THE ADSORPTION AND REACTIONS OF AROMATIC HYDROCARBONS AT METAL CATALYST SURFACES.

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SUMMARY

The adsorption and hydrogenation of aromatic hydrocarbons by alumina- and silica-supported platinum and palladium catalysts, has been studied in the temperature range 100° - 335°C, using a microcatalytic reactor flow method, with helium and hydrogen carrier gas.

The adsorption and hydrogenation of benzene and toluene on all the catalysts examined, indicates that the relative specific activities of the metals for each reaction is in the order platinum > palladium.

The studies of adsorption, carried out in helium, show that the hydrocarbons were adsorbed dissociatively: at 250°C the hydrogenolysis of toluene was observed with platinum supported on alumina and palladium supported on silica. Methane and benzene were the only products of carbon-carbon bond fission observed. A further investigation of the retained species, using ^{14}C-labelled benzene, showed that this species is inactive in molecular exchange and hydrogenation. An associatively σ- or π-bonded benzene species is unlikely to be responsible for the retention in view of the lack of reactivity found in the studies with labelled hydrocarbon.

In the reaction of benzene and toluene with hydrogen over platinum and palladium catalysts, the only observed products were cyclohexane and methylcyclohexane respectively. No cracking products were detected, indicating that both

platinum and palladium exhibit no activity for the hydrogenolysis of benzene and toluene in the temperature range used in the present study.

Well-defined activity maxima between 140°- 220°C were found for benzene and toluene with all the catalysts examined. The maxima appear to have their origins in kinetic factors associated with the reaction, rather than a result of the thermodynamics of the reaction system.

The hydrogenation of toluene was found to be greater than benzene when it was hydrogenated separately or in a mixture 1:1 (v:v) of benzene and toluene on alumina- and silica-supported platinum and palladium.

On hydrogen-covered surfaces, the adsorption is interpreted in terms of associatively adsorbed species. The chemisorbed hydrocarbon is regarded as a π-complex, which is the reactive adsorbed state of hydrocarbon in hydrogenation reaction. The hydrogen acts as a cover of the catalytic surface, preventing the formation of strongly-held species but favouring the weak adsorption of hydrocarbons and in consequence the hydrogenation of benzene and toluene.

The higher rate of toluene hydrogenation, relative to that of benzene, together with the relative positions of the maxima in the activity-temperature curves is interpreted in terms of a lower strength of adsorption of toluene on the hydrogen-precovered platinum and palladium surfaces.

CONTENTS

CHAPTER ONE

CHAPTER ONE

AN INTRODUCTION

1.1 Introduction

The development of modern concepts in heterogeneous catalysis began in 1913 with Sabatier, who was the first to suggest that catalysis proceeds through the formation of an intermediate compound on the catalyst surface (1). This idea was not extensively developed at the time, largely due to the fact that the molecular organometallic compounds which were candidates as catalytic intermediates were unknown to chemists of that era. The concept of surface intermediates in catalysis plays a very important role in present-day theories, partly as a result of the success of inorganic chemists (since 1950) in the synthesis of analogous organometallic compounds.

The concept of "active centres" in catalysis was introduced in 1925 by Taylor (2), who reasoned that catalytic activity on a solid surface was restricted to a distribution of specific sites on the surface rather than to all available sites. Taylor conceived the surface as being nonhomogeneous by virtue of the presence of a distribution of substrate atoms having different degrees of coordination with other substrate atoms; a catalytic surface was not a perfect crystalline surface. Since that time, a number of attempts to identify lattice imperfections (such as dislocations and points defects) with catalytically active centres have been made, but the effect of this heterogeneity on catalytic activity remains controversial.

Historically, catalytic chemists have distinguished between the geometric and electronic factor in catalysis. This somewhat artificial separation of solid state properties has resulted in correlation between catalytic activity and lattice spacing on the one hand, and between catalytic activity and electronic character on the other hand (3). It is now widely recognized that geometric properties of a solid are intimately related to the electronic properties, and that attempts to separate the two can be misleading.

Recent developments in catalysis seem to be returning to the concept originally introduced by Sabatier, rather than concentrating on the general electronic and geometric properties of the solids, theoretical and experimental work is concerned with properties of atoms and complexes at surfaces. The last few years have seen the development of new experimental techniques such as auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) for the examination of the adsorption of hydrocarbons at well-defined single crystal surfaces, as recently reviewed by Thomson (4) and Somorjai (5). The result has been an advance in the understanding of catalytic processes and it has provided a new impetus for studies of heterogeneous catalysis.

1.2 Adsorption

Atoms or groups of atoms which lie in the surface of a phase differ fundamentally from those within the bulk of the phase. They cannot interact symmetrically with neighbouring atoms and their effect is unbalanced. For this reason they frequently exhibit unsaturated valencies, which are capable of forming a bond with foreign atoms or molecules on the surface. This process, which is called adsorption, is of considerable interest in heterogeneous catalysis, where the reaction takes place at the interface between the catalyst and the less dense phase.

Two types of adsorption have been recognized, physical adsorption and chemisorption. Physical adsorption can, in principle, occur between all gases and all solids, no new chemical bonds are formed, the forces involved being weak and of the same type as those responsible for the cohesive properties of liquids, namely Van der Waals forces. This type of adsorption has been used in the measurement of surface areas and pure size distribution of catalysts. Chemisorption, however, involves strong forces and new chemical bonds, of similar strength to those formed between atoms in molecules, are formed between the adsorbing atom or molecule and the surface. Chemisorption is a spontaneous process and is accompanied by a decrease in the Gibbs free energy change. ΔG is negative. Further, the process of adsorption, also involves a decrease in entropy and consequently, since $\Delta G = \Delta H - T\Delta S$, adsorption will be exothermic. Measurements of the heats of adsorption reveal some information regarding the nature of the adsorbed state. From the magnitude of the heat of adsorption it is possible to confirm that adsorption has indeed occurred, and from the variation of the heat of adsorption with the extent of surface coverage (θ), deductions can be made about the type of chemisorption (6). It has been observed that the heat of adsorption decreases with increasing surface coverage. This decrease may be explained in terms of (a) the heterogeneous nature of the adsorbent surface, (b) repulsions between adjacently adsorbed molecules becoming more important as (θ) increases, and (c) electron transfer between the adsorbate and the solid surface. The last mentioned is believed to be of importance in chemisorption on oxides, while surface heterogeneity is certainly of importance in chemisorption on metals.

Catalytic solids have been shown, in many experiments and by a variety of techniques, to be heterogeneous with respect to chemisorption. The observed nature and possible sources of this heterogeneity are the subjects of much published work and an attempt is made in this chapter to summarise and evaluate the observations made, with particular emphasis on hydrocarbon adsorption on transition metals.

The chemisorption of hydrocarbons on metal plays a very important role in the catalytic process, since it is generally accepted that the chemisorption of hydrocarbons precedes its hydrogenation and since the nature of the adsorbed state has a direct bearing upon the mechanism. On the other hand, the chemisorption of hydrocarbons produces carbonaceous deposits whose characteristics depend on the substrate structure, the type of hydrocarbon chemisorbed, the rate of adsorption, and the surface temperature. The existence of inactive species on a catalyst surface has been demonstrated by stoicheiometric balance (7,8) and by the use of radioactive tracers (9, 10). Infrared spectroscopic studies have shown that on hydrogen-free metal surfaces, hydrocarbons are dissociatively adsorbed, thereby forming hydrogen-deficient residues and possibly also surface polymers (11, 12, 13). Dissociative adsorption and the formation of surface residues has also been demonstrated by field-emission microscopy (14) and low-energy electron diffraction (5). Irreversible adsorption may be demonstrated in a simple desorption experiment. However, the use of radioactive tracers permits the detection of even a small amount of irreversible adsorption. Moreover, the radioactive tracer can indicate the displaceability of irreversibly adsorbed species. A number of studies have been made to elucidate the nature of the adsorbed state by direct or indirect determination of the radioactivity of adsorbed species.

Although conventional volumetric measurements of adsorption failed to reveal any chemisorption of i-butane on SiO_2/Al_2O_3 at temperatures known to be effective for cracking, Maciver, Emmett and Frank (15) succeeded in detecting 0·003 ml/g of adsorbed i-butane at 150°C by using ^{14}C-labelled isobutane; Larson and Hall (16) classified the adsorbed i-butane on SiO_2/Al_2O_3 into three forms, as follows:

(a) removable by evacuation at 150°C, (b) unremovable by evacuation but displaceable with gas phase i-butane, (c) undisplaceable.

Inoue and Yasumori (17) classified adsorbed acetylene on cold worked Pd foil at 27°C into four types: (a) which undergoes desorption on evacuation, (b) which is removed from the surface during hydrogenation at 27°C, (c) which is not removed during hydrogenation, but is removed by treatment with hydrogen at 150°C, and (d), which remains on the surface after reduction at 150°C. It was considered that the type (b) species are the species responsible for hydrogenation and that these species can occupy two kinds of site (I) and (II). Site (I) can be identified with lattice imperfections in the (110) crystal plane which disappear on annealing at temperatures between 200 and 300°C. Site (II) can be correlated with the lattice planes or boundaries which are preferentially developed during the disappearance of the (110) plane and the growth of (111) planes at annealing temperatures of around 600°C.

Systematic studies of retention of hydrocarbons were made using two different approaches by Taylor et al. (18) and by Cormack et al. (19). Taylor et al. (18) using a microcatalytic reactor examined the adsorption of CH_4, C_2H_6, C_3H_8, C_2H_4, C_3H_6, C_2H_2 and cyclo-C_3H_6 on Pd/Al_2O_3 in the temperature range 20° to 200°C. The percentage retention of the various hydrocarbons increases in the order alkanes < cyclopropane < alkenes < acetylene. Dissociative adsorption occurred and carbon-carbon bond rupture appears to be unimportant, except at 200°C. They also point out that the palladium-alumina catalyst exhibits different degrees of heterogeneity depending upon the adsorbate hydrocarbon. Thus, for example, the retention for propylene and for ethylene were dissimilar.

In an alternative approach to retention and interaction of hydrocarbons with metals, Cormack et al. (19) examined the interaction of ^{14}C-ethylene at ambient temperature with a range of metals supported on alumina. When ^{14}C-ethylene is adsorbed onto alumina-supported nickel, ruthenium, rhodium, palladium, iridium, or platinum, it was observed that only a fraction of the initially adsorbed ethylene can be removed by hydrogenation, by molecular exchange with non-radioactive ethylene, or by evacuation. They gave the following sequence for the percentage of adsorbed ethylene unremovable from metals:

$$\begin{array}{ccccccccc} \text{Pd} & > & \text{Ni} & \simeq & \text{Rh} & > & \text{Ir} & > & \text{Pt} \\ 63{\cdot}5 & & 24 & & 22{\cdot}5 & & 16 & & 6{\cdot}5 \end{array}$$

The authors pointed out that the surfaces studied were heterogeneous in that at least two types of adsorbate-surface bonding could be recognised. The species retained was dissociatively bonded ethylene, whereas the species removed during hydrogenation was associatively bonded.

Chemisorption of ^{14}C-ethylene and ^{14}C-propylene between 20° and 350°C on Pt/Al_2O_3 and Pt/SiO_2 was studied by Altham and Webb (20). A microcatalytic reactor was used in these studies and injected pulses of hydrocarbons over the catalysts allowed quantitative data to be obtained regarding the extent of adsorption. It was observed that the retention of ethylene was greater than that of propylene under the same conditions. Mixed adsorption studies yielded interesting information. When inactive ethylene was injected on Pt/Al_2O_3 which was precovered with ^{14}C-propylene, ethylene adsorption still occurred, although the extent of adsorption was less than a "clean" surface. At 200°C and below, no radioactivity was displaced from the surface but at 350°C injections of ethylene resulted in the formation of radioactive ethane and ethylene. The authors concluded that different types of sites, and consequently different types of adsorbed species were involved in the retention of ethylene and propylene, that is, the catalyst surface showed differing degrees of heterogeneity depending upon the adsorbate hydrocarbon.

The use of radioactive tracers has demonstrated that the surface of metal catalysts are heterogeneous for hydrocarbon adsorption and as was pointed out by Webb (21) the degree of heterogeneity depends both on the surface and, to some extent, on the adsorbate molecule.

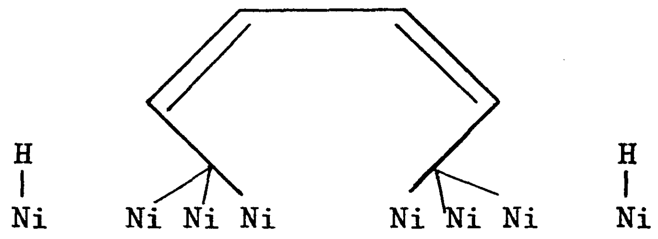
1.3 Chemisorption of Benzene

The interaction of benzene on metals has been studied almost as exhaustively as has ethylene. It is an unsaturated hydrocarbon, and as such it may undergo associative chemisorption in a manner not dissimilar to that of olefins and diolefins or, in the extreme alternative, is dissociatively chemisorbed with no interaction of the π-electron system with the surface, in which case the basic reactivity is in principle similar to that exhibited by the alkanes.

The chemisorption of benzene has been reviewed by Bond (22) and, more recently, by Moyes and Wells (23), whilst Garnett (24) has given a useful account of benzene hydrogenation, with particular reference to the role of π-complexes as intermediates in catalytic processes.

There is special interest in studying the chemisorption of benzene, due to the important role of this process in the catalytic hydrogenation-dehydrogenation of six-membered hydrocarbon rings. In an early investigation by the low frequency A.C. permeater method (25), it was shown that benzene chemisorbed on silica-supported nickel at 150°C was taken up primarily by formation of six adsorbate-surface bonds. This suggested associative adsorption with the plane of the ring parallel to the nickel surface. A subsequent examination of this system by Silvent and Selwood (26) confirmed that approximately six metal-adsorbate bonds are formed on chemisorption of benzene at 120°C and that as the adsorption temperature is raised further, the number of bonds formed increases rapidly, reaching about eighteen at 200°C. It is clear that the temperature of adsorption has a marked effect on the number of bonds formed per molecule of adsorbed benzene. The results were interpreted as associative adsorption at the lower and dissociative at higher temperatures. Six bonds formed by benzene suggest that the molecule lies flat; more than six bonds suggests not only dissociation of hydrogen but some degree of carbon-carbon rupture. It was also observed that, if hydrogen is allowed to flow over preadsorbed benzene at 100°C, it is possible to recover most of the original adsorbate in the form of cyclohexane. But if the adsorption is conducted at 200°C, the effluent vapour contains an appreciable fraction of lower molecular weight hydrocarbons, although a substantial amount of cyclohexane is still formed.

In saturation magnetization measurements Martin and Imelik (27, 28) found eight adsorbate-surface bonds when benzene was adsorbed on nickel supported on silica at room temperature. This suggests not only a dissociation of C-H bond but a C-C bond rupture. At 150°C, 25 bonds were formed corresponding to complete dissociation to H and C. The results at room temperature were interpreted by Martin and Imelik as being due to "edge on" dissociative adsorption, giving a bond number of 8. At 150°C, benzene is completely cracked with formation of Ni_3C and NiH.



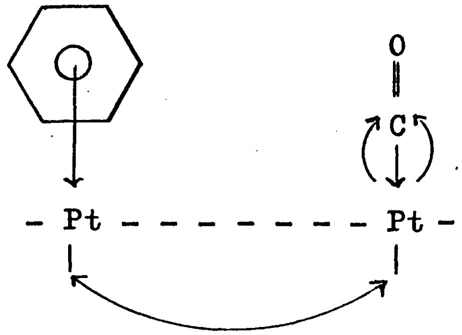
Flash-filament studies have been employed by Cratty and Hansen (29) to study benzene chemisorption on tungsten. It was observed that benzene is adsorbed rapidly and irreversibly on such surfaces. Displacement stoichiometries and surface area considerations, strongly favour a dissociative adsorption model (σ-bonded phenyl group) for this process. The irreversibly chemisorbed benzene undergoes neither exchange nor hydrogenation with preadsorbed or gas-phase hydrogen, and is therefore not an important intermediate in the catalysis of these reactions by tungsten.

Broden et al. (30) using UV-photoemission in conjunction with LEED/Auger spectroscopy studied the chemisorption and the molecular structure of benzene on the Ir(100) surface. Evidence was obtained that the adsorption of benzene at 150K does not cause any change in the geometry of the (5 x 1) LEED pattern. At 550K decomposition of the benzene molecule occurs, associated with the occurrence of a hydrogen thermal desorption peak observed on the mass spectrograph. It was assumed that the benzene molecule was bound flat with the ring parallel to the metal surface. Chemisorption occurs via π-bond formation. It was also found that the benzene molecule is surprisingly insensitive to the iridium substrate geometry. It adsorbs at low temperature with little molecular distortion and apparently retains its molecular identity remarkably well as the temperature is raised to near the dehydrogenation temperature.

Fischer et al. (31) studied the chemisorption of benzene on Pt(100) by Auger electron spectroscopy, ultraviolet photoemission spectroscopy, flash dehydrogenation and LEED. Adsorption of benzene caused a decrease in the work function proportional to coverage and corresponding to a dipole moment of 1·5D. This implies that the benzene molecule is acting as electron donor to the metal surface. UPS analysis indicated π-bonding for benzene adsorption. The authors comparing their results with those reported for iron, copper and nickel, concluded that the interaction of benzene with platinum is stronger than it is with iron, nickel and copper.

Current knowledge of application of LEED to chemisorption of hydrocarbons on platinum has been extensively reviewed by Somorjai (5). Infrared spectroscopy has found application in the investigation of surface species formed upon adsorption of different gases and vapours on supported metals. The infrared spectrum of benzene adsorbed on a Pt/Al_2O_3 sample was observed by Shopov et al. (32). A comparison with the spectra of some bulk coordination compounds enabled the authors to obtain direct evidence for π-complex formation. Subsequently, Palazov (33) examined the thermal stability and behaviour of the adsorbed benzene complex during the interaction with various gases and vapours using the infrared technique. The presence of a single band at 3050 cm^{-1} was suggested as being in accord with the formation of π-adsorbed benzene on the platinum surface. This band is characteristic for "sandwich" complexes of transition metals. The presence of the 1390 cm^{-1} band in the IR spectrum also gave evidence for π-complex formation on the catalyst surface. The surface π-complex formed after adsorption on the Pt/Al_2O_3 sample had a considerable thermal stability, but reacted readily with hydrogen and was removed by carbon monoxide subsequently adsorbed on the same sample.

