable difference in the catalytic activity of the two samples indicating that the method of preparation of a catalyst has significant influence on its activity.

D. Saturation and Oxidation of Adsorbates

(1) Styrene Oxidation Studies

Saturation of Carbon:

The modified TGA was used. First a known weight of unimpregnated Pittsburgh Activated Carbon BPL 6/16 mesh, was saturated with styrene using the set-up in Fig. 2. The concentration of styrene in the saturation stream was 6,870 ppm (vol/vol) which is well beyond the range of 2 to 100 ppm that is significant in this study. It was considered more important in this work to quickly saturate the carbon for TGA and DSC analysis so that information obtained could be applied to the design of an adsorption-oxidation system that operates within the range of concentration more typical of contaminated atmosphere. The necessity to work with 6,870 ppm became even more important, when it was determined that a given sample at that concentration, at a Flow-rate of 300 ml/min., took more than 100 minutes to be saturated. The time depends on the Flow-rate showing that adsorption is diffusion controlled.

Weight changes during adsorption were automatically recorded, until constant weight was indicated at saturation; the instrument sensitivity was set at 4 mg/in.

Oxidation Run:

Two methods were used to study the oxidation of adsorbed styrene after saturation.

Thermogravimetric Analysis (TGA)

A known weight of the saturated carbon was desorbed in air by temperature-programming at 15°C/min, in the modified TGA. In Fig. 2 air replaced the styrene stream and a counter flow of nitrogen was still maintained through the balance housing. The 900 Thermal Analyzer has controls for changing from isothermal to temperature-programming modes of operation. Weight changes during desorption were monitored by the thermobalance and the TGA was coupled to two gas chromatographs for effluent analysis of CO_2 and other components during oxidation. The effluent was sampled at different temperatures during desorption. One of the gas chromatographs was a Perkin-Elmer 154 Vapor Fractometer with a thermal conductivity detector and having a 1 meter silica-gel column ($\frac{1}{4}$ in O.D.) for CO_2 and CO analysis. The other was a Perkin-Elmer 800 Gas Chromatograph equipped with a flame ionization detector and a 1 meter Apiezon L column ($^1/8$ in O.D.) for organic intermediates analysis. A dry-ice cold trap was incorporated in the line to the gas chromatograph with thermal conductivity detector. The trapped effluents were subsequently analyzed by a GC-MS combination for positive identification of intermediate oxidation products.

The temperature-program was stopped at 400°C before any carbon burn off occured. Air Flow-rate was 300 ml/min.

Similar oxidative runs were made with carbon impregnated with different metal oxides as described before. Runs

were also made with mixed metal oxides. Effluent analysis was carried out in each case to confirm oxidation and to determine intermediate products. Retention times of authentic samples of benzene, toluene, and ethylbenzene, benzaldehyde and styrene were used to identify some of the products but confirmation was by GC-MS analysis of trapped effluent.

DSC Run.

Part of a sample saturated as above was weighed out and analyzed in the DSC. Temperature program was set at the same rate as for the TGA desorption in air at the same Flow-rate. Calibrated Flow-meters were used to regulate the rates of flow. Any oxidation was registered as an exothermic peak and the area under the peak is directly proportional to the heat of reaction. Desorption without oxidation should appear as an endothermic peak.

Heats of reaction were determined where necessary by the cut-and-weigh technique. A Xeroxed copy of the thermograms was used in order to obtain more reproducible results because of the heterogeneity of the chart paper which is used in the 900 thermal Analyzer. Metals of known heats of fusion, indium, zinc and tin were used to calibrate the instrument at two different rates of heating, $10^{o}C$/min and $15^{o}C$/min. The sensitivity of the DSC was set at a level that gave measurable peak area within the chart during oxidati[illegible] operational procedures were stipulated in t[illegible]strumental manual.

Calibration curves for the determination of calibration coefficient are shown in Fig. 4. The coefficients are used for calculating the heats of reaction, ΔH.[109]

$$\Delta H(\text{mcal/mg}) = \frac{E.A.\Delta T_S.T_S}{M.a}$$

where, E = Calibration coefficient, mcal/^oC-min

A = Peak Area, sq. in.

ΔT_S = Y-Axis Sensitivity, ^oC/in

T_S = X-Axis sensitivity, ^oC/in

M = Sample mass, mg

a = Heating Rate, ^oC/min.

Electron Spin Resonance

The oxidation state of catalysts and the nature of adsorbed pollutants were determined in some specific instances by esr technique. Measurements were made on weighed samples (10 to 15 mg) using the JEOL Spectrometer, equipped with a JEOL Electromagnet Model JM-ME-3 and a microwave unit model JES-ME-X with a rectangular cavity. The samples were contained in a quartz tube (3 MM I.D..by 300 mm long) supported by an adjustable teflon holder. The magnetic field was swept at $\pm$ 2500 gauss from a center of 3400 fauss. The modulation was at 100 khz with a power of 20 mW. Instrument settings were such as to give the optimum results and all measurements were made at room temperature in air.

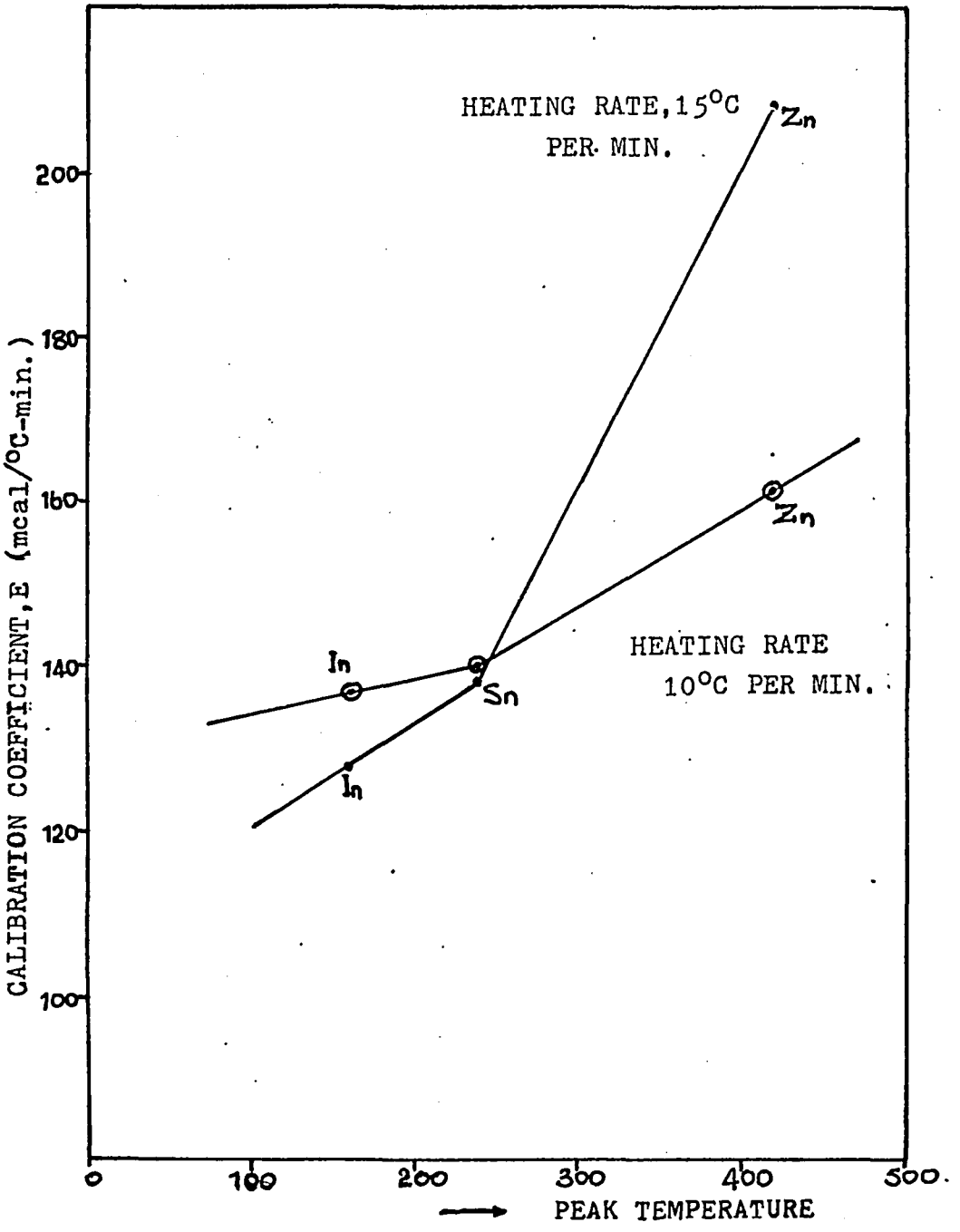


FIGURE 4. Calibration Curves For The Determination Of ΔH. Atmosphere, Air (dynamic).

RESULTS AND DISCUSSION

METAL OXIDE CATALYSTS

(A) Oxidation on Chromia-Impregnated Carbon

Fig. 5 shows DSC runs for styrene oxidation on carbon without catalyst (a), and on carbon impregnated with 1% $(NH_4)_2Cr_2O_7$ solution (2gm/3ml solution) (b). The significance of these figures can be seen when compared with Fig. 1, which contains DSC runs for unimpregnated carbon (a), and for carbon impregnated with 1% $(NH_4)_2Cr_2O_7$ solution (b). The results indicate that carbon alone catalyzes oxidation of styrene between 170 and 320°C. Impregnation with Chromia lowers the ignition temperature from 493°C to 350°C. This type of behaviour characterizes all the oxidation catalysts studied but the degree of depression varies from one catalyst to another. For styrene oxidation over Chromia-impregnated carbon, four distinct regions of reaction were observed: 90° to 140°C, 140° to 230°C, 290° to 340°C and above 350°C.

TGA-GC analysis within these temperature ranges using the set-up of Fig. 2, did not reveal any oxidation between 90° to 140° even when the size of the sample saturated with styrene was doubled. For this study, the oxidation train is as shown in Fig. 6. This set-up was used to detect the oxidation products CO_2 and H_2O within the range 140° to 230°C and above 350°C. Intermediate oxidation products were found to be benzaldehyde, benzene, ethylene, ethylbenzene and styrene.

It was necessary to know the temperature variation of

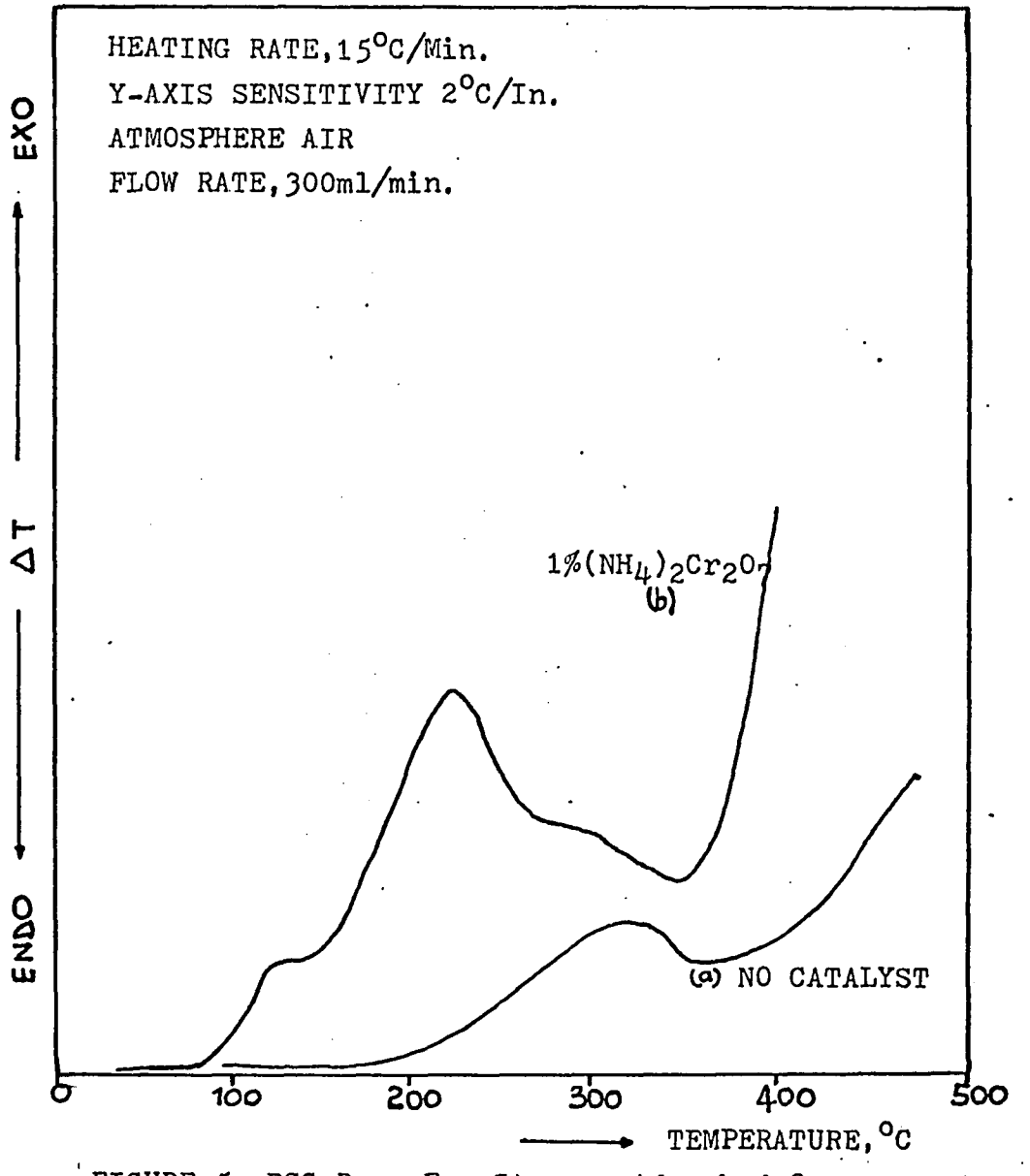


FIGURE 5. DSC Runs For Styrene Adsorbed On
(a) Carbon- No Catalyst, (b) Carbon+ 1% $(NH_4)_2Cr_2O_7$.

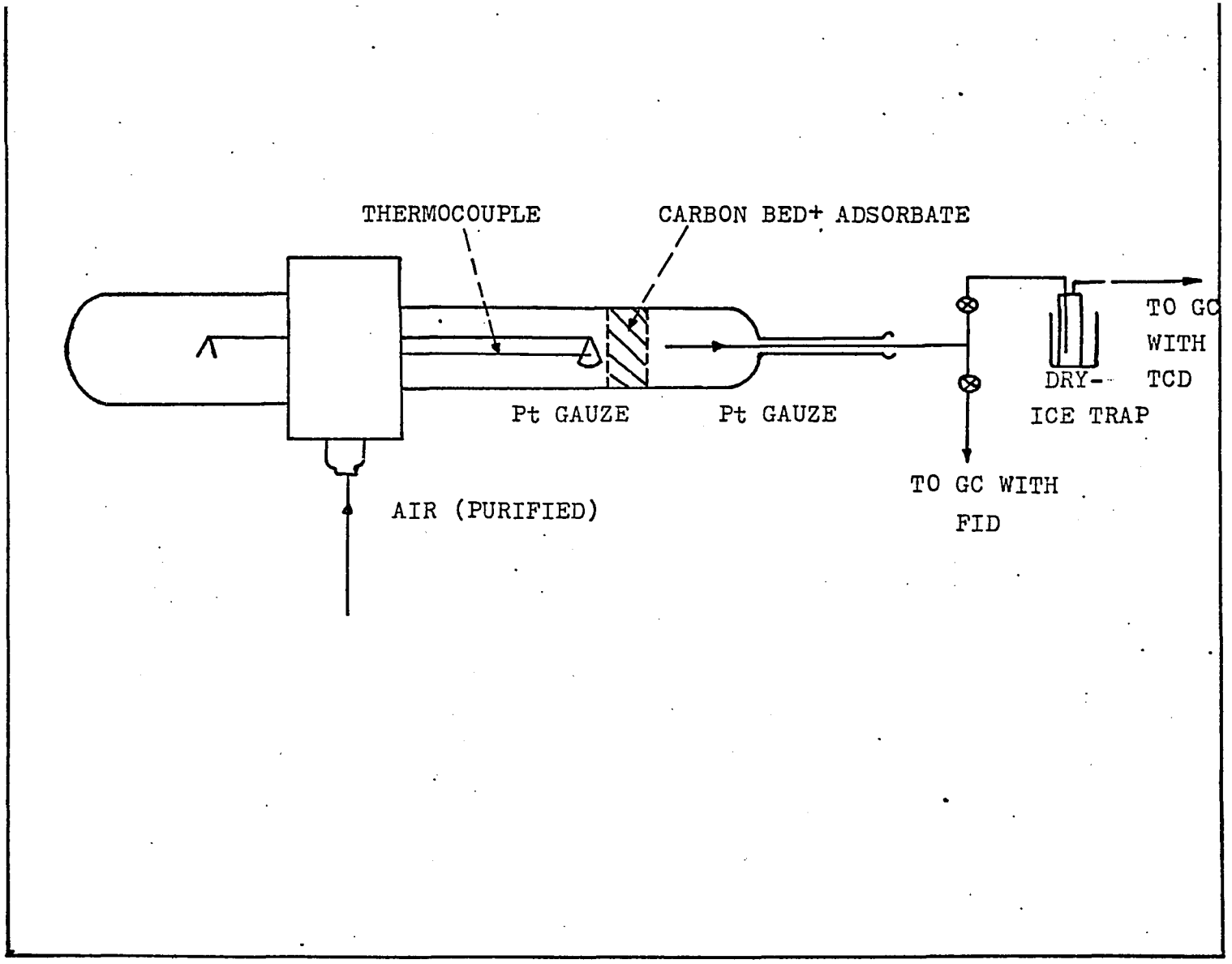


FIGURE 6. Macro-Oxidation Train For Adsorbed Pollutants. TGA-GC Analysis..

the carbon bed in Fig. 6 with respect to that of the furnace during a temperature-programmed desorption. Consequently, about 1cm depth of unimpregnated carbon was held in place at the mid-section of the original Du Ponts' TGA furnace tube by two platinum wire gauzes B and C. A Chromel-alumel thermocouple was positioned in the middle of the carbon bed and was connected to a Leeds and Northrup Co. Potentionmeter Model 700778 with capability for temperature measurement. The furnace temperature was measured by the thermocouple A.

The program was set at 15°C/min in nitrogen atmosphere to avoid any temperature difference due to oxidation and the potentiometer was quickly balanced at known furnace temperatures as indicated by thermocouple A, in order to measure temperature of the carbon bed. Voltages were recorded and the corresponding temperatures were obtained from tables. The results are shown in Fig. 7 where furnace temperature, as indicated by thermocouple A, is plotted against corresponding carbon bed temperature.

Chemisorption and Polymerization of Styrene

It is obvious from Fig. 5(b) that the endothermic reaction between 290° and 340°C is due to desorption of styrene or polysyrene. Polystyrene is suggested in view of the fact that no CO_2 was detected between 90° and 140°C, and the reaction giving rise to the exotherm within this temperature range, could therefore be either polymerization

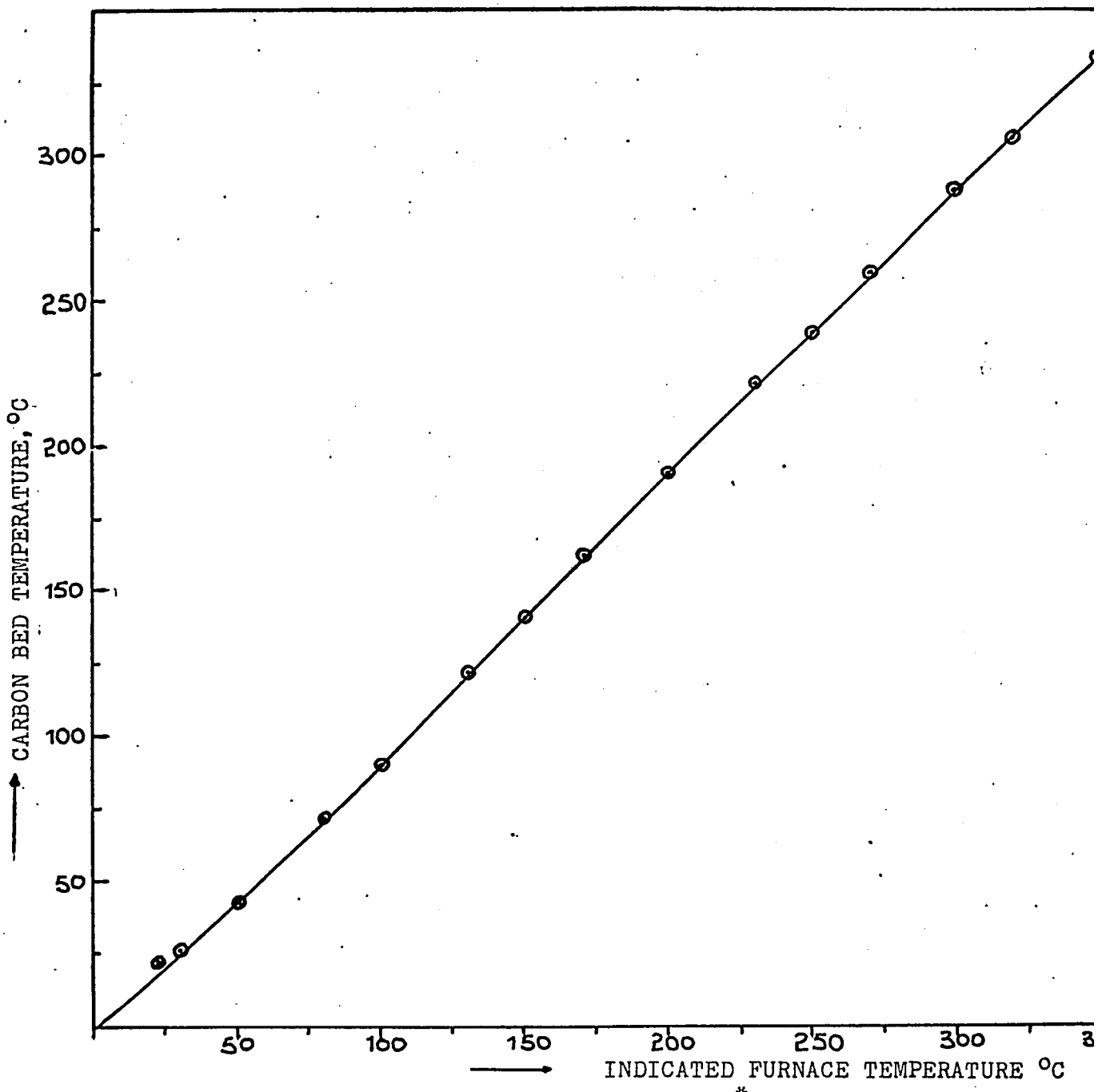


FIGURE 7. Calibration Curve For Carbon Bed* Temperature In Macro-Oxidation Of Adsorbed Pollutants.

* Carbon Bed Positioned At Center Of Furnace.

or desorption followed by chemisorption of styrene or oxygen. Oxygen will exothermically displace adsorbed substrate from the surface of carbon; this is to be expected from the much greater heat of adsorption of oxygen on carbon (70-100 kcal $mole^{-1}$)[44]. Because of the highly exothermic adsorption there is an off-set of the negative heat due to the endothermic desorption of adsorbate.

Another reasonable explanation that could be adduced is that between 90° and 140°C, styrene is undergoing oxidation by oxygen furnished by the catalyst Cr_2O_3. Support for this proposition would seem to come from the observation that this peak appeared in oxidative runs involving many other metal oxides, especially on mixed metal oxide catalysts as La_2O_3/Co_2O_3, where the 90 - 140°C peak was more pronounced (Fig. 16(b). Chemisorption of oxygen on these oxides, however, is not completely unreasonable, and could also result in an exothermic peak.

Table VI summarizes the results of effluent analysis at different temperatures during oxidation of styrene adsorbed on chromia-impregnated carbon. The products identified agreed with the results of Lehman and Brauer[45] and Madorsky et al[46], who studied the pyrolysis of polystyrene at different temperatures. The significant difference is that much lower temperatures for identical products were involved in our findings.

Polymerization and/or oxidation with Cr_2O_3 participation was further indicated by desorption in nitrogen. Fig. 8 shows a DSC of carbon saturated with styrene and of

TABLE VI

Oxidation Products Of Styrene On Chromia-Impregnated Carbon.

Temperature ranged (^{o}C)	Products identified
100 - 140	Benzene, ethylene, acetylene, Styrene.
140 - 230	Benzaldehyde, CO_2, H_2O, Styrene.
230 - 340	Styrene, toluene, ethylbenzene, benzene.
Over 340	Styrene, toluene, ethylbenzene, benzene CO_2, H_2O.

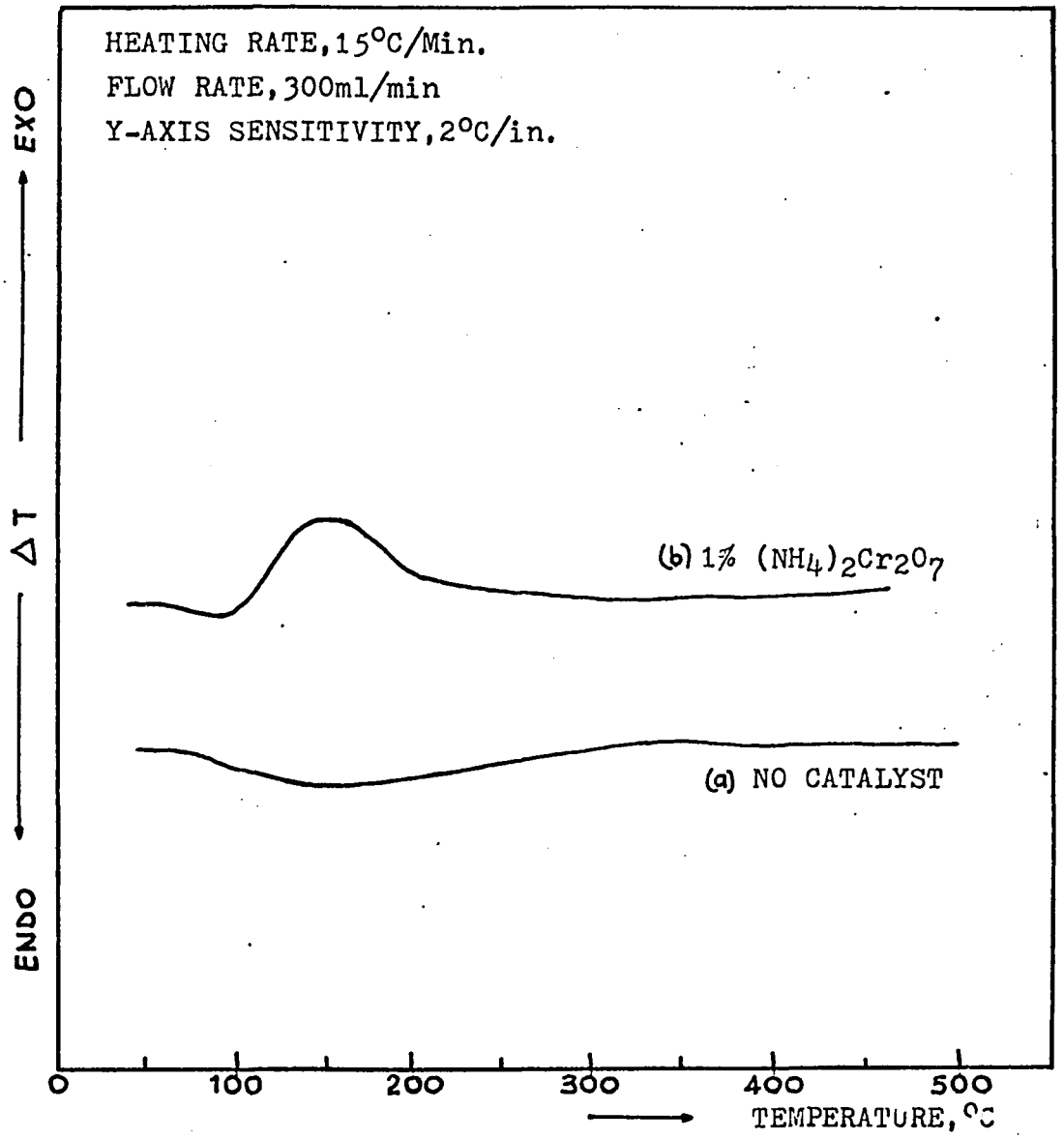


FIGURE 8. DSC Run For Styrene Adsorbed On
(a) Carbon- No Catalyst (b) Carbon + 1% $(NH_4)_2Cr_2O_7$.
Atmosphere, N_2.

chromia-impregnated carbon, saturated with styrene. An exothermic peak is shown for the impregnated carbon between 100° and 140°C. The fact that it occurs at a somewhat lower temperature than that obtained during desorption in air strongly suggests polymerization since molecular oxygen is a polymerization inhibitor[47].

The extent of polymerization, oxidation and chemisorption was determined from the TGA results. Using carbon impregnated with 1% $(NH_4)_2Cr_2O_7$, it was found that 42 to 68% of styrene was still adsorbed at 400°C. Weight losses were recorded between 90° and 230°C. For carbon without catalyst, 6 to 11% of styrene was retained at 400°C. This latter result is consistent with the fact that activated carbon has high-energy surface sites which are thought to be due to surface oxides formed during manufacture[48]. These high-energy sites adsorb some contaminants which cannot be removed completely by thermal desorption. Some polymer could be deposited at the same time.

It was noticed that the amount of styrene still adsorbed at 400°C depended on the method of preparation of the catalyst and on the initial saturation level of the carbon, which in turn depends on the concentration of styrene in the saturation stream. The extent of this adsorption is shown in Fig. 9(b) for saturation level of 0.287 mg styrene per mg activated carbon (AC). We have plotted residual weight fraction of styrene (based on initial weight of styrene adsorbed) against temperature. The data

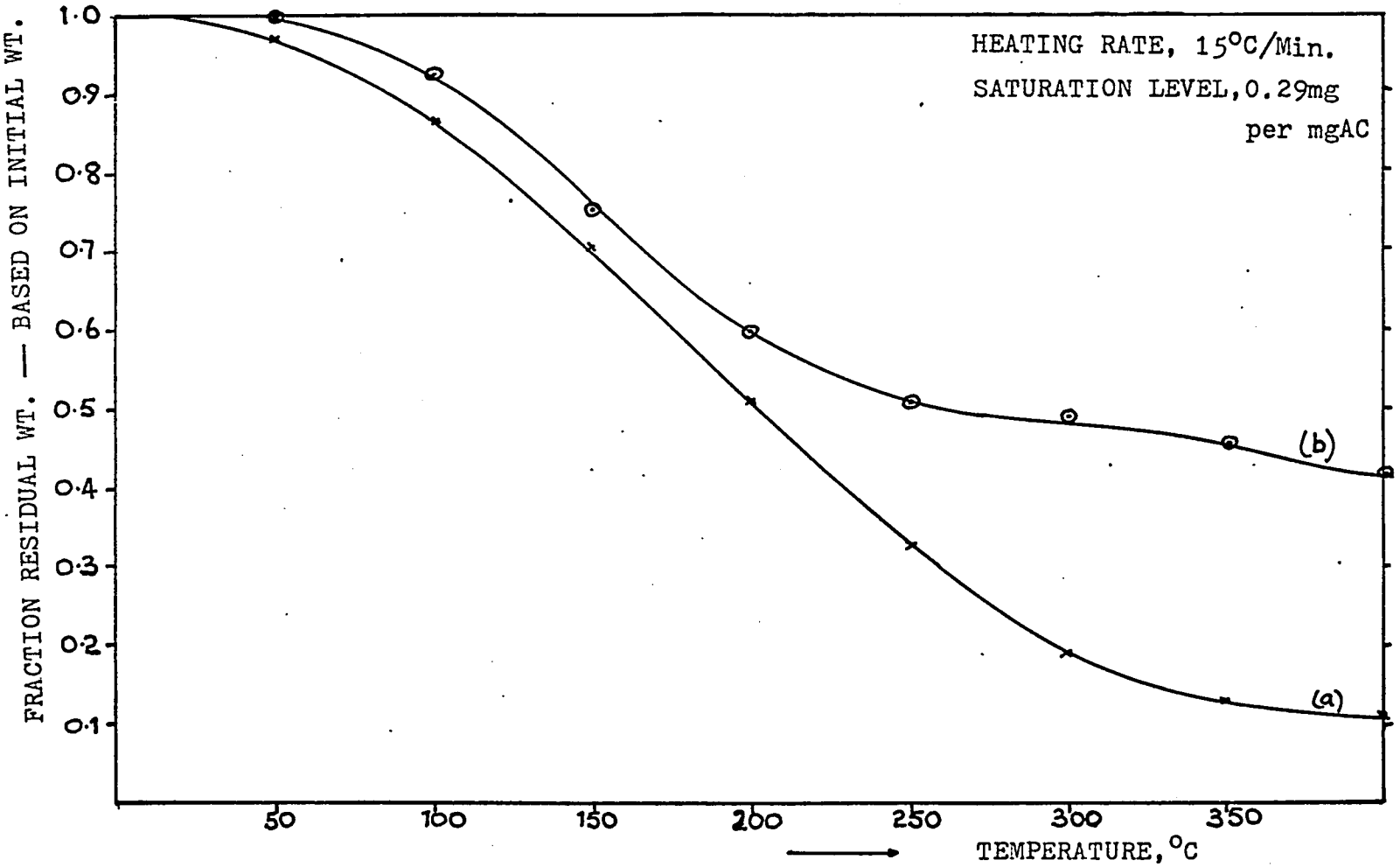


FIGURE 9. Desorption Curves For Styrene Adsorbed On (a) Carbon-No Catalyst (b) Carbon + 1% $(NH_4)_2Cr_2O_7$. Atmosphere, Air; Flow Rate, 300ml/min.

fot the desorption of styrene adsorbed on carbon without catalyst is plotted in Fig. 9(a) for comparison. The saturation level was 0.369 mg/mgAC.

That some polymerization occurred within the range 90° to 230°C was confirmed by extraction of the adsorbate with carbon tetrachloride after desorption in nitrogen to 230°C and subsequent analysis by infra-red spectroscopy. The spectrum obtained matched that of polystyrene in CCl_4[49], with characteristic frequencies at 3027.1, 2850.7, 1944, 1871, 1801.6, 1069.1 and 1028.0 wavenumbers (cm^{-1}). This is shown in Figure 10.

Enter Electron Spin Resonance (esr)

Polymerization and cracking reactions occur on chromia/alumina catalysts. Such reaction occur on acidic sites and Cr_2O_3 is a well-known amphoteric oxide. Ayscough et al[50] showed, by means of esr spectroscopy, that ethylene polymerizes over chromia on γ-alumina catalyst and this reaction is catalyzed by Cr(V) ions. The question that we attempt to answer here is whether the reaction of adsorbed styrene on chromia-impregnated carbon involved catalysis by Cr(V) or Cr(III) ions.

Turk[8] has suggested that a higher oxidation state than Cr(III) was present on carbon impregnated with $(NH_4)_2Cr_2O_7$ in view of the evolution of ammonia during impregnation at ambient temperatures. The possible reactions are as follows:

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4\ H_2O + N_2 \qquad (1)$$

$$(NH_4)_2Cr_2O_7 \longrightarrow 2CrO_3 + 2\ NH_3 + H_2O \qquad (2)$$

$$4\ CrO_3 + C \longrightarrow 2\ Cr_2O_5 + CO_2 \qquad (3)$$

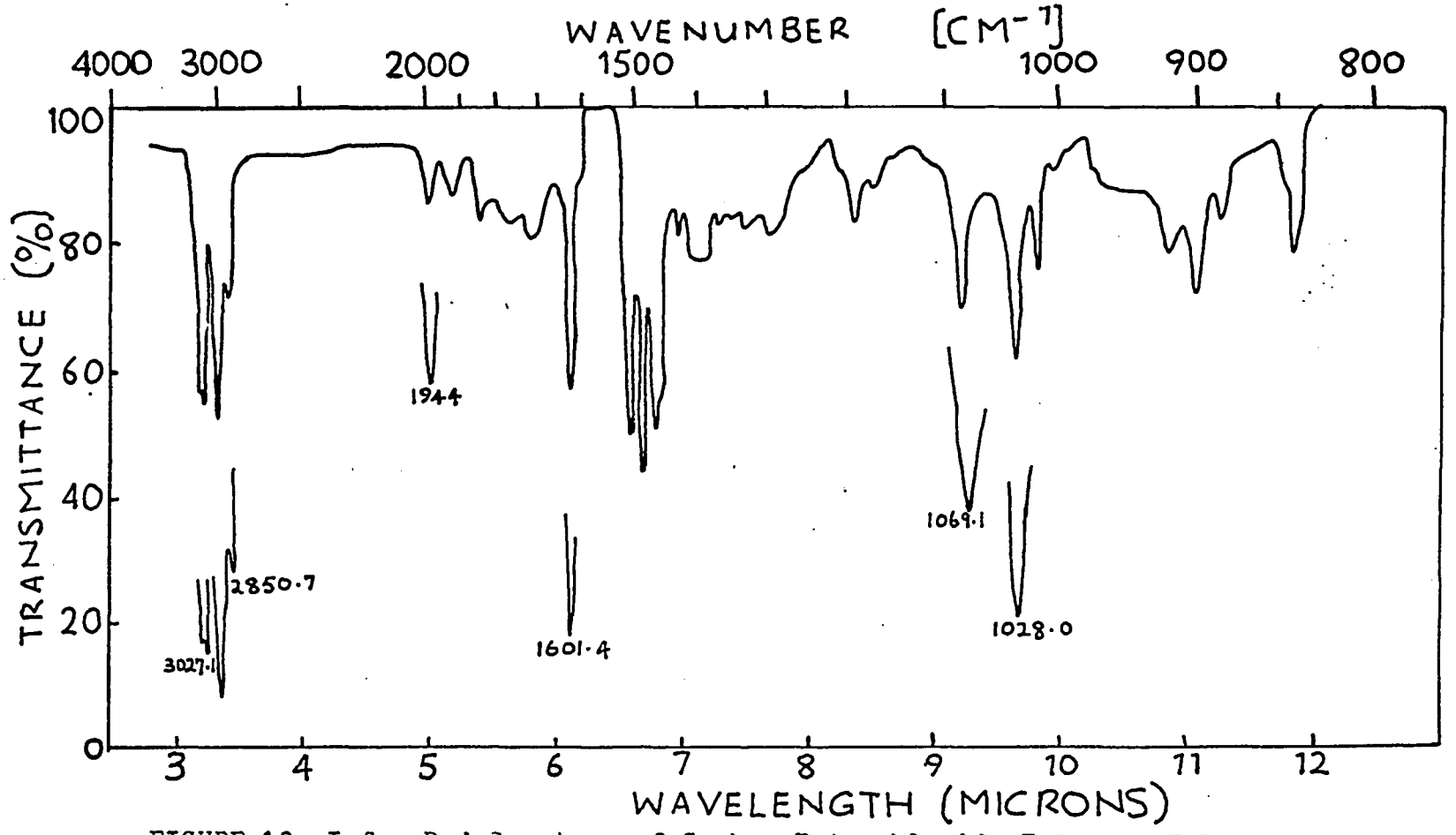


FIGURE 10. Infra Red Spectrum of Carbon Tetrachloride Extract of Styrene Residue on Carbon + 1%$(NH_4)_2Cr_2O_7$ After Desorption in N_2 to 200°C.

Reaction (3) is postulated, because of the reducing property of carbon, and it leads to the Cr(v) oxidation state. The presence of Cr(V) was confirmed by esr analysis. Fig. II shows the spectrum obtained and the sharp resonance at center with width 50 gauss and a g-valve 2.08 is assigned to Cr(V). This assignment is based on the work of O'Reilly et al[51] and of Ayscough et al[50]. There is no reported work in the literature on the esr spectrum of chromium on activated carbon. The Cr(V) resonance is seen imposed on a broad signal due to Cr(III)[50,51].

It should be noted, however, that the existence of Cr(V) in chromia catalysts, has been challenged recently by Ellison et al[52], who interprets the γ-phase resonance, assigned to Cr(V) by O'Reilly[51] and Ayscough[50], in terms of a mixed valency of the type, $-Cr^{3+}- O^{2-}-Cr^{6+}$.

Active Sites for Polymerization and Chemisorptive Reactions

The presence of Cr(V) would therefore lead one to speculate on possible polymerization catalyzed by Cr(V) in analogy with the observed reaction of ethylene; styrene is a substituted ethylene. Apart from polymerization, however, there is also the possibility of chemisorption of styrene on active sites, which could be Cr(V) or Cr(III) ions. A chemisorbed molecule is difficult to oxidize or desorb even at high temperatures.

In order to dispel all doubts about the participation of Cr(III) in this reaction, the activated carbon was

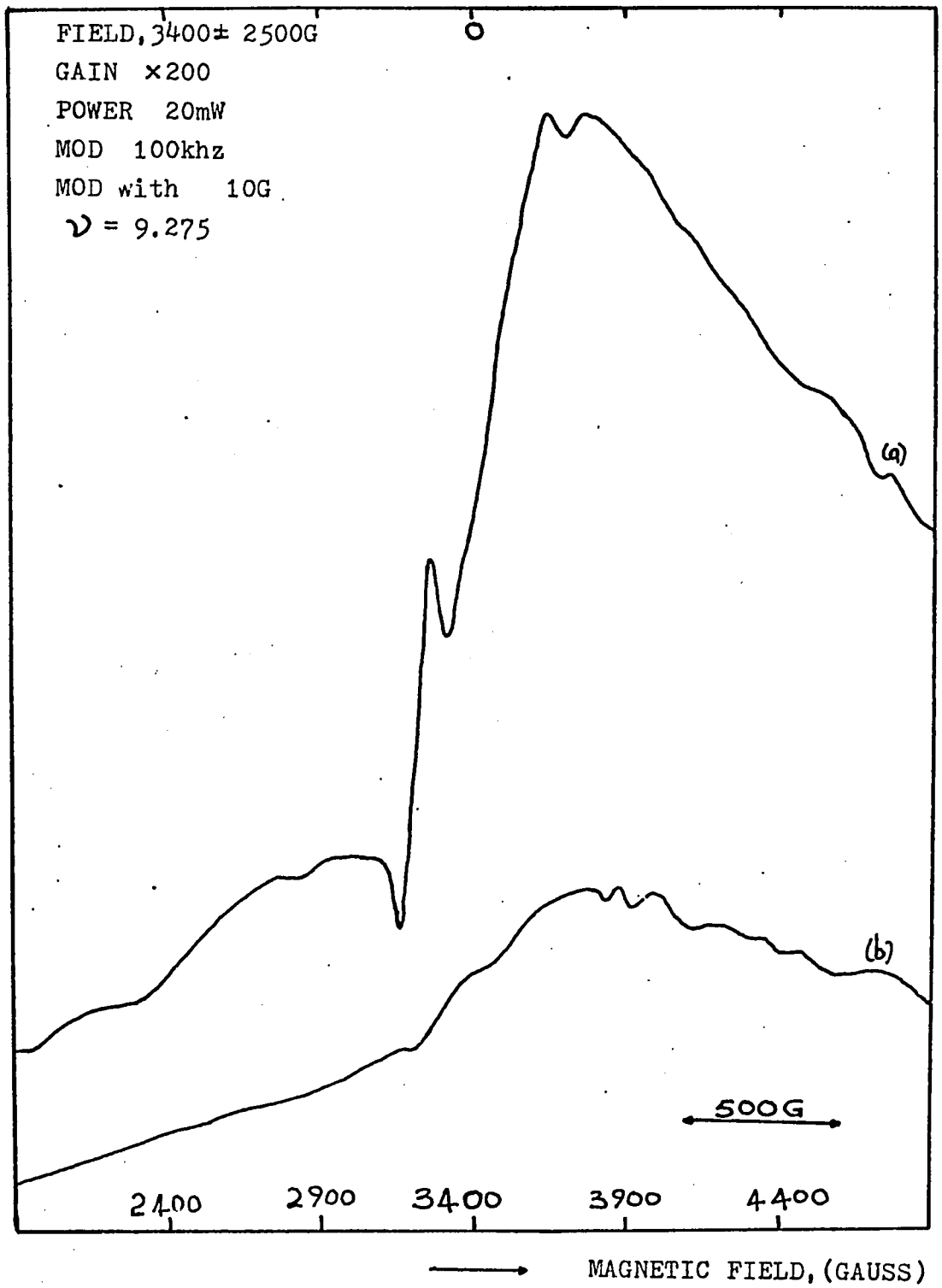


FIGURE 11. Esr Spectra Of (a) Carbon+ 1% $(NH_4)_2Cr_2O_7$ Air Decomposed At 300°C For 3hrs, (b) Carbon — No Catalyst Temperature, Ambient.

impregnated with 1% $Cr(NO_3)_3.9\ H_2O$ solution (2gm/3ml) and was decomposed in air at 300°C for 2 hours. Only Cr(III) should be present and this was confirmed by esr analysis. Fig. 12(a) shows a desorption curve for styrene adsorbed on carbon impregnated with 1% $Cr(NO_3)_3.9\ H_2O$ solution and a DSC of the same sample is shown in Fig,13(a). The saturation level was 0.428 mg/mgAC.

The desorption curve shows that 65.5% of styrene is still adsorbed at 400°C. This result is significant when we consider that the carbon impregnated with 1% $(NH_4)_2Cr_2O_7$ contained 0.0091 mg Cr_2O_3 per mg carbon and that impregnated with 1% $Cr(NO_3)_3.9\ H_2O$ contained 0.0029 mg Cr_2O_3 per mg carbon. These were calculated values. It could therefore be inferred that the retention of 65.5% styrene at 400°C might be due to chemisorptive interaction on the chromium sites. Another inference is that Cr(III) ion catalyzes the polymerization of styrene.

That chemisorptive reaction was operative was further supported by the following results. When styrene was adsorbed on carbon impregnated with 1% $Cr(NO_3)_3.9\ H_2O$ which was decomposed in air at 300°C and then heated in H_2 at 350°C for 1 hour, a desorption curve indicated that 76.5% of styrene was still adsorbed at 400°C. This is shown in Fig. 12(b). A DSC of the same sample is shown in Fig. 13(b). The saturation level was 0.452mg/mgAC.

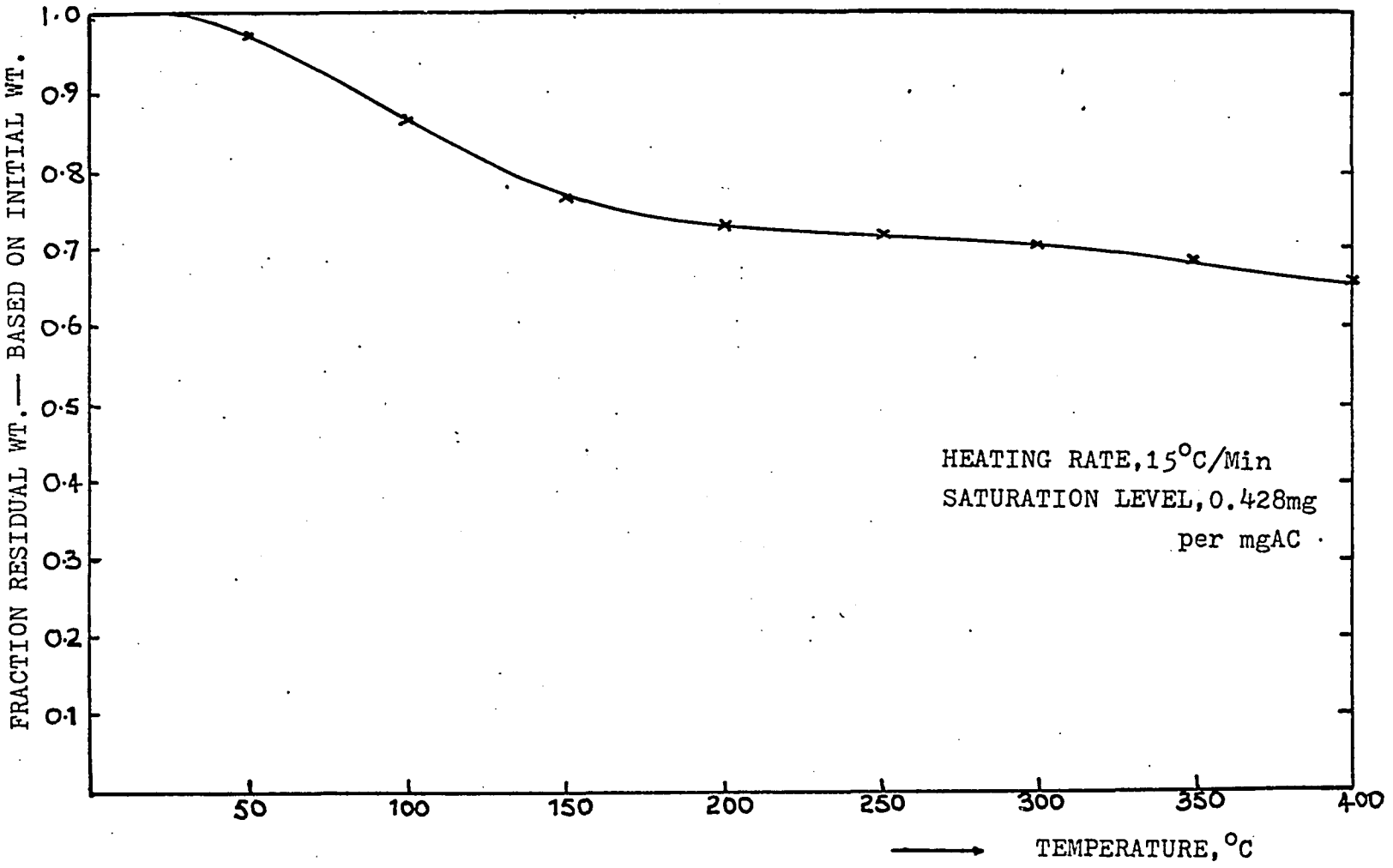


FIGURE 12(a) Desrption Curve For Styrene Adsorbed On Carbon + 1% $Cr(NO_3)_3$.
Air Decomposed At 300°C For 6hrs. Atmosphere, Air; Flow Rate, 300ml/min.

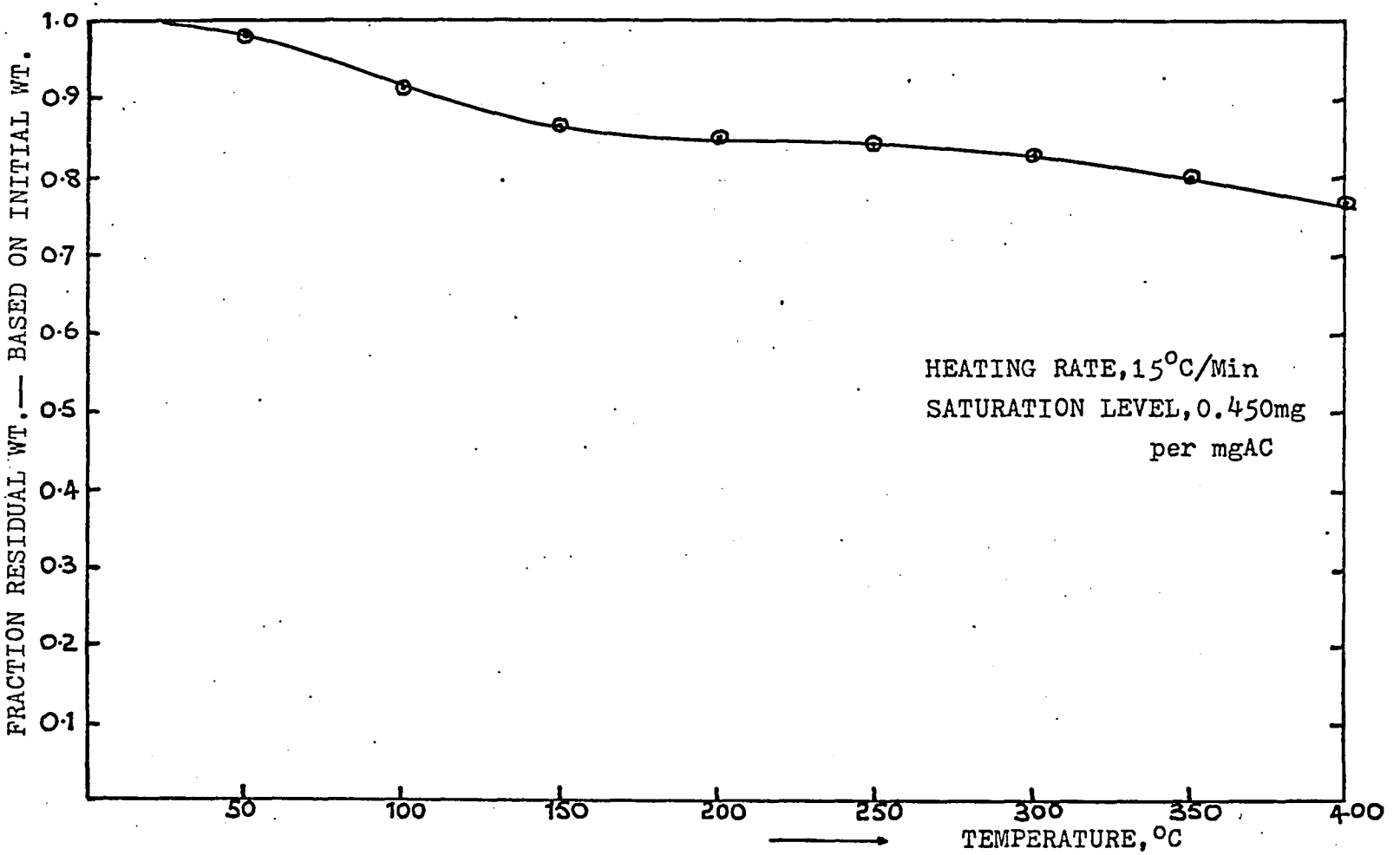


FIGURE 12 (b). Desorption Curve For Styrene Adsorbed On 1% $Cr(NO_3)_3$ Air Decomposed At 300°C For 6hrs, Followed By Reduction In H_2 At 350°C For 1hr.

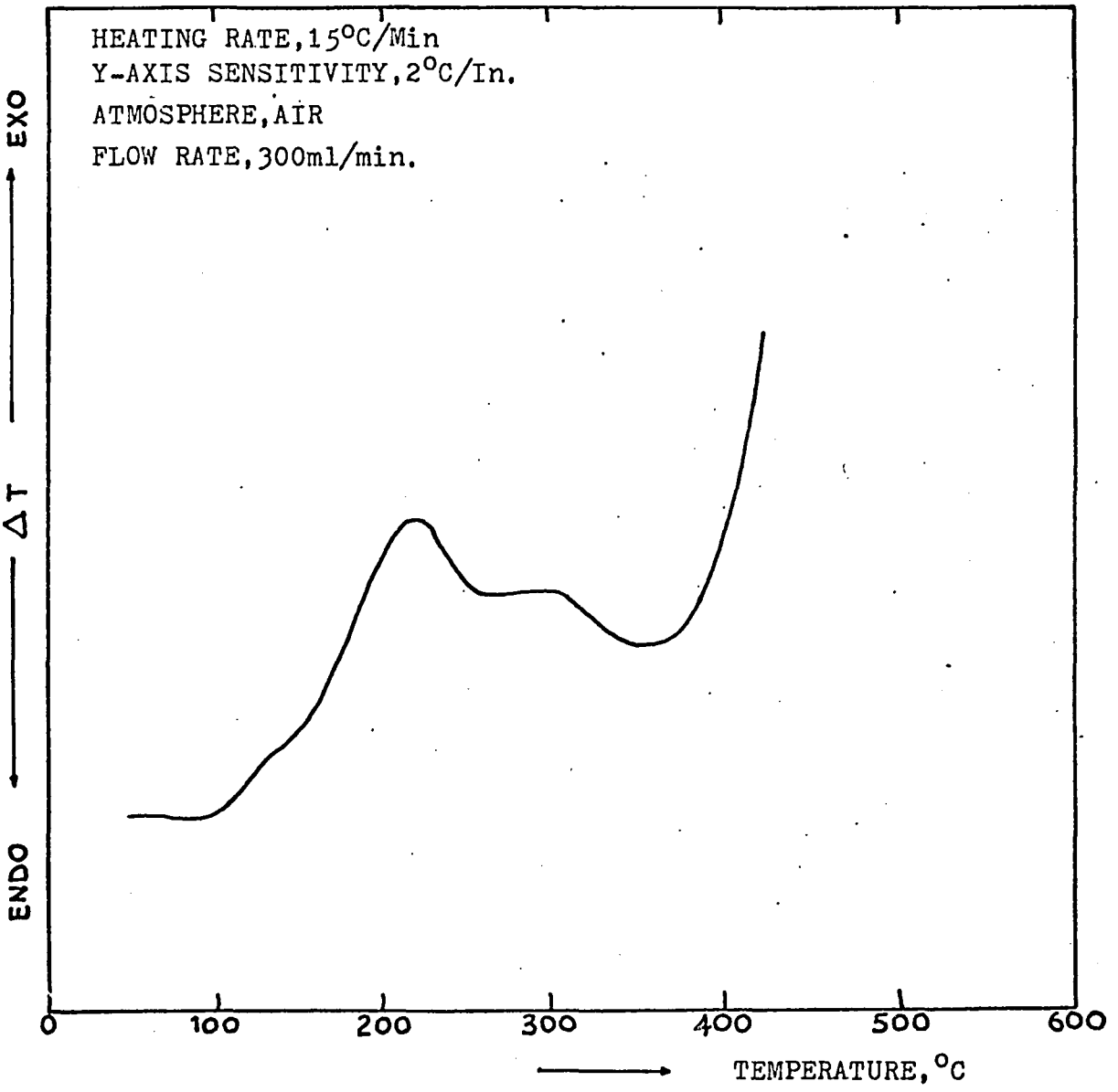


FIGURE 13(a). DSC Run For Styrene Adsorbed On Carbon Impregnated With 1% $Cr(NO_3)_3$,Air Decomposed At 300°C For 6hrs.

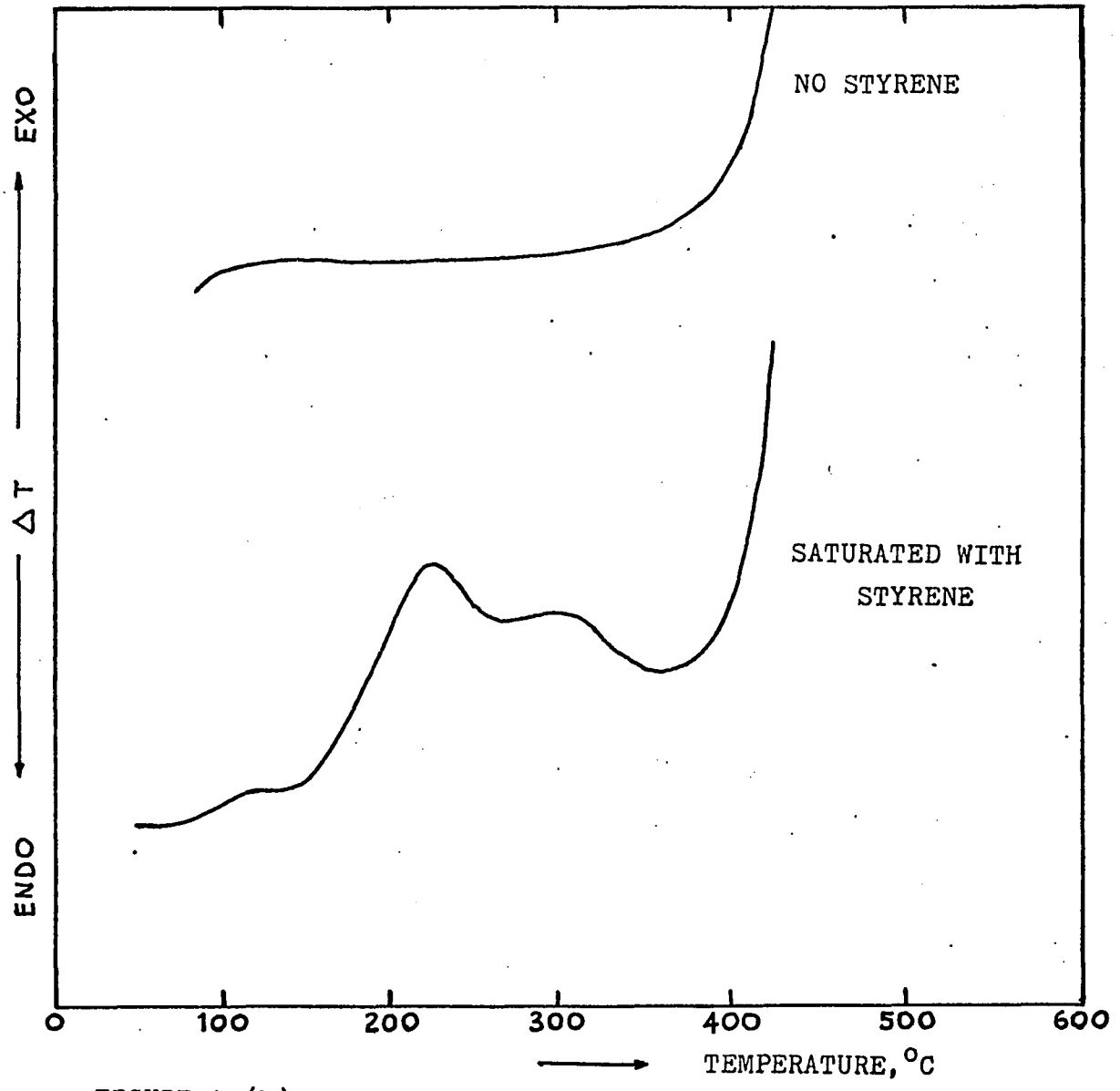


FIGURE 13(b). DSC Run Of Styrene Adsorbed On Carbon Impregnated With 1% $Cr(NO_3)_3$ Air Decomposed At 300°C For 6hrs followed By Reduction In H_2 At 350°C For 1hr.

Justification for Observed Reactions.

It had been shown by Reijen et al[53] that surface chromium ions on a chromia/alumina catalyst are either Cr(II) or Cr(III) depending on the equilibrum reaction:

$$Cr^{3+}O_n + H_2 \longrightarrow Cr^{2+}O_{n-1} + H_2O \qquad (4)$$

Arguments were adduced to show that Cr(II) ion is more favorable than Cr(III) ion for chemisorptive reactions with carbon monoxide, leading to the formation of metal-bonds of sufficient stability.

The hydrogen treatment in the present work could have resulted in one or both of the following effects:

(a) Reduction of Cr(III) to Cr(II).

(b) Reaction between H_2 and O_2^- ions chemisorbed on active chrmium ions, during decomposition in air.

The latter would generate more active sites resulting in increased reaction of styrene. This would lead to an increase in the amount of styrene adsorbed at 400°C as it was observed. The first proposition would be contrary to the result of Weller and Voltz[54] who concluded that Cr_2O_3 is thermodynamically stable at 500°C to reduction and oxidation. But it should be pointed out that supports for these reactions were silica-gel or γ-alumina. In this work we have used activated carbon as support and this could require thermodynamic data different from these of Weller and Voltz. Degree of oxidation of Cr(III) to higher oxidation states increased with decreasing chromium content and increasing oxidation temperature. At very low concentration

(about 1% by wt.) chromium appeared to be oxidized almost completely to the Cr(VI) state, However because of the carbon support, the highest oxidation state is Cr(V). No Cr(VI) was detected using the diphenylcarbazide method[55]; the impregnated carbon was digested with water for about 24 hours and the supernatent was analyzed for Cr(VI).

Large amounts of H_2 and O_2 could be adsorbed at 500°C; only a small fraction can be removed by evacuation. Excess O_2 atoms on surface of oxidized chromia occupy catalytically active sites. This was indicated by esr analysis of styrene adsorbed on carbon impregnated with 1% $Cr(NO_3)_3$ which was decomposed in air at 300°C for 3 hours. Another run was made of styrene adsorbed on carbon impregnated with 1% $Cr(NO_3)_3$, decomposed in air and then heated in H_2 at 350°C.

A sharp esr resonance with a free radical g-valve of 1.92 was obtained for the latter, whereas the former showed no resonance line apart from a broad Cr(III) resonandce. The spectra are shown in Figures (14) and (15). It seems that decomposition in air atmosphere leads to chemisorption of O_2 at active sites and these chemisorbed O_2^- ions are reduced by H_2 to generate sites free of chemisorbed oxygen. Such active sites are Lewis acid types like Cr(III) or Cr(II) ions. Interaction of several aromatic hydrocarbons with certain Lewis acids has been shown to yield positive radical-ions which are paramagnetic[56,57].

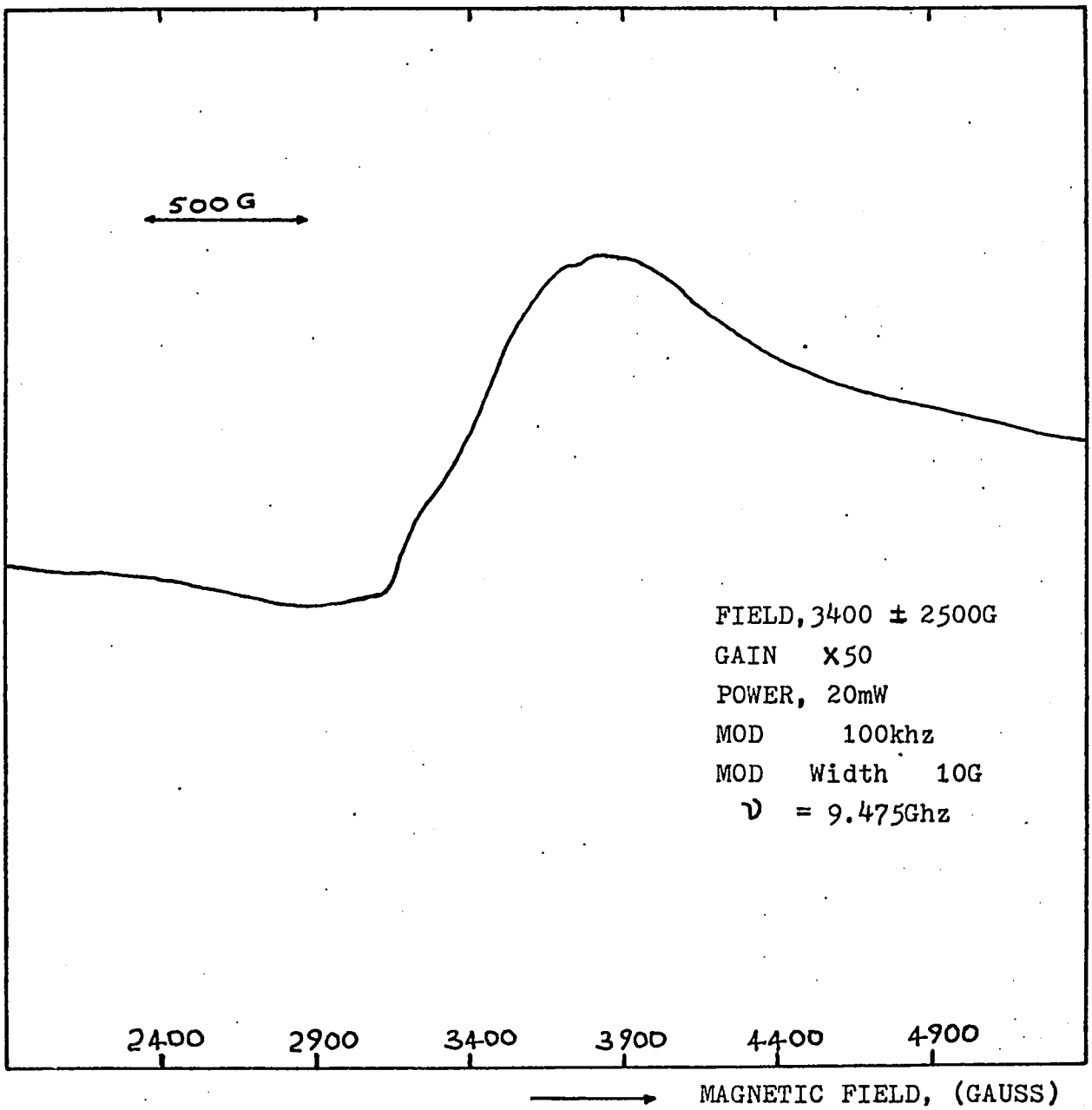


FIGURE 14. Esr Spectrum Of Styrene Adsorbed On Carbon Impregnated With 1% $Cr(NO_3)_3$ Air Decomposed At 300°C For 6hrs.

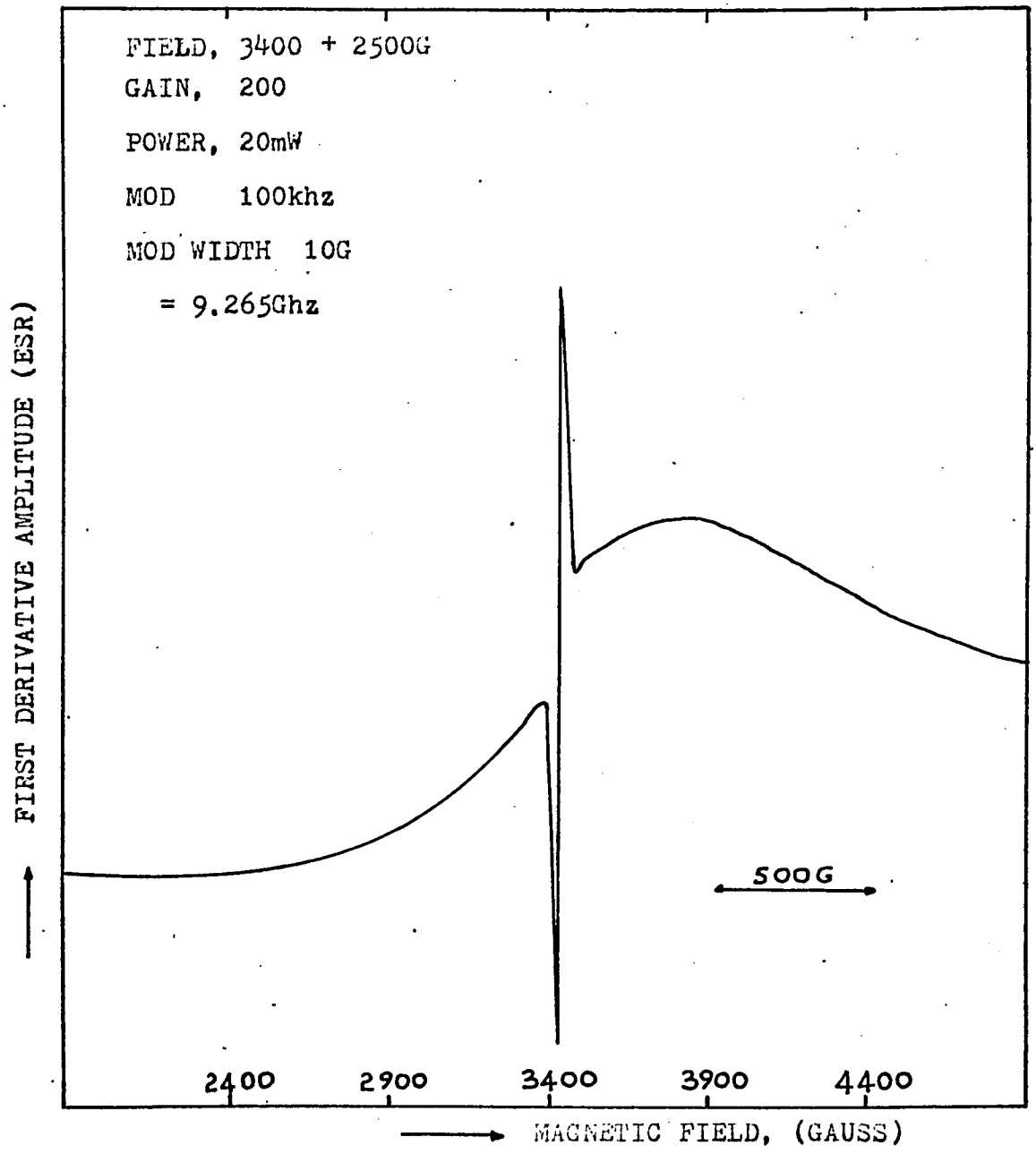


FIGURE 15. Esr Spectrum Of Styrene Adsorbed On Carbon Impregnated With 1% $Cr(NO_3)_3$, Decomposed In Air At 300°C For 6hr. Followed By Reduction In H_2 At 350°C.

These findings and that of Leftin et al[58] are contrary to the result of Fogo who showed that oxygen can accept an electron from a covalent complex of a hydrocarbon with a weaker Lewis acid site to form a paramagnetic radical-ion[59]. In all cases studied during the present investigation, no resonance absorption was observed for styrene adsorbed on carbon impregnated with metal oxide catalysts obtained by decomposition in air such as CuO, Co_3O_4, and V_2O_5. A sharp resonance absorption appeared on heating the adsorbate to 350°-400°C in oxygen and is probably due to polymer ions or to surface radical ions generated by styrene oxidation. Odd electrons in polymer molecules have been detected by Winslow et al on pre-oxidized polyvinylbenzene[60]. The observed resonance could also be due to desorption followed by chemisorption on sites devoid of chemisorbed O_2^-ions.

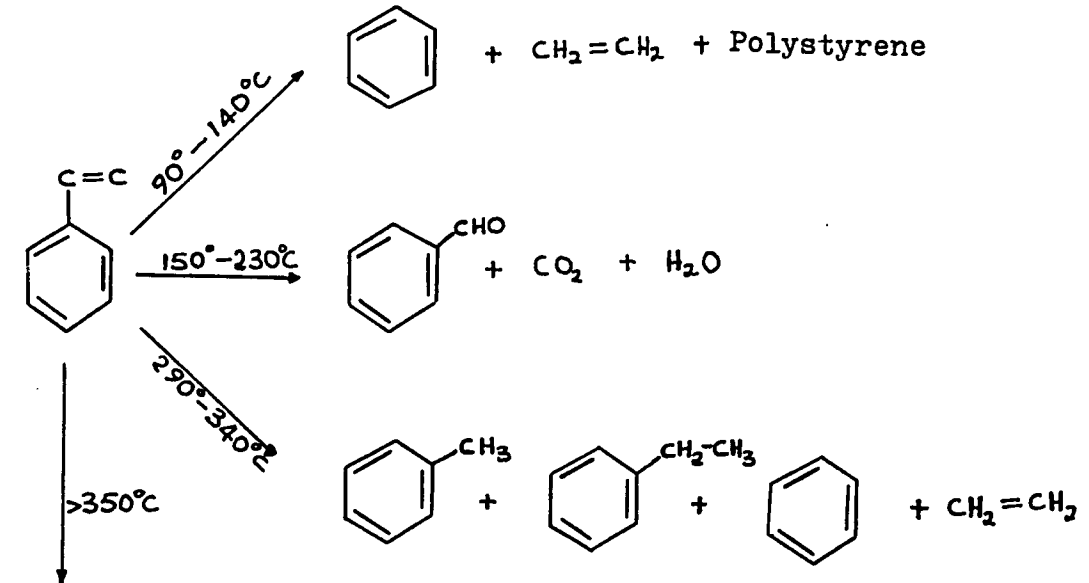
Evidence for the formation of positive radical-ions by electron transfer to oxygen from a hydrocarbon-proton complex has been reported[61]. This might be expected from interaction of the hydrocarbon with a protonic acid site on the catalyst. If H_2 adsorption leads to formation of H_2^+ions, this could explain the observed effect. This was however not confirmed.

No signal was observed for styrene adsorbed on carbon without catalyst and it can be assumed that the reactive centers involve Cr(III) or Cr(II) ions for chemisorption.

The endothermic peak observed between 290°-340°C is due to desorption of chemisorbed styrene or to depolymerization

reaction. It should be noted that for oxidation to occur, there must be diffusion of adsorbed material to the active catalyst site. This diffusion is inhibited by polymerization or strong chemisorptive adsorption and catalytic oxidation does not occur. This is why the oxidation at 150^{o}-$230^{o}C$ is not sustained until catalytic activity is restored between 240^{o}-$340^{o}C$, when styrene desorbs to release active oxidation sites. Diffusion appears to be a maximim within this temperature range and polymerization should raise the temperature of maximum diffusion and of oxidation.

The results obtained from both physical and chemical evidence, arising from gc-ms analysis, lead to the following scheme for <u>in situ</u> oxidation of adsorbed styrene on chromia impregnated carbon.



Combustion of Styrene and Carbon

(B) Oxidation With Other Metal Oxide Catalysts.