Infrared studies have been employed by Primet et al. (34) and Basset et al. (35) to study carbon monoxide adsorption and benzene chemisorption on Pt/Al_2O_3. When CO is adsorbed on platinum, two types of bonding are formed: a σ-bond and a π-bond obtained by back-bonding of metal "d" electrons to an antibonding orbital of CO. This model takes into account most of the experimental results obtained when CO is adsorbed on platinum. Various gases having electron donor or electron acceptor properties were adsorbed on platinum previously covered (surface coverage $\theta = 0{\cdot}2$) by CO. Chemisorption of Lewis bases increases the electronic density of metal and the back donation to the carbonyl group which results in a shift of the $\nu(CO)$ frequency toward low wave numbers. The fixation of electron acceptor elements such as chlorine or oxygen decreases the electronic density of the metal, the back donation is lowered resulting in a shift of the $\nu(CO)$ frequency toward high wave numbers. When benzene was adsorbed on platinum, the shift observed indicated a net "flow of charge" from benzene to platinum. This was claimed by the authors to be proof of the existence of a π-complex between benzene and platinum and as an intermediate state responsible for the catalytic hydrogenation of benzene. The π-complex which was suggested was assumed to be a kind of weak adsorption of benzene. In fact back bonding from the metal d orbitals to the benzene π^* orbitals could explain the very high thermal stability of adsorbed benzene. It would be a "surface complex" very close to π-arene complexes. The interaction between adsorbed benzene and CO would proceed through the lattice as shown below:



The chemisorption of ^{14}C-benzene on nickel, platinum, copper (36) and cobalt (37) have been examined by Tetenyi and Babernics using a flow reactor system. Nickel was examined in the greatest detail and the system was operated at atmospheric pressure in the temperature range 100-300°C. In this study the active compounds were eluted, condensed in inactive benzene, and counted in a scintillation counter. It was observed that, the quantity chemisorbed depended on the temperature of adsorption to a considerable extent; as the temperature was varied, the adsorption passed through a maximum at 140°-160°C for all the nickel catalysts examined except raney nickel, for which the authors suggested that the maximum possibly appears at temperatures below 100°C. The coverage of the surface with chemisorbed benzene was calculated to be 23-63% depending on the catalyst used. In the range of 250°-300°C, the temperature at which cyclohexane dehydrogenation occurs, the coverage with chemisorbed benzene was only 2-10%. The quantity of benzene adsorbed was smaller in all cases than the maximum amount of adsorbed hydrogen. The benzene coverages were a half to one fifth of those observed for hydrogen.

The reactivity of the adsorbed species was examined using unlabelled benzene or hydrogen. The chemisorbed benzene could be fully removed only with hydrogen, benzene removed only a part of it. The authors proposed that the two kinds of adsorption which they observed on nickel was based on an associatively adsorbed form, π- or σ-bonded, which can be displaced by benzene itself, and a dissociatively adsorbed species which required hydrogen for its removal.

The absence of adsorption on copper and a low surface coverage compared with hydrogen on platinum, were also observed in these studies.

Babernic and Tétényi (37) using a chromatographic method combined with the radioactive tracer method examined the adsorption of benzene on metallic cobalt in the temperature range 35°-200°C. It was found that below 100°C, the whole surface of the catalyst became saturated with reversibly bound benzene. This adsorption was considered to be entirely physical in nature. Above 100°C, simultaneous with a considerable decrease of the extent of reversible adsorption, irreversible adsorption and chemisorption occurred. In the range 160°-200°C only 10-12% of the coverage represented reversibly adsorbed species. The use of ^{14}C-benzene showed that about half of the benzene adsorbed at 200°C was irreversibly chemisorbed at the surface and was only removable by hydrogen treatment at 360°C. According to these authors the catalytic activities of nickel, platinum and cobalt for benzene hydrogenation are not in direct correlation with their chemisorption capacity as shown by the following comparison:

catalytic activity: Pt > Ni > Co

chemisorption capacity: Ni > Pt > Co > Cu $\simeq$ 0.

Recently the adsorption of ^{14}C-labelled benzene on raney nickel at room temperature has been studied by Candy and Fouilloux (38) using a Sartorius balance coupled to a radiomanometer. It was established that benzene was adsorbed in both a reversible and an irreversible form. The observed isotherm was discussed in terms of the Freundlich equation and was obtained at 24°C for pressure less than 1 torr. It was also observed that, for every benzene molecule irreversibly adsorbed, 5·7 hydrogen molecules were removed from the catalyst surface. The use of radiotracers showed evidence for two types of chemisorbed benzene species on the surface, both of which can be hydrogenated, one due to a single hydrocarbon-metal interaction as a π-complex and the second due to dissociative adsorption through dissociation of the carbon-hydrogen bonds of the benzene ring.

1.4 Hydrogenation of Benzene

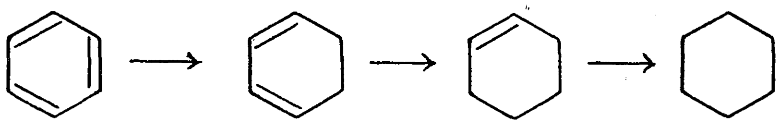
Considerable attention has been given in the past to the study of the hydrogenation of benzene over a variety of group VIII transition metal catalysts. In general, cyclohexane has been found to be the sole product, unless elevated temperatures (above 350°C) are employed, when cracking and rearrangement into a variety of products occurs. For the vapour phase hydrogenation, extensive investigations have been made using nickel (39-45), platinum (46-51) and other group VIII transition metal catalysts (52-53).

Although much work has been done on the kinetics of benzene hydrogenation mainly on nickel, there is still no consensus of opinion. The results of the kinetics studies show some discrepancies. For example, most studies of the reaction at temperatures below 100°C have shown that the hydrogenation is zero order with respect to benzene and either first or one-half order with respect to hydrogen (50, 54, 55, 56). Nicolai et al. (39), have found the reaction order with respect to hydrogen to vary with the temperature. Germain et al. (42) showed that elevation of the temperature from 120° to 192°C changes the order with respect to benzene from 0·2 to 0·48, and the order with respect to hydrogen from 0·45 to 2·5. An inhibiting effect of cyclohexane has been reported by some authors (42, 57) and has been refuted by others (39, 43). Most authors acknowledge that these reactions proceed by several sequences on the catalyst surface, but there is no agreement on their number and nature.

Balandin's multiplet theory (58), predicts a planar adsorption of benzene molecules on catalysts having appropriate geometrical structure with lattice dimensions specifically related to the size of benzene ring. On this basis Trapnell (59), proposed the formation of six covalent carbon-metal bonds on the surface, followed by the simultaneous addition of all six hydrogen atoms with no formation of intermediates between benzene and cyclohexane.

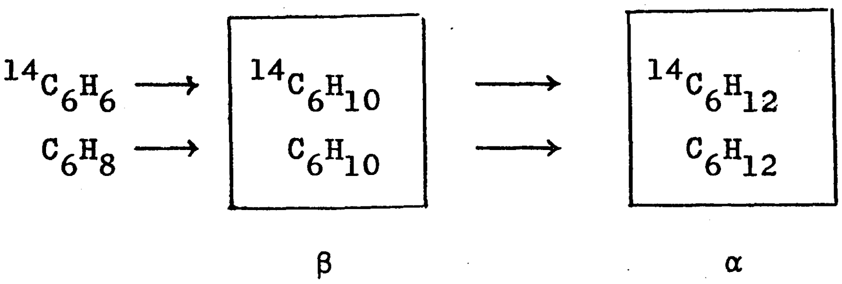
The postulation of the π-complex adsorption of the aromatic ring (22, 60, 61, 62) offered a more realistic explanation of the planar benzene adsorption, assuming that the π-electron sextet may interact with the metal surface forming species coplanar with the surface. The adsorption of benzene in this way has been postulated by several authors in the hydrogenation of benzene. According to Rooney (62) hydrogenation takes place via intermediate species π-bonded to the surface as cyclohexadienyl and cyclohexenyl π-complexes. The hydrogenation might then proceed through cycloolefins, but since these are hydrogenated more rapidly than benzene (63) their presence would be difficult to detect.

The purpose of the studies of Tetenyi and co-workers (64) was to investigate the reactivity of benzene and cycloolefins, under circumstances where they were admitted to the catalyst simultaneously, by making use of the sensitivity of detection of radiotracers. In the hydrogenation study a mixture of radioactive starting material (^{14}C-benzene) with an inactive form of the supposed intermediate (cyclohexa-1,3diene) was introduced in a pulse type microreactor in the presence of Fe, Ni, Ru, Rh, Pd, Os, Ir, Pt and Re catalysts. The authors showed that when ^{14}C-benzene and inactive cyclohexadiene reacted together with hydrogen at low conversion, the radioactivity appeared in the cyclohexene and cyclohexane. In the case of platinum, it was also established that the cyclohexadiene was radioactive. The appearance of radioactivity in the intermediate cyclohexene indicates that some of the benzene was being hydrogenated by a stepwise process:



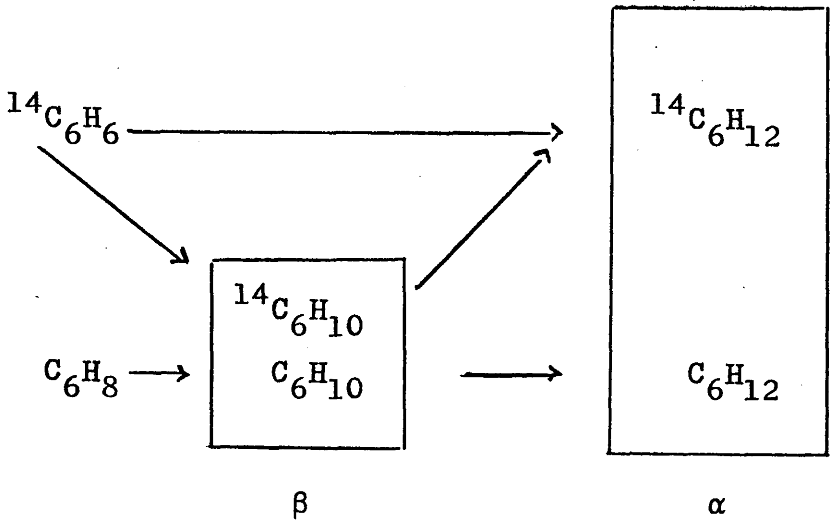
From radiotracer data, it was obvious that radioactive products could be formed only from benzene. Tetenyi and Paal (65) evaluated the different apparent role of cyclohexene in the low and high conversion of benzene to decide whether benzene hydrogenation via cycloolefins is the only route (scheme A) or whether "direct" and "stepwise" mechanisms take place simultaneously (scheme B).

The reaction conditions were chosen such that the conversion proceeded only to a small extent. Under this condition it was possible to examine the specific radioactivities of cyclohexane (α) and cyclohexene (β), and to draw conclusions about the validity of the two schemes.



$\beta \geqslant \alpha$

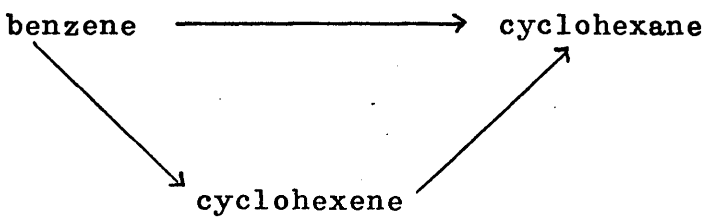
Scheme A



$\beta < \alpha$

Scheme B

In scheme A, $\beta \geqslant \alpha$. In B, $\beta < \alpha$. Since β/α values ranged between 0·01 and 0·27 over all the catalysts examined, the authors concluded that scheme B was valid.



The two apparent routes in the triangular scheme were attributed to a single mechanism which involves the π-complex adsorption of the benzene ring followed by either random or "directed" addition of hydrogen atoms.

CHAPTER TWO

CHAPTER TWO

THE OBJECT OF THE PRESENT WORK

The adsorption of hydrocarbons on metals plays an important role in the understanding of the theory of catalysis. In the study of this phenomenon it is very often found that the hydrocarbons are adsorbed to a small extent at low temperatures, while at higher temperature chemical reactions such as dehydrogenation or cracking take place on the surface of metals. The relatively small specific surface of the metals makes the quantitative determination of the adsorption difficult. In consequence, only a very few quantitative data are available concerning the adsorption of hydrocarbons by metal under conditions of catalytic reaction.

The object of the present work was to study in detail the adsorption of aromatic hydrocarbons over alumina and silica supported metal catalysts under a variety of conditions which involved reaction, retention, deactivation and regeneration. In order to obtain this information the following investigations were carried out:

(a) The evaluation of the amount retained with type of hydrocarbon.

(b) The evaluation of the amount retained with the temperature and with different catalysts.

(c) The evaluation of the amount retained with different carrier gases and with different catalysts.

(d) The study of the reactivity of adsorbed-hydrocarbon towards molecular exchange and hydrogenation, using ^{14}C-labelled hydrocarbons.

The reaction of aromatic hydrocarbons with hydrogen was examined with the following aims:

(i) To study the effect of the temperature on the hydrogenation reaction.

(ii) To study the retention under conditions of catalytic reaction.

(iii) To study the variation of hydrogenation with the type of hydrocarbon and with different catalysts.

(iv) To compare the catalytic activities of the catalysts in hydrogenation reaction.

CHAPTER THREE

CHAPTER THREE

APPARATUS AND EXPERIMENTAL PROCEDURE

3.1 Introduction

The pulse-flow microcatalytic reactor has been extensively used in catalytic research, where the small pulse size enables one to study initial interactions between surface and reactants. In this way, information about many kinetic parameters, such as intrinsic reaction rates, orders, poisoning effects and catalyst deactivation can be obtained. The technique is especially suitable when product distributions are to be examined, or the activity of different catalysts is to be compared. Both stable and radioactive isotopic tracers may be used, combined with microcatalytic reactors, to provide critical information about catalytic reactions on surfaces.

With this technique, one can determine the fate of reactant molecules as they interact with a fresh catalyst surface. In many cases the first molecules striking a surface are strongly adsorbed as some type of residue. A simple material balance taken over the first few pulses can be used to determine how many molecules are so retained. Furthermore, if these pulses involved radioactive (^{14}C, tritium, etc) labelled molecules, the quantitative determination of radioactivity in subsequent, non-radioactive pulses, indicates the extent of exchange-ability of this

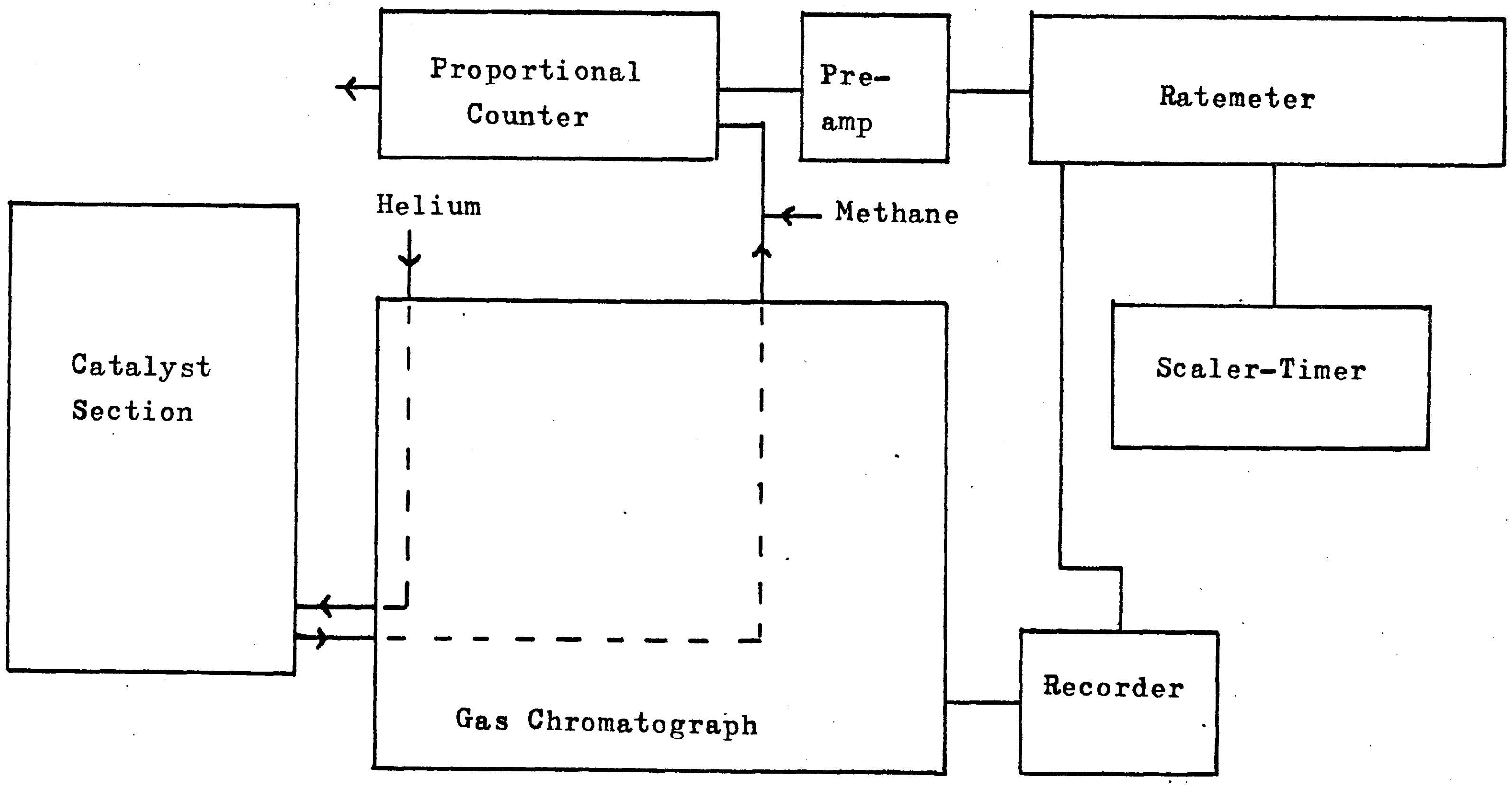


Fig. 3.1 Block Diagram of the Flow System

adsorbed material. In some cases surface compounds are formed which can be decomposed either thermally or chemically; these may actually be intermediates in overall catalytic reactions.

By use of microcatalytic reactors, one can get some idea of catalytic activities and the nature of poisoning processes. Both the activity and selectivity frequently change, as with catalyst usage. The flexibility inherent in the microcatalytic technique for varying the pulse size/ catalyst ratio and speed of analysis, allow the accumulation of considerable amounts of data, particularly when used in conjunction with isotopic tracers.

A block diagram of the flow system, which is similar to that described by Kokes, Tobin and Emmett (66) is shown together with associated instrumentation in figure 3.1.

3.2 The Catalytic Reactor and Chromatograph

A pulse-flow microcatalytic reactor coupled directly to a Beckman GC2A gas chromatograph, with a thermal conductivity detector, was used in this study.