Table VII summarizes the results obtained with CuO, Co_3O_4 or Co_2O_3, V_2O_5, La_2O_3, MnO_2 and WO_3. Oxidation of styrene to benzaldehyde, CO_2 and H_2O occurred within the range 150°-230°C as was observed for Cr_2O_3 on carbon. Polymerization and/or oxidation by oxygen furnished by catalyst occurred between 90°-140°C and desorption without oxidation occurred between 240°-340°C with CuO_2, Co_3O_4 and La_2O_3.

TABLE VII

Activity Data For Metal Oxides In Styrene Oxidation

Catalyst	Temperature (°C)		
	Polymerization and/or chemisorption	Oxidation to CO_2 and H_2O	Carbon Burn-off
Cr_2O_3	100-140	140-220	340
CuO	100-140	140-210 250-300	340
Co_3O_4	100-140	140-230	360
V_2O_5	100-150	200-280	310
WO_3	-	150-240	400
MnO_2	100-140	150-220	370
La_2O_3	100-140	140-230	350

Mixed oxide catalysts, CuO/Cr_2O_3, V_2O_5/Cr_2O_3, CuO/Co_2O_3, La_2O_3/Co_2O_3, La_2O_3/Mn_2O_3 and BaO/MnO_2 exhibited similar behaviour and the results are shown in Table VIII. All the data in Tables VII and VIII were obtained from DSC analyses.

TABLE VIII

Activity Data for Mixed Oxides in Styrene Oxidation.

Catalyst	Temperature (°C)		
	Polymerization and/or chemisorption.	Oxidation to CO_2 and H_2O	Carbon Burn-off °C
CuO/Cr_2O_3	70-125	150-220	350
CuO/Co_3O_4	90-140	150-225	330
V_2O_5/Cr_2O_3	90-140	150-230	340
BaO/Cr_2O_3	-	110-210	340
La_2O_3/Co_2O_3	70-120	150-230	385
La_2O_3/MnO_2	110-140	140-230	380
ZnO/Co_3O_4	70-120	150-220	380

Figs. 16(a), 16(b) and 16(c) show DSC curves for V_2O_5, CuO, and CO_2O_3/La_2O_3. TGA analysis of styrene adsorbed on carbon samples impregnated with metal oxides, such as V_2O_5 and mixed metal oxides, showed that much of the styrene remained adsorbed up to 400°C. Fig. 17 shows the desorption curve obtained when V_2O_5 was used. The amount retained depends on the nature of the oxide and on the method of activation.

Esr analysis did not give any resonance line until after oxidation of styrene to 400°C. Chemisorptive interaction appears to be operative. It has been shown that $LaCl_3$ on graphite forms complexes with aromatic compounds, such as benzene, ethylbenzene, and toluene[62]. The strength of the complex increases with lanthanum concentration. It can be assumed that metal oxides are active sites for the formation of chemisorbed complexes with styrene. Stronger complexes are formed with oxides containing empty d-bands, such as Cr_2O_3, La_2O_3 and V_2O_5.

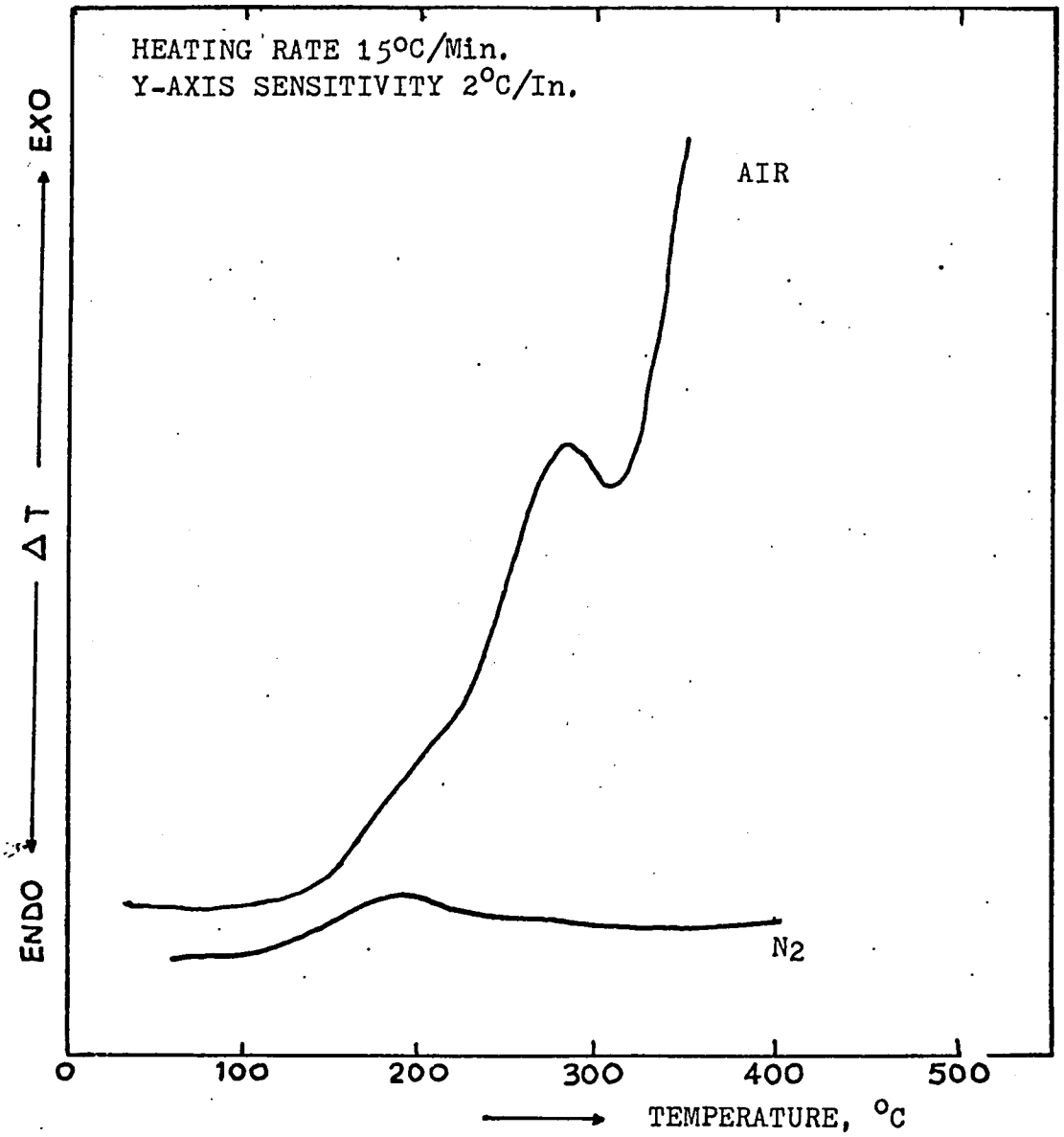


FIGURE 16(a). DSC Run For Styrene Adsorbed On Carbon Impregnated With 1% NH_4VO_3 Air Decomposed At 230°C For 3hrs. Atmosphere (i) Air, (ii) N_2.

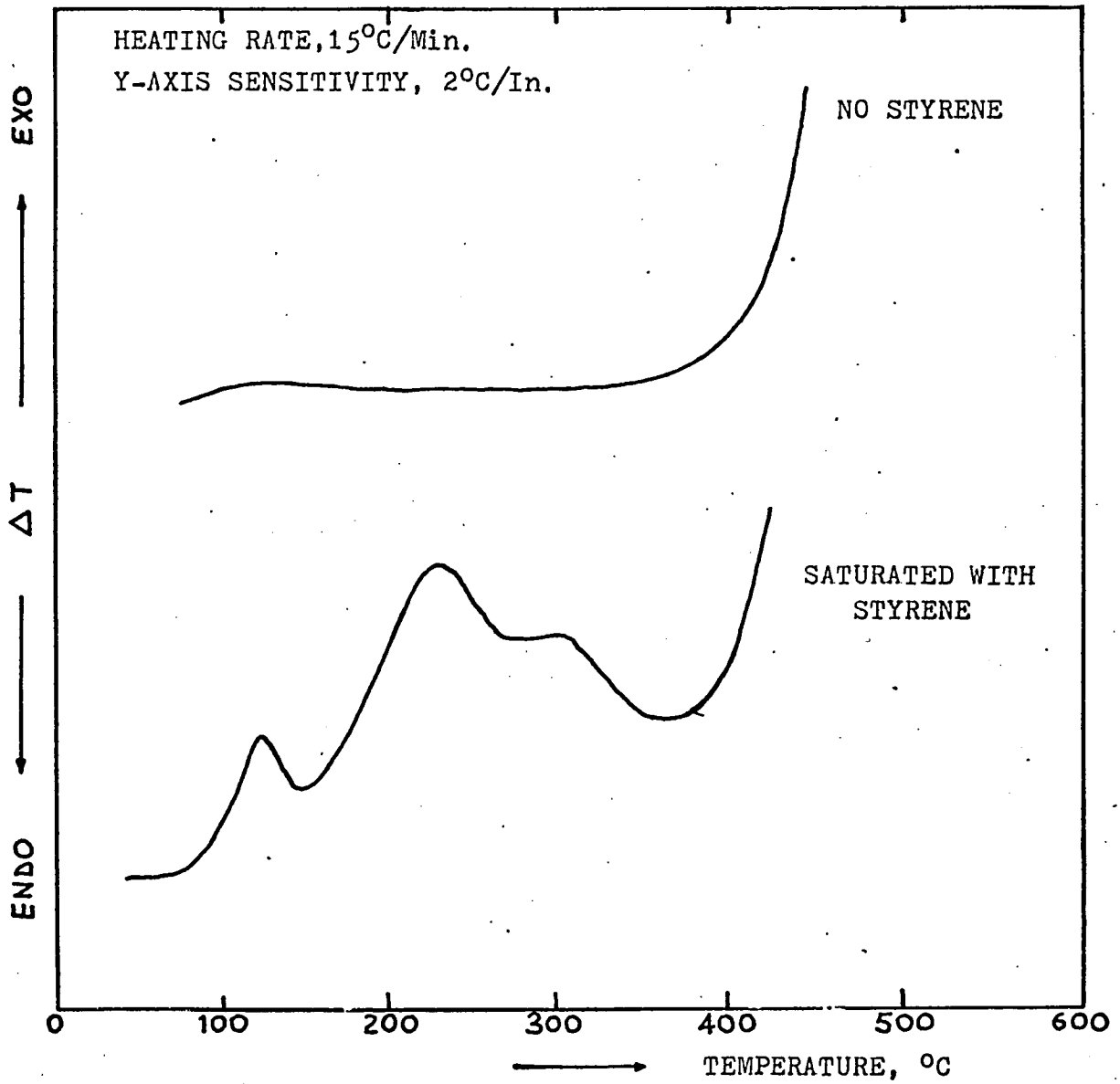


FIGURE 16 (b). DSC Run For Styrene Adsorbed On Carbon Impregnated With La_2O_3/Co_2O_3 Catalyst Activated In Air.
Atmosphere, Air; Flow Rate, 300ml/min.

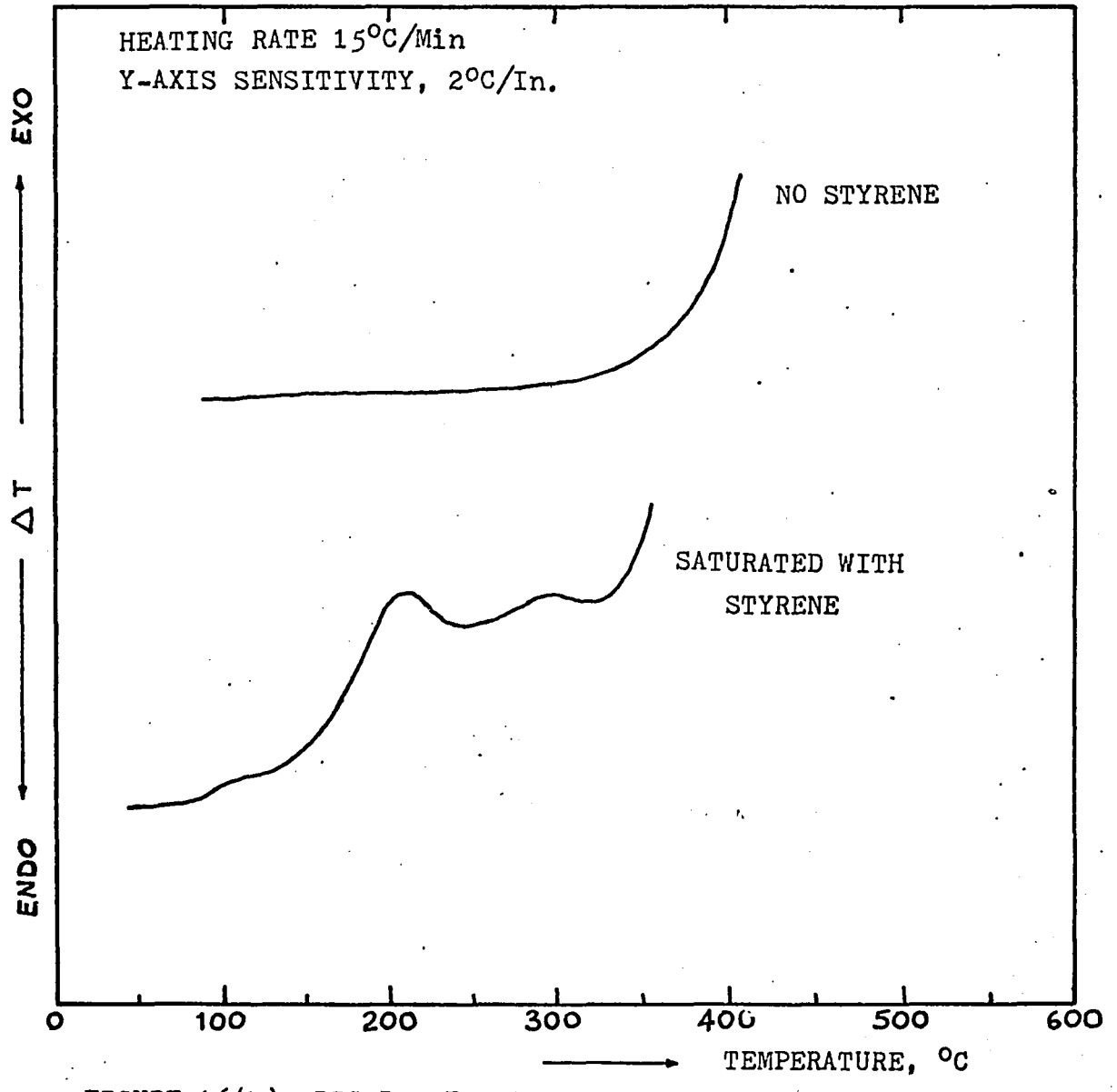


FIGURE 16(Φ). DSC Run For Styrene Adsorbed On Carbon Impregnated With 2% $Cu(NO_3)_2.3H_2O$ Air Decomposed At 320°C For 6hrs. Atmosphere, Air; Flow Rate, 300ml/min.

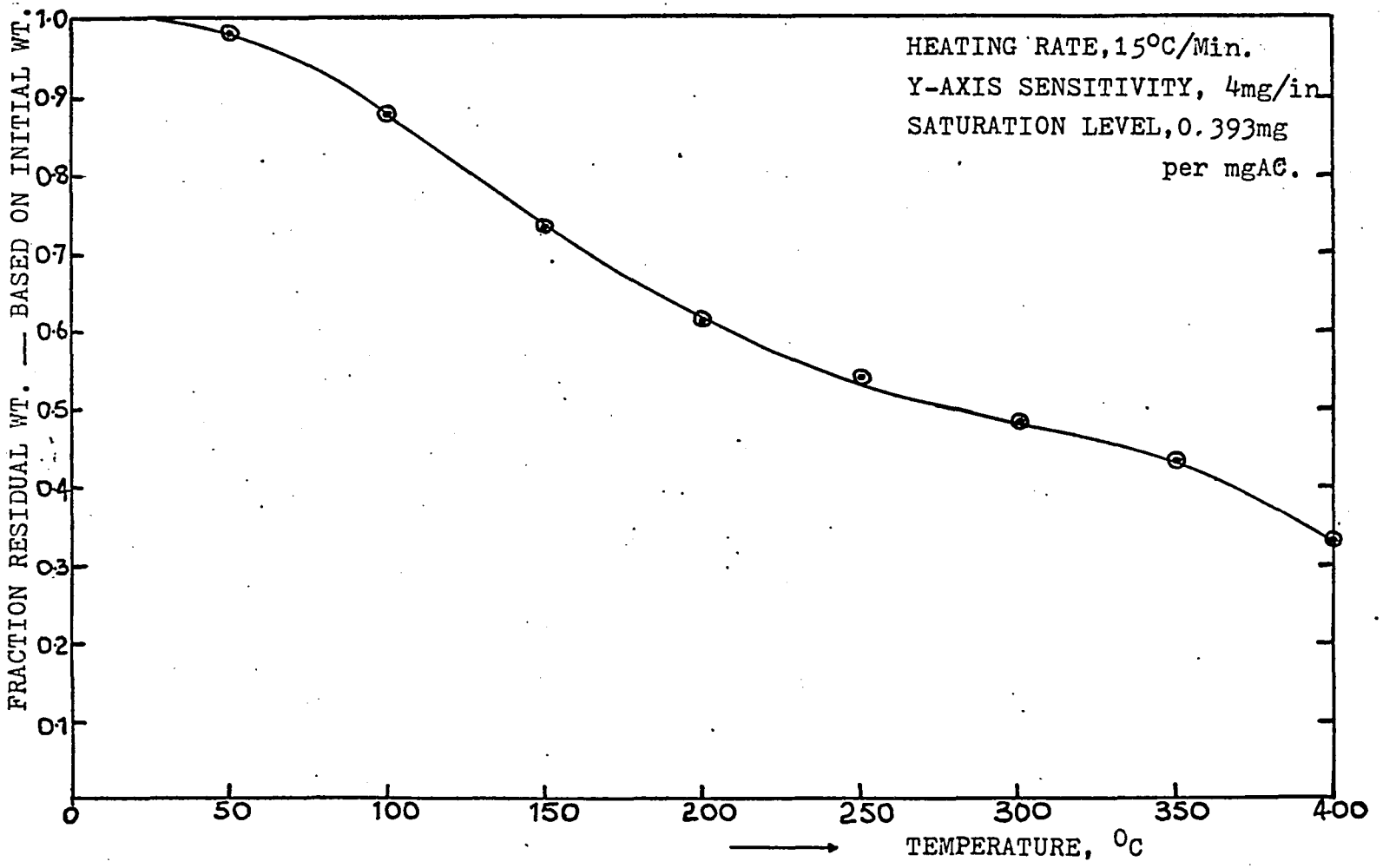


FIGURE 17. Desorption Curve For Styrene Adsorbed On Carbon Impregnated With 1% NH_4VO_3, Air Decomposed At 230°C For 4hrs. Atmosphere, Air Flow Rate, 300ml/min.

Significance Of Activating Conditions In Catalytic Activity

A significant factor in the activity of the oxides is the mode of decomposition or activation. A difference in behaviour was noticed for NH_4VO_3 decomposed under differing conditions. Fig. 18 shows DSC curves for one sample decomposed at 230°C for 2 hours and for another sample decomposed at 230°C for 12 hours. While catalytic activity is indicated between 150° and 230°C for the latter, the former is active in two regions: 150°to 250° and 250° to 300°C. The second area of activity seems to involve oxidation of the aromatic ring. We note that decomposition of NH_4VO_3 under the two differing conditions could lead to the following, (equations are not balanced).

$$NH_4VO_3 \xrightarrow[230^oC,\ 2\ hrs]{heat} V_2O_5 + V_2O_4 + N_2 + NH_3 \qquad (1)$$

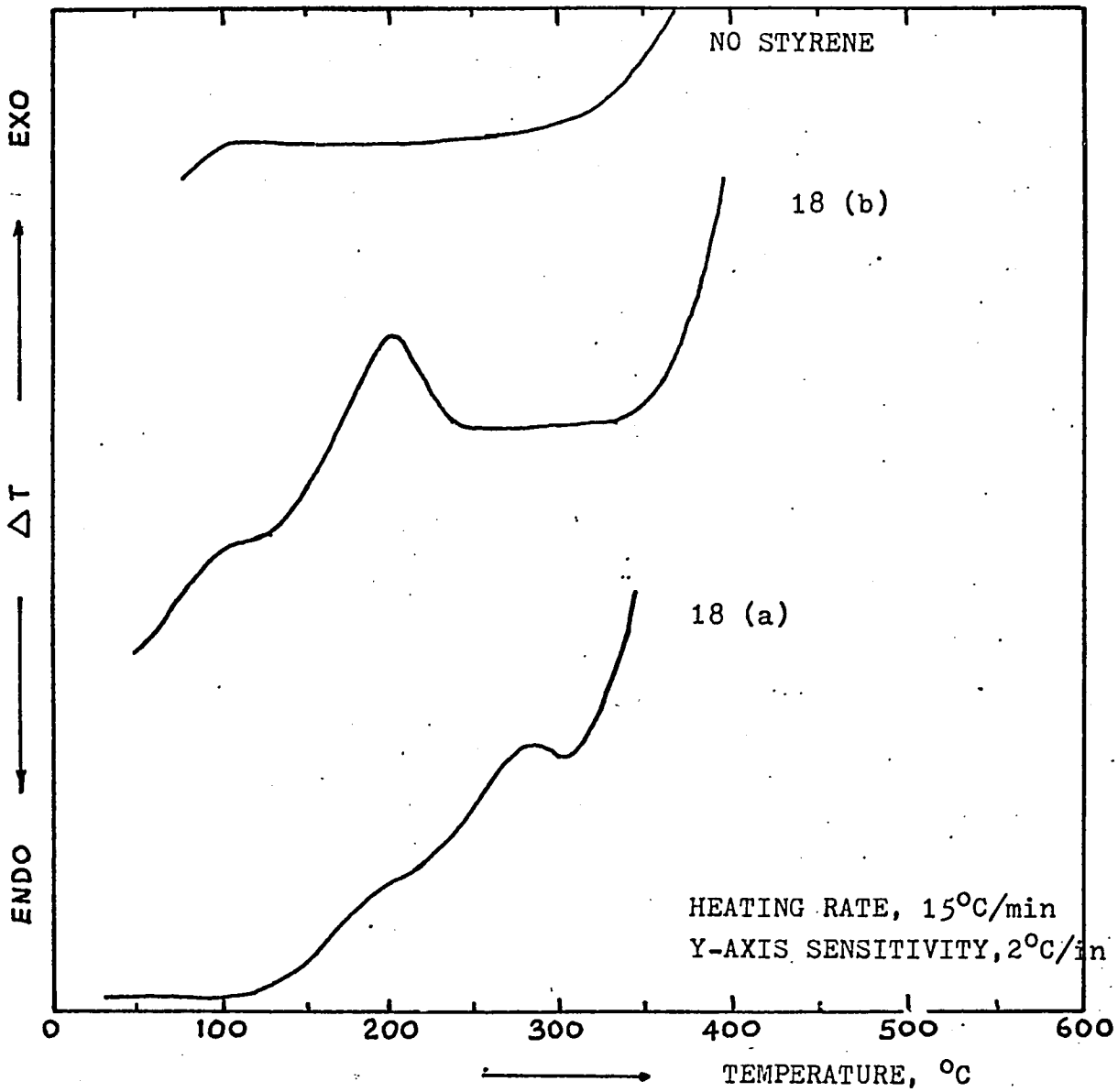
$$NH_4VO_3 \xrightarrow[230^oC,\ 12\ hrs]{heat} V_2O_4 + N_2 + NH_3 \qquad (2)$$

Esr analysis of the two differently decomposed samples as indicated, showed that:

a. the sample decomposed for 2 hours according to equation (1) has little or no signal for V_2O_4.

b. the sample decomposed for 12 hours has a strong signal for V_2O_4 as confirmed by the eight-line hyperfine resonance.

The sample which was active at 300°C was the one decomposed at 230°C for 2 hours. Fig. 19 compares the esr spectra obtained. The inference therefore is that active vanadia catalyst for styrene oxidation must



FIGURES 18 (a) and 18 (b). DSC Runs For Styrene Adsorbed On (i) Carbon+1% NH_4VO_3, Decomposed In Air At 230°C For 3hrs and (ii) Carbon+1% NH_4VO_3, Decomposed In Air At 230°C For 12hrs. Atmosphere, Air; Flow Rate, 300ml/min.

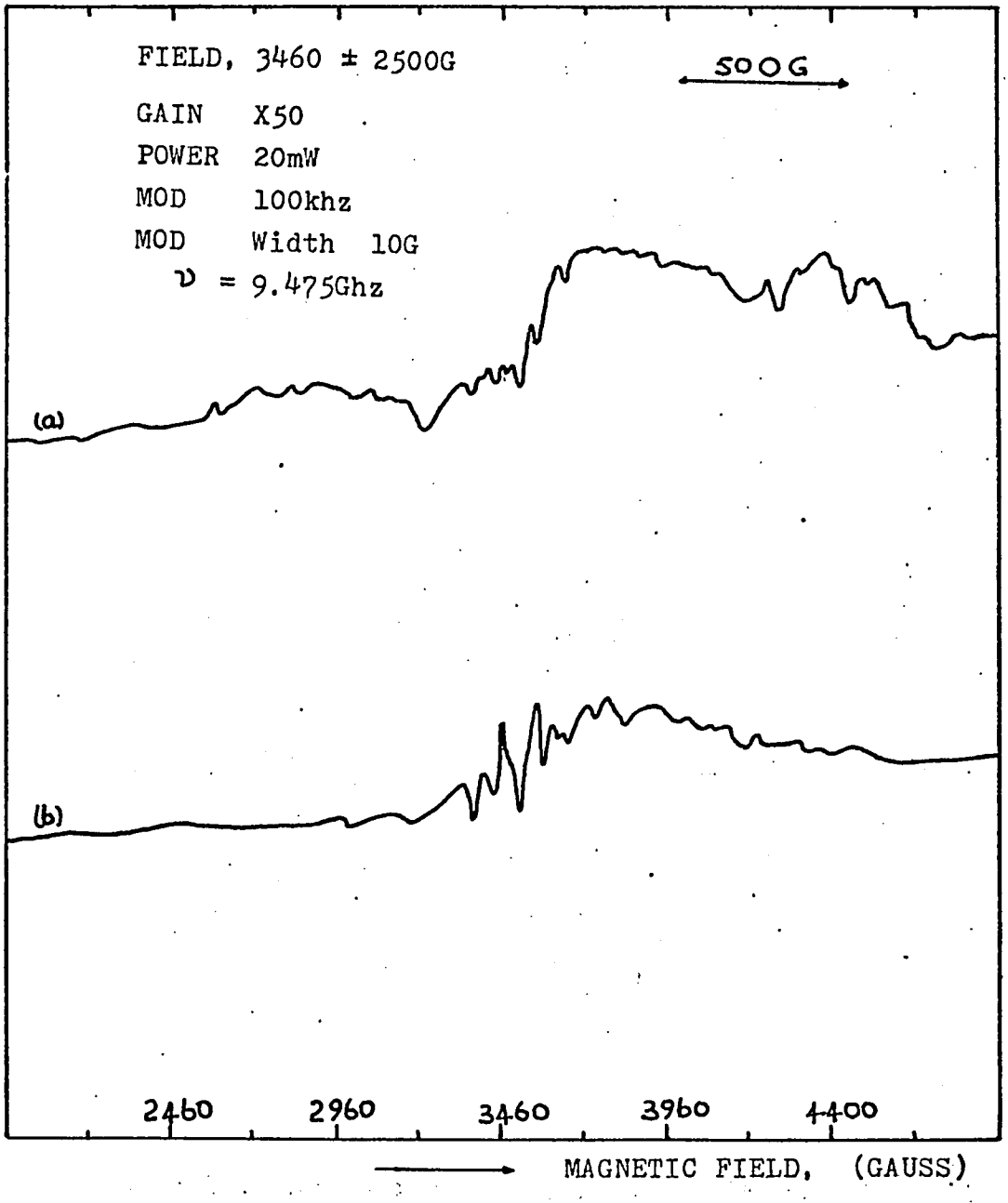


FIGURE 19. Esr Spectrum Of (a) Carbon Impregnated With 1% NH_4VO_3 Decomposed In Air For 2hrs. At 230°C. (b) Carbon Impregnated With NH_4VO_3 Decomposed In Air for 12hrs. At 230°C.

contain a mixture of V_2O_4 and V_2O_5 in the crystal lattice. Some type of equilibration between V_2O_4 and V_2O_5 yields a lattice defect necessary for catalytic activity. Simard et al[63] have shown that this type of reaction leads to $V_2O_{4.34}$ which is catalytically active in the oxidation of naphthalene to phthallic anhydride.

METAL CATALYSTS.

In view of the fact that the metal oxides have proved to be active in the oxidation of styrene to benzaldehyde, CO_2 abd H_2O and considering that they catalyze cracking of styrene to benzene, toluene and ethylbenzene and also catalyze polymerization and or chemisorptive reactions of styrene, it was imperative to study oxidation with metal catalysts. The metals studied were Cu, Ni, Pd, and Pt.

The copper was prepared by decomposition of the exalate in vacuo at 350°C, followed by mild reduction in H_2, and Ni by reduction of the oxide with H_2 at 350°C. The Pt catalyst was prepared as described on page 31. Palladium-impregnated carbon was purchased from Englehard Industries and it contained 0.2% Pd by weight. There was good evidence for selective oxidation of styrene to CO_2 and H_2O, and the anticipated pyrophoricity surprisingly was not observed.

Oxidation with Cu occurred between 150° and 300°C but the separation from carbon burn-off was poor. Nickel also showed some catalytic activity between 160°-300°C but with good separation from carbon burn-off. The palladium and platinum catalysts were very active. Palladium-impregnated carbon catalyzed the oxidation of styrene completely to CO_2 and H_2O between 200° and 320° and platinum-impregnated carbon catalyzed the oxidation between 180°-280°C. No other intermediate oxidation products, such as benzaldehyde, were detected. However, the styrene was cracked to produce toluene, ethylbenzene and benzne. Figs. 20 and 21 show DSC curves for

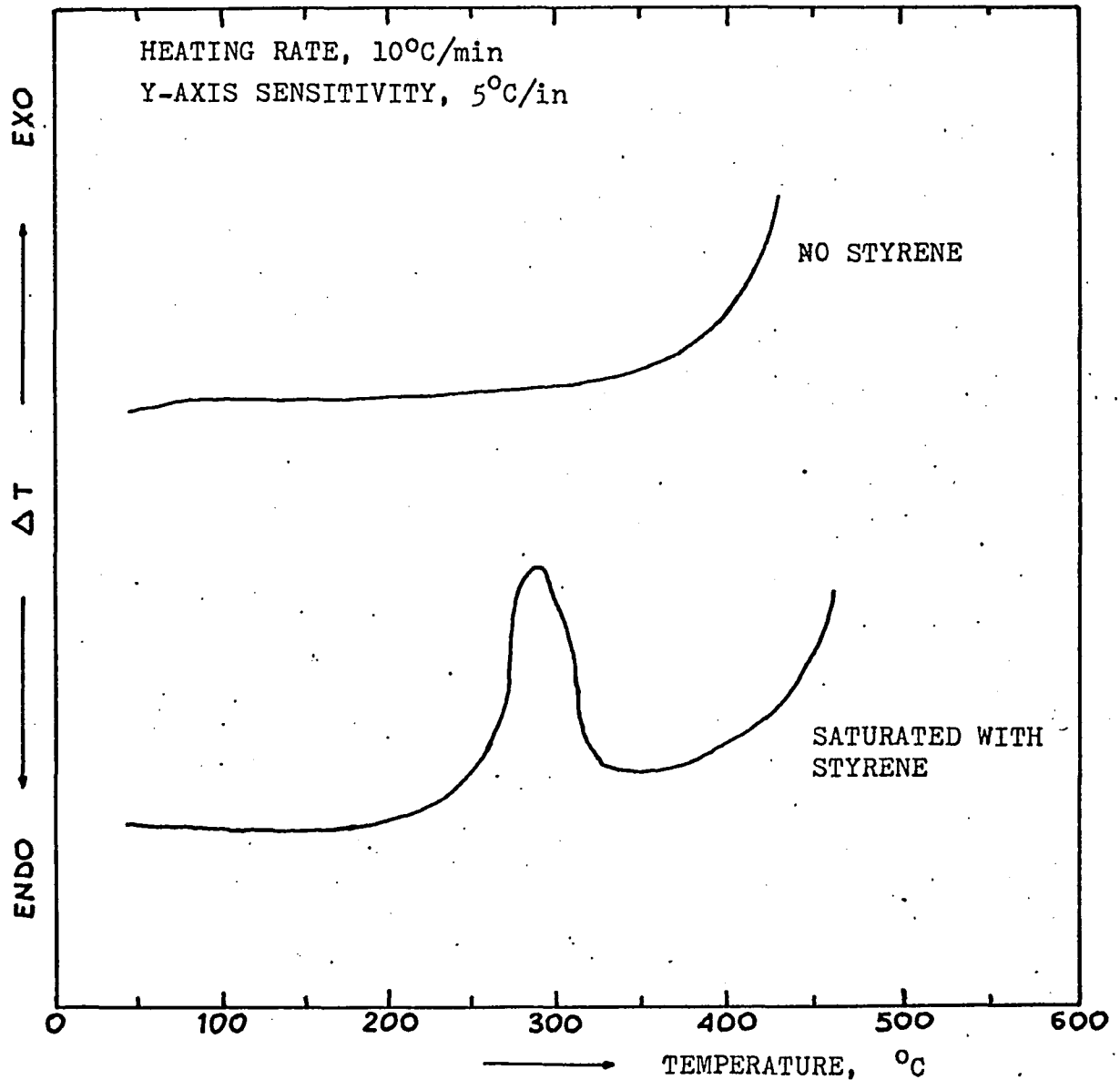


FIGURE 20 DSC Run For Styrene Adsorbed On Carbon Impregnated With 0.2% Pd. Atmosphere, Air; Flow Rate 300ml/min.

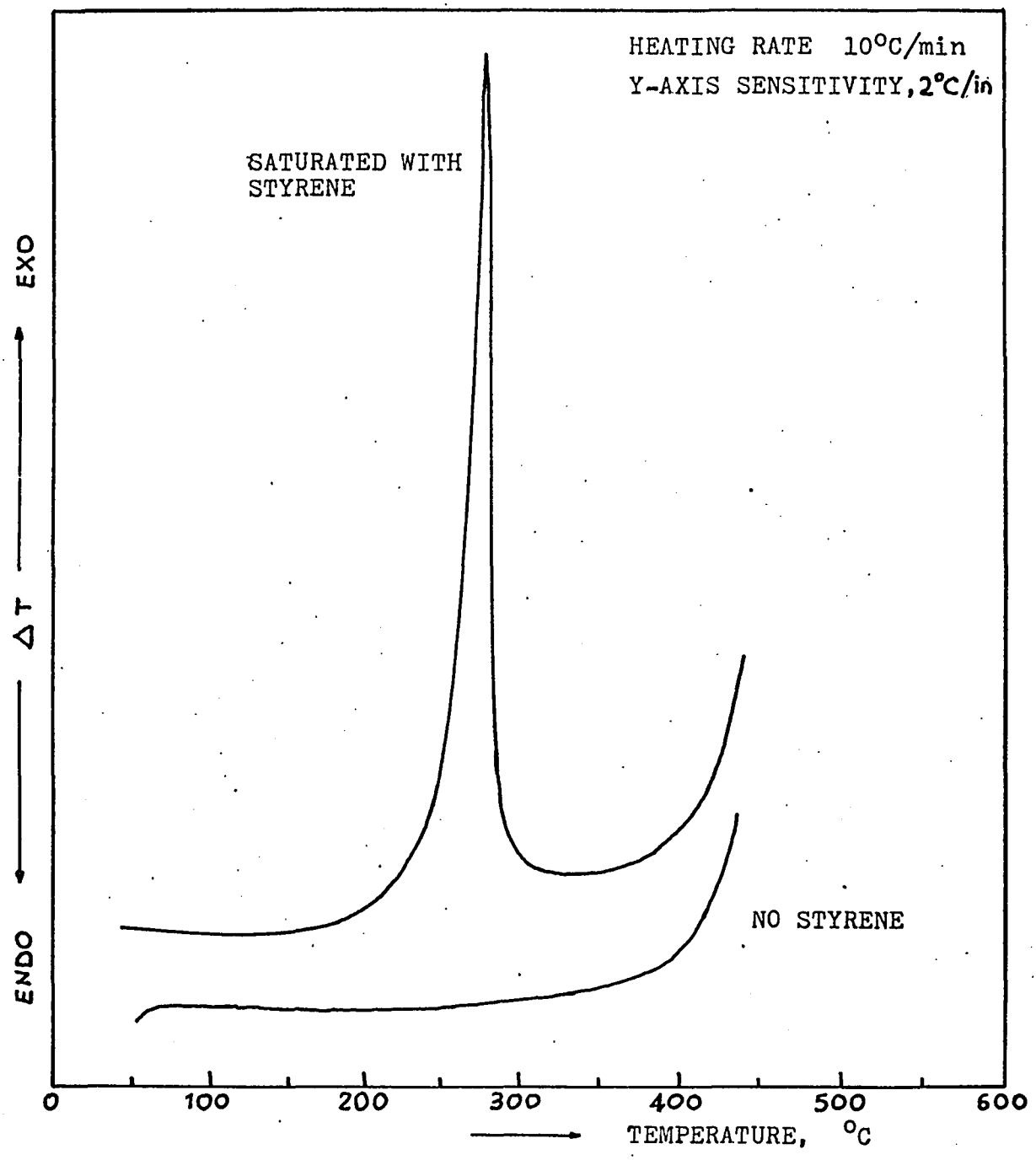


FIGURE 21. DSC Run For Styrene Adsorbed On Carbon Impregnated With 0.282% Pt, H_2 Reduced At 350°C For 2Hrs. Atmosphere, Air; Flow Rate, 300ml/min.

styrene oxidation on Pd and Pt respectively. The separation achieved in each case from oxidation of carbon is about 120°C.

TGA analysis indicated that for Pd, 6 to 8% of the styrene remained adsorbed on the carbon when the oxidation temperature had reached 400°C. This refractory behaviour is evidence for polymerization or adsorption on high energy sites. Oxidation on carbon impregnated with Pt showed complete removal of styrene at the end of the reaction. These facts are presented graphically in Fig. 22. Deposition of polymeric material on palladium-impregnated carbon lowers its activity for subsequent oxidation cycles, as is demonstrated in Part III of this investigation.

Reactions similar to those obtained with metal oxides were observed when styrene was oxidized on carbon impregnated with the platinum solution prepared as on page 31, but decomposed in air instead of in H_2. Fig. 23 shows a DSC analysis of this sample, and in Fig. 22 we have a plot of a TGA desorption run on the same sample in direct comparison with data obtained with the metals Pd and Pt. We see from Fig. 23 that some oxidation occurs at 350°C .

Charge-transfer Complexes.

An esr analysis of styrene adsorbed on palladium-impregnated carbon and on platinum-impregnated carbon, showed a strong resonance absorption for the former and no signal for the latter. This result strongly supports chemisorption of styrene at palladium sites to form some

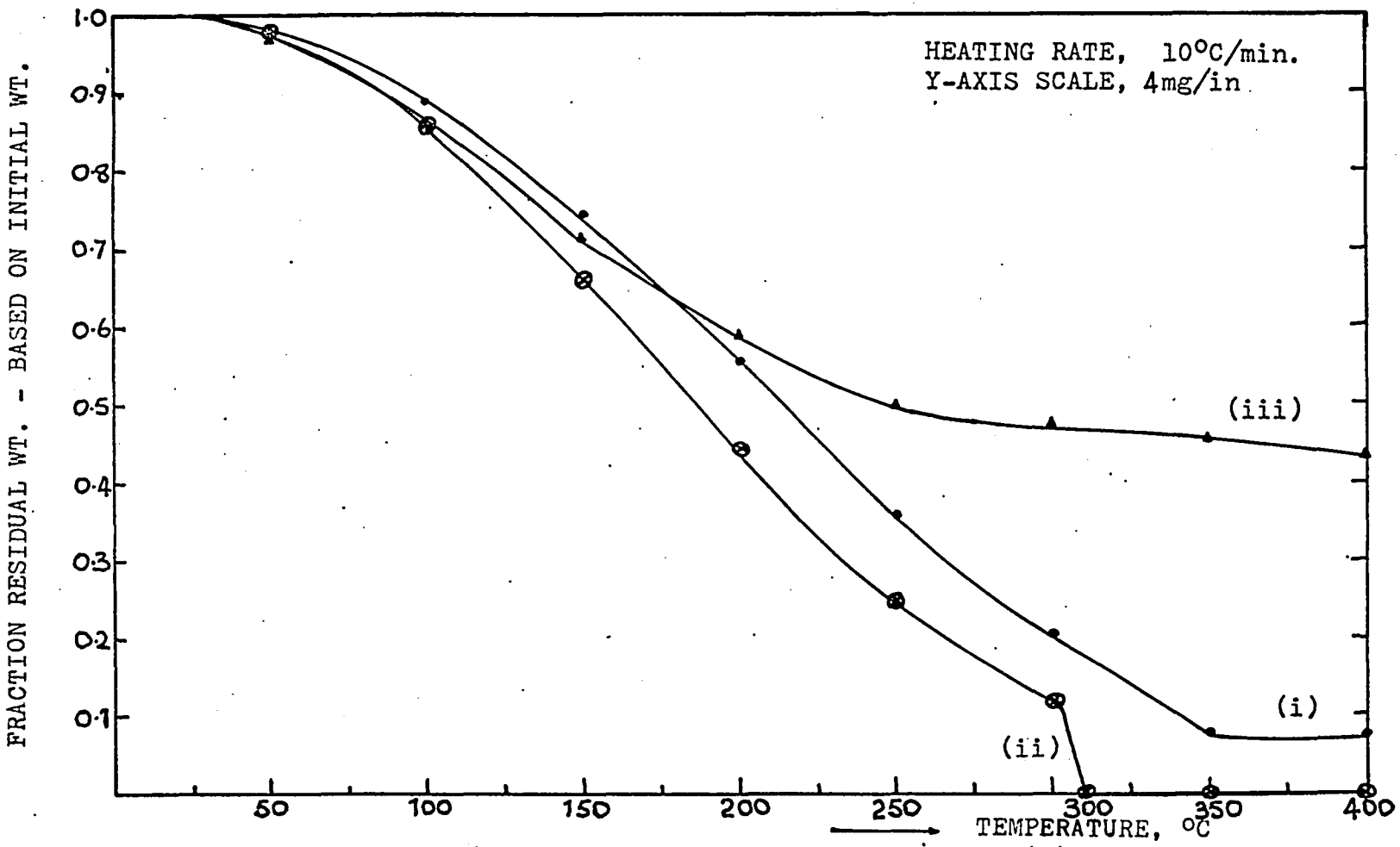


FIGURE 22. Desorption Curves For Styrene Adsorbed on (i) Carbon + 0.2% Pd, (ii) Carbon +0·282% Pt, H_2 Reduced At 350°C for 2 Hrs. (iii) Carbon +0.282% Pt, Air Decomposed at 350°C For 1hr. Atmosphere, Air Flow Rate 300ml/min.

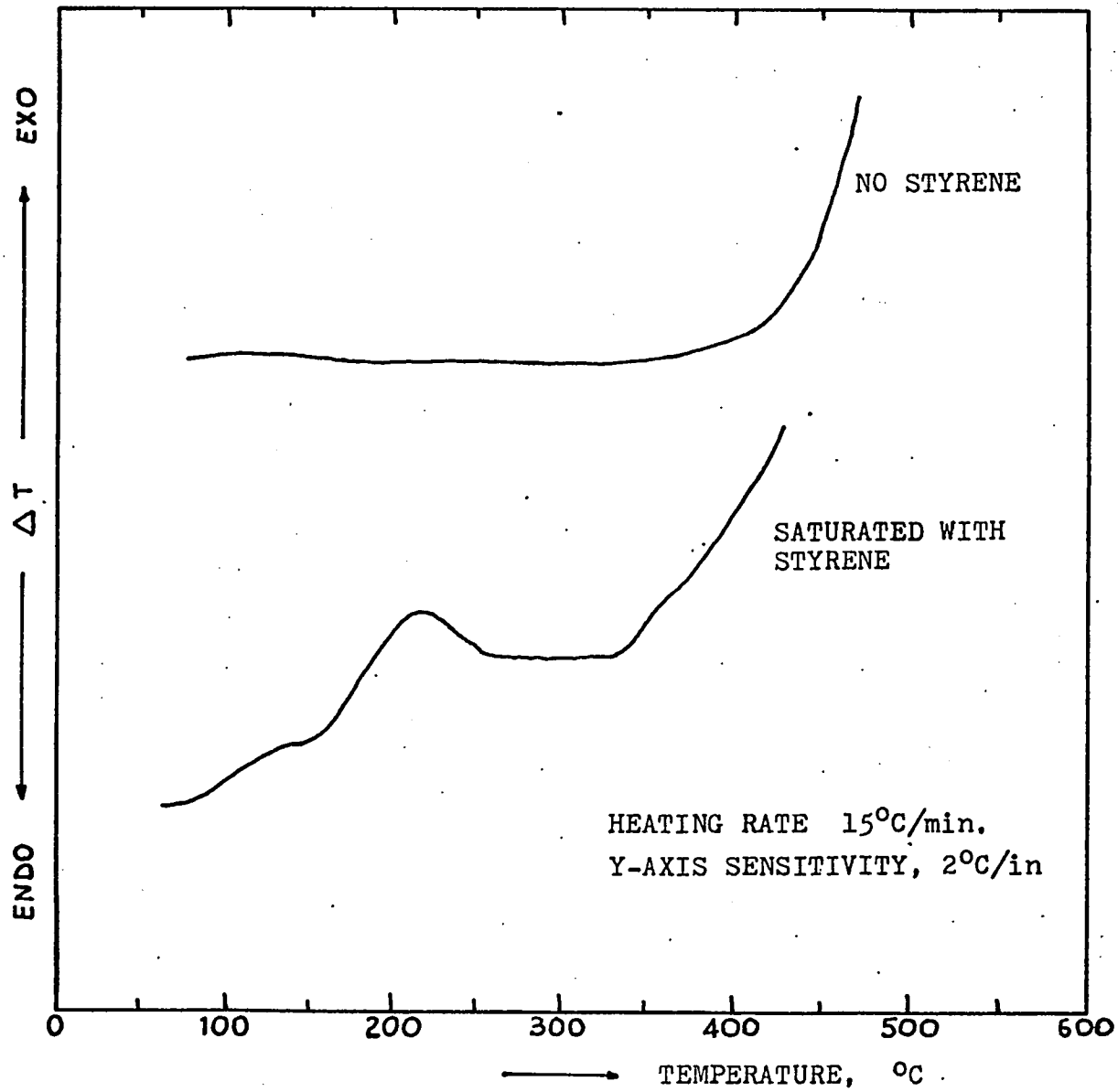


FIGURE 23. DSC Run for Styrene Adsorbed On Carbon + 0.282% Pt, Air Decomposed At 350°C For 1hr. Atmosphere, Air; Flow Rate, 300 ml/min.

type of charge-transfer complexes or dissociatively adsorbed styrene molecules. The esr spectra are shown in Fig. 24.

Turkevich et al[64] have formulated an electron transfer mechanism for catalytic reactions. Esr techniques were used to investigate the mechanism of catalytic reactions of palladium on alumina. These were cumene cracking, ethylene polymerization, and hydrogen-deuterium equilibrum reactions. They postulated that active sites were Lewis acid centers which can accept electrons from adsorbed molecules. Bronsted acid sites were discounted, contrary to the results of Rooney and Pink[57]. An electron abstraction theory was formulated for catalytic reactions of palladium, based on results with tetracyanoethylene and diphenylamie in dioxane solution. The donor levels were said to have been generated by hydrogen adsorption which then leads to the formation of protons.

Results obtained in the present investigation seem to contradict their results since a strong signal was observed for styrene adsorbed on palladium. Signals were also obtained with ethylbenzene, toluene and benzene, the largest originating from ethylbenzene. These compounds are not electron abstractors. We therefore seem to have confirmed the formation of charge-transfer complexes leading to positive radical ions which are paramagnetic[65,66].

An alternative theory is that free hydrogen atoms are present on the surface by the reaction between surface

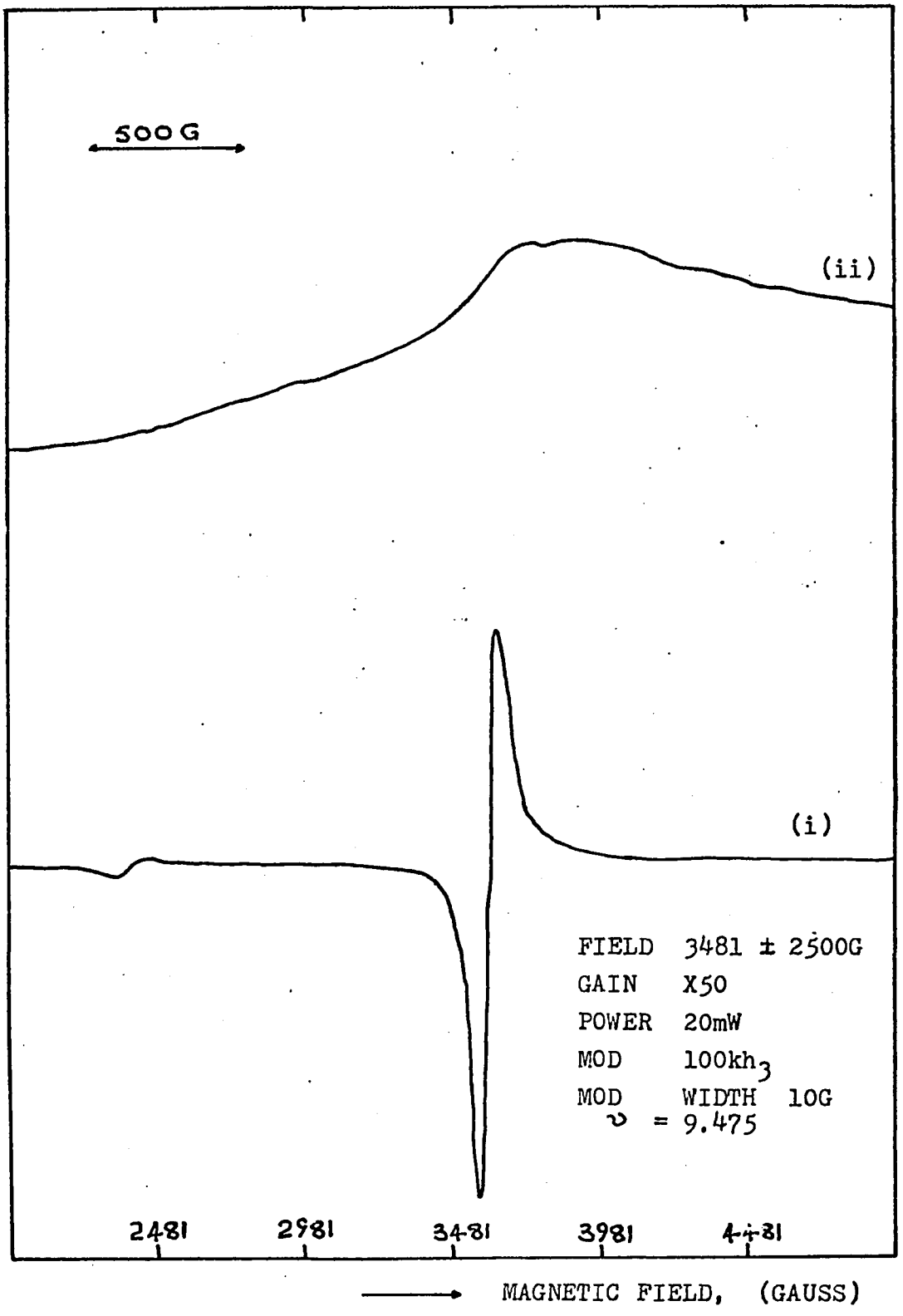


FIGURE 24. Esr Spectra Of Styrene Adsorbed On (i) Carbon + 0.2% Pd and (ii) Carbon + 0.282% Pt

protons and organic molecules.

$$H^+ + \phi \text{ ——— } H + \phi^+$$

Where ϕ = organic molecule.

This type of reaction will lead to a paramagnetic species with hyperfine splittings. Complex formation would involve empty d-bands of Pd and the absence of any observed hyperfine splitting indicates that the suggested reaction has not occurred. Besides, no signal was observed for Pt which was obtained by reduction with H_2. Charge-transfer complexes between Pd and some adsorbed molecules have been reported[66]. In fact, since oxidative reactions proceed via a free radical mechanism, the results of esr analysis are not unreasonable.

Esr signals were obtained for styrene adsorbed on Pt-impregnated carbon after oxidation to a temperature of 400°C. This could be due to surface electrons on the carbon or to polymer radicals generated by oxidation.

D. Saturation and Oxidation of Adsorbates.

(II) Studies on Oxidation of Benzene, Toluene and Ethylbenzene.

Method:

The set-up for saturation and oxidation studies was the same as described in section D.1. All catalysts investigated were as previously prepared in studies with styrene. Both metal and metal oxide catalysts were used. The concentration of pollutanats introduced from a saturator was such as to ensure rapid saturation of the carbon. Esr measurements were made on weighed samples as described before on page 35.

RESULTS AND DISCUSSION:

Metal Oxides.

Only V_2O_5 showed any detectable activity in the oxidation of benzene, toluene and ethylbenzene adsorbed on activated carbon. Chromic oxide showed slight activity for ethylbenzene oxidation. These results are surprising in view of the reported oxidation of these compounds on metal oxides such as CuO, NiO and Cr_2O_3-MoO_3 combination [68,69]. It might be that we were unable to prepare these oxides in the active form because of the carbon support. The most widely employed supports for complete oxidative reactions are γ-alumina and silica-gel. Oxidations are usually in the vapor-phase with pollutant stream passing through a bed of catalyst at usually high temperatures. Fazekas et al[70] have studied removal of hydrocarbons from gaseous CO_2 by complete oxidation over Cr_2O_3-MnO_2/γ-alumina catalyst. The minimum temperature reported was 500°C at a maximum pressure of 60 atm. In our investigation, V_2O_5 was effective between 180°—310°C but the separation from carbon burn-off was poor.

TGA analysis indicated complete removal of adsorbed benzene and toluene at 300°C without any oxidation. For ethylbenzene about 20% was still adsorbed at 300°C probably as polymeric matter resulting from polymerization of styrene, since styrene was detected as an intermediate product. A DSC curve for oxidation of ethylbenzene on V_2O_5 is shown in Fig. 25.

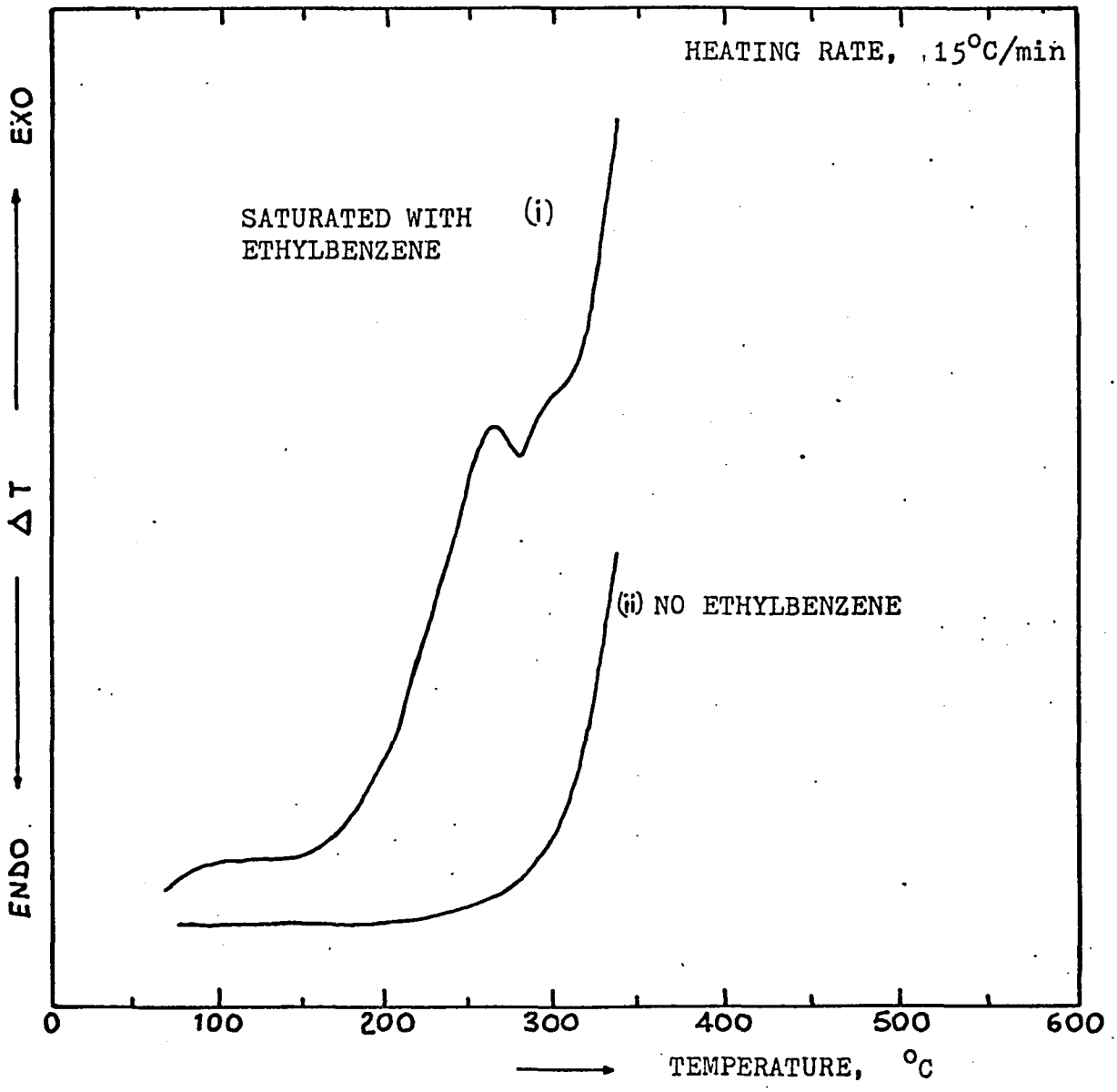


FIGURE 25. Dsc Run For (i) Ethylbenzene Adsorbed On Carbon + 1% NH_4VO_3, Air Decomposed At 230°C For 4hrs. (ii) Carbon +1% NH_4VO_3, Air Decomposed, Atmosphere, Air Flow Rate, 300ml/min.

Metal Catalysts

Results with metal catalysts were more promising. Benzene, toluene and ethylbenzene were oxidized with palladium and platimum as catalysts. TGA-GC analysis during oxidation of ethylbenzene yielded benzene, toluene and styrene, whose concentration increased with increasing temperature. Fig. 26 shows GC analysis of effluent at different temperatures. No benzaldehyde was detected and this implies that oxidation is complete to CO_2 and H_2O. The heats of reaction are shown in Table IX.

Deductions from TGA and esr Analysis

Evidence from TGA analysis indicated that some polymer or chemisorbed matter was still adsorbed on a Pd catalyst but not on a Pt catalyst when oxidation was carried to 400°C. Esr data provided an insight into the nature of the adsorbate.

Sharp esr signals were obtained when benzene, toluene, and ethylbenzebe were adsorbed on a palladium-impregnated carbon but not with platinum-impregnated carbon. This was similar to the result obtained with styrene. Ethylbenzene gave the largest signal and it was necessary to reduce the gain of the instrument amplifier. The calculated g-factor was 2.10 indicating the formation of free-radical ions or some type of charge-transfer complex. The latter conclusion is supported by the fact that the electron donating effect of the ethyl group seems to be responsible for the huge signal observed for ethylbenzene adsorbed on palladium-impregnated carbon. That the aromatic ring is involved derives from the fact that benzene also gave a signal. The

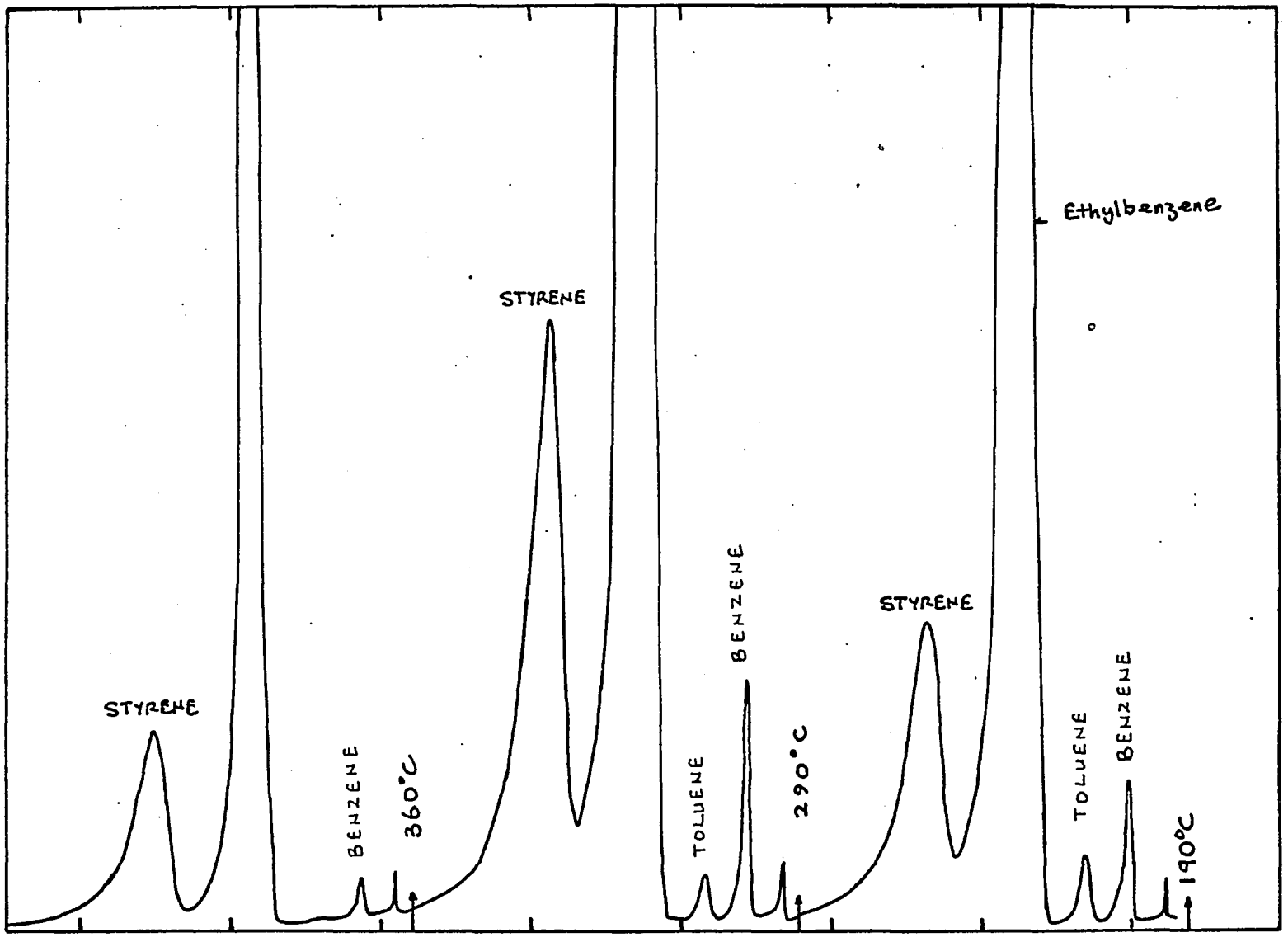


FIGURE26.TGA-GC Analysis of Effluent During Oxidation of Ethylbenzene Adsorbed on Carbon + 0.2% Pd. Samples were Taken at Different Temperatures with a Flame Ionization Detector.

esr spectra are shown in Figures 27, 28, and 29.

The results with platinum are strange in view of the fact that Ernst et al[71] obtained esr signals for toluene and ethylbenzene adsorbed on $PtO_2.2H_2O$ at 70°C. The benzene resonance appeared after 7 days at 120°C. With PdO a small signal was detected after 7 days at 120°C. The absence of signal might be due to the fact that our measurements were carried out at ambient temperatures. It appears that there is a correlation between catalyst activity in oxidation of a particular compound and the intensity of the esr signal obtained. Figures 30, 31, and 32 show the DSC of ethylbenzene, toluene and benzene adsorbed on Pd-impregnated carbon. Each measurement was on a saturated sample. Table IX gives the corresponding heats of reaction which are directly proportional to catalyst activity[72].

The separation between oxidation of adsorbate and carbon respectively was about 80°-100°C.

TABLE IX

Heats of Reaction for Oxidation of Benzene, Toluene, Ethylbenzene and Styrene on Palladium-impregnated Carbon.

Compound	Maximum Temp. for oxidation (°C).	Heat of Reaction mcal/mg.
Benzene	265	208 ± 2
Toluene	285	725 ± 7
Ethylbenzene	315	1410 ± 2
Styrene	290	954 ± 23

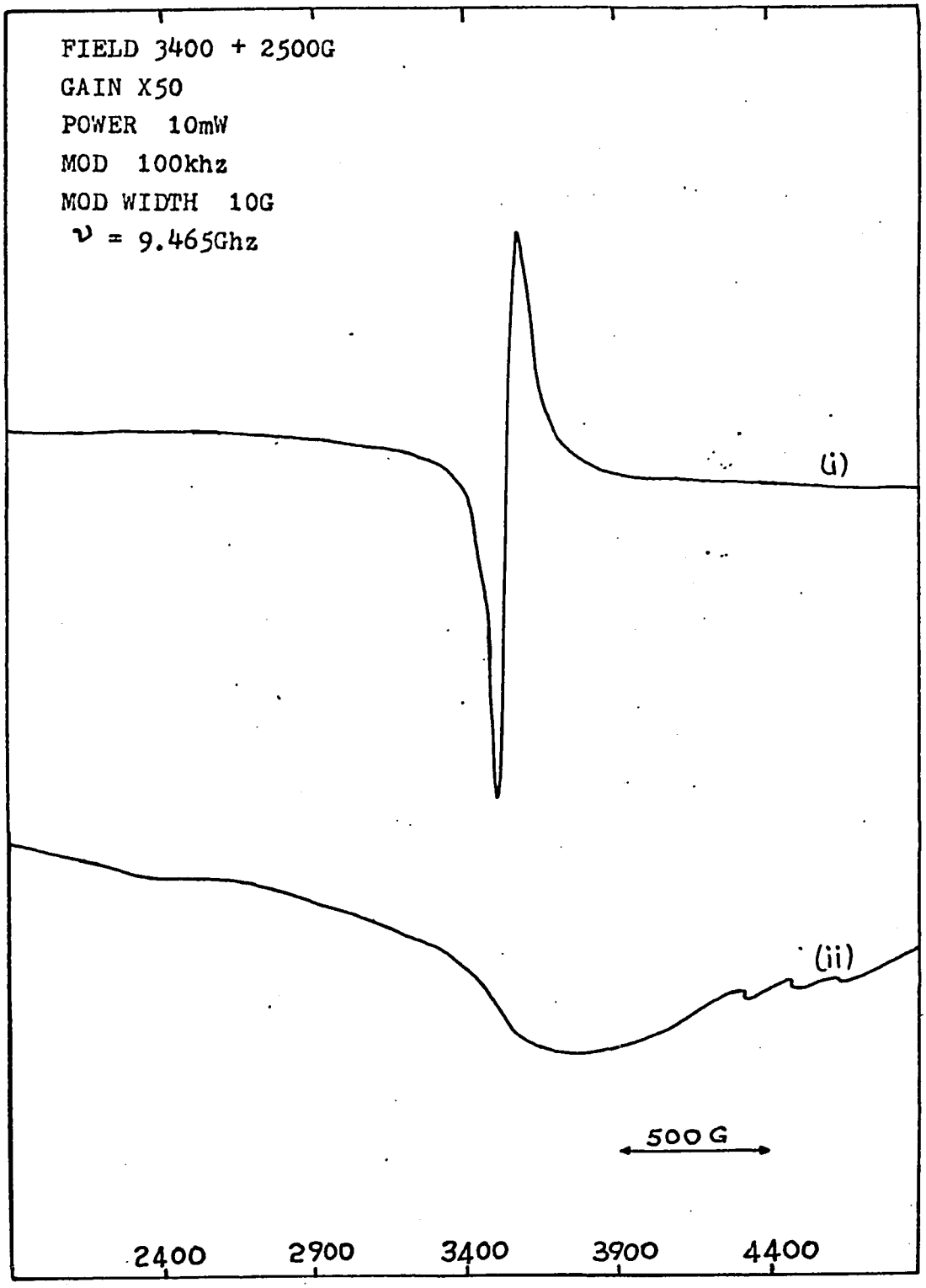


FIGURE 27. Esr Spectra of Benzene Adsorbed on (i) Carbon + 0.2%Pd and (ii) Carbon + No Catalyst. Temperature, Ambient.

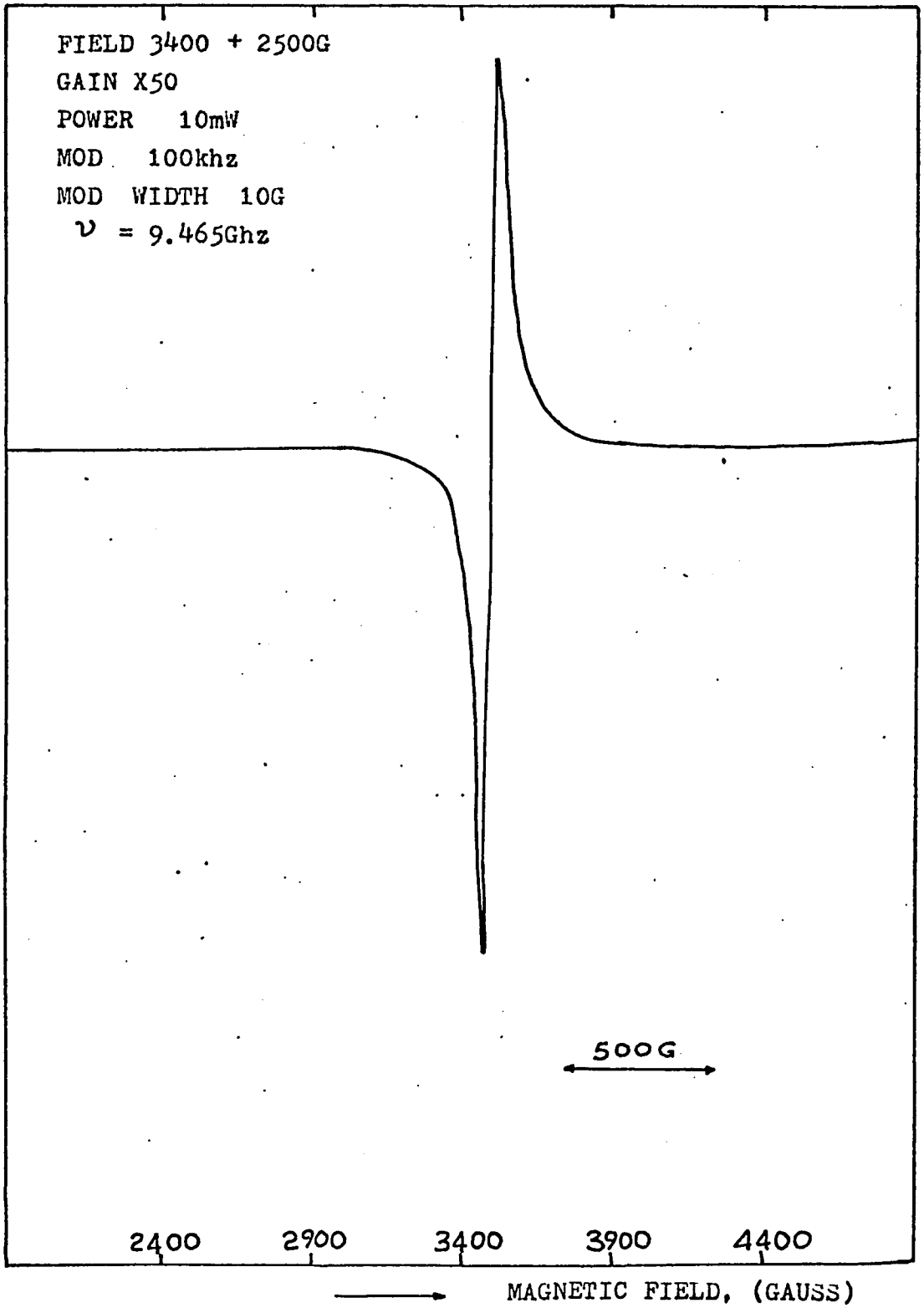


FIGURE 28. Esr Spectrum of Toluene Adsorbed on Carbon + 0.2% Pd. Temperature, Ambient.

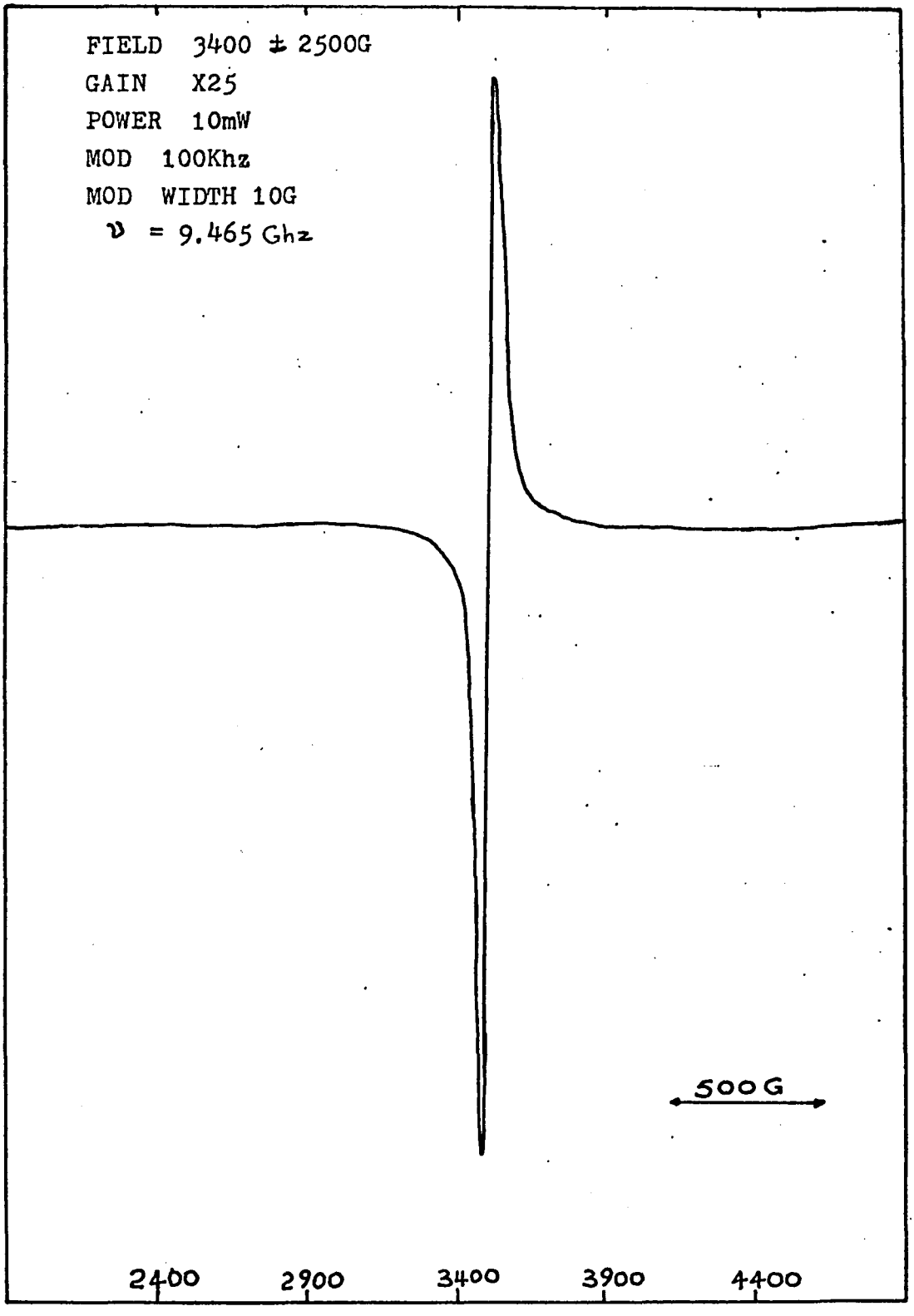


FIGURE 29. Esr Spectrum Of Ethylbenzene Adsorbed On Carbon + 0.2% Pd. Temperature, Ambient.