The detailed block diagram of the reactor section is shown in the figure 3.2. The sample line of the chromatograph, $^1/8$ - inch diameter copper tubing, is connected to a fine control valve, used to balance flow rate in the sample line, and then to a "Rotameter" gas flowmeter. This was calibrated <u>in situ</u> against a soap-bubble flowmeter at the end of the system. The "Rotameter" was thereafter used to

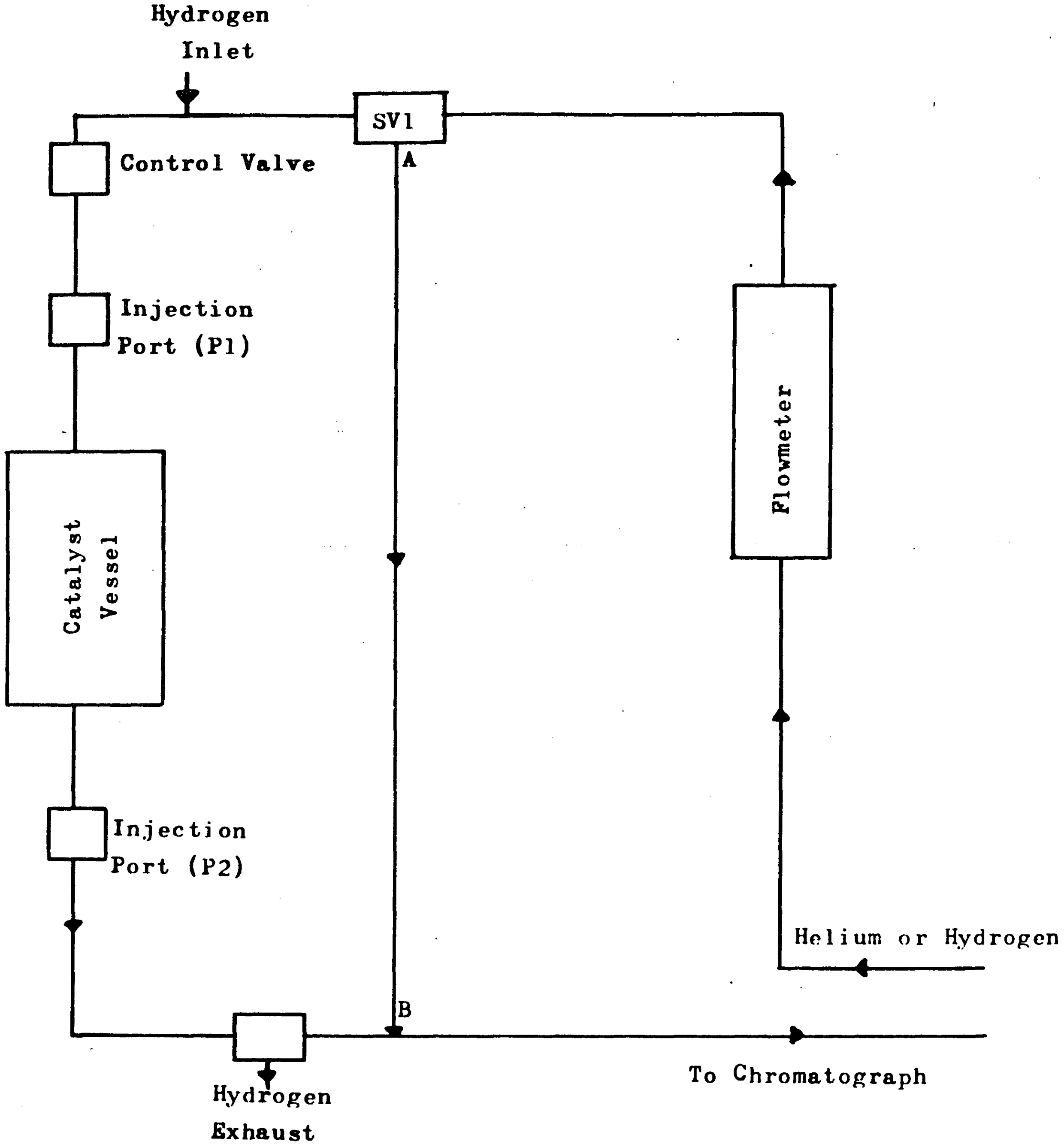


Fig. 3.2 Block Schematic Diagram of Microcatalytic Reactor

indicate the flow rate of the carrier gas before blending at the chromatograph exit, to form a counting mixture (figure 3.1 and section 3.7), when the proportional flow counter was used. From the flowmeter the line entered a rotary switch valve SV1 (Drallim Industries Ltd) where, if necessary, the carrier gas could be led directly back to the chromatograph; the junction with the chromatograph was immediately before the column. This will be referred to as the catalyst by-pass circuit.

With SV1 in its alternative position the carrier gas flow was directed into the catalyst vessel (figure 3.3). The catalyst vessel was made of "Pyrex" glass fitted at each end with Crawford connectors. The pipette-shaped Pyrex glass kept the dead volume of the vessel to a minimum, but permitted quantities of up to one gram of catalyst to be placed on the glass sinter without the catalyst bed itself acting significantly as a chromatographic column. Immediately above and below the catalyst bulb were situated injection ports (IP) which were sealed by $\frac{1}{4}$-inch serum caps. These permitted hydrocarbon samples to be introduced into the carrier-gas stream and thence onto the catalyst, or directly onto the chromatographic column for calibration purposes.

The return of the gas line to the chromatograph was made through a spring-loaded stopcock and a T-piece. This T-piece which joined the by-pass circuit and the main line, was a "Crawford Swaglok" fitting, as were all the other

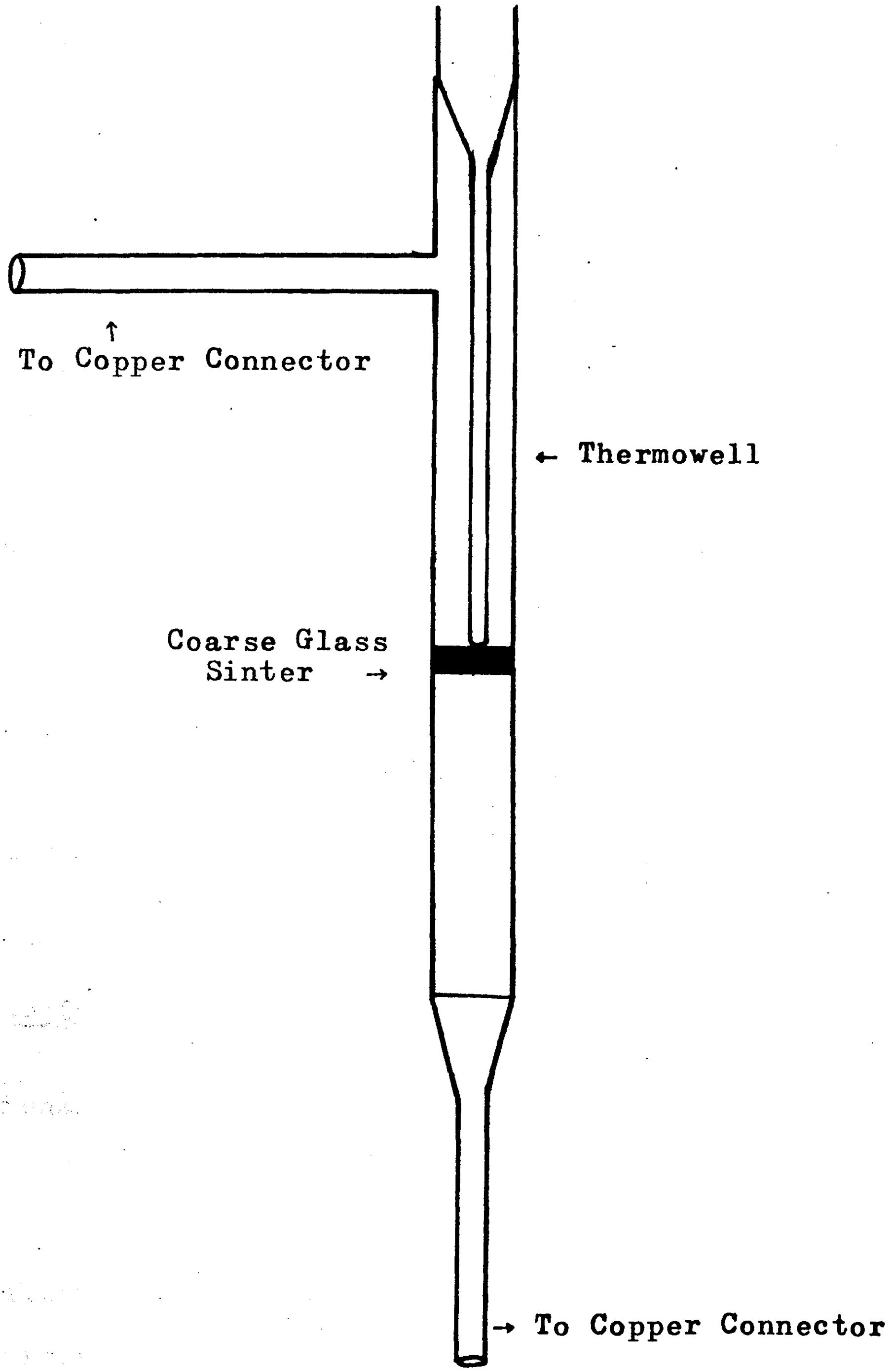


Figure 3.3 The Catalyst Vessel

couplings in the system. The provision of a spring-loaded stopcock was to permit exhaust to atmosphere of hydrogen, which entered the section through a similar T-piece after SVl, and which was used for the <u>in situ</u> reduction of the catalyst. During these reduction periods, the conditions of which are fully described in section 3.11, the carrier gas stream flowed continuously through the rest of the system via the catalyst by-pass circuit.

The temperature of the catalyst was maintained by a cylindrical electric furnace surrounding the catalyst vessel. The current to the furnace was controlled by a "Variac" variable transformer and the temperature of the catalyst was measured using a chromel/alumel thermocouple, positioned in the thermowell in the centre of the reactor vessel, connected to a "Comark" electronic thermometer (type 1602).

3.3 High Vacuum System

A conventional vacuum line was used for the storage of gases to be used as reference in the chromatographic analysis. This included facilities for storing several gases, purification by fractionation, and transfer of gases to sample vessels at measured pressures greater than atmospheric.

The system was maintained at a pressure of 10^{-4} Torr or better by means of an oil diffusion pump backed by a rotary pump. The system is shown schematically in figure 3.4.

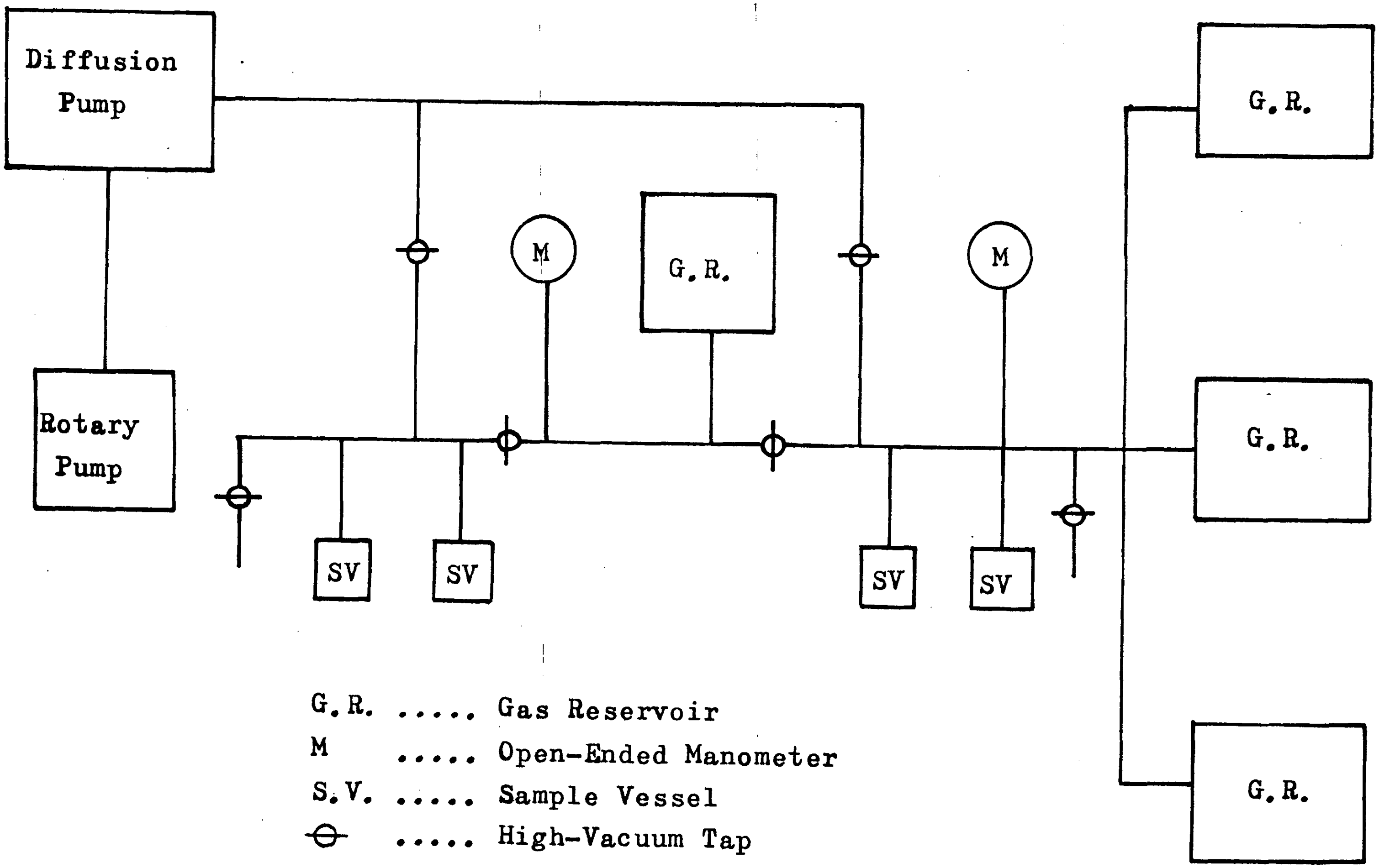


Figure 3.4 Vacuum Line Diagram

3.4 Gas and Liquid Syringes

Gas tight syringes or liquid syringes (Hamilton Co.) were used to transfer samples from storage vessel to the flow system. When Chaney adaptors are fitted to the syringe a reproducibility of the injection size of 0·01% is claimed. Syringes of 10 µl (liquids), 1·0 ml and 10 ml (gases) capacity were used in the present studies.

3.5 Materials

(a) The catalysts, containing 5% w/w metal supported on "aerosil" silica (Degussa Ltd) or γ-alumina (Degussa Ltd) were prepared by adding an aqueous solution of the metal chloride, containing the required weight of metal, to an aqueous suspension of the support. The excess water was evaporated off and the supported salt finally dried in an air oven at 150°C. The supported salts were reduced, as required, by *in situ* reduction in the catalyst vessel at 350°C using hydrogen at a flow rate of 30 ml/min. The B.E.T. surface areas of the reduced catalysts and the metal surface areas were determined as described in sections 3.9 and 3.10.

(b) Helium, used as carrier gas in the studies of adsorption of hydrocarbons, was passed through a 5 A molecular sieve trap cooled in liquid nitrogen, then through a trap containing a reduced 1% palladium on tungsten oxide catalyst and finally dried by passage over $Mg(ClO_4)_2$.

Hydrogen, used in the reduction/activation of the catalyst and hydrogenation of hydrocarbons, was obtained from the British Oxygen Co. Ltd. This was passed through an "Engelhard Deoxo Hydrogen Purifier" which had the effect of lowering any oxygen impurity to less than 1 p.p.m. by conversion to water vapour. That it did not require periodic regeneration suggested that the purifier did not retain the vapour produced. A 5A molecular seive trap maintained at -195°C was therefore inserted in this line. Finally the hydrogen was passed over a 1% Pd/WO_3 catalyst to remove any remaining traces of oxygen.

Methane, used to form a counting mixture with the helium, was the "CP Grade" of Air Products Ltd., who quote the purity as greater than 99%, nitrogen at less than 0·77% being the principal impurity. Since this gas did not pass over the catalyst its purity was less critical and it was used as supplied.

Nitrogen (B.O.C., Oxygen-Free Grade) used as carrier gas in the measurements of metal surface area, was passed through a trap containing a 1% palladium on tungsten oxide catalyst, to remove trace amounts of oxygen, and then through a molecular sieve trap (Linde 5A) cooled to 80 K to remove traces of water vapour.