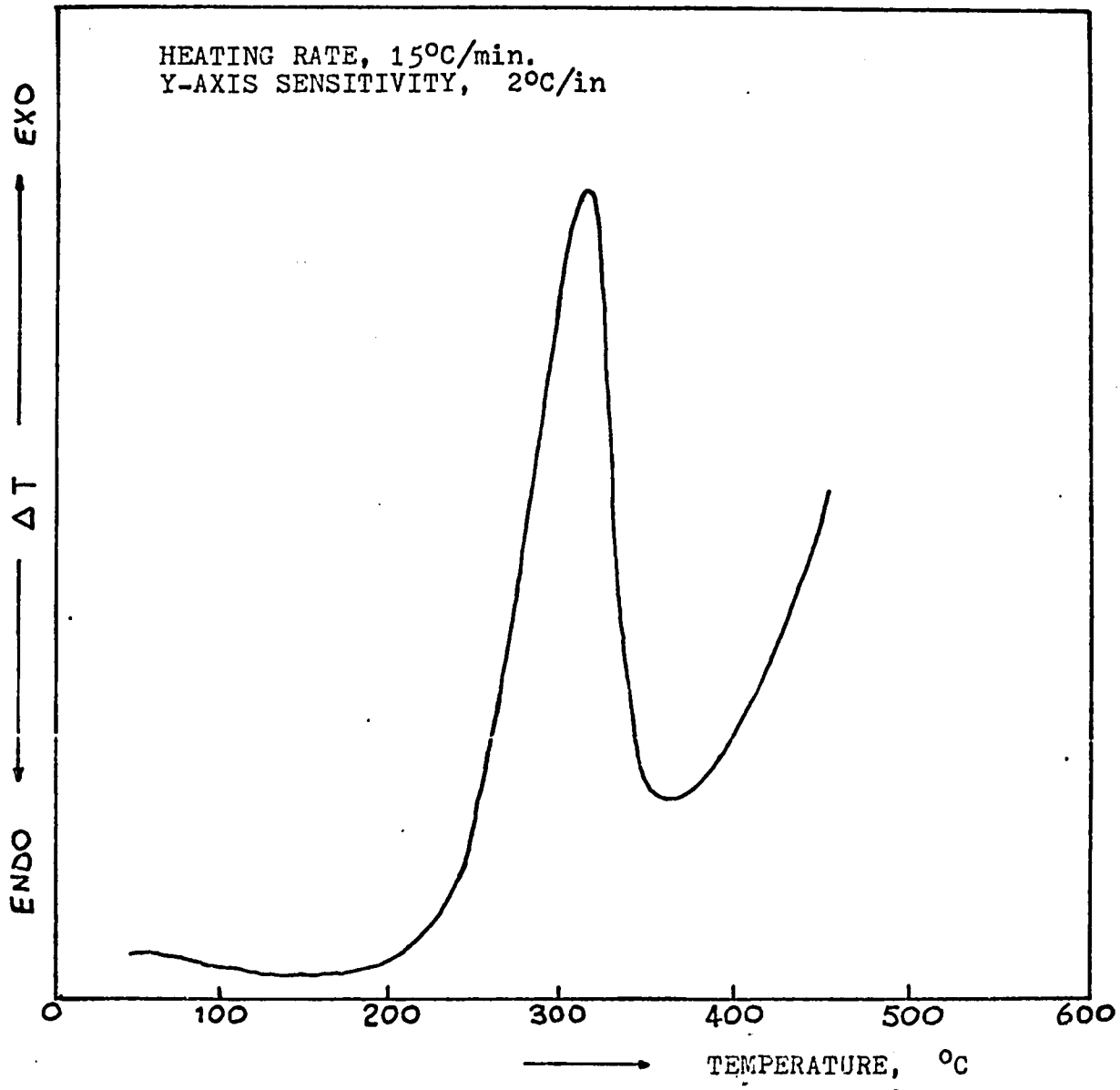


FIGURE 30. DSC Run For Ethylbenzene Adsorbed On Carbon + 0.2%Pd. Atmosphere, Air; Flow Rate, 300ml/min.

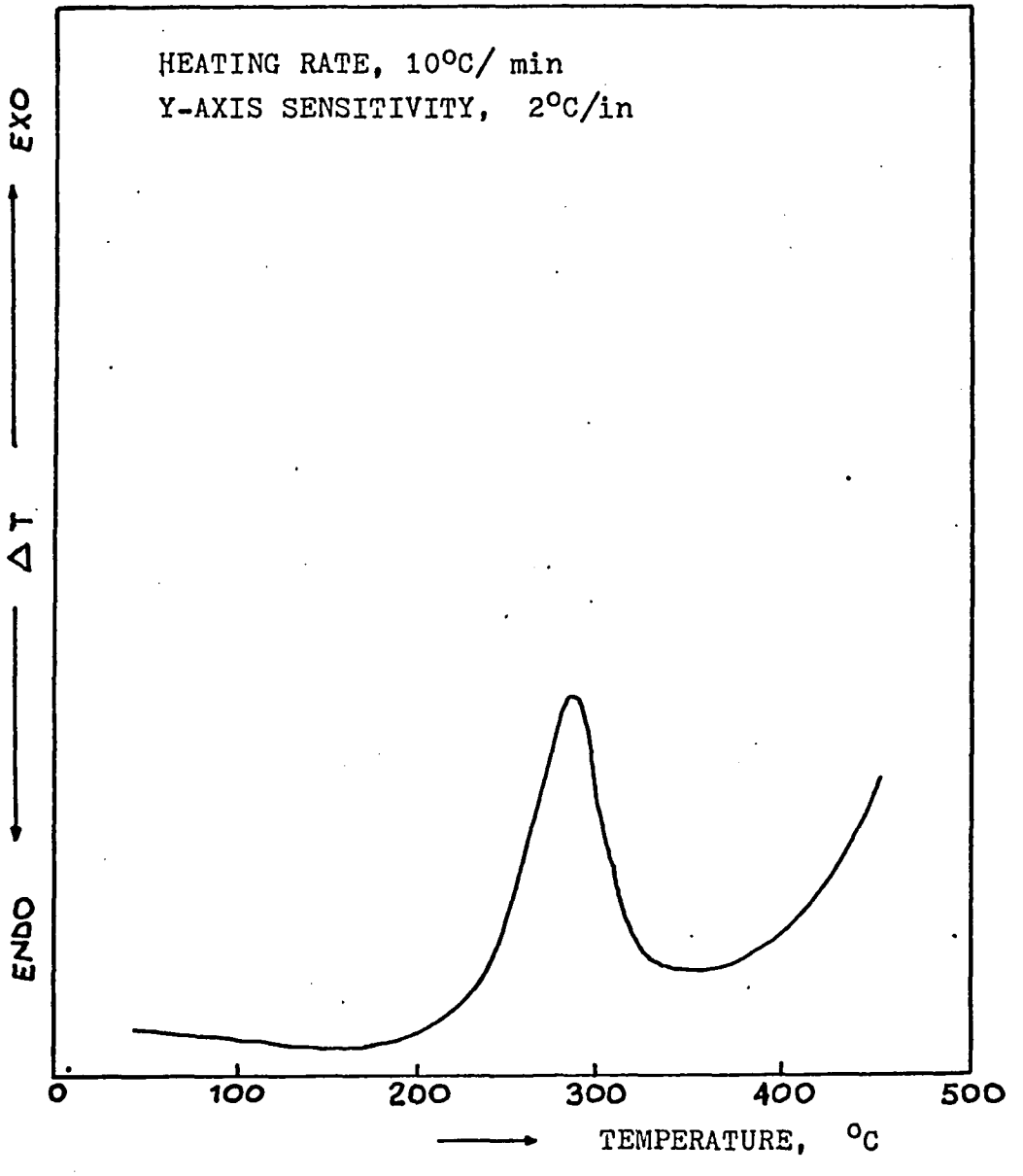


FIGURE 31. DSC Run For Toluene Adsorbed On Carbon + 0.2% Pd. Atmosphere, Air; Flow Rate 300ml/min.

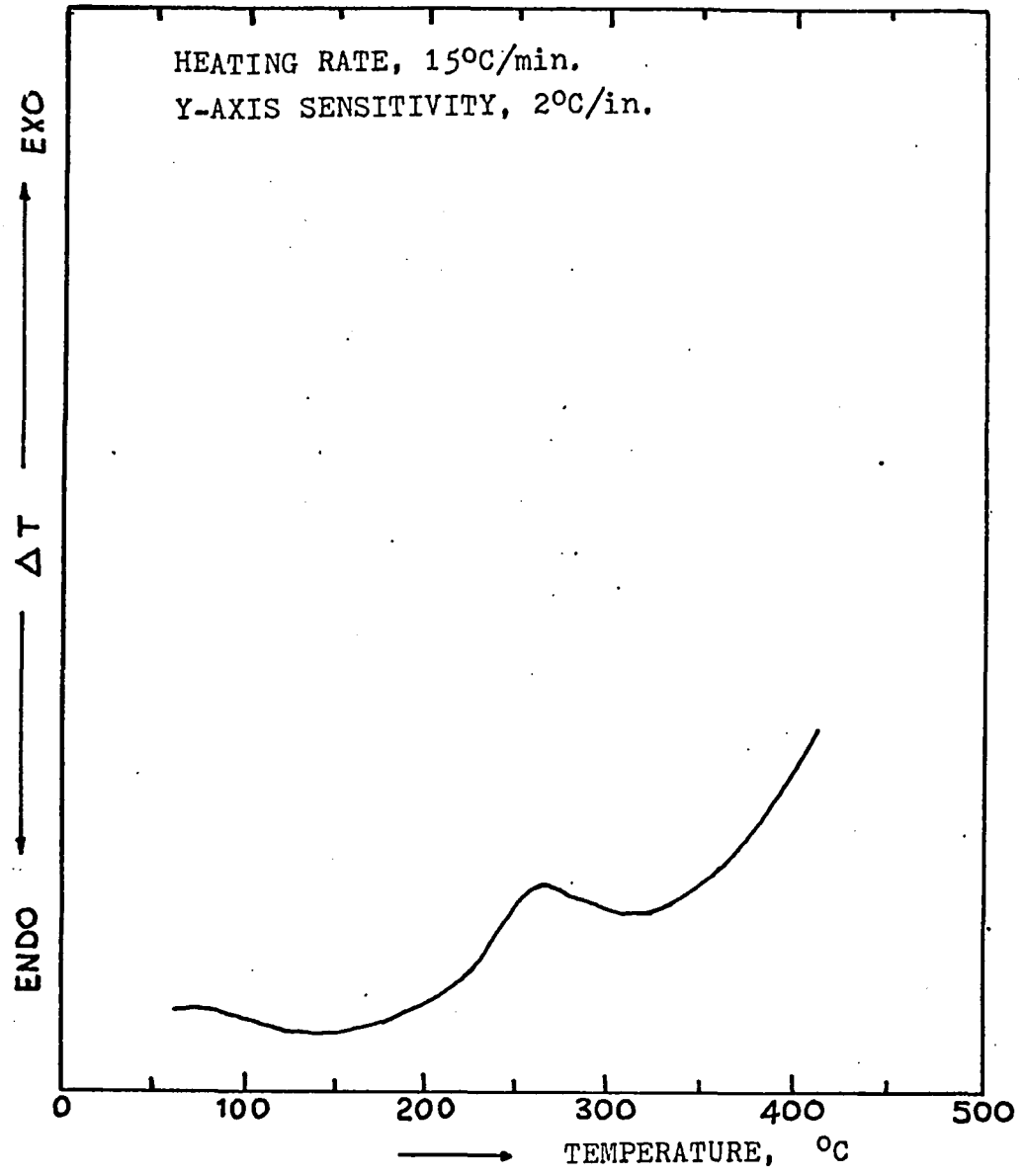


FIGURE 32. DSC Run For Benzene Adsorbed On Carbon + 0.2% Pd. Atmosphere, Air; Flow Rate 300ml/min.

For oxidation of benzene on Pt-impregnated carbon, the heat of reaction was calculated to be 608 $\pm$ 6 mcal/mg. Comparison with the figure of 208 $\pm$ 2 mcal/mg for Pd-impregnated carbon would suggest that platinum is about three times more active than palladium for the oxidation of the benzene ring.

Conclusions.

Metal Oxides (CuO, Cr_2O_3, Co_2O_3, MnO_2 and V_2O_5) are active in the oxidation of styrene to benzaldehyde, CO_2 and H_2O at 140° to 230°C. Mixed oxide catalysts (CuO/Cr_2O_3, CuO/Co_2O_3, La_2O_3/Co_2O_3, La_2O_3/MnO_2, V_2O_5/Cr_2O_3 and BaO/Cr_2O_3) are also active within the same range of temperature. However their activity is impaired by polymerization and/or chemisorptive reactions.

The metallic catalysts, Pd and Pt effect complete oxidation of styrene to CO_2 and H_2O at 150° to 310°C. With platinum there is no deposit of polymeric matter at the end of the reaction. The temperature range during oxidation depends on the heating rate.

Benzene, toluene and ethylbenzene can be completely oxidized to CO_2 and H_2O on palladium and platinum-impregnated carbons at 150°-280°C but not on carbons impregnated with metal oxides, except V_2O_5 which shows some activity for oxidation of ethylbenzene but with poor separation from carbon burn-off.

The most significant result in this study is that for unimpregnated carbon there is a deposit of 8-10% of polymeric material at 400°C butthere is a complete burn-off of styrene and ethylbenzene on platinum-impregnated carbon. The desorption of adsorbates without oxidation is not a serious disadvantage, since a potential concentration effect can be achieved with activated carbon. For example, styrene at 150 ppm can be transferred from one air stream to another

at average concentrations of 0.2-3.2% by volume and this gives rise to concentration by a factor of 14 to 212. If full advantage is taken of the concentrating effect the volume of contaminated air to be scrubbed or incinerated can be reduced by a factor of 212. This represents significant savings. For example, the fuel requirements per unit volume of air can be reduced. A cycling oxidation and incorporation of a catalytic after-burner would help eliminate the discharge of pollutant or intermediates to the atmosphere.

The electron spin resonance (esr) results suggest that it is probable that oxidative regeneration of catalyst takes place by a radical mechanism. Rooney and Pink[72] have advocated that radical-ion formation occurred when aromatic molecules are adsorbed on catalysts like silica-alumina.

Also Leftin and Hall[73] have shown by spectrophotometric technique that tri-phenylmethane and related hydrocarbons are adsorbed as carbonium ions at Lewis acid sites on the surface of silica-alumina catalyst, by hydride-ion abstraction. With diphenyl ethylene, 2-butene and ethylene, Webb[74] proposed two different species, one probably a carbonium ion, the other believed to be a charge-transfer complex formed by adsorption of the olefin at a non-acidic site.

Evidence from this work indicates some type of charge transfer complex for benzene, toluene, ethylbenzene and styrene adsorbed at Lewis acidic centers or on non-acidic

sites like Pd. The absence of esr signal on platinum-impregnated carbon in the present investigation could be due to the low concentration of Pt on the carbon. Nicolau, C.S. et al[75] have obtained esr spectra on charcoal at the concentration of 1 to 5% by weight. (Our Pt-impregnated carbon contained 0.3% Pt by weight). It should be mentioned that the esr spectra in this work were run at room temperaure whereas Ernst et al[71] carried out their measurements at 70°C.

Oxidation catalysts are therefore sites for radical-ion formation and this is in keeping with the accepted mechanism of catalytic oxidations[76].

Good separation of about 120°C was obtained between oxidation of styrene and of carbon for the metal oxides. Palladium-and platinum-impregnated carbon were highly reactive in the oxidation of styrene, benzene, toluene and ethylbenzene. The separation between oxidation of styrene and of carbon was 80°C on palladized carbon and 100°C on platinized carbon. The carbon support was not pyrophoric even at 450°C.

No carbon monoxide was detected in all the oxidation reactions. This is reasonable in view of the fact that carbon monoxide can be oxidized on carbon or on carbon, impregnated with metal oxide catalysts[78,79].

PART II

CATALYTIC OXIDATION OF OXYGENATED ORGANIC COMPOUNDS

INTRODUCTION

Having considered the oxidation of adsorbed hydrocarbons in Part I, consideration will now be given to oxygenated organic compounds of non-aromatic type. Study of the oxidation of oxygenated compounds is important in air pollution control since most of them have been identified with branched chain ketones and aldehydes. They produce plant damage, eye irritation, rubber cracking and odor. The development of a method for the control of these compounds is therefore of tremendous importance.

In the present investigation we are interested in the oxidation of the acrylates such as methyl methacrylate, ethylacrylate and n-butylacrylate and on the oxidation of methylethyl ketone.

Turk[8] has reported on the catalytic reactivation of carbon using methylethyl ketone as sorbate. The type of data he obtained are quite different from the thermal analytical data we hope to obtain, especially with regards to the separation achieved between oxidation of sorbate and of the sorbent.

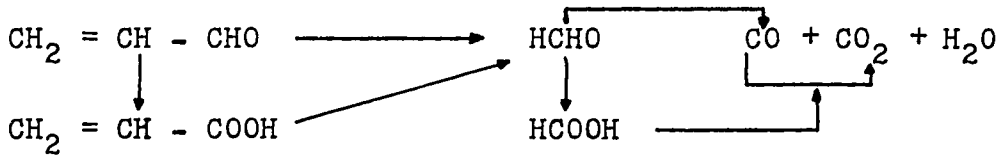
Acrylic monomer has been observed to cause contact dermatitis on persons working in orthopedics by penetration of rubber gloves[80]. We are therefore interested in the acrylates because of this type of health hazards. Their control by catalytic oxidation is expected to raise the problem of polymerization, as was the case in the oxidation of styrene. Almost all the reports in the literature on the oxidation reactions of the acrylates, dealt with mechanism and kinetics.

Kinetics and Mechanism of Oxidation

Saltanov[81] has reported on the kinetics of the vapor-phase oxidation of organic substances containing the waste waters from acrylate industries, over CuO/Cr_2O_3 catalyst.

The mechanisms for the thermal or oxidative degradation of acrylic polymers such as polyethyl acrylate were studied by Conley[82]. Kinetics of the oxidation of ethylmethyl acrylate in the presence of phenolic compounds has been investigated by several workers[83,84].

Gorshkov *et al*[85] studied the kinetics of oxidation of various aldehydes and acids over a bismuth-molybdenum catalyst. The scheme of acrolein oxidation was given as



We have studied complete oxidation of the acrylates adsorbed on carbon impregnated with different catalysts. No attempt was made to elucidate the mechanism of the oxidation reactions. Emphasis was placed on evaluation of catalysts for *in situ* complete oxidation of adsorbates on activated carbon.

Shulz and Henrici[86] have recently studied the oxygen-inhibited polymerization of methyl methacrylate by a simple dilatometric technique in which the length of the well-defined inhibition periods were used to estimate the rate of oxidation of the monomer during the inhibition periods.

The study of mixtures of pollutants would be of great interest in view of the fact that phenols retard vinyl

polymerization in air. This would favor the burn-off of the adsorbate without deposit of polymeric matter. Inhibition of the oxidation and polymerization of methyl methacrylate by phenols has been studied by Caldwell and Ihrig[84]. A synthetic mixture of methylmethacrylate, ethylacrylate and toluene has been studied in the present investigation in ratios that are typical in industrial effluents.

EXPERIMENTAL

A. OXIDATION OF METHYLETHYLKETONE (MEK).

B. OXIDATION OF ACRYLATES.

A. Oxidation of Methylethylketone (MEK).

Method:

As in Part I, there were two methods of investigation. The first involved the use of the modified TGA apparatus as shown schematically in Fig. 2 for the saturation of the carbon samples already impregnated with catalysts as described in Part I. Metal oxides, mixed oxides and the metals Pd and Pt were investigated for in situ oxidation of MEK adsorbed on activated carbon.

For each saturation run, 2 ml of MEK was used in the saturator at ice temperature, the carrier gas flow-rate being maintained at 290 ml/min. Each run took about 40 minutes at pollutant concentration of 29,000 ppm (vol/vol) for a sample weighing between 45 and 60 mg.

DSC Studies

A portion of the saturated sample was analyzed in the DSC in order to determine the range of temperature over which oxidation occurred and to measure the heat of reaction in some cases. Also by carrying out the desorption (oxidation) at different rates of temperature program it was possible to calculate the activation energy for any particular catalyst according to the method of Amenomiya et al[87]. For example, the activation energy for oxidation on carbon impregnated with V_2O_5 was determined and compared with the literature value.

TGA Studies

Desorption and oxidation in air was then carried out on a saturated sample in the TGA. Weight changes during

desorption were monitored with increasing temperature for all catalysts studied. It was possible to determine if oxidation occurred by visual observation of the TGA curve and by TGA-GC analysis of effluent for CO_2 at different temperatures as described in Part I.

RESULTS AND DISCUSSION

DSC Analyses

Tables X, XI and XII show the results obtained for oxidation of MEK on carbon impregnated with metal oxide catalysts, mixed metal oxide catalysts and the metal catalysts Pd and Pt respectively. All the data were derived from DSC analyses.

TABLE X

Data For MEK Oxidation On Metal Oxide Catalysts.

Heating Rate = 10°C/min. Flow Rate = 300 ml/min.

Atmosphere = Air Y-axis sensitivity = 2°C/in.

Catalyst	Oxidation Temperature (°C)	Carbon Support Burn-off (°C)	Heat of Reaction (mcal/mg).
Cr_2O_3	80 - 155	345	202 ± 9
None	90 - 180	400	210 ± 2
V_2O_5 (2%)	60 - 140	310	428 ± 36
V_2O_5 (1%)	90 - 160	300	430 ± 5
Co_3O_4	90 - 185	350	162 ± 0

TABLE XI*

Data For MEK Oxidation On Mixed Metal Oxide Catalysts.

Catalyst	Oxidation Temperature (°C).	Carbon Support Burn-off (°C).	Heat of Reaction (mcal/mg).
CuO/Co_3O_4	80 - 150	320	242 ± 0
V_2O_5/K_2SO_4	100 - 162	310	148 ± 4
V_2O_5/KOH	90 - 180	290	359 ± 9
BaO/K_2O	60 - 160	310	282 ± 4
CuO/Cr_2O_3	80 - 175	320	197 ± 4
V_2O_5/Cr_2O_3	70 - 160	315	341 ± 9

TABLE XII*

Data For MEK Oxidation On Pd and Pt Catalysts.

Catalyst	Oxidation Temperature (°C).	Carbon Support Burn-off (°C).	Heat of Reaction (mcal/mg).
Pd	100 - 230	380	370 ± 4
Pt	90 - 185	385	463 ± 3
Pd/V_2O_5	100 - 185	325	362 ± 10

* The experimental conditions are the same as those used for the derivation of Table X.

It was observed that vanadia-impregnated carbon was the most active for the oxidation of MEK to CO_2 and H_2O. Typical DSC runs are shown in Figures 33 and 34 for carbon impregnated with 2% solution and 1% solution of NH_4VO_3 respectively. It is evident that oxidation occurs at a lower range of temperature with increasing amount of V_2O_5, and this may suggest participation of the oxide, which would lead to a lower oxidation state after a number of oxidation cycles.

TGA Analyses

TGA analysis indicated that about 4% of MEK (based on the initial amount adsorbed at saturation) was still adsorbed on the carbon at the end of the exothermic oxidative reaction for the specific case of carbon impregnated with 1% NH_4VO_3. The amount retained appears to increase with increasing vanadia concentration. Fig. 35 shows a typical TGA desorption (oxidation) for MEK in air atmosphere. We see that at the end of the oxidation around (130°C) some MEK is still adsorbed; the reference point for complete desorption is A on the curve. Data generated from TGA desorption curves are compared in Fig. 36, where residual weight fraction of MEK is plotted against temperature. We observe that for carbon impregnated with V_2O_5/KOH, there is complete removal of MEK at the end of the oxidative reaction. This is illustrated in Fig. 37. DSC analysis indicated that oxidation occurred between 90° and 175°C. Table XIII gives data for the residual amount of MEK at the end of the oxidative reaction for several other catalysts.

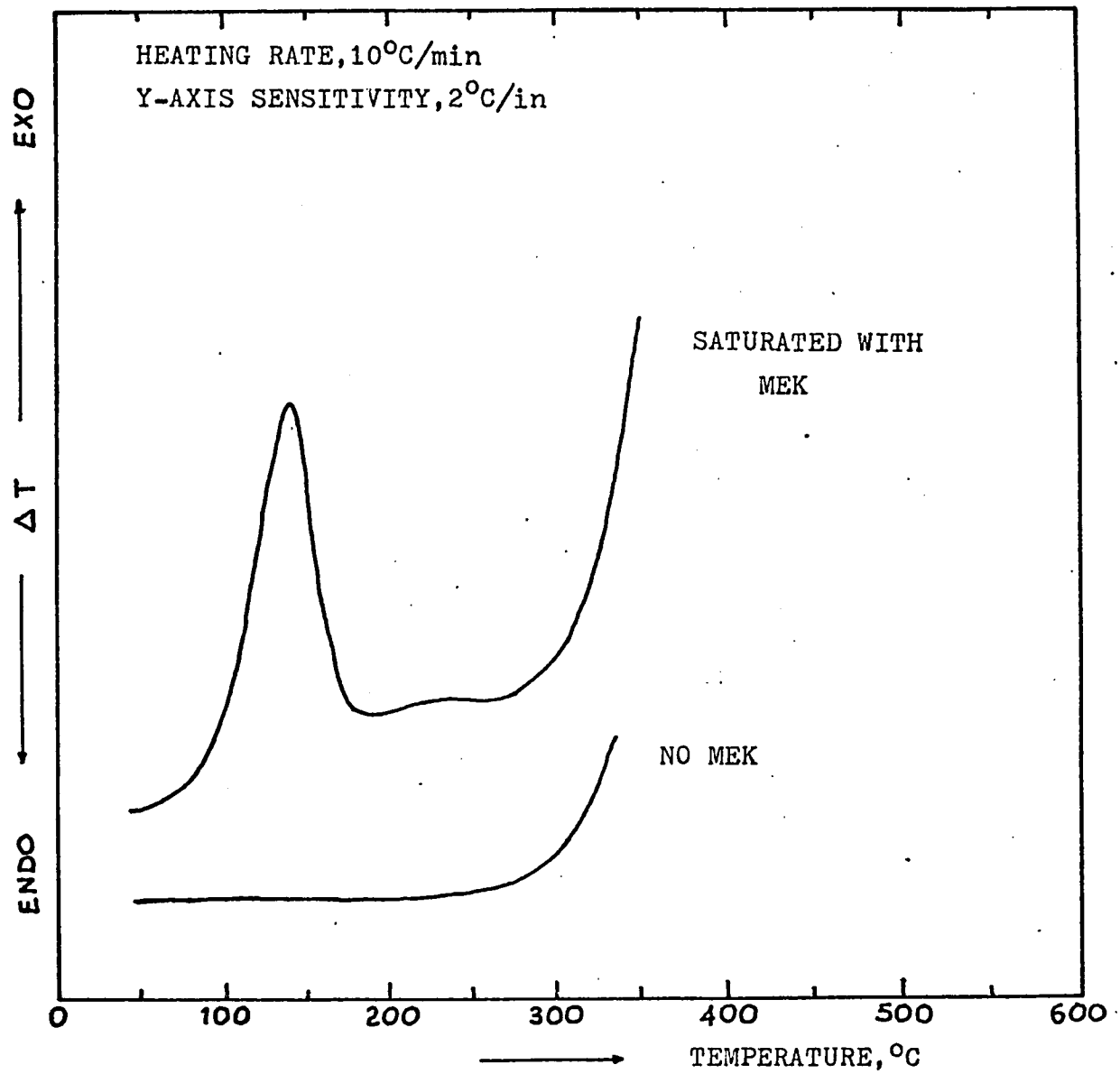


FIGURE33. DSC Run For Metyl Ethylketone Adsorbed On Carbon Impregnated With 2% NH_4VO_3, Air Decomposed at 230°C For 12hrs. Atmosphere, Air; Flow Rate, 250°C.

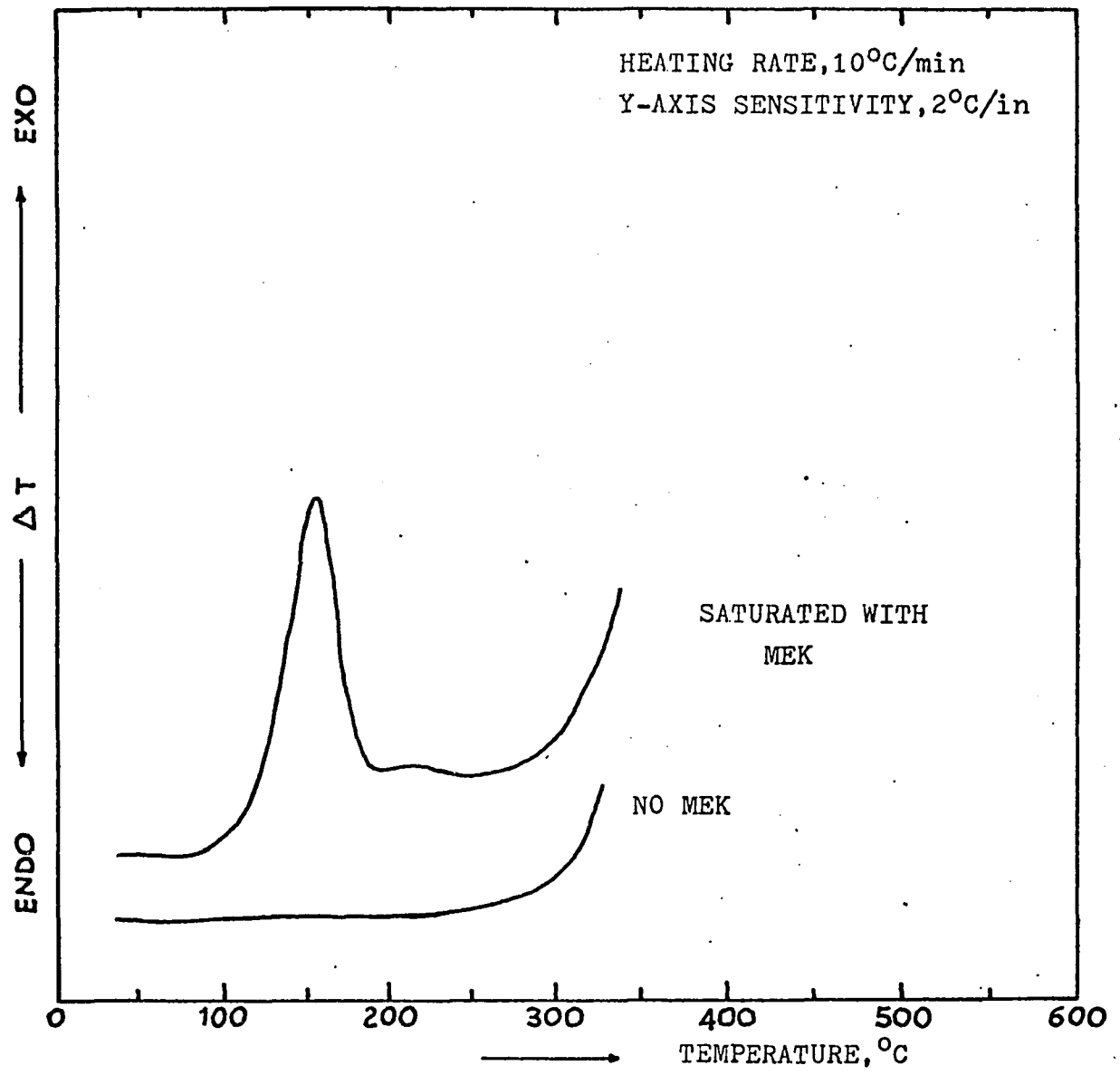


FIGURE 34. DSC Run for Methyl Ethylketone Adsorbed On Carbon Impregnated With 1% NH_4VO_3, Air Decomposed at 230°C For 12hrs. Atmosphere, Air; Flow Rate, 250°C/min

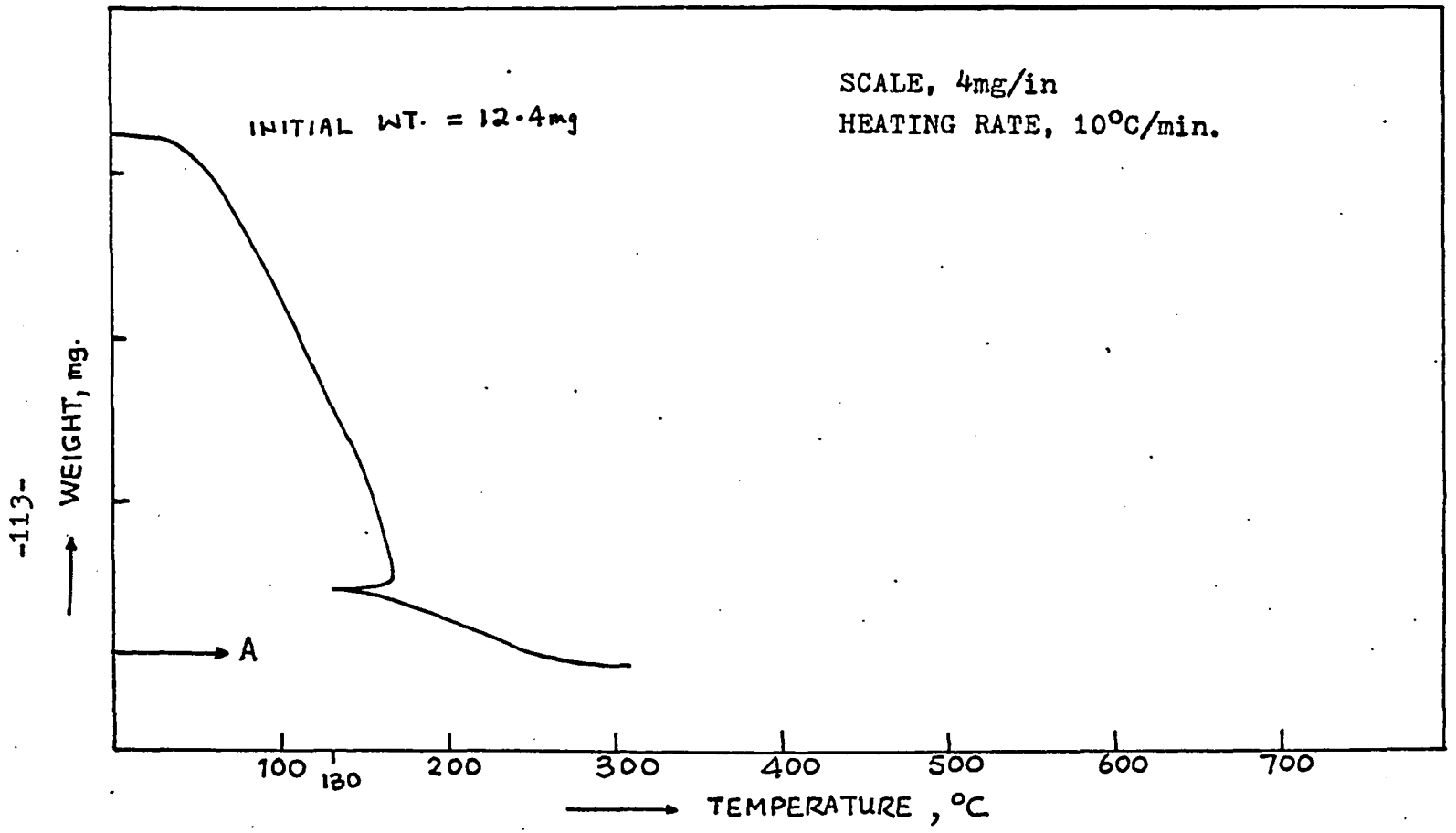


FIGURE 35. TGA Desorption(Oxidation) Curve For MEK Adsorbed on Carbon Impregnated With V_2O_5. Reference Point For Complete Removal of Adsorbate. is,A.

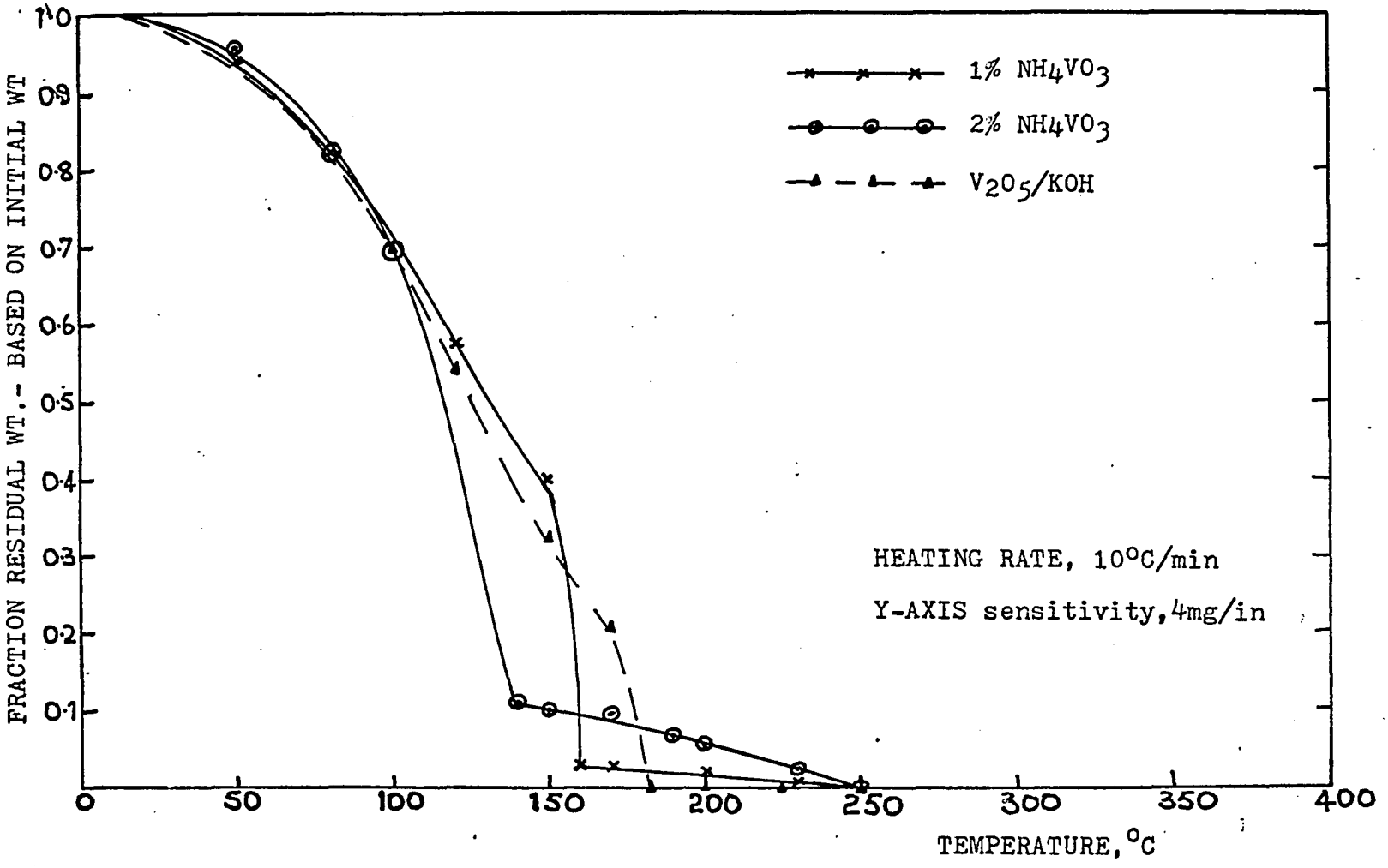


FIGURE 36. TGA Desorption Curves For Methyl Ethylketone(MEK) Adsorbed On Oxide Catalysts. Atmosphere, Air; Flow Rate, 250ml/min.

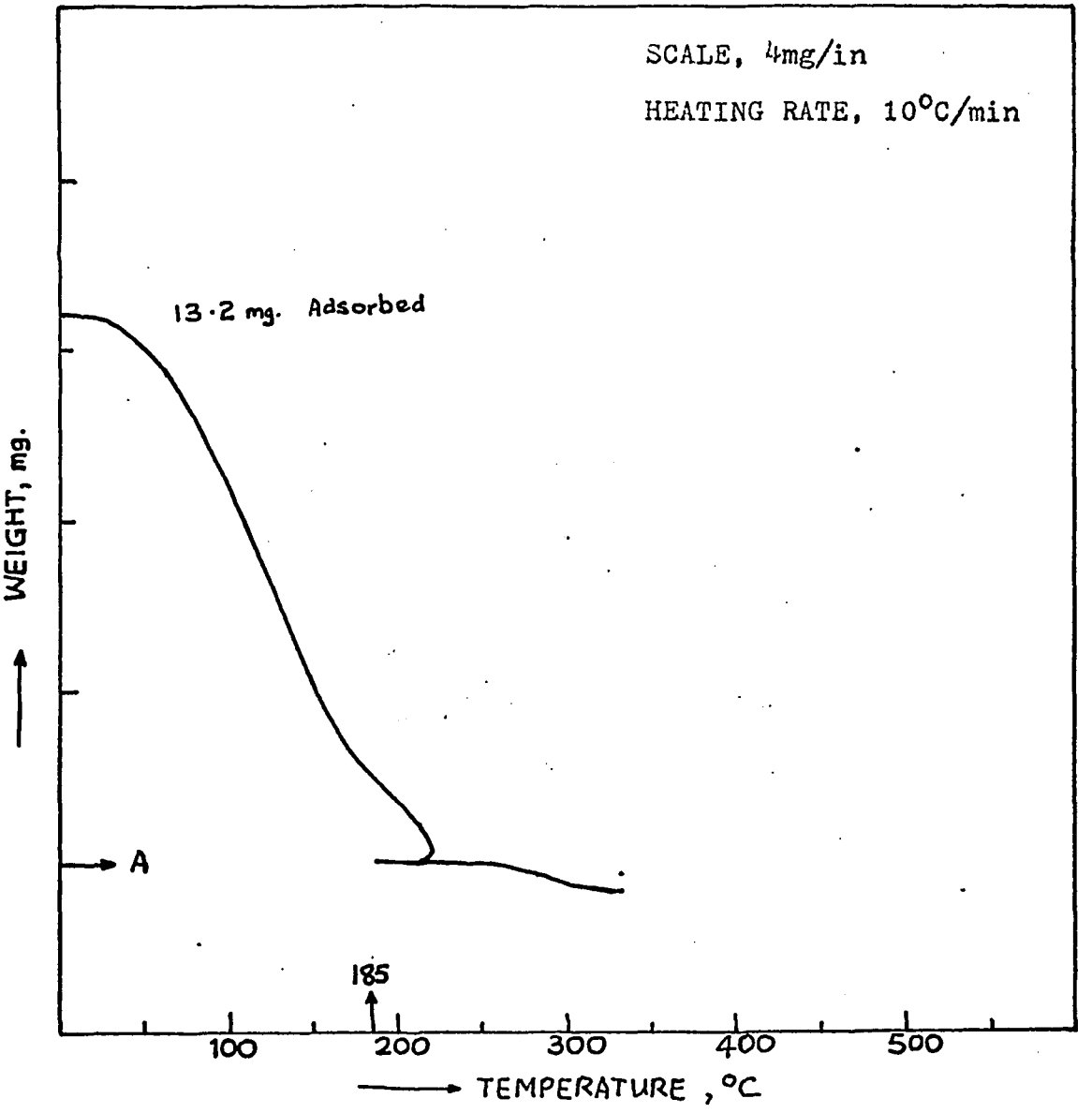


FIGURE 37. TGA Desorption(Oxidation) Curve for MEK Adsorbed on Carbon + V_2O_5/KOH. Point A, is Reference For Complete Removal of Adsorbate.

TABLE XIII

Desorption Data For MEK Adsorbed On Various Catalysts.

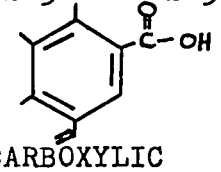
Catalysts	Initial Saturation Level (mg/mg AC)	Residual Wt. Fraction at end of oxidation	% Residual Wt. - Based on initial Wt.
V_2O_5 (1%)	0.268	0.0526	5.26
V_2O_5 (2%)	0.290	0.109	10.9
V_2O_5/KOH	0.295	0.000	0.00
V_2O_5/K_2SO_4	0.293	0.078	7.76
V_2O_5/Cr_2O_3	0.290	0.992	9.23
Pd	0.308	0.111	11.1
Pt	0.304	0.000	0.00
No Catalyst	0.300	0.036	3.60

An Attempt To Explain Observed Results

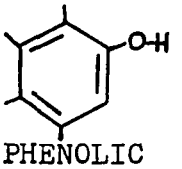
The observed results could be explained by either of two postulates, First we propose that the MEK could be chemisorbed on the catalyst surface, a proposition that is supported by the fact that the amount adsorbed increases with catalyst concentration in the case of V_2O_5. The other proposition is that some type of aldol condensation occurred with vanadia-impregnated carbon, leading to the deposit of polymeric matter.

Aldol condensation is usually acid or base catalyzed but ketones do not often form aldols by self-condensation with bases as catalysts and are generally stable to aqueous alkalies[88]. Acid-catalyzed aldol condensation usually proceed directly to the $\alpha\beta$-unsaturated carbonyl compound, the intermediate β-hydroxy compound having only transitory existence.

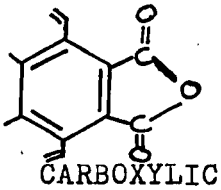
Since the effect of KOH was to prevent the deposit of MEK at the end of the oxidative reaction, acid-catalyzed aldol condensation is postulated. The acidity could be due to V_2O_5 or Cr_2O_3. Also acidic groups, such as



CARBOXYLIC



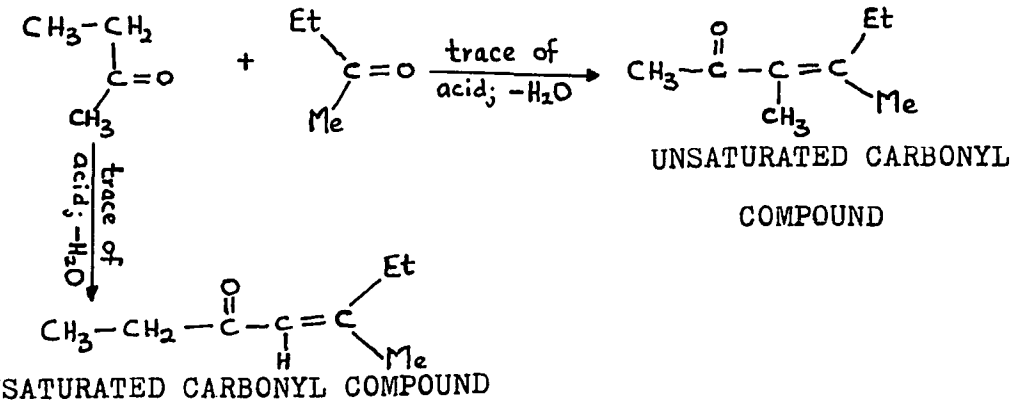
PHENOLIC



CARBOXYLIC ACID ANHYDRIDE.

have been identified on the surface of activated carbon by direct and indirect methods[89]. Each or both groups could then catalyze the reaction. It was observed that with V_2O_5/K_2SO_4 impregnated on the carbon, some MEK was still retained at the end of the oxidation reaction. This seems

to strengthen our proposition that acid-analyzed aldol condensation of MEK is operative. With unimpregnated carbon, about 3.6% of MEK was still adsorbed and this is probably due to chemisorption or formation of polymeric aldol condensation products. These results are shown in Table 13. The expected products from MEK condensation would be:



Oxidation on palladium-impregnated carbon seems to confirm the presence of some polymeric material since the oxidation was maximum at 210°C as shown in Fig. 38.

With Pt-impregnated carbon there was excellent oxidation of MEK to CO_2 and H_2O in the range of 90° to 185°C at a heating rate of 10°C per minute. The oxidation products were detected by gas chromatographic analysis of effluent using a thermal conductivity detector. A DSC curve of platinum-impregnated carbon saturated with MEK is shown in Fig. 39. From TGA analysis we observed complete removal of MEK at the end of the oxidation, indicating no deposit of polymeric matter.

The separation between oxidation of adsorbate and of

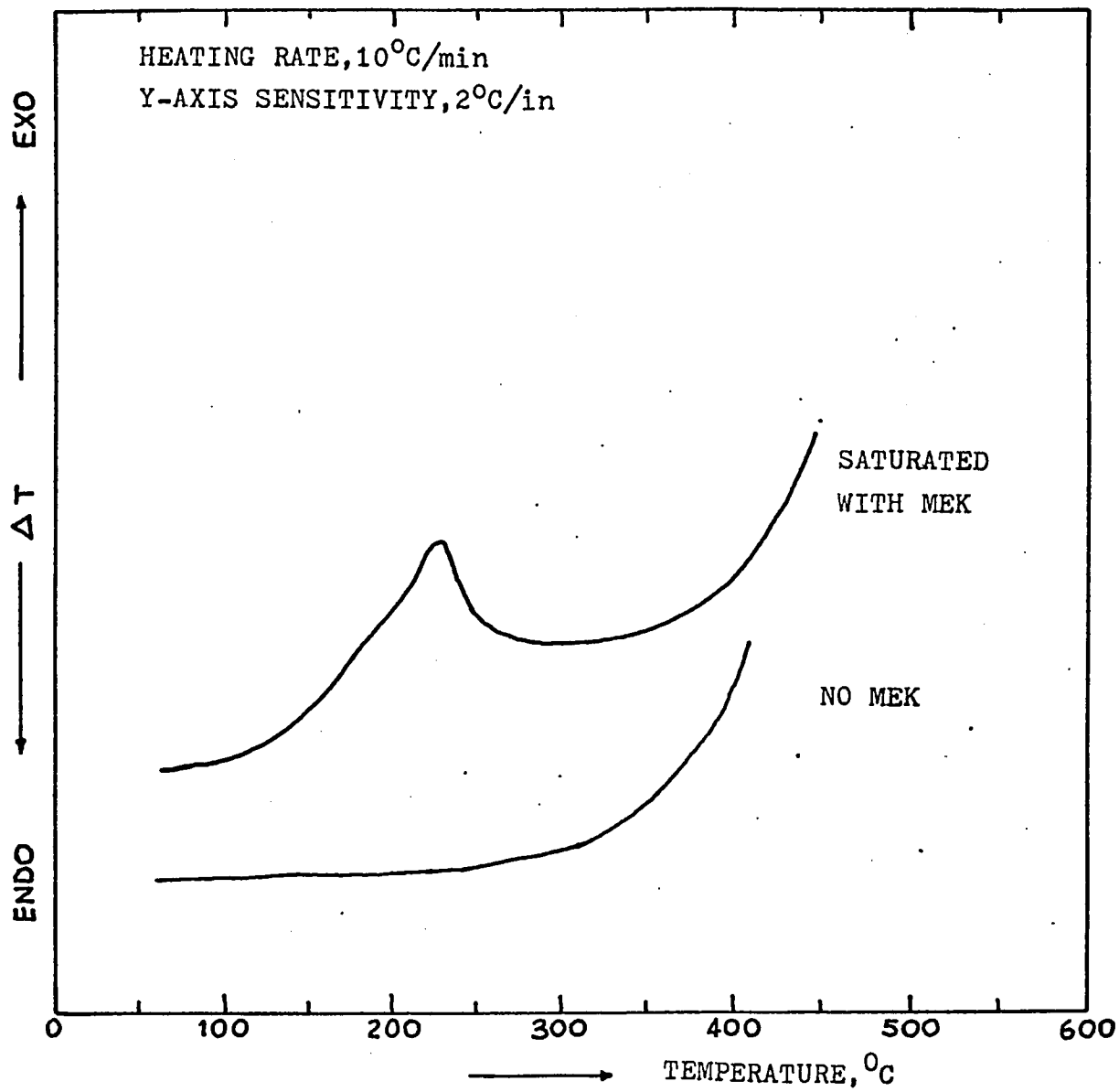


FIGURE 38. DSC Run For MEK Adsorbed On Carbon Impregnated With 0.2% Pd. Atmosphere, Air; Flow Rate, 250°C.

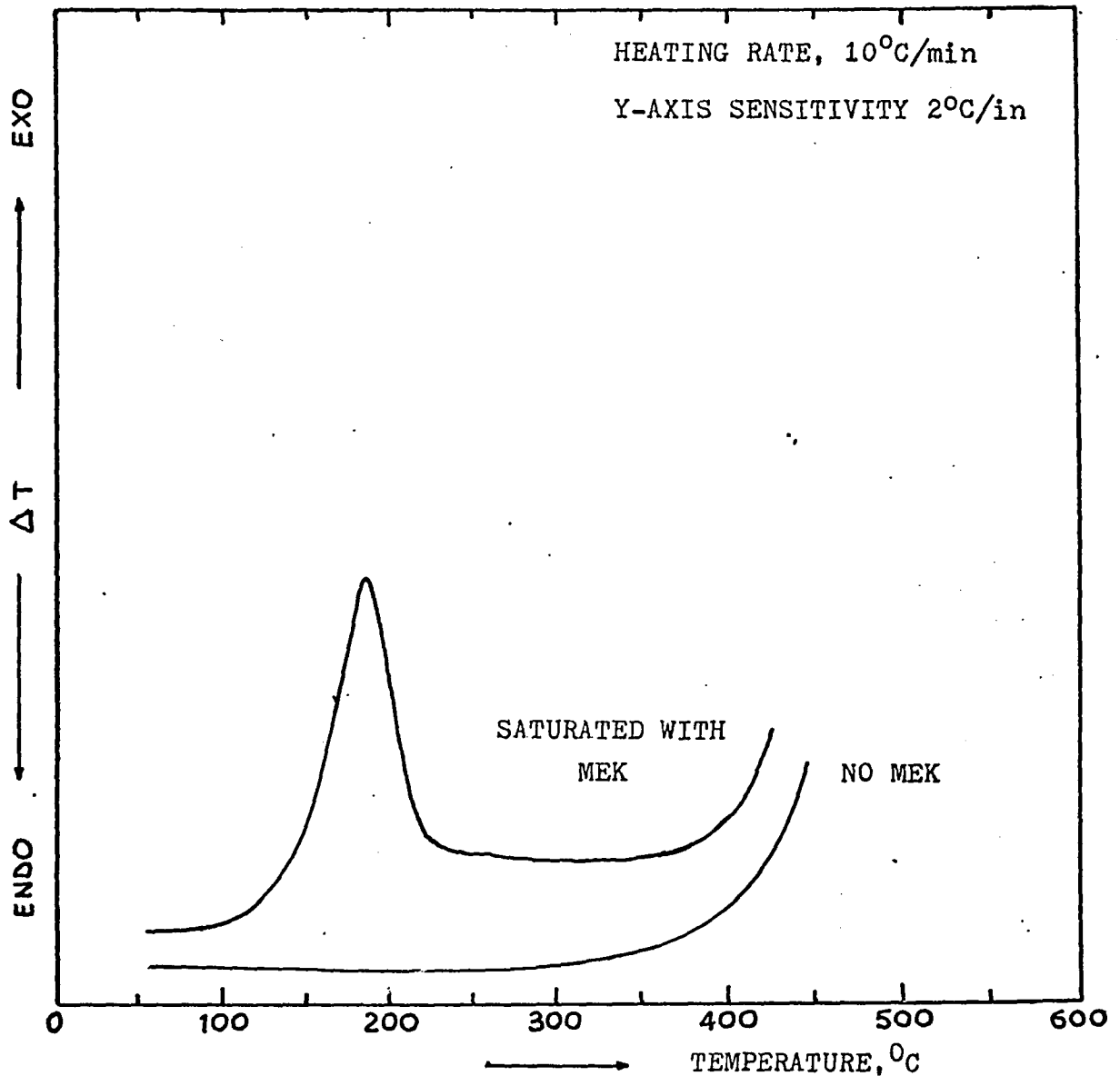


FIGURE 39. DSC Run For MEK Adsorbed On Carbon Impregnated With 0.282% Pt. Air Decomposed and H_2 Reduced at 350°C For 1hr. Flow Rate, 250ml/min; Atmosphere, Air.

carbon for the different catalysts is shown in Tables X, XI, and XIII. The lowest temperature for maximum oxidation was 140°C for carbon impregnated with 2% solution of NH_4VO_3. The minimum temperature at which oxidation commenced was 80°C.

Determination of Activation Energy

Using the method of Amenomiya et al[87], the activation energy for oxidation of MEK on vanadia-impregnated carbon was evaluated as 26.1 kcal/mole. The equation is

$$2 \log T_m - \log\beta = \frac{E}{2.303\ RT} + \log \frac{E\nu_m}{R\ K_o}$$

where, T_m = maximum temperature of oxidation,

β = heating rate (°C/min).

E = Activation energy of Surface Reaction (kcal/mole).

R = Gas constant (1.987 cal/°K mole).

k_o = constant

ν_m = monolayer amount of reactant

We note that $T_m = T_o + \beta t$

where, t is time in sec, and T_o = initial temperature. The assumption in the use of this equation is that the reaction must be a surface reaction and since we are considering in situ oxidation its use here is reasonable. Thecalculated value of 26.1 kcal/mole for E compares favorably with the value of 30 kcal/mole per mole given by Simard et al[90], for V_2O_4-catalyzed oxidation reactions. In fact, the figure they reported was for o-xylene with vanadia supported on silicon carbide.

Esr analysis of the catalyst used in this work indicated the presence of V_2O_4(Part I). For very accurate determination

of activation energy, the temperature program must be varied over a wide range. Using the DSC we only had the capability of going as far as 30°C/min as compared with a rate of 180°C/min used by Amenomiya et al[87]. Fig. 40 shows a plot of 2 log T_m - logβ against $1/T_m$ from which the activation energy was determined; the slope is equal to E/2.303 R.

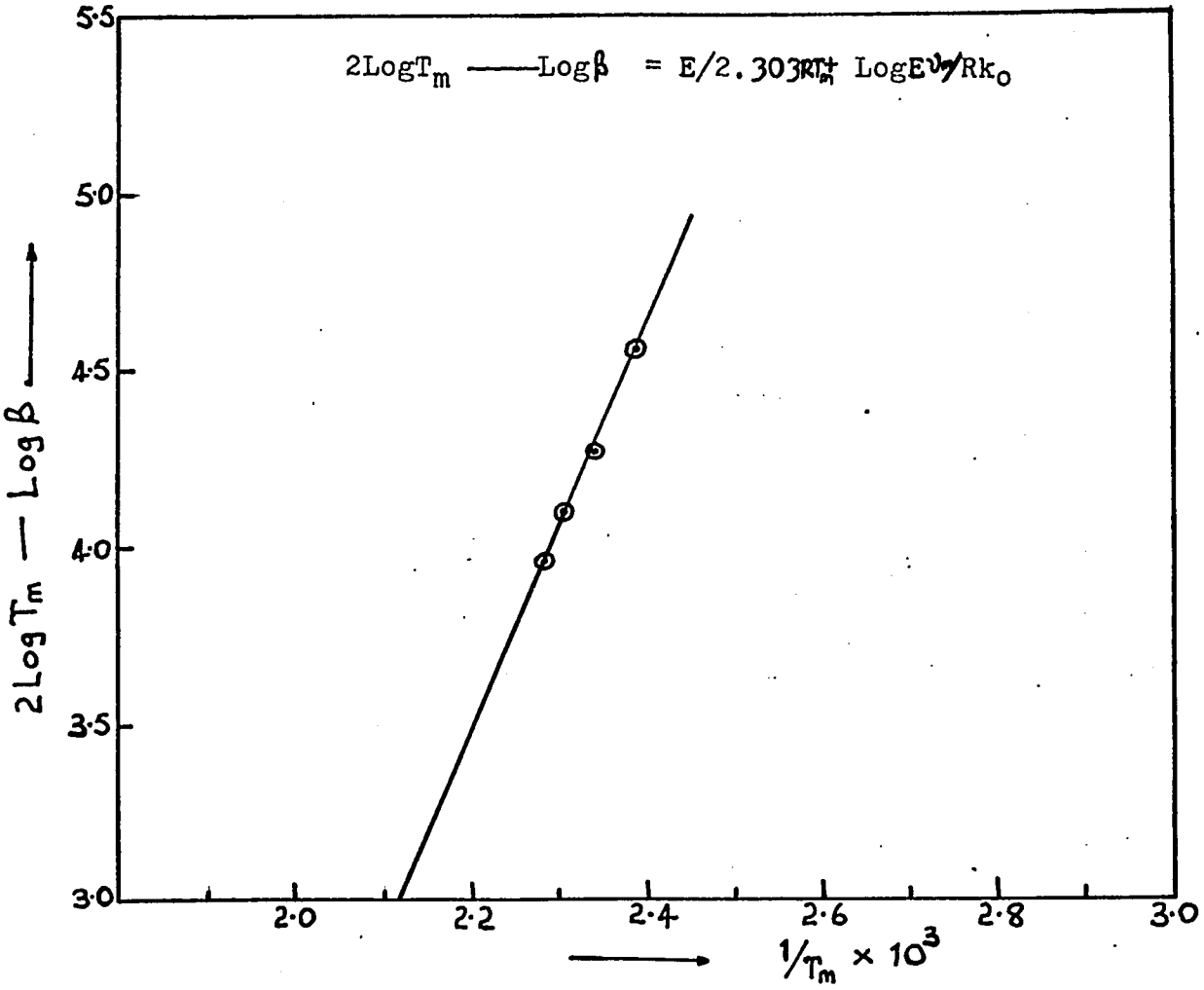


FIGURE 40. Plot Of $2\log T_m$ —— $\log\beta$ V $1/T_m$ For The Determination Of Activation Energy, E, In Oxidation Of Methyl Ethylketone Adsorbed on Carbon Impregnated With 1% NH_4VO_3.

B. Oxidation Of Acrylates.

Method:

Table XIV gives the specifications of the acrylates used. The saturation procedure was as described in Part I, using the set-up of Fig. 2. For methylmethacrylate (MMA) and ethyl acrylate (EA) the bubbler was kept at ice temperature to maintain a low vapor pressure. Ambient temperature was employed for n-butyl acrylate (n-BA).

TGA and DSC analysis were performed on samples using different catalysts as previously described. Emphasis in this section was placed on the separation between oxidation of carbon and of adsorbate. TGA-GC analysis was carried out to confirm oxidation to CO_2 and H_2O as described elsewhere.

A mixture of ethyl acrylate, methyl methacrylate and toluene in the ratio of 1 : 8 : 19 (by weight) was investigated with vanadia-platinum-and palladium-impregnated carbon. In order to ensure that all three components were adsorbed on the carbon about 1 ml of the mixture was taken and the vapor was passed through a bed of catalyst weighing about 2 gm. TGA-DSC determinations were then performed on the saturated sample.

The temperature program was stopped at 400°-$450^{\circ}C$ when all the adsorbed material had been desorbed.

TABLE XIV

Acrylates —— Sources And Specifications

Compound	Manufacturer	Molecular Wt.	Boiling Point	Odor Threshold
Methyl methacrylate	Aldrich Chem. Comp. Inc.	100.12	100°C	100 ppm
Ethyl Acrylate	Celanese Chem. Corp.	100.12	99.8°C	25 ppm
n-Butyl Acrylate	Celanese Chem. Corp.	128.17	145-6°C	-

RESULTS AND DISCUSSION.

Metal Oxides And Metal Catalysts

Figures 41, 42 and 43 show DSC curves for methylmethacrylate, ethylacrylate and n-butyl acrylate oxidation on vanadia-impregnated carbon. For n-butyl acrylate, oxidation commenced at 150°C and was complete at 275°C. Without catalyst there is evidence of oxidative reaction between 160° and 350°C. Methylmethacrylate and ethylacrylate were also oxidized on vanadia within the same range of temperature. The oxidation products detected were CO_2 and H_2O and unoxidized acrylate.

Other metal oxide catalysts, CuO, MnO_2, Co_2O_3 and Cr_2O_3 impregnated on activated carbon were not suitable for oxidizing the acrylates.

Runs on the mixture of methylmethacrylate, ethylacrylate and toluene showed that selective oxidation occurs with V_2O_5. Fig. 44 shows a DSC run on the mixture indicating that oxidation occurs in two distinct regions: 180°-250°C. The first range is due to oxidation of the acrylate and the second corresponds to the oxidation of toluene. It would appear that the heat of oxidation of the acrylates did not contribute enough thermal energy to initiate oxidation of toluene within a lower temperature. However, it should be noted that this could be achieved if the configuration during desorption is altered to that where the air stream flows through a bed of the catalyst instead of over it as was used in this investigation.

With the metal catalysts Pt and Pd, there is evidence of

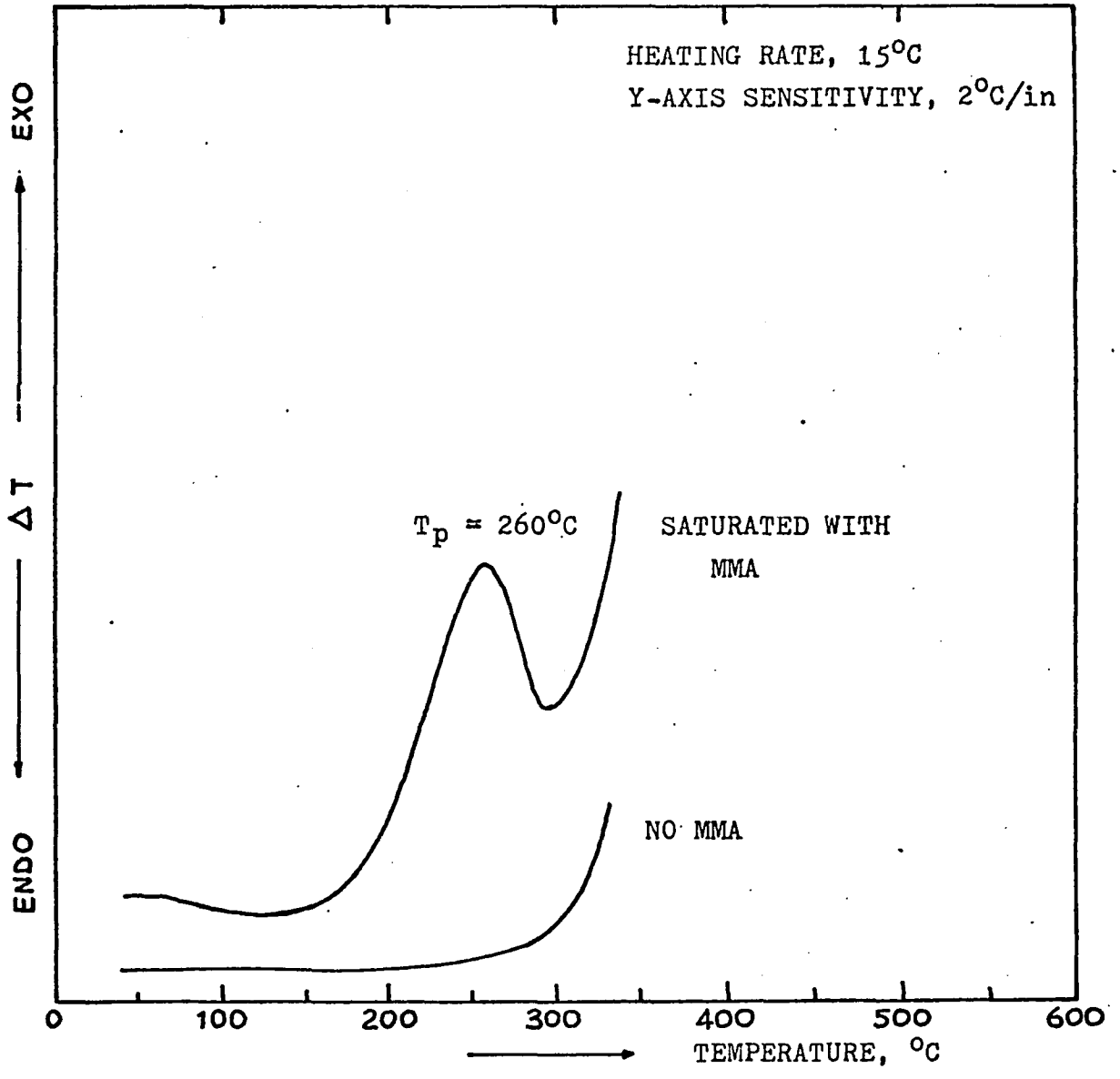


FIGURE 41. DSC Run For Methyl Methacrylate (MMA) Adsorbed On Carbon Impregnated With 1% NH_4VO_3, Air Decomposed at 230°C For 3hrs. Atmosphere, Air; Flow Rate, 250ml/min

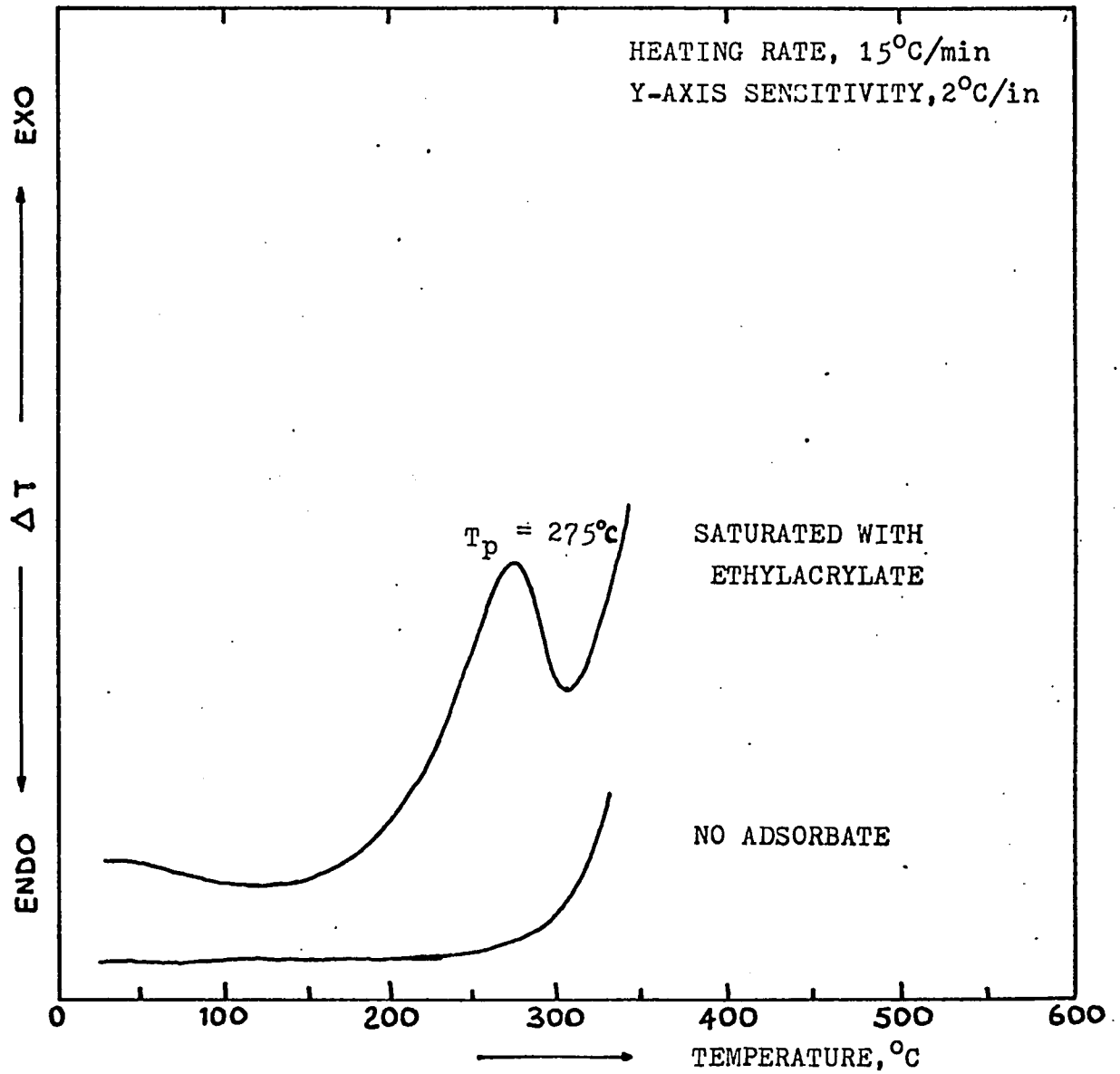


FIGURE 42. DSC Run For Ethylacrylate Adsorbed On Carbon Impregnated With 1% NH_4VO_3, Air Decomposed at 230°C For 3hrs. Atmosphere, Air; Flow Rate, 250°C.

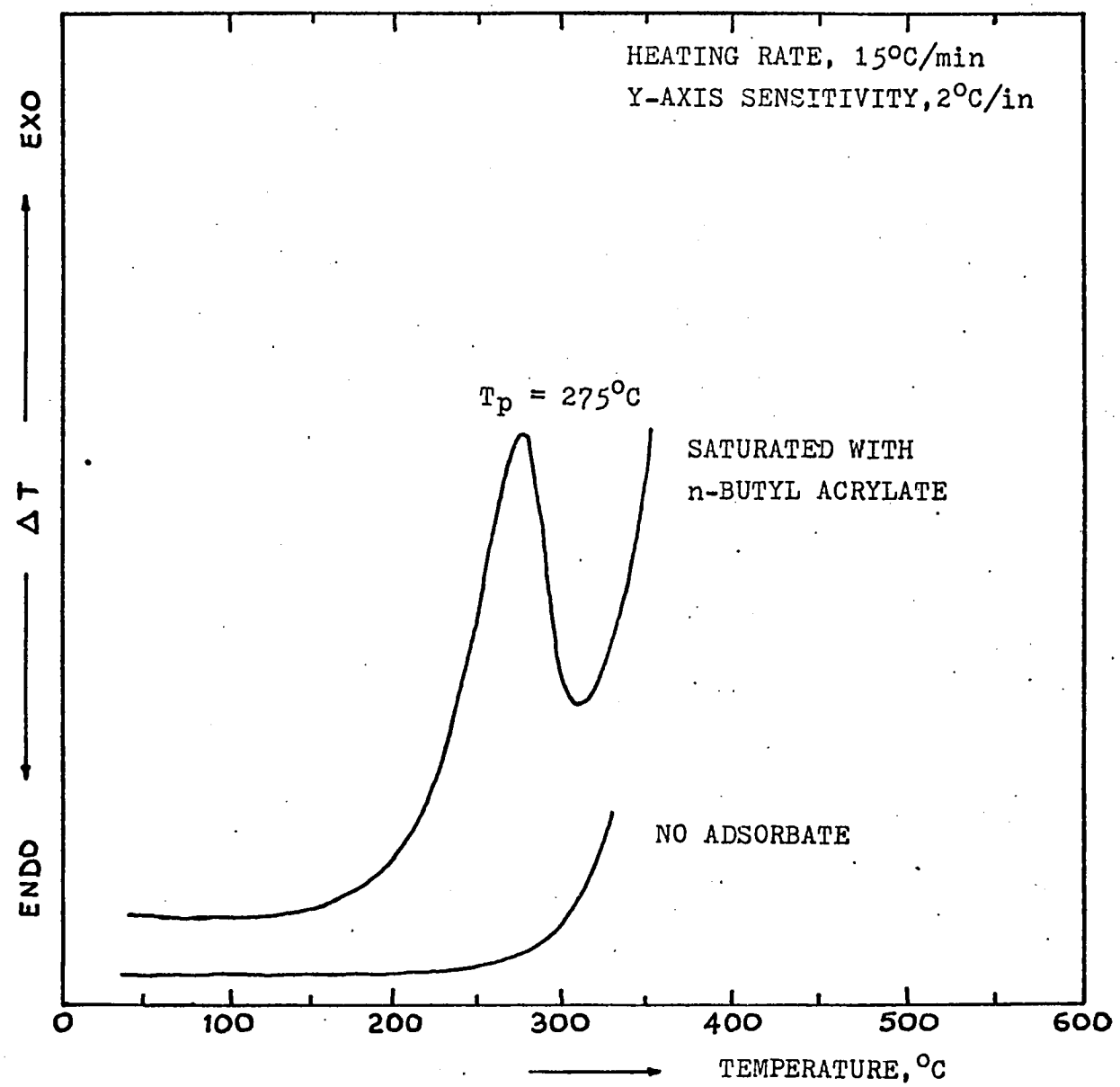


FIGURE 43. DSC Run For n-Butyl Acrylate Adsorbed On Carbon Impregnated With 1% NH_4VO_3, Air Decomposed At 230°C For 3hrs. Atmosphere, Air; Flow Rate, 250°C.