(c) ^{14}C-carbon monoxide, was prepared by the reduction of ^{14}C-carbon dioxide (Radiochemical Centre, Amersham) with metallic zinc. The apparatus used is shown in figure 3.5. It consists of a storage vessel and converter which was

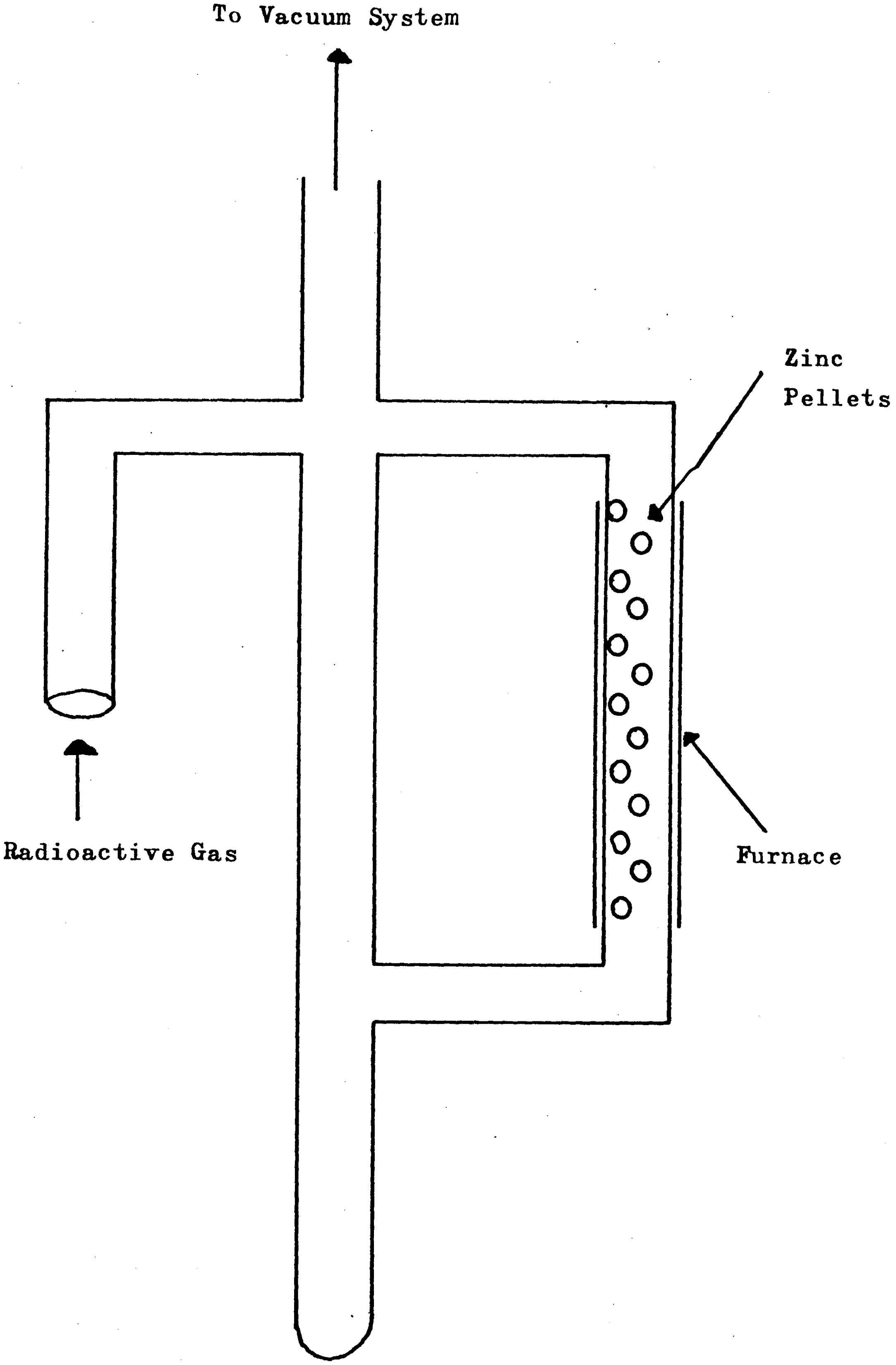


Figure 3.5 Reaction Vessel for Reduction of ^{14}C-carbon Dioxide.

constructed from a 15 cm length of Pyrex tubing 25 mm in diameter. A thermocouple was attached to the outside wall and the converter was then placed in a furnace. 50 grams of zinc pellets (about 6 mm in diameter) were made from a moistened mixture containing 95% by weight zinc dust and 5% aerosil silica. The silica was used in order to give greater porosity and to prevent clogging. The zinc pellets were dried at 110°C for 24 hr before being placed in the converter. They were degassed by heating to 320°C under vacuum pumping. Over 99·9% conversion was accomplished by circulating the $^{14}C-CO_2$ through the converter at 400°C for 36 hr.

(d) But-1-ene, cis-but-2-ene, trans-but-2-ene and buta-1:3-diene used in the chromatographic analysis were obtained from Matheson Company. These hydrocarbons contained no impurities detectable by gas chromatography and were merely degassed before use.

(e) N-hexane, cyclohexane, cyclohexene, benzene and toluene, ultra and analar, were obtained from B.D.H. Ltd., the purity level was determined by gas chromatography.

(f) ^{14}C-labelled benzene was supplied by the Radiochemical Centre, Amersham. The ampoule, containing 50 μCi of benzene of specific activity 40-60 mCi/mmol, was diluted to 1600 counts/μl with non-active benzene before use.

3.6 The Gas Chromatography System

Analysis of hydrocarbons was carried out by gas chromatography using a 100 cm 15% tricresyl phosphate-on-chromosorb P 30-60 mesh column. The column was operated at 70°C with helium or hydrogen as carrier gas at a flow rate of 60 ml/min and a filament current of 200 mA. The column gave excellent separation of the reaction products and unreacted hydrocarbons. A typical chromatographic trace is shown in figure 3.6. Quantitative results were obtained by computing the area of the peaks obtained using an "Allbrit" fixed arm planimeter.

A calibration was incorporated in every experiment in order to eliminate error due to day to day fluctuations in ambient and instrumental conditions. If the experiment was particularly long, the calibration was repeated at frequent intervals. The calibration usually consisted of a number of replicate injections of the initial reactant dose and all possible products, from which the sensitivity of each component relative to the reactant was determined.

3.7 Gas Proportional Counter

The use of radiotracers allows one to investigate the behaviour of labelled molecules on adsorption, desorption and displacement, during uninterrupted study of a surface process. A proportional flow counter similar to the design of Schmidt-Bleek and Rowland (67) was used in the radiochemical analysis, which could efficiently detect

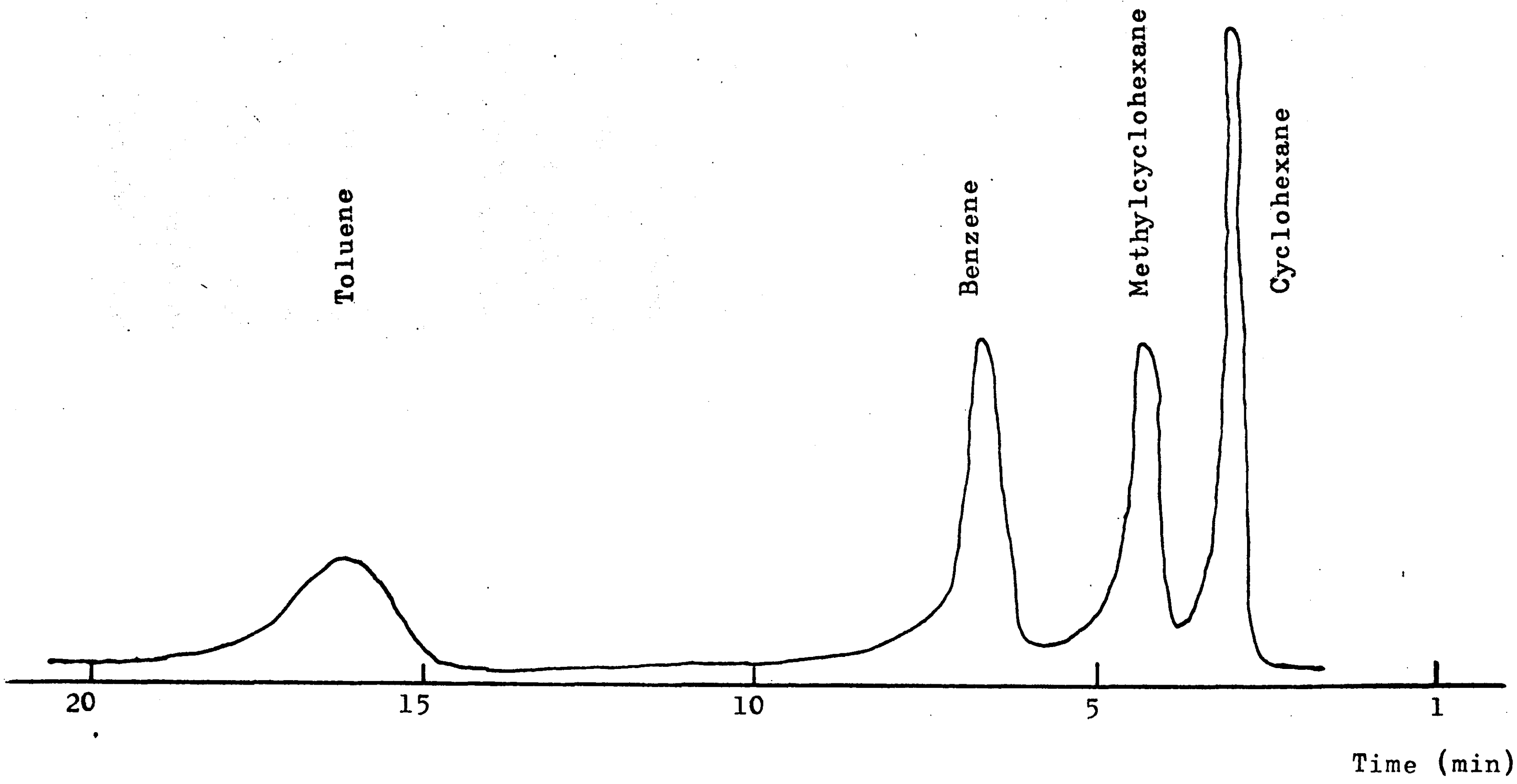


Figure 3.6 Chromatographic Analysis of a Sample of Hydrocarbons at 70°C.

radioactivity in the gases eluted from the chromatograph. The details of the counter are shown in figure 3.7.

The counter was connected to the outlet from the gas chromatograph and was operated using a filling of helium and methane in the ratio (10:1) at a flow rate of 60 ml/min. The ratio helium/methane is critical in order to obtain a plateau of length greater than 200 volts and slope less than 3% per 100 volts (68). The proportion of methane was accurately controlled by a needle valve which was located on the methane supply line before the junction with the chromatograph exhaust.

The proportional counter was connected to an Ekco M5024B Scaler-Timer. The 5050B Ratemeter was equipped with an amplifier, pulse-height analyser, ratemeter and high voltage supply and provided the following facilities.

(a) Ratemeter: Rate information is displayed on a meter having a 3 inch scale calibrated in pulse per second (pps). The rate range is 3 to 10^6 pps. Seven time constants can be selected from 0·1 to 100 seconds.

(b) Amplifier: Amplifier gain is adjustable in six switched steps from x 10 up to x 500 and a range of integrating and differentiating time constants are provided for selection of any desired frequency response within pass band of the basic amplifier.

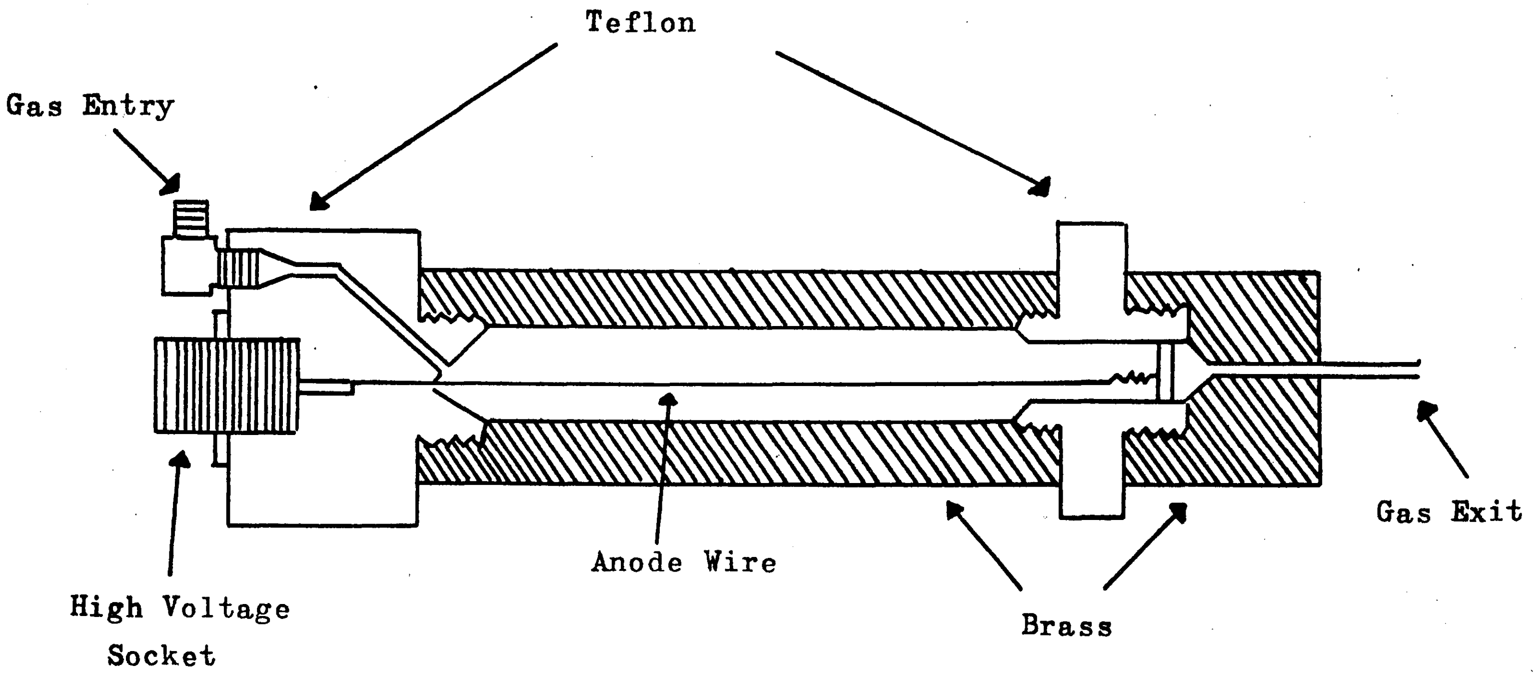


Figure 3.7 The Proportional Counter

(c)	Pulse-Height Analyser:	The pulse-height analyser (PHA) has three modes of operation. The dual disc, the proportional gate and the linear gate. The proportional gate mode, where the gate width is proportional to lower discriminator voltage, was used in these series of experiments.
(d)	Power:	Stabilised HV power, continuously variable from +10 V to +3 kV, was connected to counter externally via a coaxial socket.

The high speed scaler-timer M5024B (Ekco) was connected to the output from the pulse-height analyser and the scaler 100 mV recorder output was fed to a "Servoscribe" potentiometric recorder, where the activity in the eluted components was displayed as peaks. From the area of the peaks the total number of counts in the sample could be measured. In practice it was more usual to use the recorder tracer to determine when to start and stop counting with the scaler.

3.8 Operation of the Counter

It had been found (68) that the best counting conditions, in terms of plateau length and slope, were achieved with a helium to methane ratio of 10:1; as a helium flow rate of 60 ml/min had to be maintained for chromatographic separation, the methane flow was fixed at 6 ml/min. The gases were blended at a T-piece junction of the gas lines at the entrance to the counter. The amplifier was set at attenuation of 50 db. The pulse shaping controls of differentiation and integration were each set at 1·0 μ secs. The ratemeter setting was 1000 pps with a time constant of 10 secs. With these settings and using a ^{137}Cs external source the variation of count rate against applied voltage was investigated for a helium to methane ratio of 10:1. The plateau is shown in figure 3.8. With the counting mixture a plateau of length of 200 volts was regularly achieved.

The performance of the counter, like that of the chromatograph, was dependent upon day to day experimental conditions. Consequently before beginning the injection of labelled compounds over the catalyst, it was necessary to investigate the efficiency of the counter and reactant activity during each experiment. The efficiency of the counter was determined with the applied voltage set at the centre of the plateau and since 1·0 μl of benzene was always used, this quantity was injected into the flow stream with the external source near the counter. No fall from the plateau count rate, which corresponded precisely with that expected, was observed during the passage of benzene. The activity of reactant was determined from a number of replicate injections, which allowed the number of counts per μl in each injection to be compared.

Although conditions in similar experiments were kept

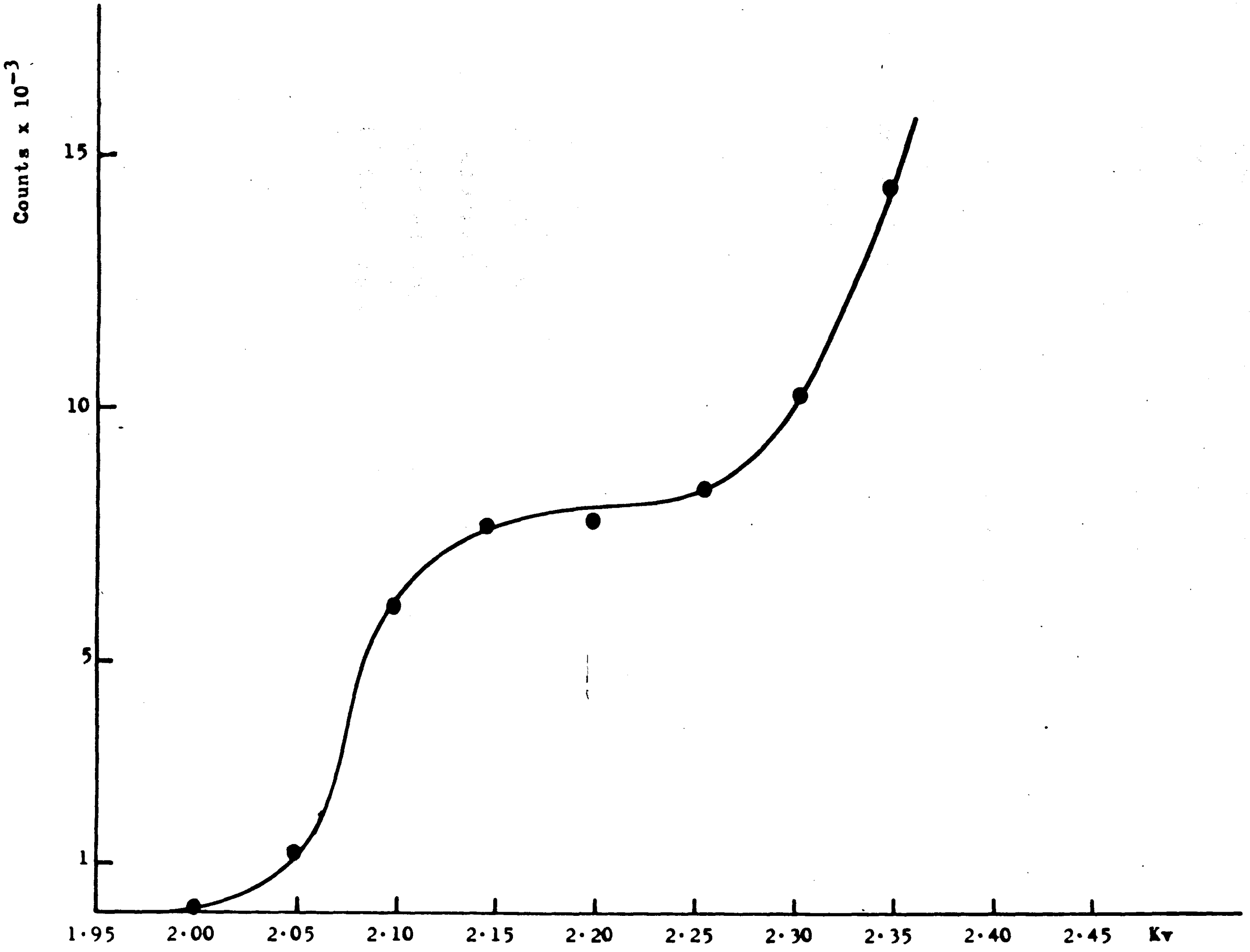


Figure 3.8 The Plateau

as uniform as possible it was not practicable to reproduce the exact sensitivities in both chromatograph and counter on every occasion and hence the necessity for regular calibration.

3.9 B.E.T. Surface Area

The surface areas of the catalysts were determined from the physical adsorption of nitrogen. This involved the measurement of the isotherm at liquid nitrogen temperature.

The essential features of the apparatus are shown in the figure 3.9. This consisted of two gas storage vessels and a mercury reservoir connected to a U-tube, which permitted measurements of the variation of volume of gas with pressure. The catalyst whose surface area was to be determined was contained in the bulb B, and was kept at 77 K in liquid nitrogen during the measurements.

The apparatus was evacuated by opening all the taps except those on the gas reservoirs. When a good vacuum was obtained, the taps at the top of the right-hand limb of the mercury U-tube were closed and then four sets of measurements were made as follows:

1. With volume B evacuated, tap (1) closed and helium in the system, a set of eight readings of V and P were taken by adjusting the height of the mercury level in the U-tube. By using the gas laws the volume of the dead-space above the zero mark on the burette was obtained.
2. The measurements in part 1 were repeated with the same sample of helium, but with tap (1) open and liquid nitrogen

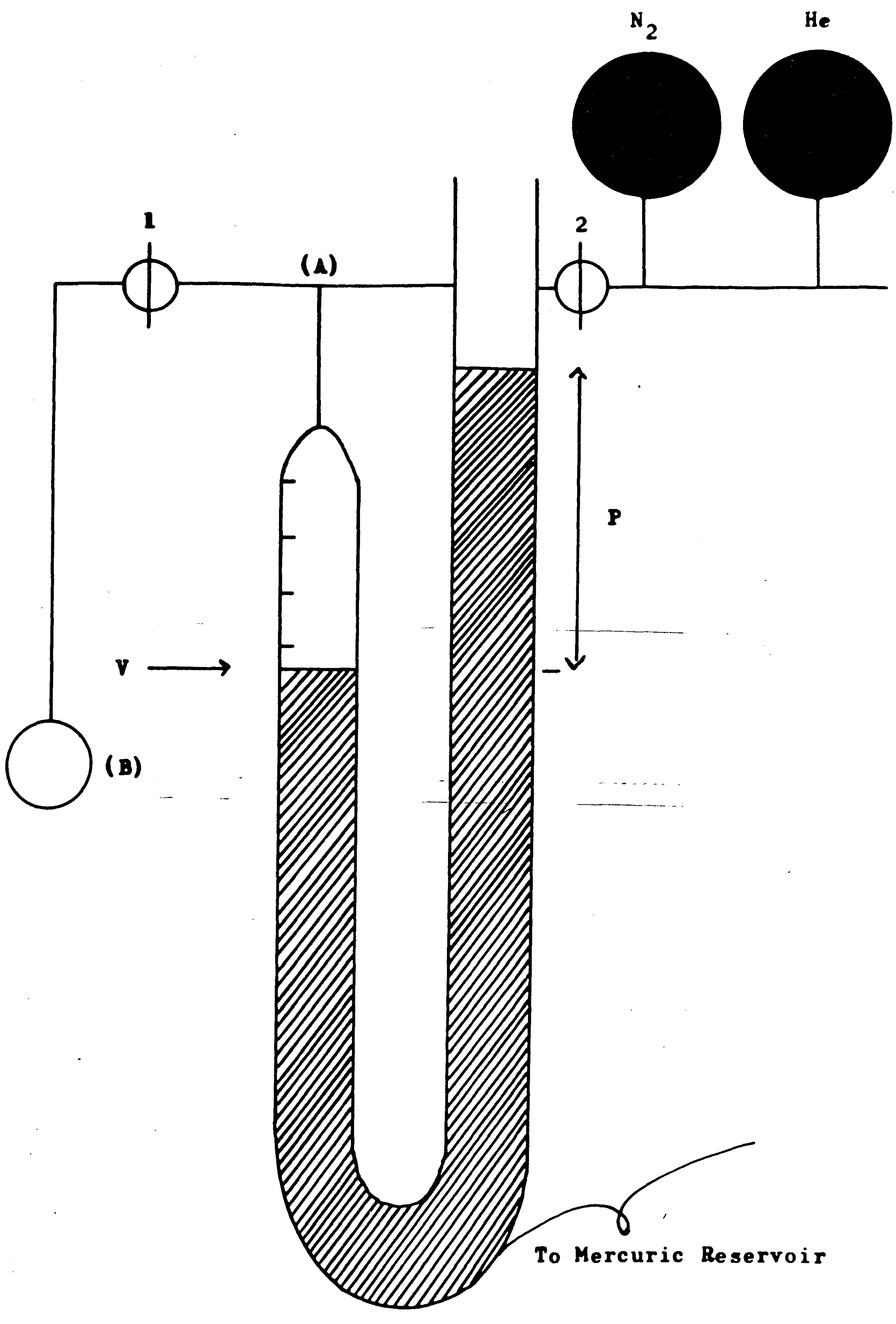


Figure 3.9 Nitrogen B.E.T. Adsorption System

surrounding the bulb containing the catalyst. The difference between the measurement and that made in part 1 allowed the determination of the effective volume of section B, that is the volume which is not occupied by the solid. Helium was used for the calibrations since it is not adsorbed even at liquid nitrogen temperatures. A plot of V against $\frac{T}{p}$ was constructed.

3. The apparatus was evacuated and step 1 was repeated using nitrogen instead of helium. The same dead-space volume was obtained with nitrogen.

4. Step (2) was repeated with the same sample of nitrogen as was used in step (3). The volume adsorbed at any particular pressure (ΔV) was determined from the difference between the volume coordinates on the reference plot in step (2) and the V vs $\frac{T}{p}$ plot obtained in step (4).

Following the B.E.T. equation:

$$\frac{p}{x(p^\circ - p)} = \frac{1}{c.x_m} + \frac{1}{x_m} \cdot \frac{p}{p^\circ} \qquad (3.1)$$

where x = amount adsorbed at pressure p;

p° = saturation vapour pressure of the gas at the adsorption temperature;

x_m = quantity of gas required to form a monolayer;

c = a constant for any particular gas/solid system,

a straight line plot of $\frac{p}{x(p^\circ - p)}$ against $\frac{p}{p^\circ}$ was made. From the gradient and the intercept of this graph a value of x_m was calculated and then converted to an area by assuming that each nitrogen molecule occupies $16 \cdot 2 \mathring{A}^2$ of surface.

3.10 Adsorption of ^{14}C-carbon Monoxide

The adsorption of carbon monoxide has been used many times to determine the surface metal area of supported catalysts. It is thought to adsorb specifically on the metal in a non-dissociative form and the relatively simple and well understood molecular structure allows a good estimate of the ratio of adsorbed molecules to surface metal atoms.

The apparatus used for the adsorption studies is shown schematically in figure 3.10. Using this system, the catalysts could be activated and then covered by ^{14}C-carbon monoxide by injecting pulses of known size into a nitrogen carrier gas stream and thence onto the catalyst. Adsorptions were followed by a Geiger-Muller detector coupled to a scaler ratemeter and chart recorder. A temperature of 20°C was maintained by a cylindrical electric furnace controlled by a West Guardian temperature programmer.

0·3-0·4g of the reduced catalyst was placed in the reactor between silica-wool plugs. Pretreatment of the catalyst was carried out, before each adsorption, by heating to 693 K for 1hr in oxygen, followed by flowing nitrogen at 693 K for 10 min and finally heating in a hydrogen flow for 1hr at 653 K. After activation, the catalyst was cooled in hydrogen to ambient temperature and then maintained in a flow of nitrogen.

^{14}C-carbon monoxide was prepared by reduction of ^{14}C-carbon dioxide of specific activity 59 mCi/mmol obtained

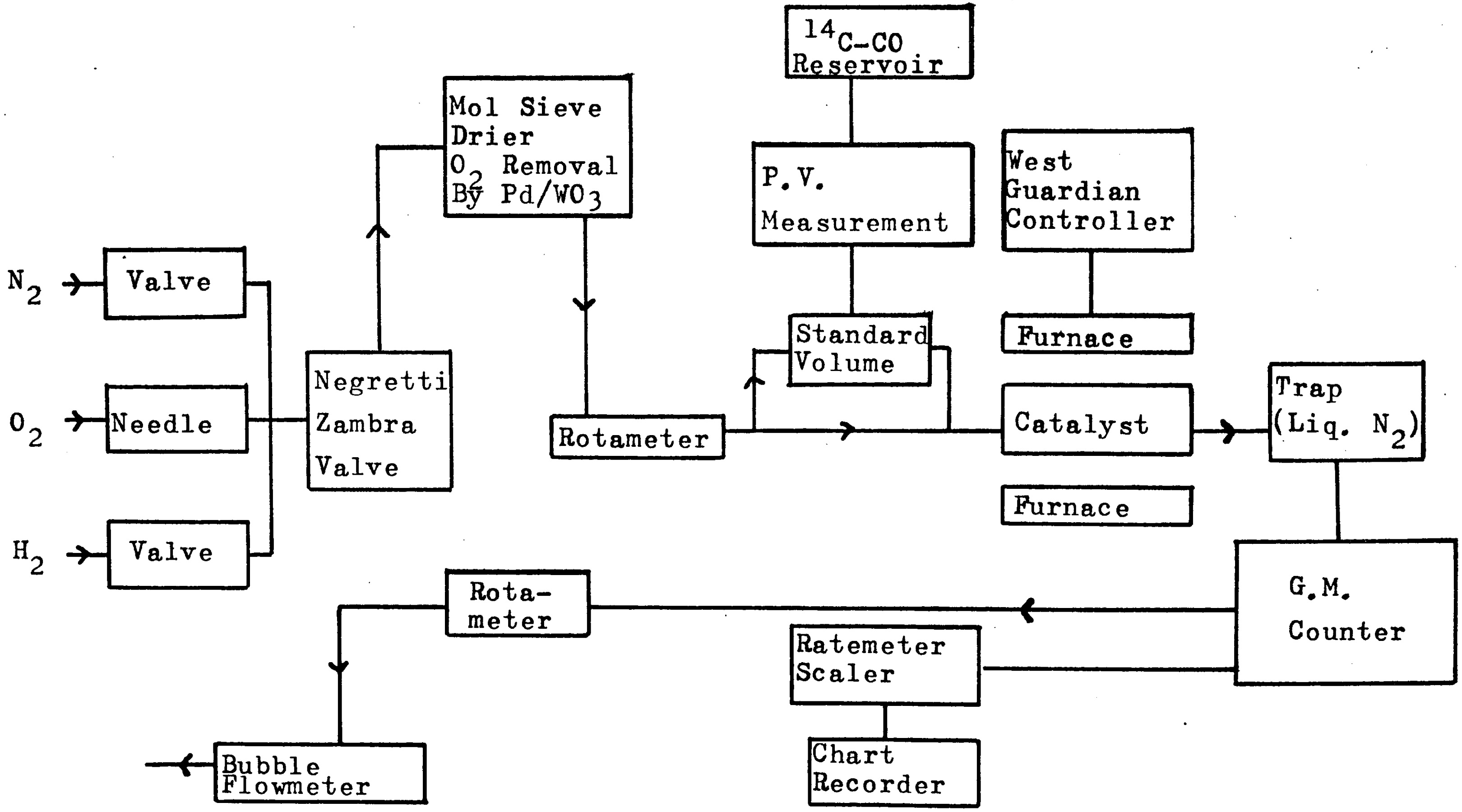


Figure 3.10 Flow System for Adsorption of ^{14}C-CO

from the Radiochemical Centre, Amersham. ^{14}C-carbon monoxide was diluted in a 500 cm^3 reservoir with non-radioactive carbon monoxide to a total pressure of 70 torr. 2·15 cm^3 samples, at a measured pressure of between 30 and 50 torr, were then injected into the nitrogen carrier gas stream and hence onto the catalyst. Amounts of ^{14}C-carbon monoxide adsorbed on the catalyst were determined from the difference between the calibration pulse peak area and the peak area obtained following the injection of comparable size pulses onto the catalyst. When a freshly activated catalyst was subjected to a series of carbon monoxide pulses at 5 min intervals, the first pulse was completely adsorbed and, thereafter, decreasing amounts were adsorbed with each successive pulse, until after nine or ten pulses the peak area obtained from the G.M. counter was similar to that obtained in the calibration pulse. From these series of adsorptions the number of ^{14}C-CO molecules adsorbed per gramme of catalyst was calculated, and assuming that 1 ml of CO occupies 2·39 m^2 (69), the surface metal area was obtained.

3.11 Experimental Procedure

(a) Studies of hydrocarbon retention by the platinum and palladium catalysts.

These series of experiments were conducted in helium as the carrier gas and were designed to investigate the variation in the amount of aromatic hydrocarbons adsorbed by the catalyst at a series of temperatures, namely 100°C, 150°C, 200°C and 250°C. These temperatures were chosen to give a wide range in which a change in the mode of adsorption of a hydrocarbon might occur.

A typical experiment was conducted in the following manner:

i) the reaction vessel was removed from the flow system at the Swagelok connections.

ii) 0·1g catalyst was placed in the bulb portion of the reactor and was held in place by a plug of silica-wool.

iii) the reaction vessel was reassembled into the flow system and surrounded by an electric furnace. Heat shields were arranged above the top and below the bottom of the furnace. The thermocouple was inserted into the thermowell provided in the vessel and new serum caps were put into the injection ports.

iv) the hydrogen line was connected to the catalyst side of the switch valves and hydrogen was passed over the catalyst at 30 ml/min. After hydrogen had been allowed to flow over the reaction vessel to displace the air from the system the temperature of the catalyst was raised to 350°C. At this temperature the reduction/activation was carried out for 6 hours.

v) at the end of the reduction period the flow of hydrogen was stopped and the switch valve SV1 turned to direct the He flow over the catalyst. To remove the bulk of the gas phase hydrogen from the system and clean the catalyst, the helium was allowed to pass through the reactor at the reduction temperature for 30 min and then for two hours at reaction temperature. During this period, the chromatograph filament current was turned up to 200 mA, the column temperature was increased to the working temperature of 70°C.

vi) as the catalyst was cooling to the required temperature, calibration injections of 1·0 μl were made into IP2, the calibration port. Usually four injections were sufficient to illustrate the reproducibility of the injection technique and detection system. Successive injections were then made over the catalyst at each temperature, and calibration injections were repeated periodically.

(b) Studies involving ^{14}C-benzene adsorption on the catalysts.

The second series of experiments was designed to investigate some of the properties of, and hence obtain information about, the nature of the adsorbed species retained by the catalysts when exposed to ^{14}C-benzene. The procedure in these experiments was essentially similar to that described in the previous section (a). The counter plateau and stability were checked using the ^{137}Cs source and a background determination was made while the helium was passing over the catalyst immediately before beginning the hydrocarbon injections. After calibration, injections of ^{14}C-benzene were made until saturation of the catalyst was achieved. These were followed by injection of either inactive benzene or hydrogen depending on the aim of the particular experiment.

(c) Studies involving the hydrogenation of aromatic hydrocarbons on the catalysts.

The reaction of aromatic hydrocarbons with hydrogen was examined using 0·005g of platinum and 0·1g palladium catalysts, at a series of temperatures between 105°C and 335°C. These experiments were conducted in hydrogen which is the reactant and carrier gas simultaneously. The catalyst samples were activated immediately before use at 350°C for 16hr in a stream of hydrogen and then the samples were cooled in a hydrogen stream to reaction temperature. Following this procedure, the activity of the catalyst was determined at both decreasing and increasing temperatures, the determinations were repeated at least twice at each temperature. A time interval of 15-25 min between individual tests was necessary for changing the catalyst temperature. 1·0 μℓ of hydrocarbon was injected onto a freshly reduced catalyst and the composition of the products determined from the chromatograph. The components were identified by comparing their retention times with those of pure substances used as calibration in each experiment.

(d) Studies of competitive hydrogenation of benzene and toluene on the catalysts.

In these series of experiments 1·0 μℓ of a mixture

1:1 (v/v) of benzene and toluene was injected on platinum and palladium catalysts. The studies were carried out in the same range of temperatures and with a similar procedure to that described in the section (c).

CHAPTER FOUR

CHAPTER FOUR

THE RESULTS

4.1 Catalyst Characterization

For the comparison of the catalytic activities of different catalysts, it is desirable to separate the two factors involved, namely the available surface area of the active phase and its activity normalized per unit of surface area. Very often in catalysis research it is essential to discover what proportion of the total surface area is active, in order to facilitate interpretation of the results. The determination of the surface areas of the catalysts were carried out using B.E.T. method and adsorption of carbon monoxide.

4.1.1 B.E.T. Surface Area

In the measurements of total surface areas of the catalysts by physical adsorption, nitrogen was used as adsorbate. In a typical physical adsorption experiment 0·2 – 0·3 g of catalyst sample was placed in a glass sample tube and adsorptions were performed as described in the section 3.9. The results obtained are shown in tables 4.1 – 4.4.

Plots of $\frac{p}{x(p^o-p)}$ against p/p^o are shown in the figures 4.1 and 4.2. Each straight line plot was extrapolated to $p/p^o = 0$. The intercept obtained from this

TABLE 4.1 Adsorption Data for Nitrogen on 0·2076 g 5% Pt/SiO_2 Catalyst at 77 K.

$V(cm^3)$	p(mmHg)	$p/_{p^o}$	$\frac{p}{x(p^o-p)} \times 10^{20}$
30·5	218·52	0·29	0·19
29·5	236·00	0·31	0·20
28·5	256·52	0·34	0·21
27·5	280·95	0·37	0·23
26·0	310·53	0·41	0·26
25·0	347·06	0·46	0·30
24·0	393·33	0·52	0·35

TABLE 4.2 Adsorption Data for Nitrogen on 0·2851 g 5% Pt/Al_2O_3 Catalyst at 77 K.