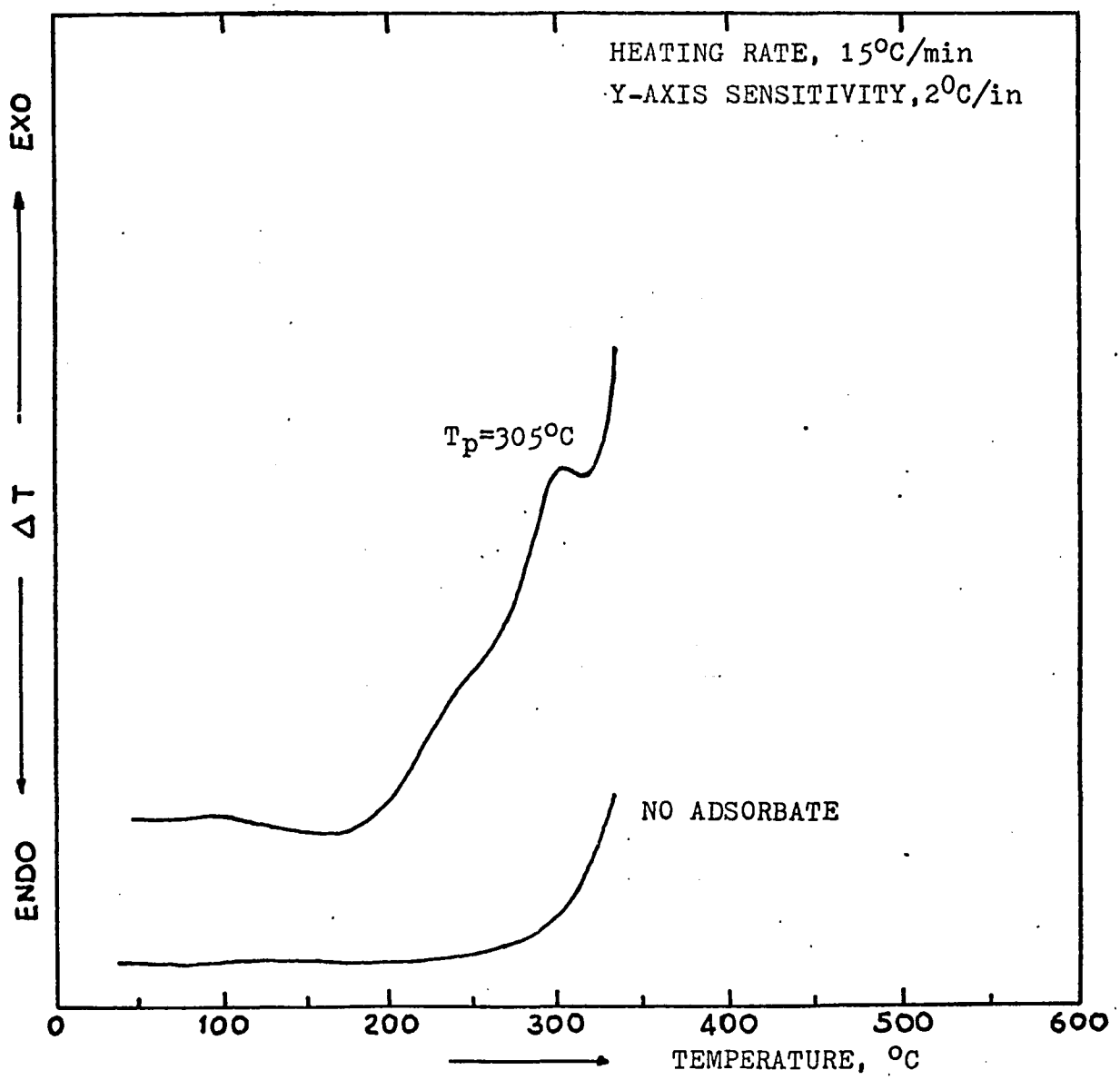


FIGURE 44. DSC Run For a Mixture Of Methyl Methacrylate, Ethylacrylate and Toluene Adsorbed On Carbon Impregnated With 1% NH_4VO_3, Air Decomposed For 3hrs. Atmosphere, Air Flow Rate, 250ml/min.

selective oxidation of adsorbates within 160° to 270°C. Typical results are shown in Figs. 45 and 46 for the DSC of methylmethacrylate adsorbed on Pt- and Pd-impregnated carbon respectively. TGA analysis indicated complete removal of adsorbate at 300°-350°C. Figure 47 shows a DSC run for a mixture of ethylacrylate, methylmethacrylate, and toluene adsorbed on Pt-impregnated carbon. Oxidation occurred between 150°-250°C.

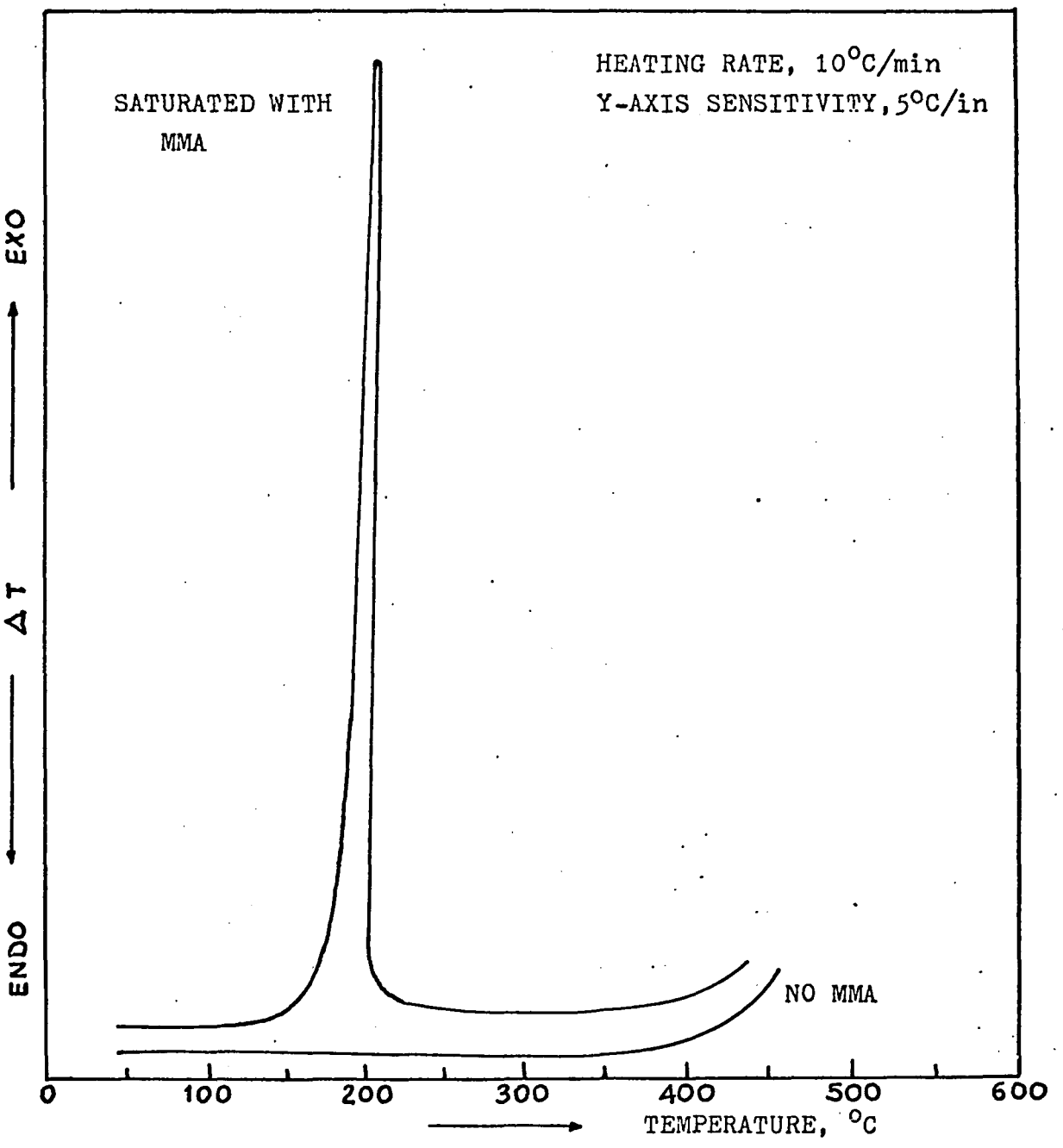


FIGURE 45. DSC Run For Metyl Methacrylate (MMA) Adsorbed On Carbon Impregnated With 0.282% Pt, Air Decomposed and H_2 Reduced at 350°C For 1hr. Atmosphere, Air; Flow Rate, 250ml/min.

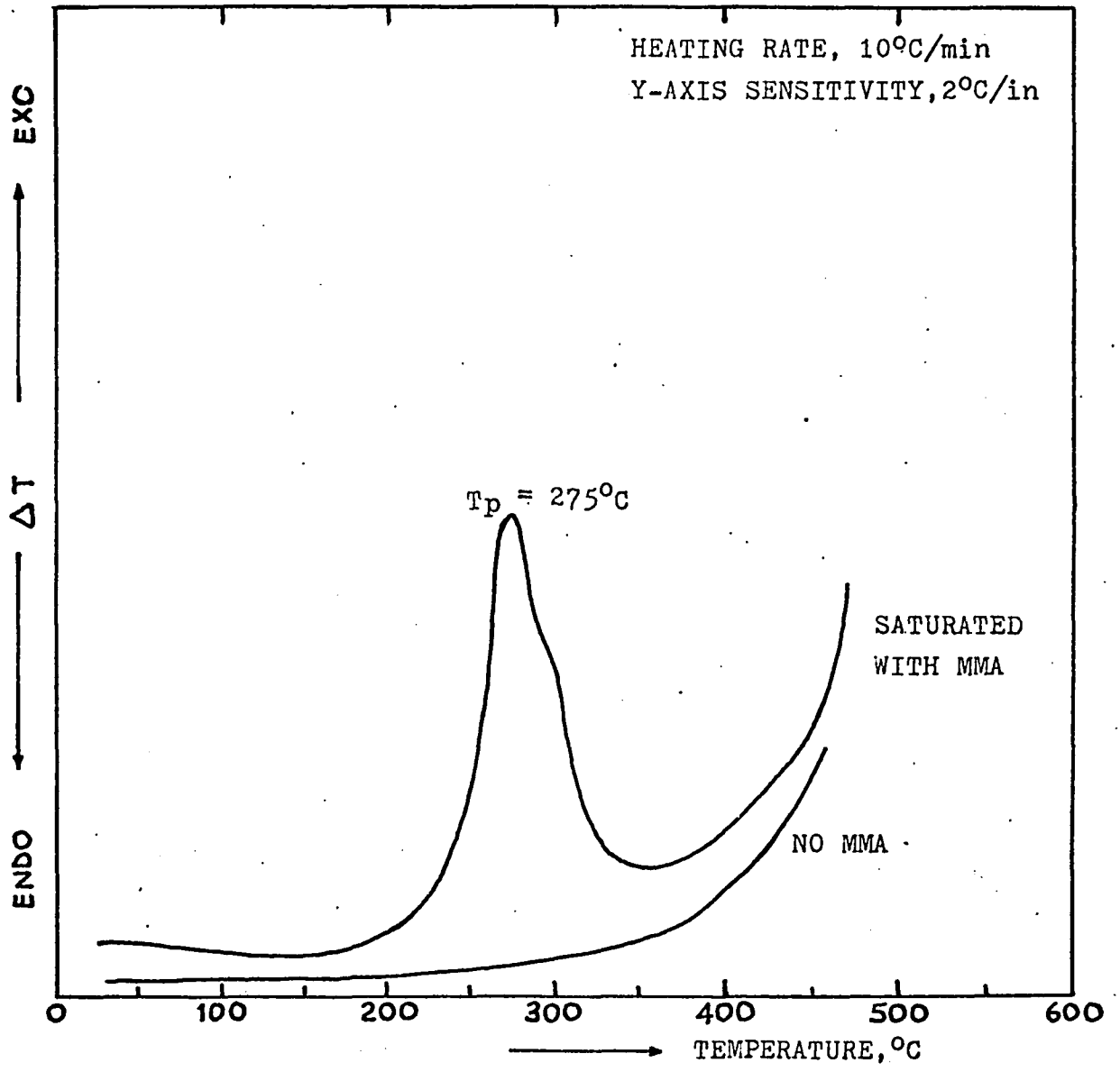


FIGURE 46. DSC Run For Methyl Methacrylate (MMA) Adsorbed On Carbon Impregnated With 0.2% Pd. Atmosphere, Air; Flow Rate, 250ml/min.

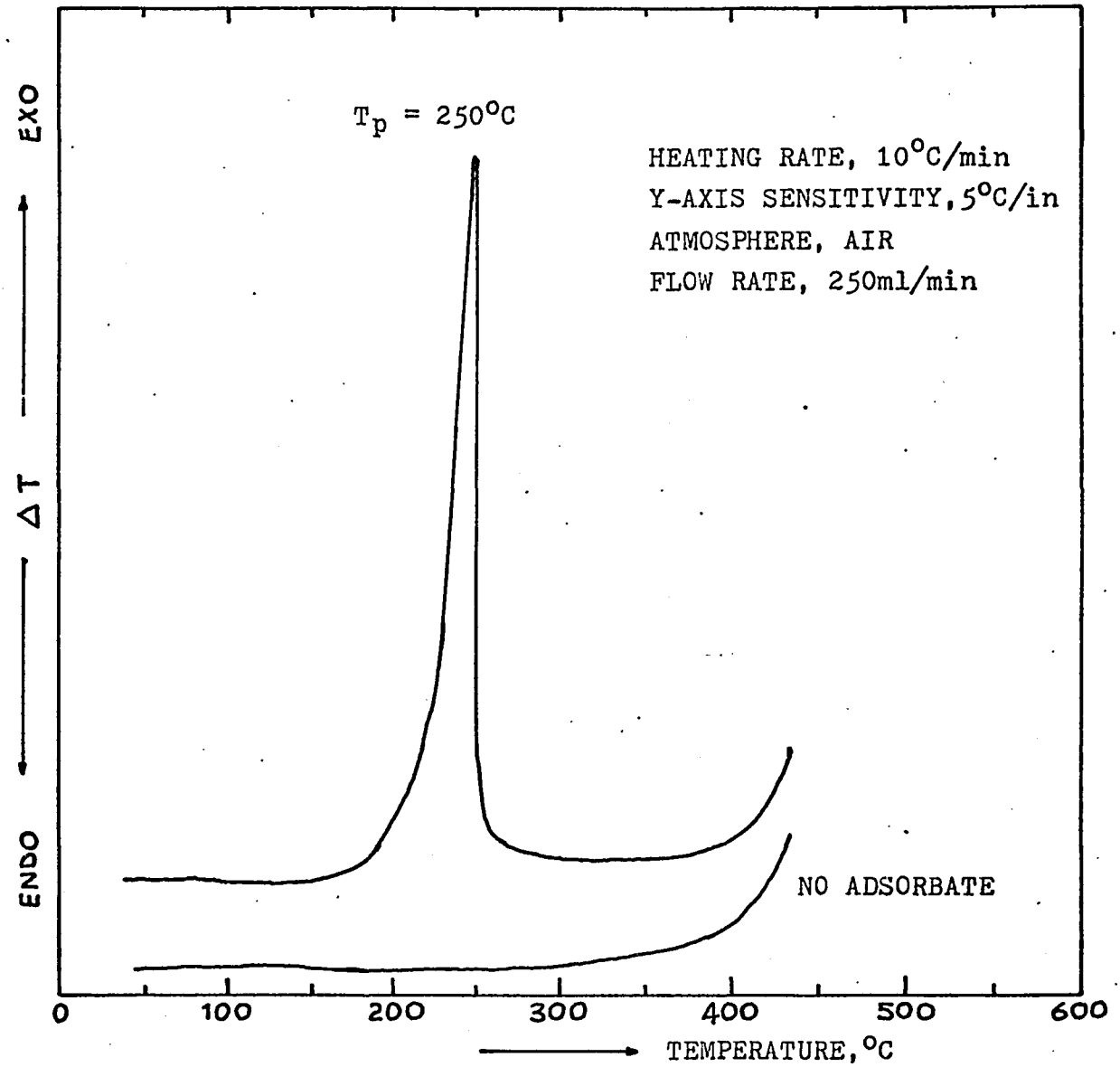


FIGURE 47. DSC Run For a Mixture Of Methyl Methacrylate Ethylacrylate, and Toluene Adsorbed On Carbon Impregnated With 0.282% Pt, Air Decomposed and H_2 Reduced at 350°C For 1hr.

Conclusion.

It has been demonstrated that MEK can be oxidized to non-polluting CO_2 and H_2O on vanadia, platinum and palladium-impregnated activated carbon. Vanadia seems to be the most suitable of the oxides tested although there is a deposit of polymeric matter. This can be prevented by a mixed catalyst containing V_2O_5 and KOH, and this leads to the postulate that the polymerization is acid-catalyzed. Flockhart and Pink[91] had noticed a decrease in polymerization when KOH was added to acid-catalyst which enhanced the reaction.

The general separation achieved between oxidation of adsorbate and the base carbon is about 160°C for vanadia, 150°C for palladium and 200°C for platinum. This is a sure evidence for the selective oxidation of the MEK.

The acrylates, methylmethacrylate, ethylacrylate and n-butyl acrylate can be selectively oxidized on vanadia-impregnated carbon. Gas chromatographic evidence suggests that the oxidation is complete to CO_2 and H_2O. However a substantial amount of the adsorbate is desorbed without oxidation and this would require a cycling adsorption-desorption system.

A mixture of ethylacrylate, methylmathacrylate and toluene is excellently oxidized on palladium-impregnated carbon. Oxidation of adsorbates occur before carbon burn-off. Very interestingly, the carbon mass is not pyrophoric at 400°C, the maximum temperature reached during the oxidation cycle.

PART III

ADSORPTION-REGENERATION STUDIES

INTRODUCTION

In Parts I and II we have considered the evaluation of catalysts for in situ oxidation of pollutants adsorbed on activated carbon. Emphasis was placed on obtaining catalysts that would initiate oxidation of pollutants at low temperatures without oxidizing the base carbon. The temperature difference between oxidation of adsorbate and of carbon adsorbent is therefore of primary importance. Results obtained in Parts I and II show that significant separations are possible in some cases and we now come to a very important section of the present investigation. As stated earlier, the ultimate objective is to develop a cycling adsorption-oxidation system, for the control of pollutants at low concentration. In the concentration range 10 ppm and over, regeneration or reactivation of the activated carbon is an economic necessity in order for the adsorption systems to be competitive with thermal incineration, catalytic incineration, or liquid absorption.

In both water and air purification systems, activated carbon is widely employed in adsorption because of its non-polar nature; organic materials are adsorbed in preference to polar compounds, particularly water. Polar adsorbents, such as silica gel-activated alumina and molecular sieves, are not used because pollutant mixtures invariably contain moisture which would prevent adsorption of organic pollutants. When the carbon is spent it is usually necessary to regenerate it for further use. The

economics of the regeneration process depends on the development of an effective method for the regeneration of the spent carbon with good yield.

Reactivation Of Granular Carbon

Granular carbon has been reactivated on a commercial scale for a number of years and several methods have been used while new techniques are constantly being developed. In solvent recovery applications, low temperature steam is used as regenerating agent because of several desirable properties. Other methods used in the reactivation of carbon are:

1. Thermal regeneration in a kiln.
2. Hot air or inert gas.
3. Vacuum.
4. Vacuum plus heat.

Thermal regeneration is used when the adsorbed material cannot be adequately removed by the other techniques listed. Hot air can be used when the pollutants are to be destroyed in a downstream incinerator or furnace. Vacuum is applicable in conjunction with down-stream recovery equipment. Incineration can also be considered in conjunction with vacuum regeneration schemes. When heat is applied with vacuum higher molecular weight materials are released.

Hot air regeneration in combination with incineration has been reported by Mattia[92]. More recently chemical regeneration of spent carbon has been developed and patented by Maier[93] and by Sontheimer et al[94], who used dimethylformamide

optionally containing 5% HCO_2H to extract organic substances at 150°-3°C.

In some cases reduction at 450°-650°C with hydrogen has been used to regenerate activated carbon[95]. Microwave technique has also been patented by Schnelin and Schumacher[96].

Strongly adsorbed contaminants can be removed from carbon by oxidation at 600° to 700°C in the presence of air or steam. However, a portion of the carbon (3 to 15%) is also oxidized during each regeneration cycle. Turk[8] has reported on catalytic reactivation of the spent carbon in air-purification systems. Data were presented for regenerative studied employing MEK as sorbent. Adsorptive capacity of carbon after four cycles of oxidation was given but there was no report on the state of the catalyst or on the mass changes during repeated cycles of oxidation.

In the present investigation we have evaluated different catalytic systems as possible candidates for applications in an adsorption process. It is shown in Parts I and II that reactivation of spent carbon by <u>in situ</u> oxidation of adsorbed material without affecting the carbon is feasible. Instead of the high temperatures usually encountered in most regeneration systems, oxidation has occurred at a temperature as low as 140°C. Major emphasis in these studies was placed on determining the temperature difference between oxidation of the adsorbed contaminant and that of the base carbon. Non-selective oxidation is preferred, and results have shown that these separations are possible in some cases. A separation of 120°C has been achieved for some pollutants with certain

catalysts. This is significant when we realize that in situ oxidation at high temperatures is extremely difficult to control; the reaction is highly exothermic and run-away oxidation can occur.

Cycling Adsorption-Oxidation System

When hot gas, steam, or vacuum is used for regeneration there is commonly a quantity of residual material left in the carbon. Results from Parts I and II show that with certain catalysts this disadvantage can be offset. The objective of developing a cycling adsorption-oxidation system for the control of air pollutants at low concentration seems to be feasible. The important question that we attempt to answer in this section are:

a. Is there any weight loss or loss in adsorptive capacity of the activated carbon during repeated oxidation cycles on a proven catalyst?

b. Does the catalyst retain its activity during these cycles or is there an irreversible loss in activity?

Saturation capacity is here defined as the total amount of matrial adsorbed on the activated carbon, at the conditions of use. This of course increases with pollutant concentration at a given temperature. From adsorption standpoint, however, the working capacity of the adsorbent is of fundamental importance during regeneration. The difference between saturation capacity and residual capacity is defined as working capacity. Working capacity can differ significantly from saturation capacity in systems where carbon is

regenerated. Joyce et al[97] have found that working capacity is independent of saturation capacity

Attempts have been made by some workers to answer the first question. Olcott[98] has studied the use of regenerable carbon beds for weakly adsorbed contaminants. Regeneration was by vacuum desorption for only a few cycles. Faulkner et al[99] used air for regeneration studies with benzene at a concentration of 150 $\pm$ 10 ppm (vol.per vol.). Degree of regeneration accomplished ranged from a low of 43% to a high of 92%. That is, 43-92% of the saturation capacity was restored. The saturation capacity of the carbon after a high of 25 cycles of oxidation with methylmethacrylate adsorbed on vanadia-impregnated carbon has been determined in this work. Capacities were also determined after 5 to 10 cycles in cases where time was the restraining factor. Catalyst behaviour was monitored by DSC analysis and by esr spectroscopic measurements on samples. The heat of reaction as determined from the area under the DSC curve, was correlated with catalyst activity. Esr spectra were used to determine the oxidation state of the catalyst.

The second question has not been answered anywhere in the literature, for the type of system we are considering. Catalyst behaviour has been monitored in oxidative reactions involving hydrocarbons when catalysts were unsupported on γ-alumina or other inert material. We have data showing the behaviour of catalysts when supported on activated carbon during repeated oxidations. A detailed report of studies

carried out on a cycling adsorption-desorption system has recently been published[100]. The merits and demerits of regenerating spent carbon with steam and non-condensable vapors at elevated temperatures were reviewed. It was suggested that the adsorbed material could be disposed of in a separate unit by catalytic or thermal incineration. There was nothing on *in situ* oxidation of the pollutant; a subject that is our main concern in the present investigation.

EXPERIMENTAL

Method:

Catalysts which proved to be effective in the oxidation of specific pollutants were employed in the regenerative studies. These were V_2O_5, Pt, Pd, and Cr_2O_3. The sorbates used were methylmethacrylate, styrene, toluene and methylethyl ketone. A general procedure for all regenerative runs is herewith described.

A known weight of the impregnated carbon was saturated isothermally at ambient temperature, with the vapor of the pollutant of interest. The method of introduction of the sorbate vapor and the set-up for the analysis have already been described in Part I.

After saturation, the adsorbate was oxidized by passing air at the rate of 300 ml/min. over the sample. The temperature program was set at the rate of 15°C/min during studies with methylmethacrylate using V_2O_5-impregnated carbon, but was set at 10°C/min. in studies involving methylethyl ketone, toluene and styrene. The catalysts were V_2O_5/KOH, Pd, and Pt respectively. The program was stopped when all the adsorbed material had been desorbed, that is when the original weight of the carbon was recovered. In some cases, such as toluene, when it was not possible to recover the original weight even when oxidation was carried up to a temperature as high as 400°C with Pd as catalyst, it was necessary to stop programming at that point.

For methyl methacrylate the saturation-oxidation

cycle was repeated 25 times using the same sample of vanadia-impregnated carbon under identical conditions. The concentration of pollutant in the saturation stream was maintained reasonably constant for effective and more meaningful comparison of saturation capacity.

DSC analysis was carried out on the saturated sample at different stages of the saturation-oxidation cycles in order to monitor the activity of the catalyst with increasing cycles. The heat of reaction was correlated with catalyst activity.

Also esr measurements were carried out on vanadia-impregnated carbon employed during runs with methyl methacrylate and methylethyl ketone. Runs were made on the fresh catalyst and on samples obtained at different stages in the cycling oxidation.

Regeneration of palladium-impregnated carbon was studied using toluene as sorbate, while styrene was employed in regeneration studies involving platinum-impregnated carbon and chromia-impregnated carbon. For V_2O_5/KOH-impregnated carbon MEK was employed. In all these latter studies we could only run 5 to 10 cycles because of the consistraint imposed by the time required for each cycle. A cycle takes about 2 hours on average at a pollutant concentration of over 4,000 ppm (vol/vol.).

RESULTS AND DISCUSSION.

Methylmethacrylate - V_2O_5 System.

DSC runs of carbon impregnated with 1% NH_4VO_3 and saturated once with methylmethacrylate, as well as that of the same sample saturated with methylmethacrylate after 24 oxidations are shown in Figs. 48 and 49. By comparing the areas under the curve, which are directly proportional to the heats of reaction, we conclude that the catalyst activity has decreased considerably after 24 oxidations. The heats of reaction were 293 $\pm$ 6 mcal/mg and 190 $\pm$ 5 mcal/mg respectively.

From TGA analysis it was evident that the carbon has lost 4.08% of its weight after 24 cycles, but the saturation capacity of the carbon did not show very significant variation. The concentration of methylmethacrylate in the saturation stream was kept reasonably constant at 4230 $\pm$ 5 ppm (vol/vol). The TGA data are shown in Table XV. Adsorption curves at various stages of regeneration are shown in Fig. 49(a).

The observed result could be explained by the following arguments. First we note that the method of temperature program required heating the carbon to a temperature well above the maximum temperature necessary for the oxidation of methylmethacrylate. The maximum temperature for oxidation is ascertained from a DSC analysis. One could therefore expect smaller weight loss if oxidation is carried out at or below the temperature where oxidation is maximum.

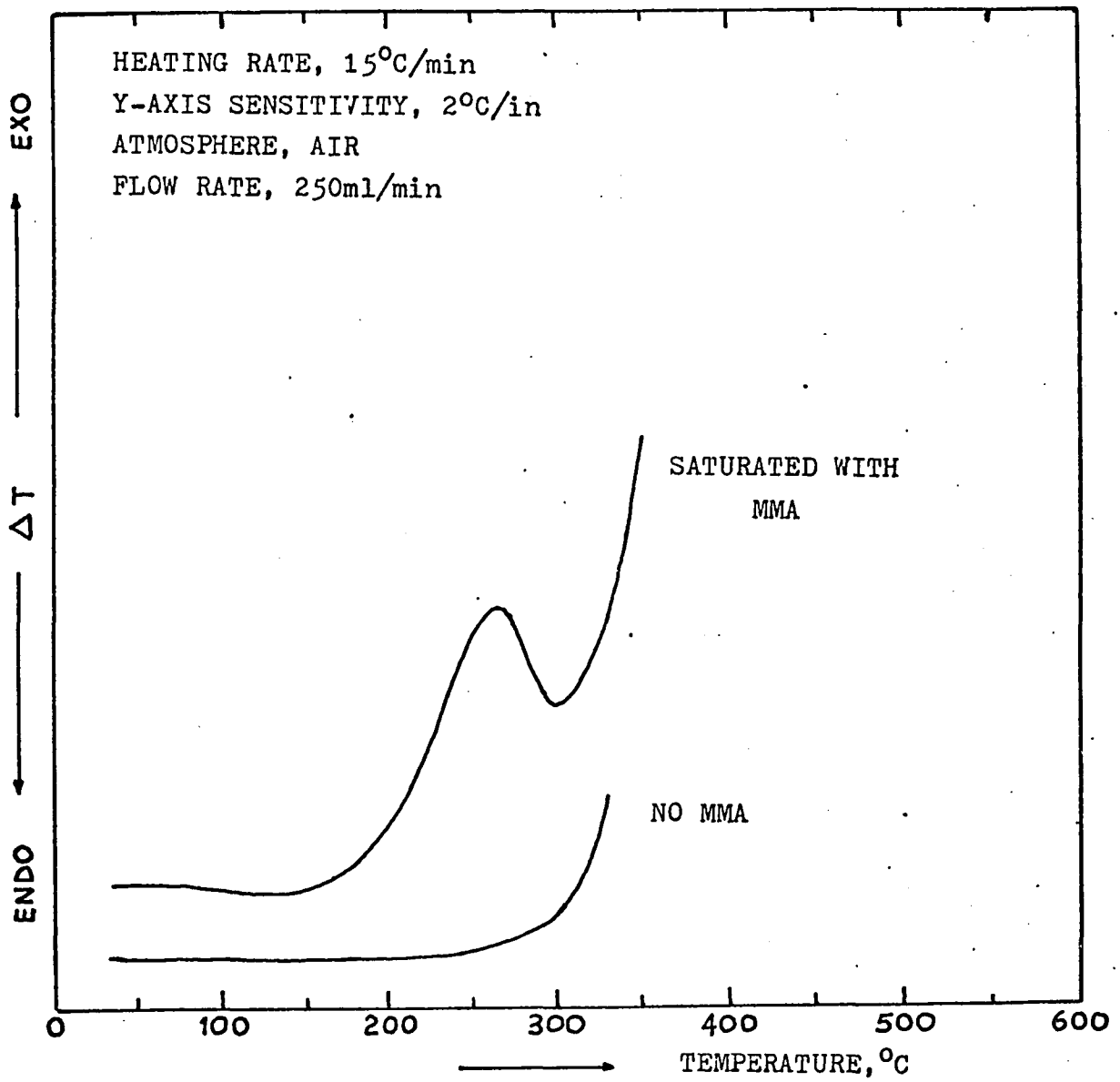


FIGURE 48. DSC Run For Metyl Methacrylate (MMA), Adsorbed On Carbon Impregnated With 1% NH_4VO_3, Prior To Regeneration Cycles.

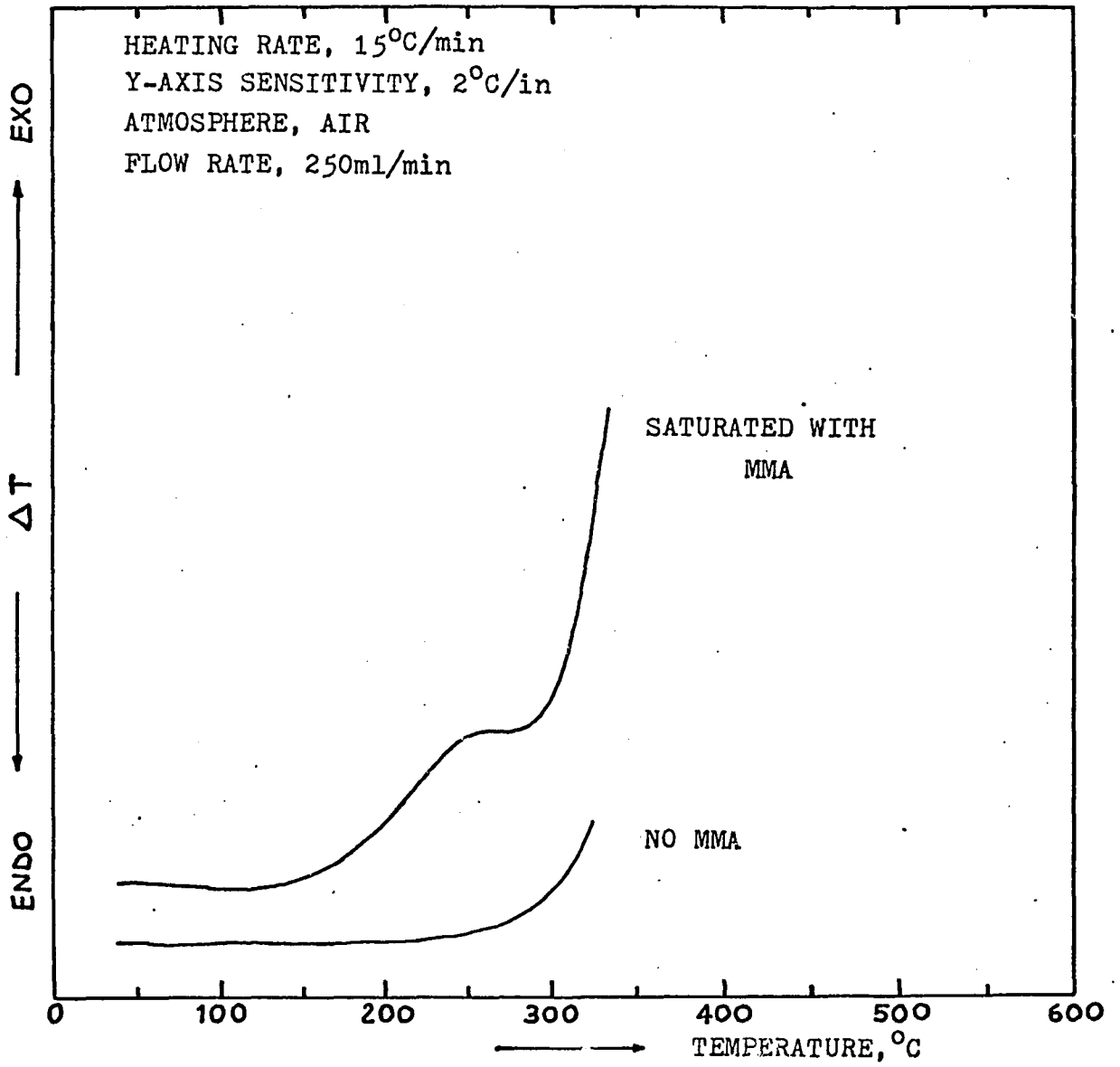


FIGURE 49. DSC Run For Metyl Methacrylate Adsorbed On Carbon Impregnated With 1% NH_4VO_3, After 24 Regenerations.

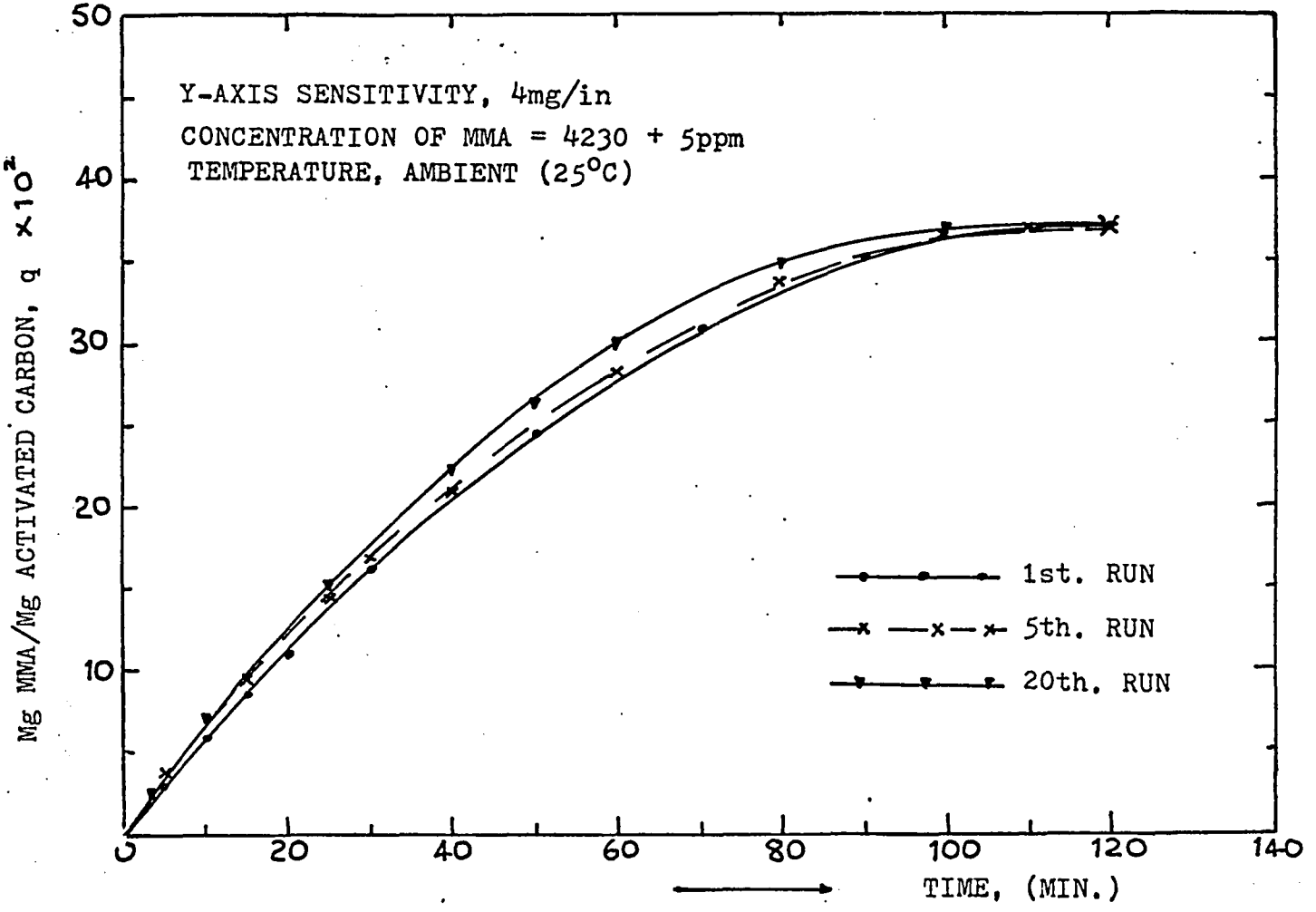


FIGURE 49(a). Adsorption Curves For Carbon Impregnated With 1% NH_4VO_3, At Different Stages Of Regeneration Using MMA as Sorbate.