$V(cm^3)$	p(mmHg)	$p/_{p^o}$	$\frac{p}{x(p^o-p)} \times 10^{20}$
27·5	217·04	0·29	0·20
26·5	234·40	0·31	0·22
25·5	254·78	0·34	0·24
25·0	279·05	0·37	0·25
24·5	308·42	0·41	0·28
24·0	344·71	0·45	0·31

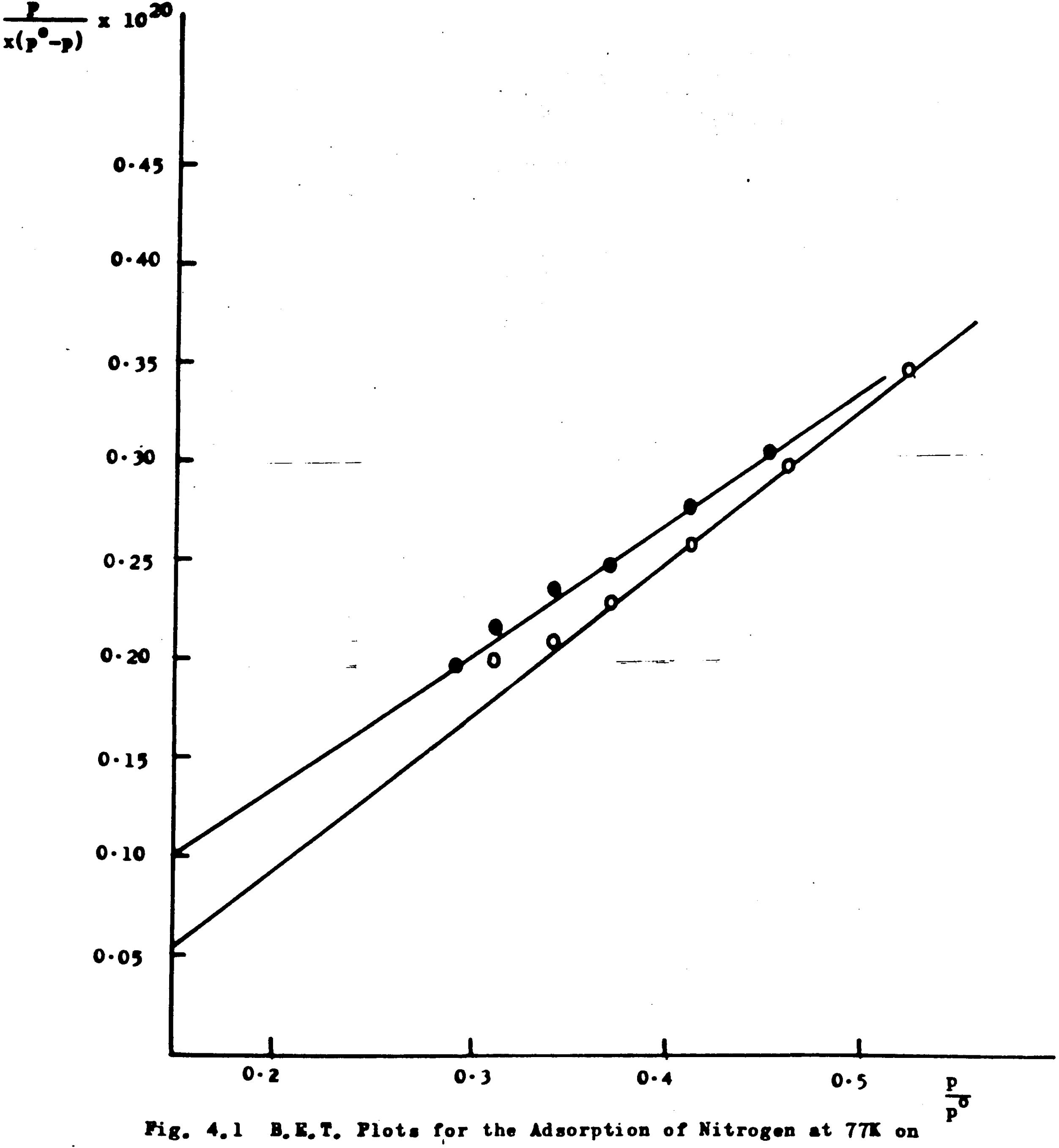


Fig. 4.1 B.E.T. Plots for the Adsorption of Nitrogen at 77K on ● Pt/Al_2O_3 and on O Pt/SiO_2.

TABLE 4.3 Adsorption Data for Nitrogen on 0·2022 g 5% Pd/SiO_2 Catalyst at 77 K.

$V(cm^3)$	p(mmHg)	$p/_{p^o}$	$\frac{p}{x(p^o-p)} \times 10^{20}$
38·0	218·52	0·29	0·15
35·0	236·00	0·31	0·17
32·5	256·52	0·34	0·19
30·0	280·95	0·37	0·21
27·5	310·53	0·41	0·25
24·5	347·06	0·46	0·30

TABLE 4.4 Adsorption Data for Nitrogen on 0·3036 g 5% Pd/Al_2O_3 Catalyst at 77 K.

$V(cm^3)$	p(mmHg)	$p/_{p^o}$	$\frac{p}{x(p^o-p)} \times 10^{20}$
28·33	220·4	0·29	0·20
27·71	235·6	0·31	0·21
26·46	258·4	0·34	0·23
25·50	281·2	0·37	0·25
24·31	311·6	0·41	0·28
23·55	342·0	0·45	0·31

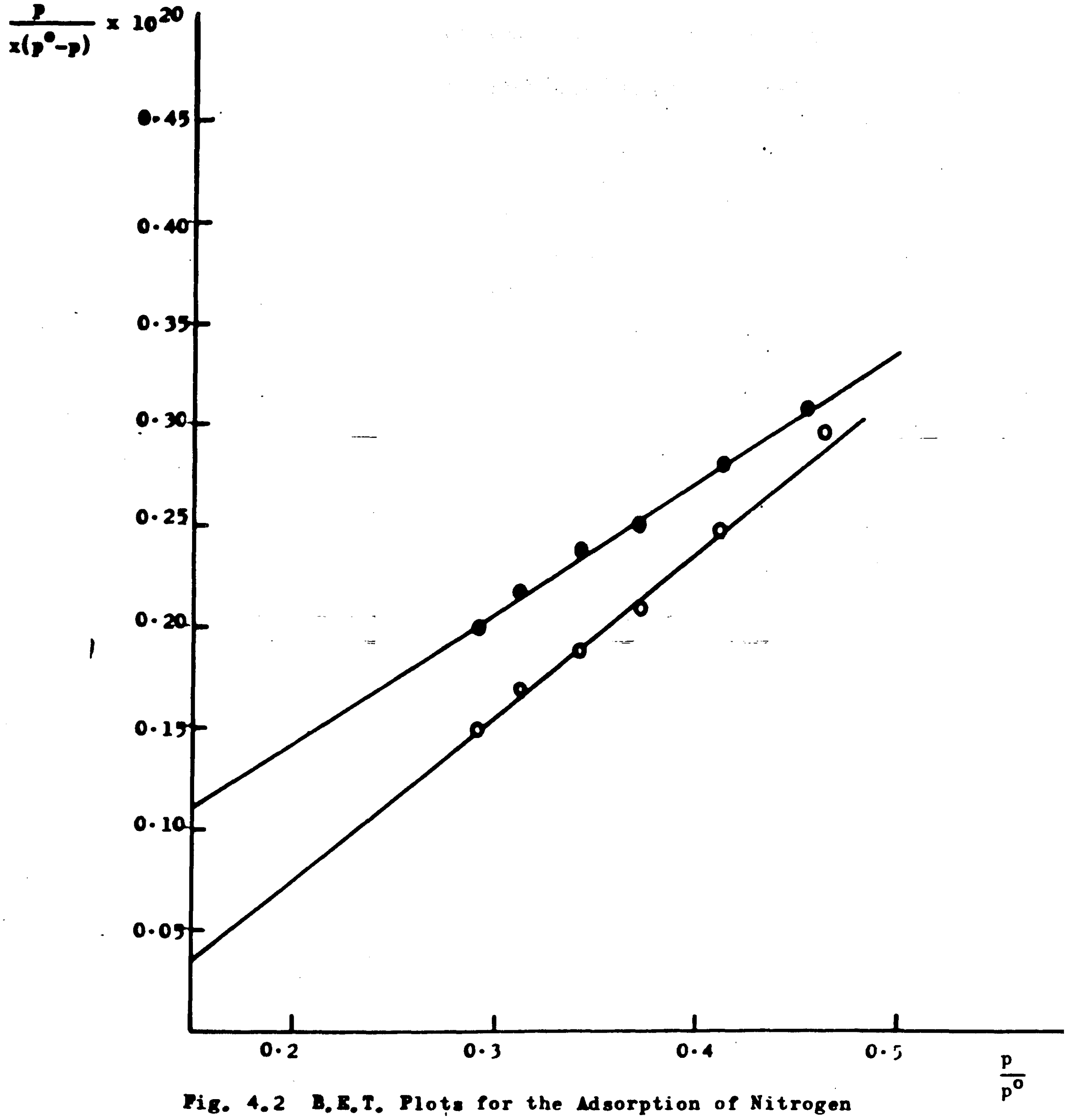


Fig. 4.2 B.E.T. Plots for the Adsorption of Nitrogen at 77K on ● Pd/Al_2O_3 and on O Pd/SiO_2

extrapolation along with the slope of the straight line permitted the determination of the quantity of gas required to form a monolayer and hence the surface area, assuming that each nitrogen molecule occupies 16·2 Å of surface. The values obtained for the surface areas of the catalysts are shown in table 4.5.

TABLE 4.5

B.E.T. Surface Areas

Catalyst	Total Surface Area (m^2/g)
5% Pd/Al_2O_3	162·21
5% Pt/Al_2O_3	164·97
5% Pd/SiO_2	197·01
5% Pt/SiO_2	195·09

4.1.2 Adsorption of ^{14}C-Carbon Monoxide

In the study of specific metal areas of supported metal catalysts, chemisorption methods represent the most useful technique. Carbon monoxide chemisorption is commonly used as a direct quantitative method. The basis of the method is the existence of conditions where CO will chemisorb selectively on the metal but not on the support. The amount of carbon monoxide adsorbed at room temperature is defined as a "CO monolayer" and consequently defines the concentration of CO active surface sites on the catalyst.

^{14}C-labelled CO, which specifically adsorbed on the metal, in a nitrogen flow-stream was passed over each of the platinum and palladium catalysts. The concentration of the adsorbate in the effluent gas was determined by G.M. counting as described in section 3.10. Eischens and Pliskin (70) from infrared studies have suggested that, on γ-alumina supported platinum, half of the chemisorbed CO is in the bridged structure, while on silica-supported platinum not more than 15% CO is in bridged form. According to Scholten and Van Montfoort (71), the chemisorption of CO on palladium supported on alumina occurs with 50% in the linear and 50% in the bridged form. The infrared results of Palazov et al (72) revealed that both bridged and linear species exist on palladium supported on silica-catalysts. From these observations and assuming that 1 ml of carbon monoxide occupies $2{\cdot}39\ m^2$ of surface, the number of active sites on the catalyst were then calculated and the surface metal areas of the catalysts were obtained. Table 4.6 shows the results obtained with the various catalyst samples.

4.2 Studies of Hydrocarbon Retention by the Platinum and Palladium Catalysts

The adsorption experiments were conducted in helium as carrier gas at atmospheric pressure, and were designed to investigate the variation in the amount of hydrocarbon adsorbed by the catalyst with temperature and with the

TABLE 4.6

Carbon Monoxide Chemisorption

Catalyst	CO Monolayer Coverage (Molecules/g Catalyst)	Total Metal Atoms Exposed	Surface Metal Area (m^2/g Catalyst)
5% Pd/Al_2O_3	$(1{\cdot}53 \pm 0{\cdot}05) \times 10^{19}$	$(2{\cdot}3 \pm 0{\cdot}06) \times 10^{19}$	$1{\cdot}42 \pm 0{\cdot}03$
5% Pt/Al_2O_3	$(1{\cdot}72 \pm 0{\cdot}05) \times 10^{19}$	$(2{\cdot}58 \pm 0{\cdot}02) \times 10^{19}$	$1{\cdot}63 \pm 0{\cdot}02$
5% Pd/SiO_2	$(1{\cdot}52 \pm 0{\cdot}00) \times 10^{19}$	$(2{\cdot}28 \pm 0{\cdot}00) \times 10^{19}$	$1{\cdot}45 \pm 0{\cdot}01$
5% Pt/SiO_2	$(2{\cdot}12 \pm 0{\cdot}05) \times 10^{19}$	$(2{\cdot}44 \pm 0{\cdot}05) \times 10^{19}$	$2{\cdot}02 \pm 0{\cdot}05$

nature of the hydrocarbon.

The measurements were carried out in the flow system reactor described earlier (3.2), and a ratio of 1·0 μℓ hydrocarbon to 0·1g catalyst was used. The amount of adsorbed hydrocarbon was evaluated from the difference in area of the chromatograms of the products and of the hydrocarbon calibrations.

Results of the adsorption studies of benzene and toluene are given in the following sections and the presentation includes the complete analysis of the experiments for each hydrocarbon at each temperature investigated.

4.2.1 Benzene Adsorption on 5% Pt/Al_2O_3

1·0 μℓ of benzene was injected onto a freshly reduced catalyst at 100°, 150°, 200° and 250°C. In each case the extent of the retention, by the catalyst, was examined with the same sample and regeneration of the surface was carried out, after each series of experiments at a given temperature, in a stream of hydrogen at 350°C for six hours followed by treatment in the helium stream before further dosing with benzene was commenced. The results obtained are shown in table 4.7.

From these results it can be seen that, the saturation of the surface was achieved after one injection of hydrocarbon. The amount retained on the catalyst is practically constant in the range of temperature between 100° and 250°C as shown in table 4.8, where the ratio $\left(N_{C_6H_6}/N_{sites}\right)$ is

TABLE 4.7

Complete Analysis for Benzene on 5% Pt/Al_2O_3

Injection No.	Amount of Benzene Recovered (µℓ)	% Benzene Retained
A. Benzene Injections (1·0 µℓ) at 100°C		
1.	0·570	43·00
2.	0·570	43·00
3.	0·570	43·00
4.	0·570	43·00
5.	0·570	43·00
B. Benzene Injections (1·0 µℓ) at 150°C		
1.	0·570	43·00
2.	0·570	43·00
3.	0·570	43·00
4.	0·570	43·00
5.	0·570	43·00
C. Benzene Injections (1·0 µℓ) at 200°C		
1.	0·560	44·00
2.	0·560	44·00
3.	0·560	44·00
4.	0·560	44·00
5.	0·560	44·00
D. Benzene Injections (1·0 µℓ) at 250°C		
1.	0·550	45·00
2.	0·550	45·00
3.	0·550	45·00
4.	0·550	45·00
5.	0·550	45·00

the number of molecules of benzene adsorbed per surface metal site, as determined by carbon monoxide adsorption.

TABLE 4.8

Total Retention of Benzene by Pt/Al_2O_3 Catalysts

Temperature (°C)	$10^{-4} \times \frac{\text{g Benzene}}{\text{g Catalyst}}$	Molecules on Catalyst	$\frac{N_{C_6H_6}}{Nsites}$
100°	37·67	$2{\cdot}91 \times 10^{18}$	0·340
150°	37·67	$2{\cdot}91 \times 10^{18}$	0·340
200°	38·54	$2{\cdot}98 \times 10^{18}$	0·348
250°	39·42	$3{\cdot}04 \times 10^{18}$	0·356

4.2.2 Benzene Adsorption on 5% Pd/Al_2O_3

The retention of benzene was examined on Pd/Al_2O_3 catalyst under the same conditions as those used with the Pt/Al_2O_3 catalyst; the object being to compare the activity of the metals in adsorption phenomena of benzene. The results obtained are shown in table 4.9. With this catalyst, as with Pt/Al_2O_3, one injection was necessary to reach reproducible behaviour, but from the data obtained, it can be seen that the amount retained on Pd/Al_2O_3 was less than on Pt/Al_2O_3 at each temperature. Table 4.10 shows the results obtained from multiple injections of benzene.

TABLE 4.9

Complete Analysis for Benzene on 5% Pd/Al_2O_3

Injection No.	Amount Benzene Recovered (μℓ)	% Benzene Retained
	A. Benzene Injections (1·0 μℓ) at 100°C	
1	0·640	36·00
2	0·640	36·00
3	0·640	36·00
4	0·640	36·00
5	0·640	36·00
	B. Benzene Injections (1·0 μℓ) at 150°C	
1	0·640	36·00
2	0·640	36·00
3	0·640	36·00
4	0·640	36·00
5	0·640	36·00
	C. Benzene Injections (1·0 μℓ) at 200°C	
1	0·630	37·00
2	0·630	37·00
3	0·630	37·00
4	0·630	37·00
5	0·630	37·00
	D. Benzene Injections (1·0 μℓ) at 250°C	
1	0·630	37·00
2	0·630	37·00
3	0·630	37·00
4	0·630	37·00
5	0·630	37·00

TABLE 4.10

Total Retention of Benzene by Pd/Al_2O_3 Catalysts

Temperature (°C)	10^{-4}x $\frac{\text{g Benzene}}{\text{g Catalyst}}$	Molecules on Catalyst	$\frac{N_{C_6H_6}}{\text{Nsites}}$
100°	31·63	$2{\cdot}44 \times 10^{18}$	0·315
150°	31·63	$2{\cdot}44 \times 10^{18}$	0·315
200°	32·51	$2{\cdot}51 \times 10^{18}$	0·324
250°	32·51	$2{\cdot}51 \times 10^{18}$	0·324

4.2.3 Benzene Adsorption on 5% Pd/SiO_2

The retention of benzene was carried out on Pd supported on silica at 100°, 150°, 200° and 250°C. The procedure in these experiments was essentially similar to that described in the previous section. These studies were carried out to investigate possible effects of the support in the adsorption of benzene. The results obtained are shown in table 4.11. From the results obtained on Pd/SiO_2 it can be seen that the reproducible behaviour was achieved after two injections over the catalyst. The amount retained by Pd catalyst in this case was greater than Pd supported on alumina. Table 4.12 shows the analysis of retention of benzene by Pd/SiO_2.

TABLE 4.11

Complete Analysis for Benzene on 5% Pd/SiO_2

Injection No.	Amount Benzene Recovered (μl)	% Benzene Retained
	A. Benzene Injections (1·0 μl) at 100°C	
1	0·560	44·00
2	0·580	42·00
3	0·580	42·00
4	0·580	42·00
5	0·580	42·00
	B. Benzene Injections (1·0 μl) at 150°C	
1	0·550	45·00
2	0·580	42·00
3	0·580	42·00
4	0·580	42·00
5	0·580	42·00
	C. Benzene Injections (1·0 μl) at 200°C	
1	0·550	45·00
2	0·580	42.00
3	0·580	42·00
4	0·580	42·00
5	0·580	42·00
	D. Benzene Injections (1·0 μl) at 250°C	
1	0·550	45·00
2	0·580	42·00
3	0·580	42·00
4	0·580	42·00
5	0·580	42·00

TABLE 4.12

Total Retention of Benzene by Pd/SiO_2 Catalyst

Temperature (°C)	$10^{-4} \times \frac{\text{g Benzene}}{\text{g Catalyst}}$	Molecules on Catalyst	$\frac{N_{C_6H_6}}{N_{sites}}$
100°	75·33	$5{\cdot}83 \times 10^{18}$	0·759
150°	76·21	$5{\cdot}89 \times 10^{18}$	0·767
200°	76·21	$5{\cdot}89 \times 10^{18}$	0·767
250°	76·21	$5{\cdot}89 \times 10^{18}$	0·767

4.2.4 Summary

The adsorption results from benzene on Pt/Al_2O_3, Pd/Al_2O_3 and Pd/SiO_2 are summarised in table 4.13.

4.2.5 Toluene Adsorption on 5% Pt/Al_2O_3

The retention of toluene was examined on 5% Pt/Al_2O_3 at the same temperatures as those studied with benzene. 1·0 μl of toluene was injected into the helium stream above 0·10 g of the catalyst, which had been reduced/reactivated at 350°C and cooled to reaction temperature. The conditions were kept as similar as possible to those used in the adsorption of benzene, with the object of comparing the adsorption capacity of the catalysts with different hydrocarbons. The data obtained are shown in table 4.14. With this hydrocarbon two injections were necessary before the saturation of the surface was achieved. The number of molecules retained by

TABLE 4.13

Retention of Benzene Adsorbed on Various Catalysts

t	5% Pt/Al_2O_3		5% Pd/Al_2O_3		5% Pd/SiO_2	
(°C)	10^{-4}x $\frac{\text{g Benzene}}{\text{g Catalyst}}$	$\frac{N_{C_6H_6}}{N\text{sites}}$	10^{-4}x $\frac{\text{g Benzene}}{\text{g Catalyst}}$	$\frac{N_{C_6H_6}}{N\text{sites}}$	10^{-4}x $\frac{\text{g Benzene}}{\text{g Catalyst}}$	$\frac{N_{C_6H_6}}{N\text{sites}}$
100°	37·67	0·340	31·63	0·315	75·33	0·759
150°	37·67	0·340	31·63	0·315	76·21	0·767
200°	38·54	0·378	32·51	0·324	76·21	0·767
250°	39·42	0·356	32·51	0·324	76·21	0·767

TABLE 4.14

Complete Analysis for Toluene on 5% Pt/Al_2O_3

Injection No.	Amount Toluene Recovered (μℓ)	% Toluene Retained
	A. Toluene Injections (1·0 μℓ) at 100°C	
1.	0·500	50·00
2.	0·560	44·00
3.	0·560	44·00
4.	0·560	44·00
5.	0·560	44·00
	B. Toluene Injections (1·0 μℓ) at 150°C	
1.	0·490	51·00
2.	0·550	45·00
3.	0·550	45·00
4.	0·550	45·00
5.	0·550	45·00
	C. Toluene Injections (1·0 μℓ) at 200°C	
1.	0·510	49·00
2.	0·570	43·00
3.	0·570	43·00
4.	0·570	43·00
5.	0·570	43·00
	D. Toluene Injections (1·0 μℓ) at 250°C	
1.	0·510	49·00
2.	0·570	43·00
3.	0·570	43·00
4.	0·570	43·00
5.	0·570	43·00

the catalyst was similar at each temperature. At 250°C a very small amount of benzene was observed in the chromatogram. Table 4.15 shows the results obtained from multiple injections of toluene.

TABLE 4.15

Total Retention of Toluene by Pt/Al_2O_3

Temperature (°C)	$10^{-4} \times \frac{\text{g Toluene}}{\text{g Catalyst}}$	Molecules on Catalyst	$\frac{N_{C_7H_8}}{\text{Nsites}}$
100°	81·24	$5{\cdot}33 \times 10^{18}$	0·622
150°	82·97	$5{\cdot}44 \times 10^{18}$	0·635
200°	79·52	$5{\cdot}21 \times 10^{18}$	0·609
250°	79·52	$5{\cdot}21 \times 10^{18}$	0·609

4.2.6 Toluene Adsorption on 5% Pd/Al_2O_3

The adsorption of toluene, measured at four temperatures on the same sample of catalyst is presented in table 4.16. One injection only was necessary to reach the reproducible behaviour on this catalyst. The variation of the amount retained by Pd/Al_2O_3 with temperature is practically constant and was less than the amount retained by Pt/Al_2O_3 under the same conditions. The results obtained from multiple injections of toluene on Pd/Al_2O_3 are shown in table 4.17.

TABLE 4.16

Complete Analysis for Toluene on 5% Pd/Al_2O_3

Injection No.	Amount Toluene Recovered (μl)	% Toluene Retained
A. Toluene Injections (1·0 μl) at 100°C		
1.	0·570	43·00
2.	0·570	43·00
3.	0·570	43·00
4.	0·570	43·00
5.	0·570	43·00
B. Toluene Injections (1·0 μl) at 150°C		
1.	0·570	43·00
2.	0·570	43·00
3.	0·570	43·00
4.	0·570	43·00
5.	0·570	43·00
C. Toluene Injections (1·0 μl) at 200°C		
1.	0·580	42·00
2.	0·580	42·00
3.	0·580	42·00
4.	0·580	42·00
5.	0·580	42·00
D. Toluene Injections (1·0 μl) at 250°C		
1.	0·580	42·00
2.	0·580	42·00
3.	0·580	42·00
4.	0·580	42·00
5.	0·580	42·00

TABLE 4.17

Total Retention of Toluene by Pd/Al_2O_3

Temperature (°C)	$10^{-4} \times \frac{\text{g Toluene}}{\text{g Catalyst}}$	Molecules on Catalyst	$\frac{N_{C_7H_8}}{N\text{sites}}$
100°	37·28	$2{\cdot}44 \times 10^{18}$	0·315
150°	37·28	$2{\cdot}44 \times 10^{18}$	0·315
200°	36·41	$2{\cdot}38 \times 10^{18}$	0·307
250°	36·41	$2{\cdot}38 \times 10^{18}$	0·307

4.2.7 Toluene Adsorption on 5% Pd/SiO_2

The results obtained for adsorption of toluene on palladium supported on silica at 100°, 150°, 200° and 250°C are shown in table 4.18. At 250°C, carbon-carbon bond fission was observed in the first injection of toluene; the products of hydrogenolysis were methane and benzene. Two injections were necessary before reproducible behaviour was achieved. Table 4.19 shows the results obtained for total retention of toluene on 5% Pd/SiO_2.

TABLE 4.18

Complete Analysis for Toluene on 5% Pd/SiO_2

Injection No.	Amount Toluene Recovered (μℓ)	% Toluene Retained
	A. Toluene Injections (1·0 μℓ) at 100°C	
1.	0·630	37·00
2.	0·660	34·00
3.	0·660	34·00
4.	0·660	34·00
5.	0·660	34·00
	B. Toluene Injections (1·0 μℓ) at 150°C	
1.	0·625	37·50
2.	0·660	34·00
3.	0·660	34·00
4.	0·660	34·00
5.	0·660	34·00
	C. Toluene Injections (1·0 μℓ) at 200°C	
1.	0·635	36·50
2.	0·650	35·00
3.	0·650	35·00
4.	0·650	35·00
5.	0·650	35·00
	D. Toluene Injections (1·0 μℓ) at 250°	
1.	0·591	40·90
2.	0·630	37·00
3.	0·630	37·00
4.	0·630	37·00
5.	0·630	37·00

TABLE 4.19

Total Retention of Toluene by Pd/SiO_2

Temperature (°C)	$10^{-4} \times \frac{\text{g Toluene}}{\text{g Catalyst}}$	Molecules on Catalyst	$\frac{N_{C_7H_8}}{N\text{sites}}$
100°	61·49	$4{\cdot}02 \times 10^{18}$	0·525
150°	61·92	$4{\cdot}05 \times 10^{18}$	0·529
200°	61·92	$4{\cdot}05 \times 10^{18}$	0·529
250°	67·46	$4{\cdot}41 \times 10^{18}$	0·576

4.2.8 Summary

The adsorption results for toluene on Pt/Al_2O_3, Pd/Al_2O_3 and Pd/SiO_2 are summarised in table 4.20.

4.3 Studies Involving ^{14}C-Benzene Adsorption on the Catalyst

These series of experiments describe a further study of the adsorption of benzene on platinum and palladium using carbon-14 as tracer in an attempt to understand further the nature and reactivity of adsorbed species at the metal surfaces. The procedure, detailed in section 3.11 involved five injections of labelled benzene onto a freshly reduced catalyst at 100°, 150°, 200° and 250°C.

The results for the radiochemical analysis of the reactor eluant are given in the following sections and the presentation includes details of a study of the reactivity

TABLE 4.20

The Retention of Toluene Adsorbed on Various Catalysts

t	5% Pt/Al_2O_3		5% Pd/Al_2O_3		5% Pd/SiO_2	
(°C)	$10^{-4} x \frac{\text{g Toluene}}{\text{g Catalyst}}$	$\frac{N_{C_7H_8}}{N\text{sites}}$	$10^{-4} x \frac{\text{g Toluene}}{\text{g Catalyst}}$	$\frac{N_{C_7H_8}}{N\text{sites}}$	$10^{-4} x \frac{\text{g Toluene}}{\text{g Catalyst}}$	$\frac{N_{C_7H_8}}{N\text{sites}}$
100°	81·24	0·622	37·28	0·315	61·49	0·525
150°	82·97	0·635	37·28	0·315	61·92	0·529
200°	79·52	0·609	36·41	0·307	61·92	0·529
250°	79·52	0·609	36·41	0·307	67·46	0·576

of the retained species in molecular exchange and hydrogenation reaction.

4.3.1 Benzene Exchange on 5% Pt/Al_2O_3

1·0 μℓ of hydrocarbon was injected onto the catalyst at a fixed temperature in the range 100° to 250°C. The catalyst surface was first saturated with ^{14}C-benzene by injecting successive pulses (usually five) of 1·0 μℓ benzene onto the catalyst until reproducible behaviour was achieved. This was followed by four injections each of 1·0 μℓ of inactive benzene over the catalyst and the reactor eluant was analysed for radioactivity. The results obtained are shown in table 4.21. In this and the ensuing tables, the activities are expressed as counts per microlitre. These were obtained by dividing the total integrated counts from the flow counter by the volume of hydrocarbon as determined by the gas chromatograph.

4.3.2 Hydrogenation of Benzene Residues on the Platinum Catalyst

The catalyst pretreatment was again standard and multiple injections of radioactive hydrocarbon were made onto the surface. This was followed for three injections of 5 ml of hydrogen onto the catalyst and the results obtained are shown in table 4.22.

TABLE 4.21

Radiochemical Analysis of Eluant from ^{14}C-Benzene Adsorption on 5% Pt/Al_2O_3

Temp (°C)	Substance Injected	Adsorption µℓ	cpµℓ x 10^{-3}	% Benzene Retained	Exchange as % Adsorption
	Molecular Exchange				
100°	$^{14}C-C_6H_6$	0·430	0·45	43·00	-
	$^{12}C-C_6H_6$	0·410	0·00	41·00	-
150°	$^{14}C-C_6H_6$	0·430	0·45	43·00	-
	$^{12}C-C_6H_6$	0·420	0·00	42·00	-
200°	$^{14}C-C_6H_6$	0·440	0·43	44·00	-
	$^{12}C-C_6H_6$	0·430	0·00	43·00	-
250°	$^{14}C-C_6H_6$	0·450	0·42	45·00	-
	$^{12}C-C_6H_6$	0·450	0·00	45·00	-

TABLE 4.22

Radiochemical Analysis of Eluant from ^{14}C-Benzene Adsorption on 5% Pt/Al_2O_3. (Specific Activity $1{\cdot}0 \times 10^3$ counts/μℓ)

Temp (°C)	Substance Injected	Adsorption μℓ	Adsorption cpμℓx10^{-3}	% Benzene Retained	Hydrogenation as % Adsorption (cyclohexane)
100°	$^{14}C-C_6H_6$	0·430	0·45	43·00	-
	H_2(5 ml)	-		-	3·00
150°	$^{14}C-C_6H_6$	0·420	0·46	42·00	-
	H_2(5 ml)	-		-	3·00
200°	$^{14}C-C_6H_6$	0·430	0·45	43·00	-
	H_2(5 ml)	-		-	1·00
250°	$^{14}C-C_6H_6$	0·440	0·43	44·00	-
	H_2(5 ml)	-		-	-

4.3.3 Benzene Exchange on 5% Pd/Al_2O_3

The exchange reaction on Pd catalyst was examined under the same conditions and in the same range of temperature as with the Pt catalyst. Table 4.23 shows that, the injection of inactive benzene onto Pd catalyst, after it had been exposed to ^{14}C-benzene resulted in the recovery of inactive benzene only, at all temperatures used.

TABLE 4.23

Radiochemical Analysis of Eluant from ^{14}C-Benzene Adsorption on 5% Pd/Al_2O_3. (Specific Activity $1\cdot0 \times 10^3$ counts/μℓ)

Temp (°C)	Substance Injected	Adsorption μℓ	Adsorption cpμℓ x 10^{-3}	% Benzene Retained	Exchange as % Adsorption
	Molecular Exchange				
100°	$^{14}C-C_6H_6$	0·37	0·37	37·00	-
	$^{12}C-C_6H_6$	0·36	0·00	36·00	-
150°	$^{14}C-C_6H_6$	0·36	0·35	36·00	-
	$^{12}C-C_6H_6$	0·34	0·00	34·00	-
200°	$^{14}C-C_6H_6$	0·37	0·37	37·00	-
	$^{12}C-C_6H_6$	0·34	0·00	34·00	-
250°	$^{14}C-C_6H_6$	0·37	0·37	37·00	-
	$^{12}C-C_6H_6$	0·36	0·00	36·00	-

4.3.4 Hydrogenation of Benzene Residues on the Palladium Catalyst

TABLE 4.24

Radiochemical Analysis of Eluant from ^{14}C-Benzene Adsorption on 5% Pd/Al_2O_3. (Specific Activity $1 \cdot 0 \times 10^3$ counts/μl)

Temp (°C)	Substance Injected	Adsorption μl	cpμl x 10^{-3}	% Benzene Retained	Hydrogenation as % Adsorption (cyclohexane)
	Hydrogenation				
100°	$^{14}C-C_6H_6$	0·36	0·35	36·00	-
	H_2(5 ml)	-	-	-	-
150°	$^{14}C-C_6H_6$	0·37	0·37	37·00	-
	H_2(5 ml)	-	-	-	-
200°	$^{14}C-C_6H_6$	0·37	0·37	37·00	-
	H_2(5 ml)	-	-	-	-
250°	$^{14}C-C_6H_6$	0·37	0·37	37·00	-
	H_2(5 ml)	-	-	-	-

4.3.5 Hydrogenation of Benzene Residues on the Palladium Supported on Silica

Having established a general lack of reactivity for the residues of benzene on platinum and palladium supported on alumina, the investigation on 5% Pd/SiO$_2$ was conducted less extensively and only the hydrogenation of the species retained was examined. The results obtained are shown in table 4.25.

TABLE 4.25

Radiochemical Analysis from ^{14}C-Benzene Adsorption on 5% Pd/SiO$_2$. (Specific Activity $9{\cdot}8 \times 10^2$ counts/μℓ)

Temp (°C)	Substance Injected	Adsorption μℓ	Adsorption cpμl x10^{-3}	% Benzene Retained	Hydrogenation as % Adsorption (cyclohexane)
100°	$^{14}C-C_6H_6$	0·86	0·84	43·00	-
	H_2(5 ml)	-		-	1·00
150°	$^{14}C-C_6H_6$	0·87	0·85	43·50	-
	H_2(5 ml)	-		-	0·50
200°	$^{14}C-C_6H_6$	0·87	0·85	43·50	-
	H_2(5 ml)	-		-	0·50
250°	$^{14}C-C_6H_6$	0·87	0·85	43·50	-
	H_2(5 ml)	-		-	-

4.3.6 Summary

From the results presented in this section, it can be seen that, no exchange of residues occurred when inactive benzene was injected over a catalyst which had been dosed previously with ^{14}C-benzene, although adsorption of benzene still occurred, as was shown in tables 4.22 - 4.23. Hydrogen treatment of the catalyst, after saturation of the surface with ^{14}C-benzene, resulted in the formation of small amounts of radioactive cyclohexane between 100° to 200°C with platinum on alumina and palladium on silica catalysts. Unfortunately the small amounts make quantitative estimations difficult.

4.4 Studies Involving the Hydrogenation of Aromatic Hydrocarbons on the Catalysts

The reaction of aromatic hydrocarbons with hydrogen was studied over platinum and palladium catalysts in a flow reactor system at atmospheric pressure. The experiments were conducted in hydrogen as carrier gas and were designed to investigate the variations of the extent of hydrogenation of benzene and toluene with temperature. The procedure adopted in these series of experiments was detailed in section 3.11.C and the results for each of the catalysts studied are given in the following sections.

4.4.1 Hydrogenation of Benzene on Platinum Catalysts

The catalytic hydrogenation of benzene over 5% platinum supported on silica or alumina was examined using 0·005g catalyst in the temperature range 100° to 335°C by the micro-reactor chromatographic pulse method. The measurements were made with the same sample and a constant flow rate of 60 ml/min. At a given temperature the conversion of benzene was the same, independent of whether the temperature was increased progressively or was decreased from experiment to experiment. From the chromatographic analyses the fraction of benzene converted to cyclohexane was obtained as a function of the temperature of the catalyst. It was also observed that, the hydrogenation of benzene depends on the temperature to a considerable extent, the formation of cyclohexane increased in extent as the temperature was raised from 105°-215°C and then decreased as the temperature was further raised to 335°C. The conversion of benzene passed through a maximum at 160°-240°C on Pt/Al_2O_3 and between 130°-220°C on Pt/SiO_2 as are shown in figure 4.3.