TABLE XV

Methylmethacrylate Oxidation Data.

Initial weight of activated carbon.....46.5 mg.

Temperature of adsorption.....25°C.

Concentration of methylmethacrylate in N_2 stream...4,230 ± 5 ppm.

Run N°	Saturation Capacity (mg/mg AC)	Total Weight lost after oxidation (320°C)
1	0.370	0.3
5	0.372	0.3
10	0.372	1.0
20	0.371	1.9
24	0.363	1.9
25	0.355	1.9

Sintering And Change In Oxidation State.

The decrease in catalyst activity after several cycling oxidations could possibly be due to sintering of the catalyst. The surface area of a catalyst decreases during use so that there is an irreversible loss in activity which occurs more rapidly the higher the catalyst temperature. A promoter usually helps to suppress surface changes in the catalyst.

One other reason that could account for the observed decrease in catalyst activity is that a change in the oxidation state occurred by the following reactions,

$$2\ V_2O_5 + C \longrightarrow 2\ V_2O_4 + CO_2 \qquad (1)$$

$$V_2O_5 + C \longrightarrow V_2O_3 + CO_2 \qquad (2)$$

Esr measurements could be used to determine which reaction is favored under the conditions of the experiment. Reaction(2) is expected to yield no signal at ordinary temperatures for V_2O_3[101], and reaction (1) should give a signal characteristic of V_2O_4. Fig. 50 shows the initial esr signal for vanadia-impregnated carbon decomposed at 230°C for 12 hours and Fig. 51 shows esr signal of the same sample after 24 cycling oxidations using methylmethacrylate as sorbate. The enhanced signal intensity in Fig. 51 is due to conversion of V_2O_5 to V_2O_4 as indicated in reaction (1). The eight-line hyperfine splitting is due to V_2O_4[102]. In some heterogenous oxidations catalyzed by metal oxides, it is believed that there is a redox cycle in which the hydrocarbon reacts with the oxide ions in the catalyst lattice which are then replaced by the reduced

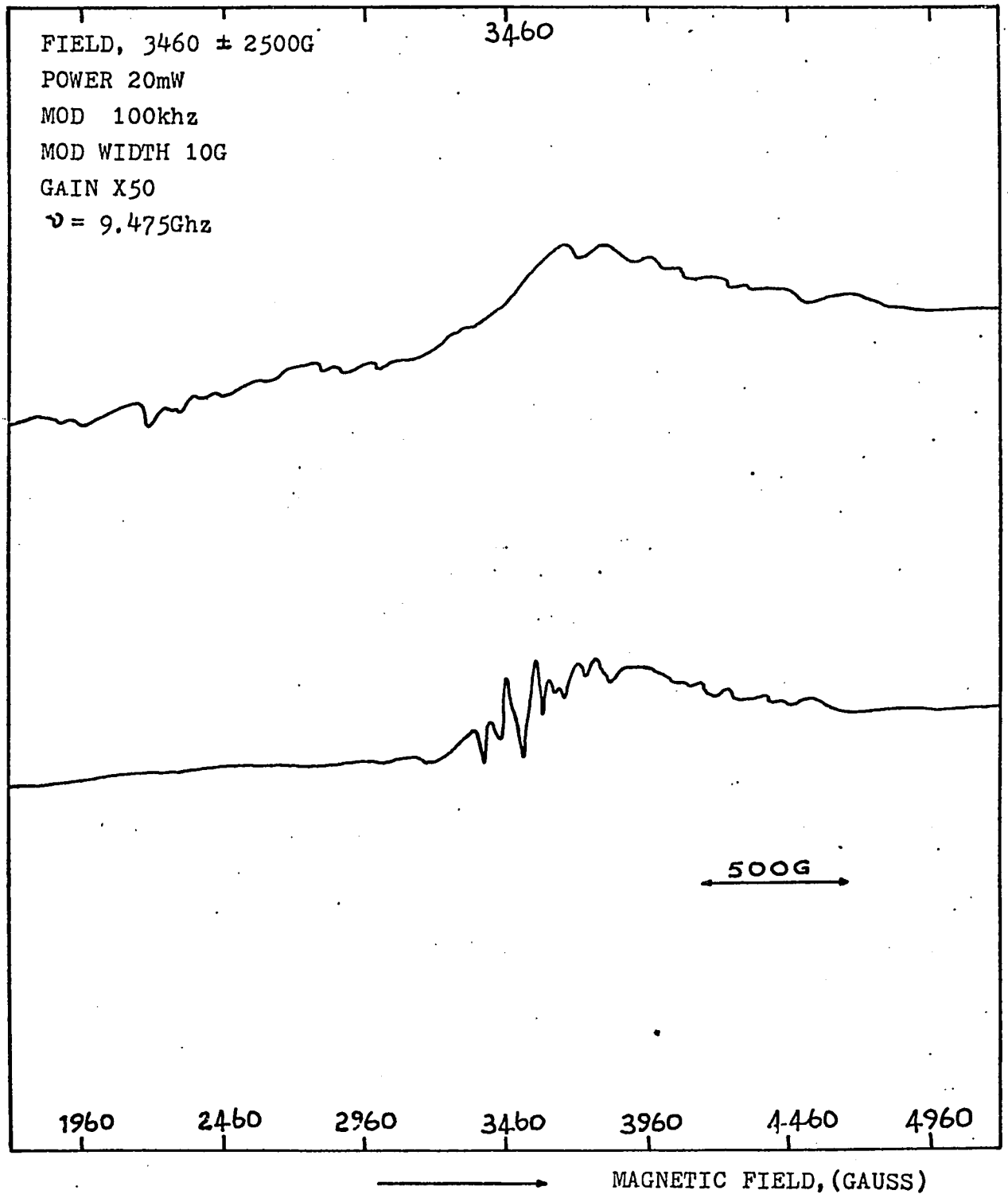


FIGURE 50. Esr Spectrum Of Carbon Impregnated With 1% NH_4VO_3, Prior To Regeneration.

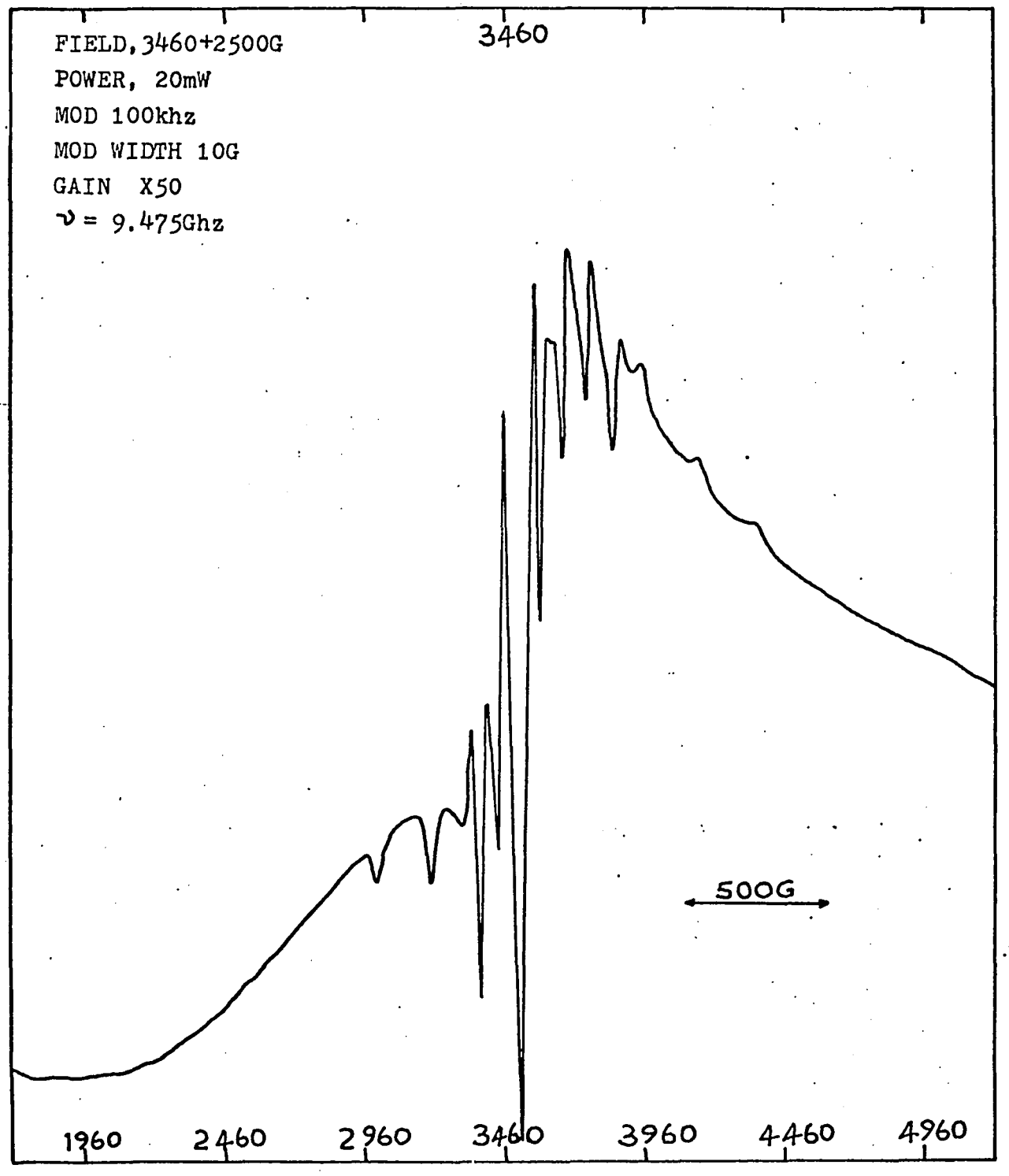


FIGURE 51. Esr Spectrum Of Carbon + 1% NH_4VO_3, After 24 cycles Of Oxidation On The same Sample.

catalyst reacting with gaseous oxygen:

$$RH \longrightarrow RH^{+}(ads) + e$$

$$RH^{+}(ads)^{+}\ O^{2-} \longrightarrow \text{Products} + e$$

$$\tfrac{1}{2}O_2 + 2e \longrightarrow O^{2-}(ads)$$

This type of reaction does not seem to be occurring in the cycling oxidation of methylmethacrylate on vanadia-impregnated carbon because of the enhanced esr signal for V_2O_4. Reduction of V_2O_5 to V_2O_4 appears to be operative.

One important consideration regarding the chemical nature of a catalyst is that its physico-chemical properties should not change as it is used. In some cases the valency states of a metal oxide are changed when it is used as a catalyst for hydrocarbon oxidation. Reduction to a lower oxide-producing a change in the equilibrum unit cell size-is sometimes particularly rapid when fuel-rich mixtures are used. Simard *et al*[63] and Iofle and co-workers[102b] have observed the conversion of V(V) to V(IV) during oxidation of hydrocarbons. Activity of V_2O_5 was attributed to equilibration between V_2O_5 and V_2O_4 to yield defect structures in the crystal lattice. Loss in activity in the present investigation after several cycles of oxidation on vanadia-impregnated carbon is therefore due to a preponderance cf V_2O_4.

We could also attribute the loss in activity to deposition of polymeric matter on active catalyst surface. If this is the case, activity could be restored by treatment of the spent carbon with steam.

Free Electrons Participation.

Finally, we note that activated carbon has free electrons on its surface as demonstrated by esr measurements by Harker et al[103,104].

The electrons would be expected to participate in donor-acceptor complex formation and this has been experimentally verified by Harker et al[104] for the adsorption of NO_2 on active carbon. The adsorption closely follows the trend of the concentration of unpaired electrons in the carbon. Consequently if free electrons participated in the oxidation of methylmethacrylate on vanadia-impregnated carbon, there could be a loss of free electrons. The carbon could still retain its adsorptive capacity but its catalytic role would be diminished. Catalytic oxidative reactions are known to proceed by a free radical mechanism and the formation of free radicals may require free electrons on the carbon surface. A decrease in free electrons has been observed when activated carbon was treated with oxygen at 250°C for 30 minutes[104]. Siedlewski[105] has thoroughly investigated the role of free radicals in the oxidation of SO_2 to SO_3 on activated carbon. Samples of carbon characterized by the strongest signal in the resonance spectrum have the maximum catalytic activity. The process of catalytic oxidation therefore occurs with the participation of free radicals.

In this study, we have carried out 25 oxidations for a total period of 500 minutes, on the same carbon sample. This would be expected to lead to a decrease in free electrons and hence of catalytic activity.

Styrene-Chromia System.

Data from runs on chromia-impregnated carbon using styrene as sorbate, showed that the initial saturation capacity of 0.26 mg styrene per mg activated carbon decreased to 0.12 mg styrene per mg activated carbon after one regeneration. This implies a decrease in working capacity of 55% and no further runs were made after the second saturation-oxidation cycle. The conclusion is that the deposit of polymeric matter and/or chemisorption must be avoided if an efficient system is to be set up. That this is so is implicit in the result obtained with a styrene-platinum system.

Styrene-Platinum System.

Data for regenerative studies on platinum-impregnated carbon, using styrene as sorbate are presented in Table XVI. The initial saturation capacity of 36.8% at a styrene concentration of 8700 $\pm$ 140 ppm (vol/vol) had decreased to 34.2% after six oxidations on the same sample at the same concentration. Saturation capacity was previously defined as the total weight increase at saturation based on the initial weight of impregnated carbon. The working capacity of the carbon is 88% of the initial value (100%) after 6 cycles of oxidations, where working capacity is defined as the saturation capacity minus the residual capacity. The decrease in working capacity is probably due to chemisorption of oxygen on the carbon or on the catalyst surface leading to the formation of the metal oxide. In fact it has been observed that metal catalysts, like nickel and platinum, become covered with transient layers of the corresponding oxide during oxidative reactions[106].

TGA data indicate a net increase in weight of the carbon by 3.4% at the end of the 6 cycles but this is not due to deposition of polymeric matter since all the styrene adsorbed was shown to be completely desorbed at the end of the oxidation. The temperature of complete desorption was 310°C, although DSC analysis indicated that oxidation of styrene was maximum at 280°C. Oxidation of carbon begins at 380°C, which gives a separation of 100°C.

Fig. 52,53 show DSC curves for oxidation of styrene

TABLE XVI

Styrene Oxidation Data

Initial weight of impregnated activated carbon	41.0 mg
Concentration of styrene in N_2 stream	8700 ± 140 ppm.
Temperature of adsorption	25°C

Run N°	Saturation Capacity (mg/mg AC).	Working Capacity (1%)	Total weight lost after oxidation (310°C)
1	0.368	100.0	0
2	0.340	96.5	0
3	0.335	92.5	+ 0.4
4	0.325	91.0	+ 0.2
5	0.346	89.7	+ 1.2
6	0.342	88.0	+ 1.4

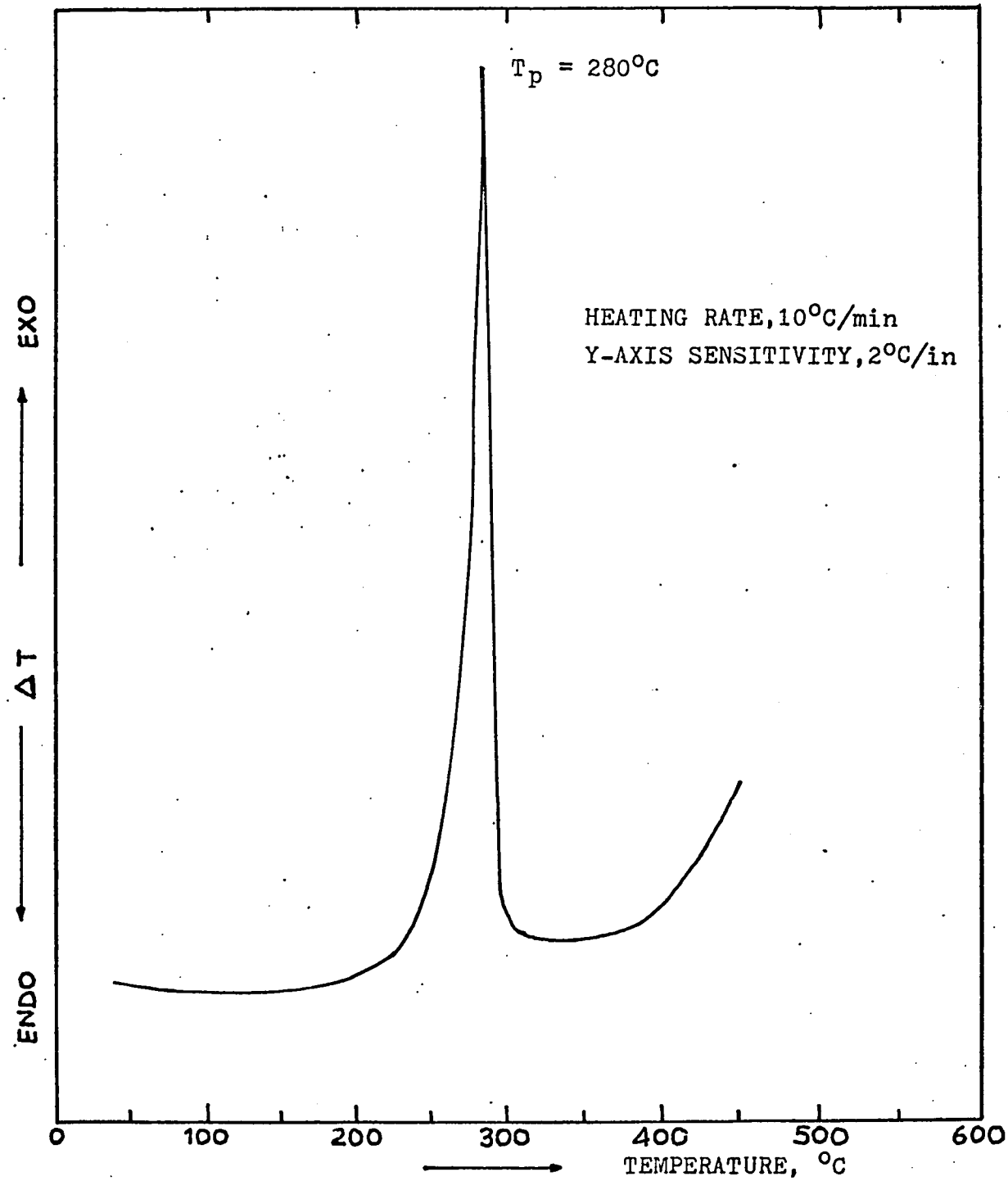


FIGURE 52. DSC Run For Styrene Adsorbed On Carbon Impregnated With 0.282% Pt Prior To Regeneration Cycles. Atmosphere, Air Flow Rate, 250ml/min

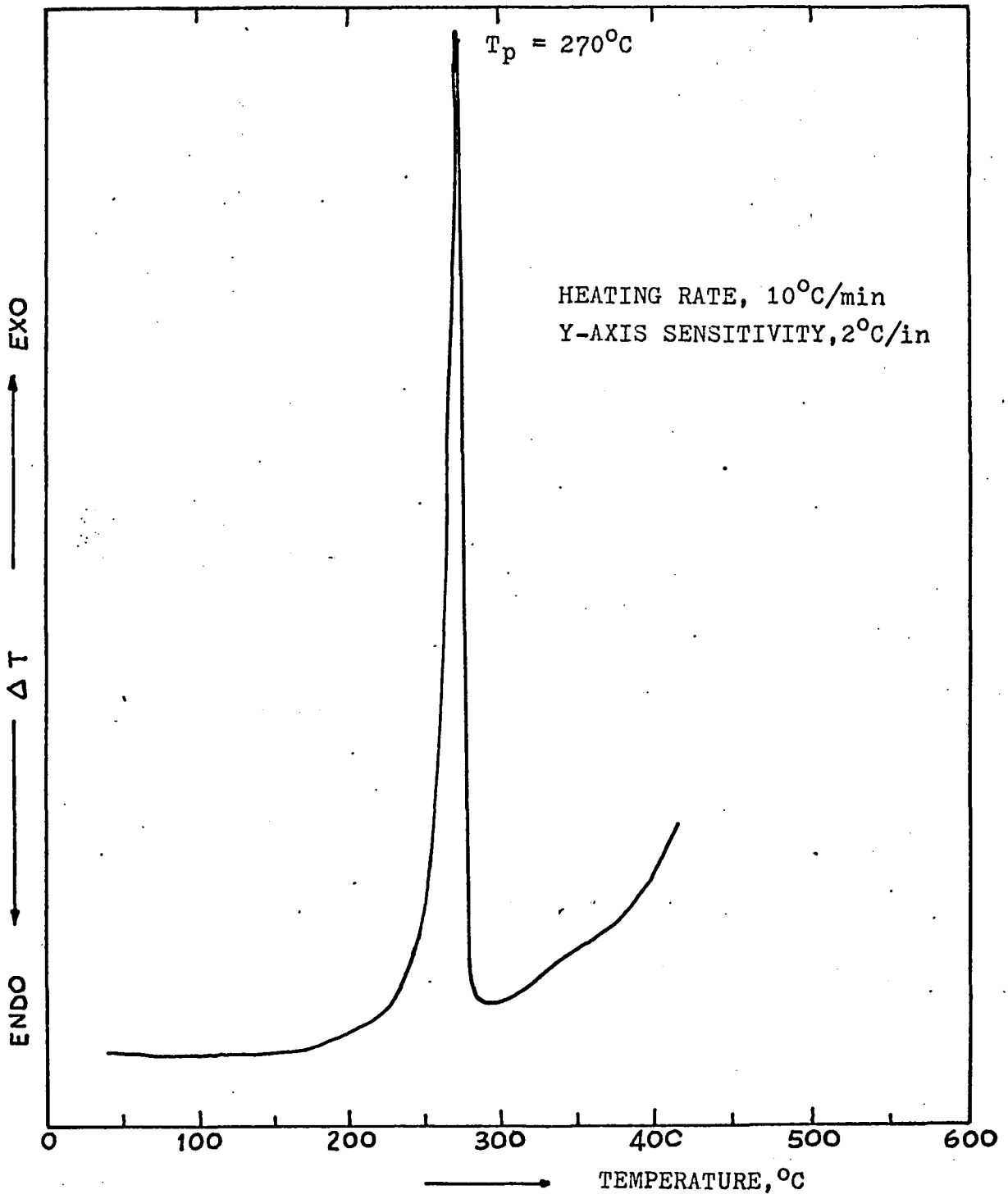


FIGURE 53. DSC RUN For Styrene Adsorbed On Carbon Impregnated With 0.282% Pt After Six (6) Regenerations. Atmosphere, Air Flow Rate, 250ml/min.

adsorbed on a fresh sample of platinum-impregnated carbon and of styrene adsorbed on the sample after 6 repeated cycles, respectively. We observe that the catalyst is still very active after 6 repeated oxidations. The respective heats of reaction are 830 $\pm$ 4 mcal/mg and 834 $\pm$ 8 mcal/mg respectively as determined from the areas under the curve. This behaviour is contrary to the result obtained with vanadia-impregnated carbon and chromia-impregnated carbon, where in the latter case activity seems to have been inhibited by polymerization and/or chemisorption of styrene. It would appear that the platinum catalyst is being continuously activated by the repeated cycles. Poisoning has not occurred.

Toluene-Palladium System.

In the regenerative runs involving toluene on palladium-impregnated carbon, the catalyst activity deteriorated after 9 cycles. This is illustrated in Figs 54 and 55 in which are given the initial DSC run on the fresh palladium-impregnated carbon saturated with toluene and a DSC run on the same sample saturated with toluene after 10 repeated oxidations. The area under the curve is proportional to the heat of reaction which is an index of catalyst activity. There is a trend towards a decreasing saturation capacity of the carbon with increasing cycles of oxidation. Table XVIII shows that the adsorptive capacity decreased by 4.8% after 9 cycles, probably as a result of incomplete toluene burn-off, but there is no net loss in weight of the carbon sample, even though the temperature program was stopped at 420°C. The trend towards a decreasing saturation capacity with increasing number of oxidations is depicted in Fig. 56, where we have plotted mg toluene adsorbed per milligram activated carbon against time.

Elovich Equation.

The widely employed Elovich equation[107,108] could also be used to show the adsorption characteristic of an activated carbon sample during a regenerative adsorption-oxidation process.

TABLE XVII

Toluene Oxidation Data

Initial weight of carbon	53,2 mg.
Concentration of toluene in N_2 stream	5,300 ppm
Temperature on adsorption	25°C

Run N°	Saturation Capacity (mg/mg AC)	Total Weight lost after oxidation (420°C)
1	0.339	0
4	0.310	+ 0.8
7	0.303	0
9	0.291	0
10	0.281	0

This equation is given as:

$$\frac{dq}{dt} = a \exp (- \alpha q)$$

where, q = amount of pollutant adsorbed at time t,

and a and α are coefficients which are dependent on temperature and concentration. The integrated form is

$$q = \frac{2.3}{\alpha} \log (t + t_o) - \frac{2.3}{\alpha} \log t_o$$

where $t_o = \frac{1}{a\alpha}$, an integration constant. When $t >> t_o$, this equation reduces to,

$$q = \frac{2.3}{\alpha} \log t - \frac{2.3}{\alpha} \log t_o$$

However, the regeneration data for repeated cycles indicate that a slight increase in regeneration temperature may be

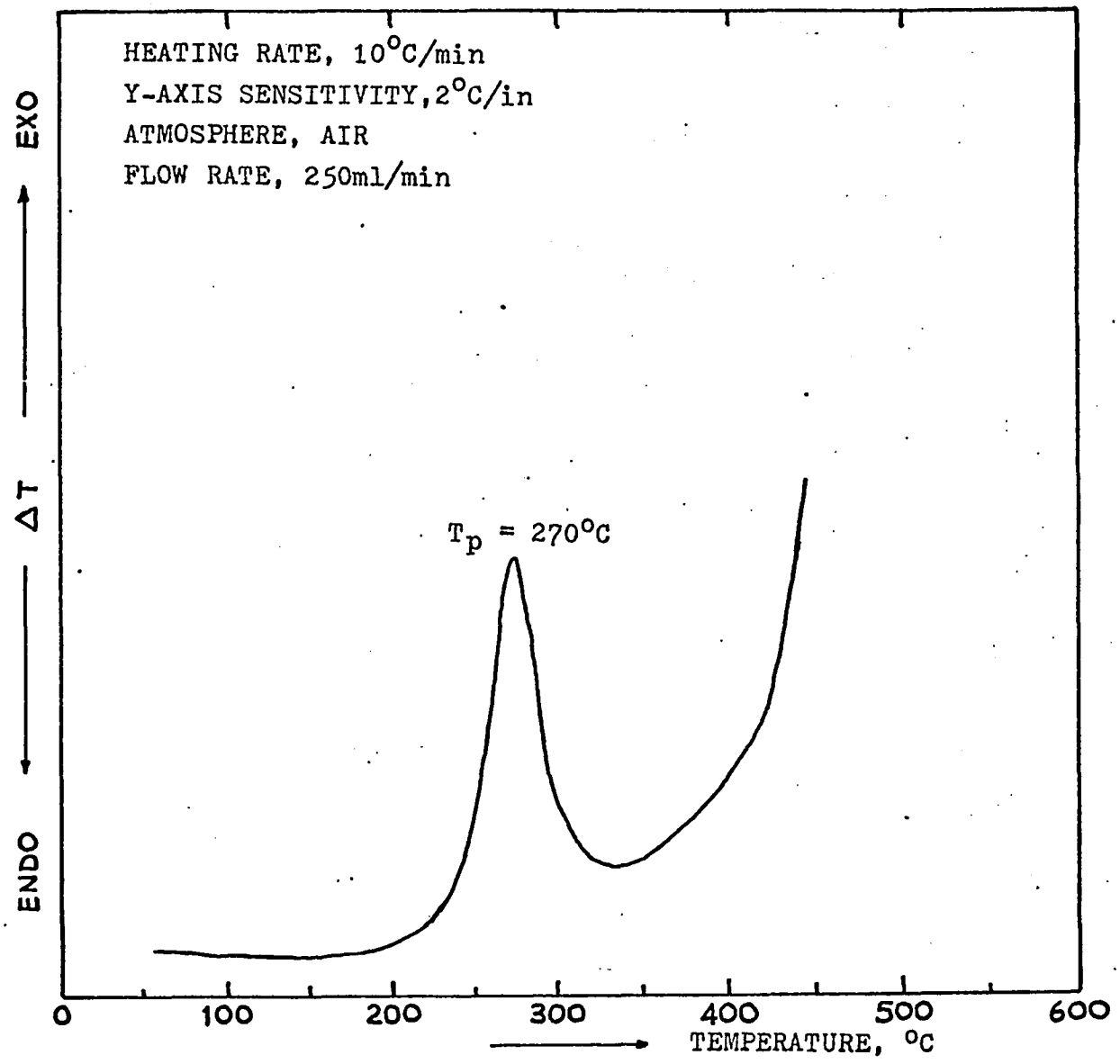


FIGURE 54. DSC Run For Toluene Adsorbed On Carbon Impregnated With 0.2% Pd, Prior To Regeneration Cycles.

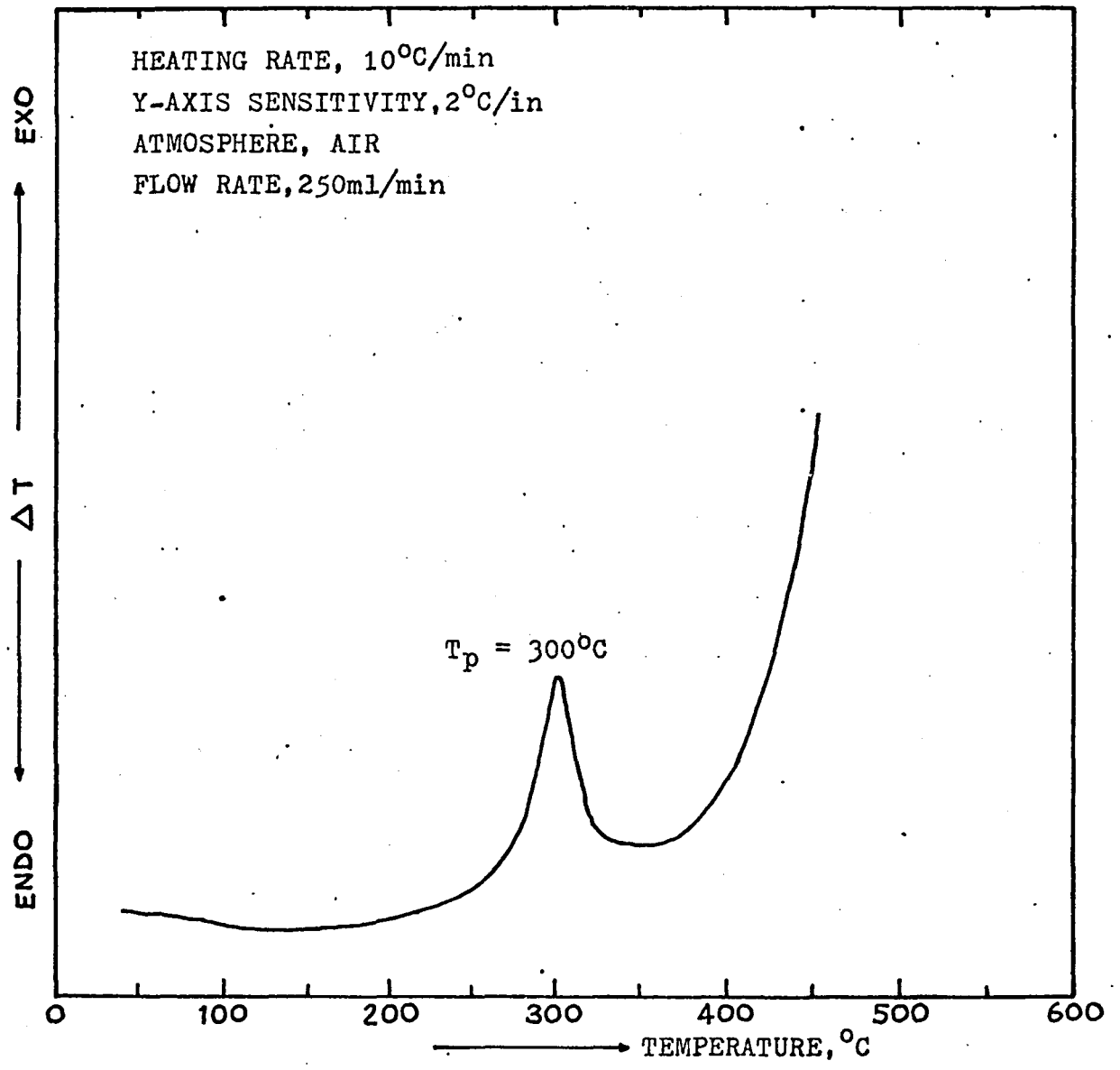


FIGURE 55. DSC Run For Toluene Adsorbed on Carbon Impregnated With 0.2% Pd, After Nine (9) Regeneration Cycles.

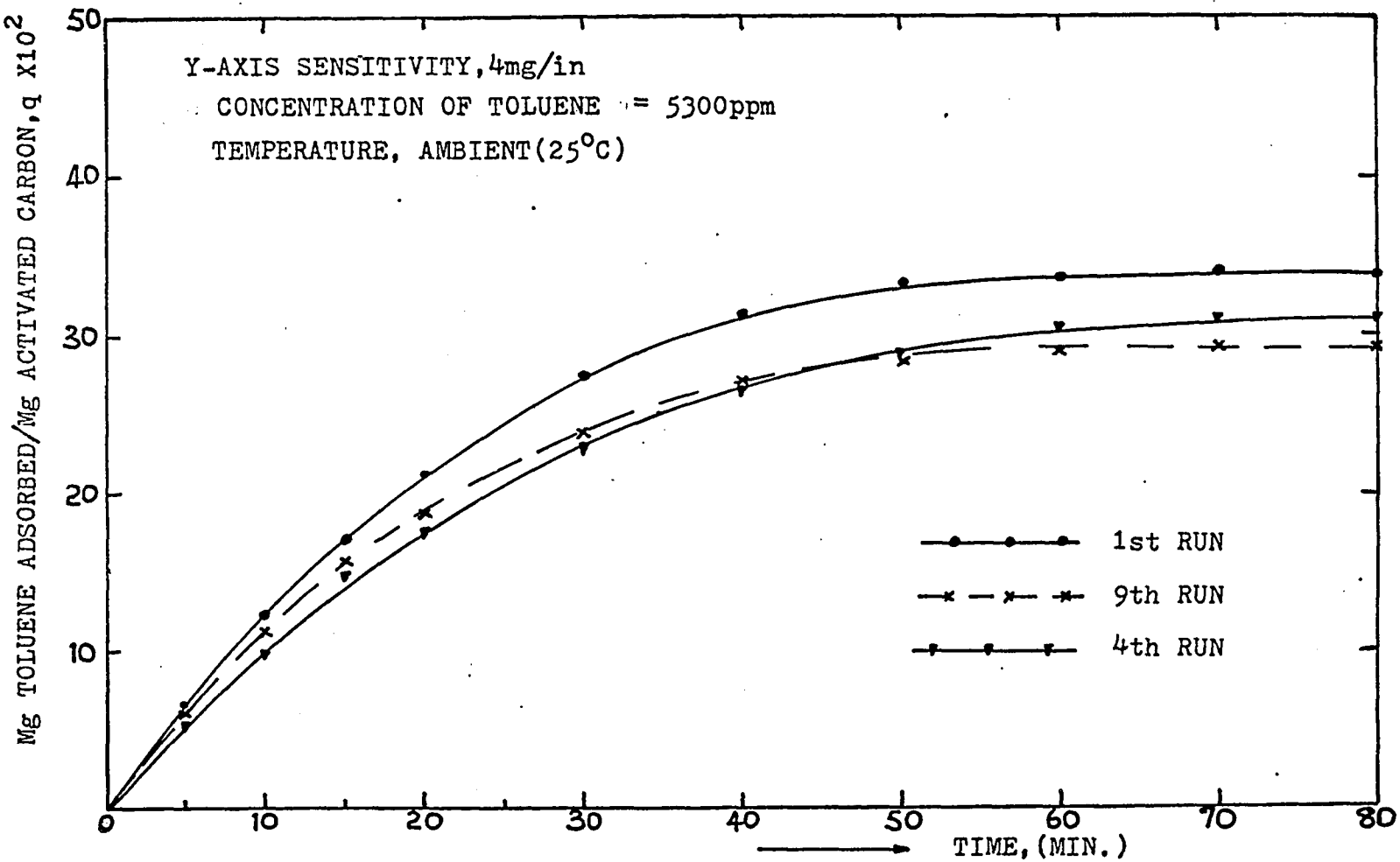


FIGURE 56. Adsorption Curves For Toluene On Carbon Impregnated With 1% NH_4VO_3, At Various Stages Of Regeneration.

required with time. This is evident from Fig. 54 and 55 where the temperature for maximum oxidation of toluene has increased from the initial value of 270° to 300°C after 9 cycles. This is probably due to minor catalyst poisoning which is absent for catalysts such as platinum.

Conclusion:

These data clearly demonstrate that regeneratable carbons can be developed which are capable of removing organic contaminants from air and which can be regenerated in situ by low temperature oxidation without significant loss of adsorptive capacity.

The absolute carbon adsorptive capacities (0.3 - 0.4 g/g) after impregnation are high and not substantially below those of the unimpregnated carbon (0.4 g/g). Of course, these figures are dependent on the concentration of pollutant in the saturating stream.

Oxidation of contaminants occurred at a temperature of 140°-290°C, whereas carbon oxidation occurred at 300°-400°C. Generally a temperature difference of 150° to 200°C between contaminant and carbon oxidation was observed. With this substantial difference in oxidation temperature control of the regeneration process is feasible.

The regenerating conditions are determined by the nature of the contaminant and by the nature of the catalyst. For instance, with vanadia as catalyst regeneration can be achieved at a temperature as low as 100°C using methylethyl ketone as sorbate. All indications are that platinum-impregnated carbon appears to be the most favorable regeneratable system for all the categories of pollutants. We found that all the compounds studied in the present investigation were selectively oxidized to CO_2 and H_2O using platinum-impregnated carbon containing 0.248% platinum

by weight. A maximum separation of 200°C was achieved between oxidation of contaminant and of carbon. The ignition temperature of carbon was 400°C, a phenomenon that would definitely ensure non-pyrophoricity of the sorbent during catalytic regeneration.

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