4.4.2 Hydrogenation of Benzene on Palladium Catalysts

In the reaction of benzene with hydrogen over 5% palladium catalysts, 0·1g palladium supported on silica or alumina was used. 1·0 μl of benzene was injected onto a freshly reduced catalyst and the extent of the hydrogenation of the injected benzene was obtained as a function of the temperature. The same phenomenon as with the platinum

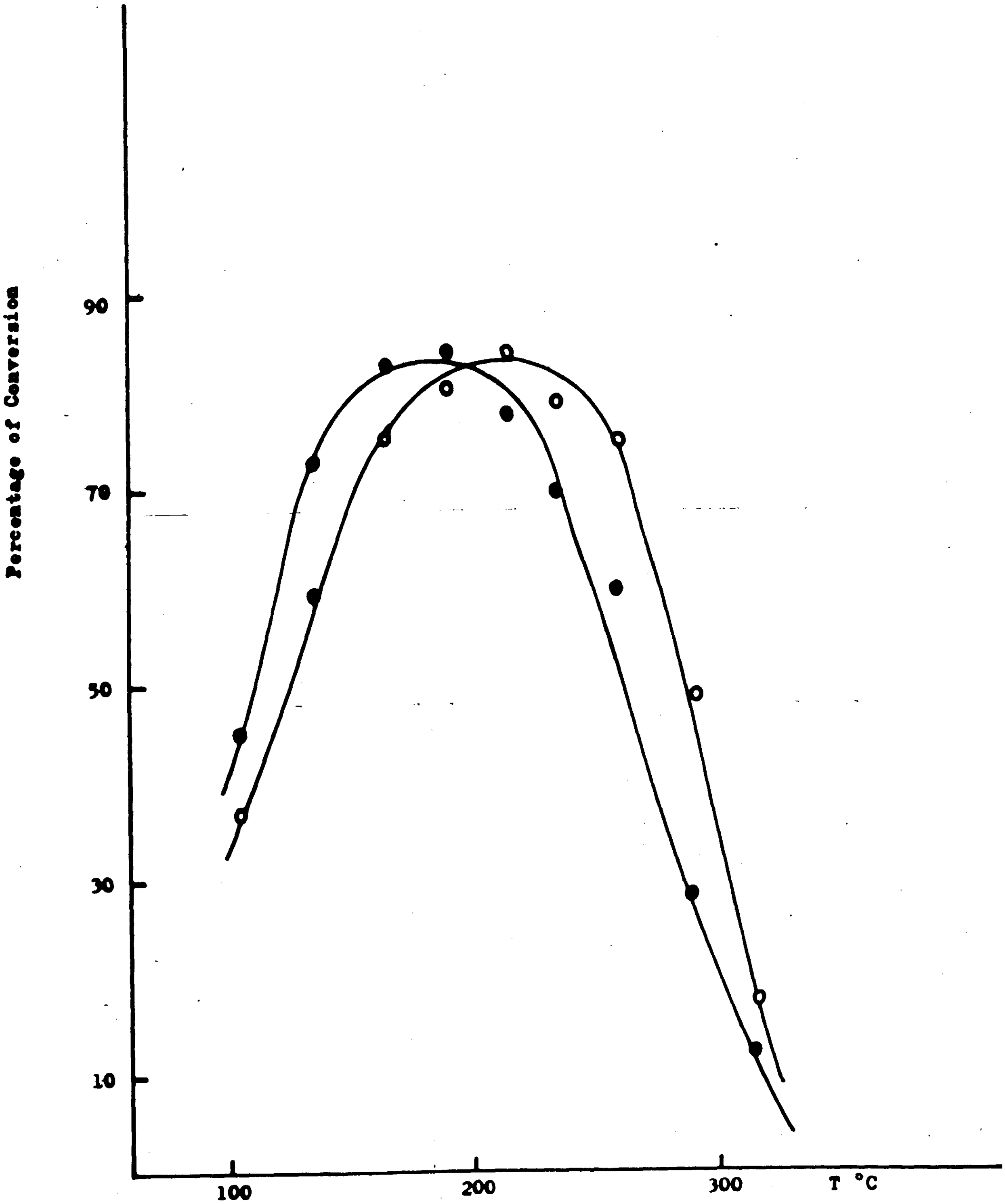


Fig. 4.3 Hydrogenation of Benzene on Alumina- and Silica-Supported Platinum Catalysts (O = Pt/Al_2O_3 , ● = Pt/SiO_2)

catalysts was found with Pd/SiO_2 and Pd/Al_2O_3. The yield of cyclohexane increased initially when the temperature was raised, but then decreased again at higher temperatures. The extent of hydrogenation was less than that over platinum catalysts. It is also apparent that, in the case of palladium catalysts, the rate of hydrogenation has a definite maximum in the region 150°-260°C. Figure 4.4 shows the effect of the temperature on the conversion of benzene with the palladium catalysts.

4.4.3 Hydrogenation of Toluene on Platinum Catalysts

The hydrogenation of toluene was examined using 0·005g 5% platinum supported on silica or alumina at series of temperatures between 100° to 335°C. The runs were conducted at atmospheric pressure and a flow rate of 60 ml/min. In the reaction of toluene with hydrogen, methylcyclohexane was the only product of hydrogenation; the hydrogenolysis of toluene was not observed in the temperature range used in these experiments. The percentage conversion of toluene to methylcyclohexane was obtained from the chromatographic analysis as a function of the temperature of the catalyst. With toluene the same phenomena as for benzene was found, the formation of methylcyclohexane increased as the temperature was raised to 190°C and then decreased as the temperature was raised to 335°C. The conversion of toluene passed through a maximum at 160°-220°C as can be seen in figure 4.5.

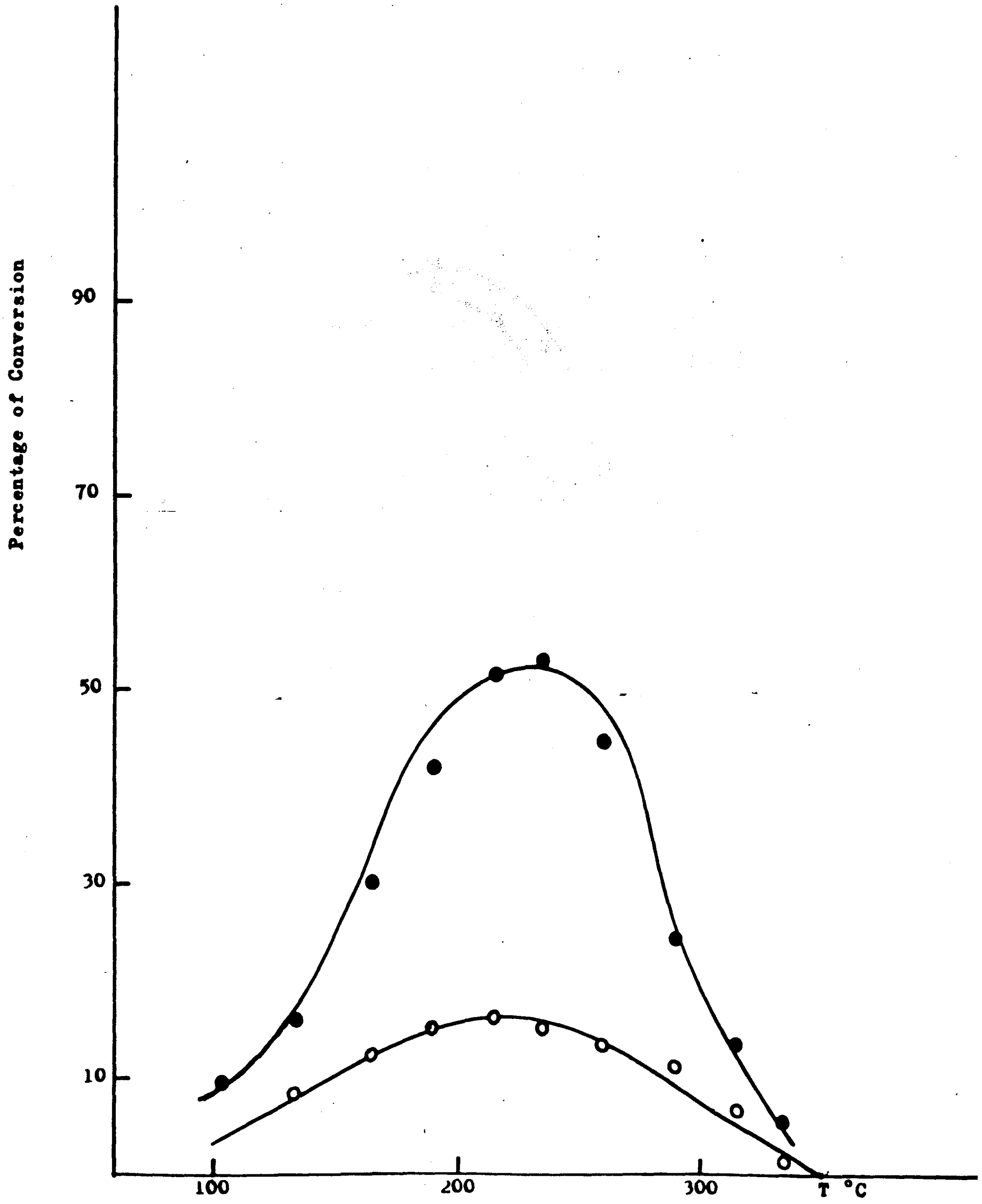


Fig. 4.4 Hydrogenation of Benzene on Palladium Catalysts
(O = Pd/Al_2O_3 , ● = Pd/SiO_2).

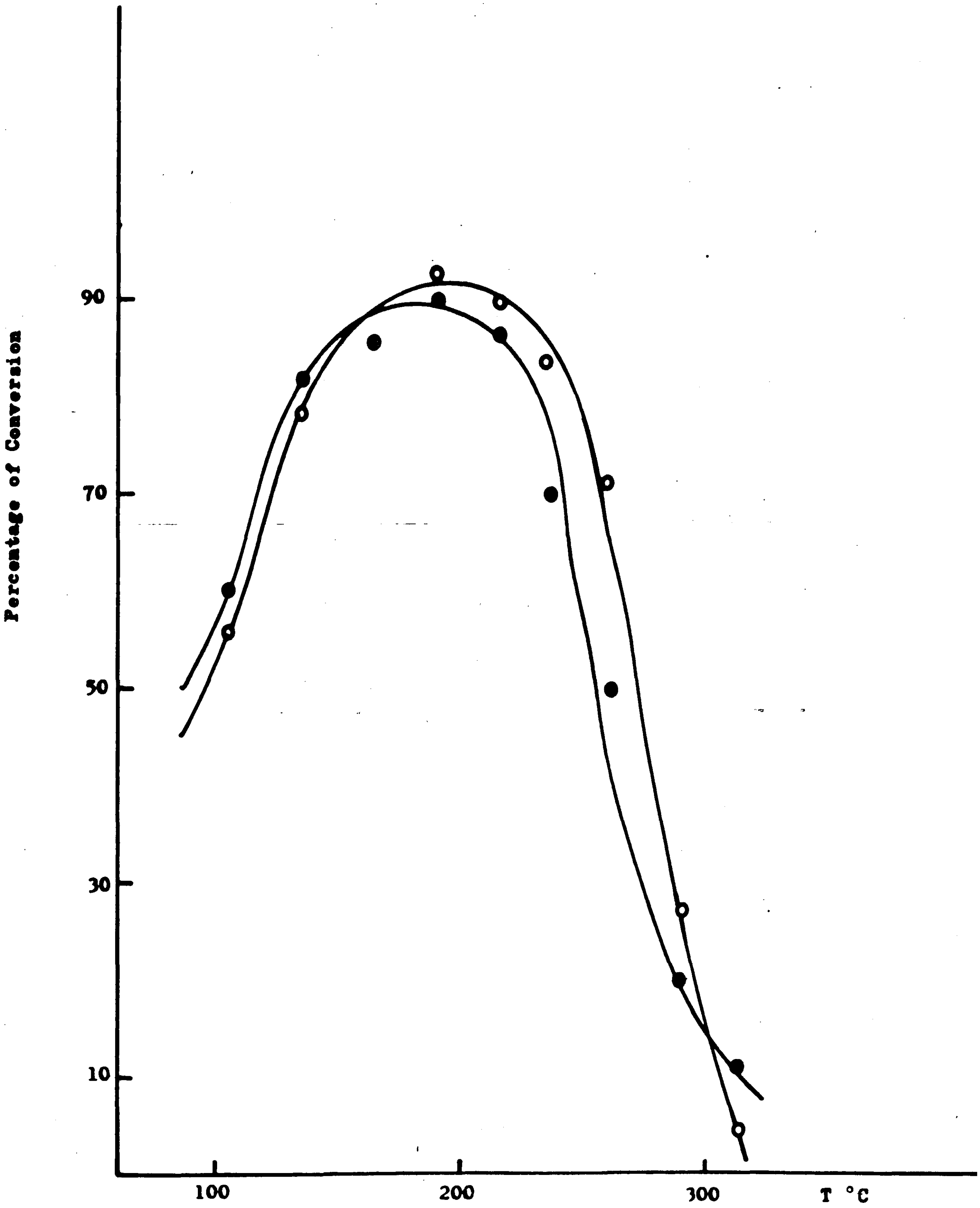


Fig. 4.5 Hydrogenation of Toluene on Alumina- and Silica-Supported platinum (O = Pt/Al_2O_3 , ● = Pt/SiO_2)

4.4.4 Hydrogenation of Toluene on Palladium Catalysts

The catalytic hydrogenation of toluene on 5% palladium supported on silica or alumina was carried out using 0·1g catalysts. The procedure was similar to that described in the section 3.11.C. In the case of palladium catalysts, the maxima were found between 180°- 240°C. In figure 4.6 are shown the effects of the temperature on the conversion of toluene as a function of temperature over palladium catalysts.

4.4.5 The Turnover Number for Benzene and Toluene Hydrogenation over Platinum and Palladium Catalysts

The chemisorption of ^{14}C-carbon monoxide, described in section 4.1.2, allowed the determination of the number of active sites on the catalysts used in these studies, as shown in table 4.26.

TABLE 4.26

Catalyst	Amount of Catalyst (g)	$\frac{\text{Active Sites}}{\text{g Catalyst}}$
5% Pt/Al_2O_3	0·005	$4{\cdot}27 \times 10^{17}$
5% Pt/SiO_2	0·005	$4{\cdot}49 \times 10^{17}$
5% Pd/Al_2O_3	0·100	$7{\cdot}74 \times 10^{18}$
5% Pd/SiO_2	0·100	$7{\cdot}66 \times 10^{18}$

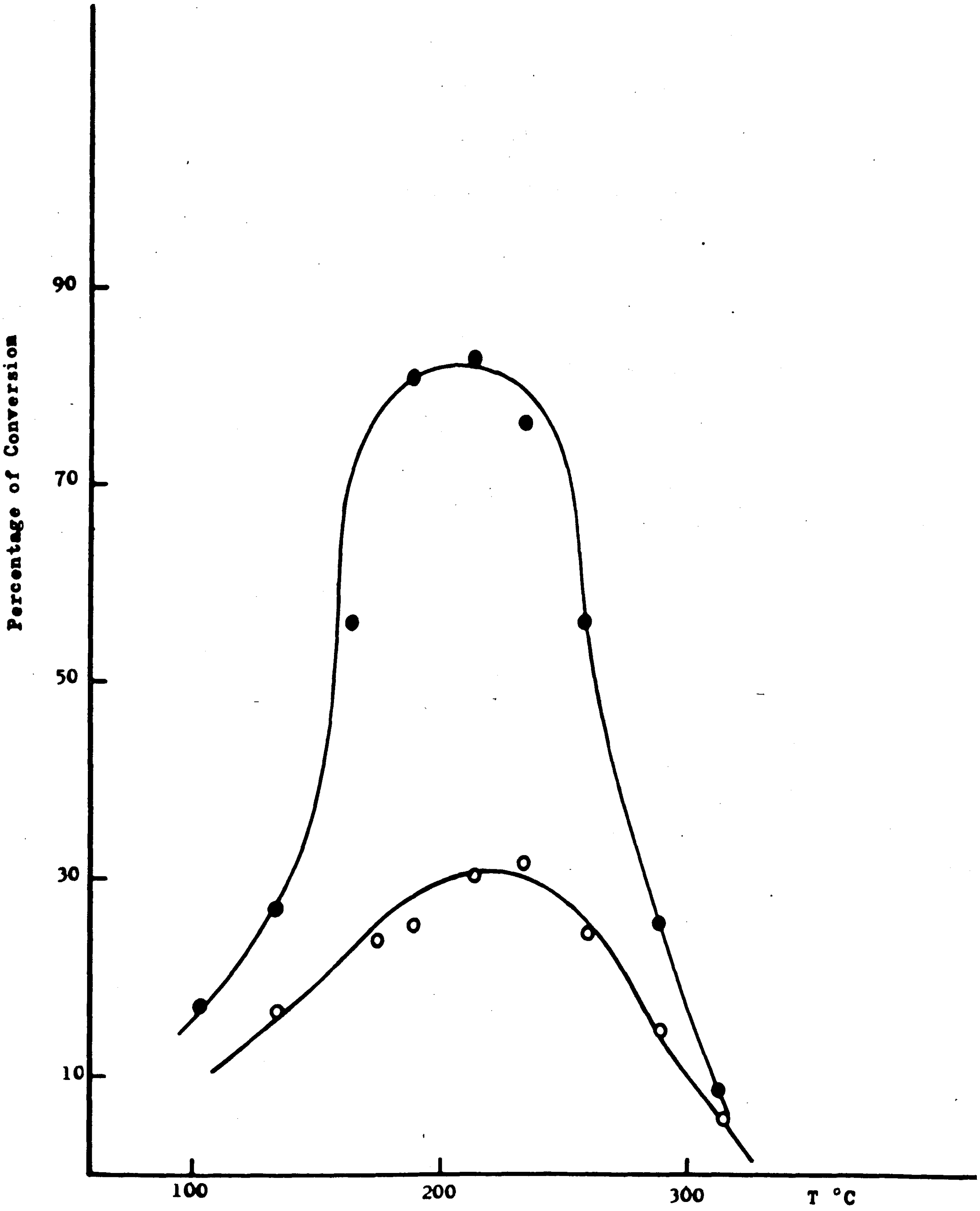


Fig. 4.6 Hydrogenation of Toluene on Palladium Catalysts (O = Pd/Al_2O_3 , ● = Pd/SiO_2)

Using the values given in table 4.26, "Turnover Number" (N_T) [molecules of benzene or toluene transformed into cyclohexane or methylcyclohexane per active site per sec] were calculated for each hydrocarbon at each temperature measured. The catalyst systems studied and the resulting turnover number (N_T), are given in tables 4.27-4.30.

TABLE 4.27

N_T Values of Benzene on Platinum Catalysts

t (°C)	% Conversion of Benzene on Pt/Al_2O_3	(N_T)	% Conversion of Benzene on Pt/SiO_2	(N_T)
105°	36·92	5·86	44·83	6·77
135°	59·34	9·42	72·52	10·95
165°	75·16	11·93	83·07	12·55
190°	80·43	12·77	84·39	12·75
215°	84·39	13·40	77·80	11·75
235°	79·11	12·56	69·88	10·55
260°	75·16	11·93	60·65	9·16
290°	48·79	7·75	28·58	4·32
315°	17·14	2·73	12·25	1·85
335°	4·05	0·64	1·36	0·21

TABLE 4.28

N_T Values of Benzene on Palladium Catalysts

t (°C)	% Conversion of Benzene on Pd/Al_2O_3	(N_T)	% Conversion of Benzene on Pd/SiO_2	(N_T)
105°	-	-	9·53	0·084
135°	8·17	0·072	15·47	0·137
165°	12·25	0·107	30·33	0·268
190°	14·97	0·131	42·19	0·373
215°	16·33	0·143	51·72	0·457
235°	14·97	0·131	53·08	0·469
260°	13·61	0·119	44·92	0·397
290°	12·25	0·107	24·50	0·217
315°	6·81	0·060	13·61	0·120
335°	1·35	0·012	5·63	0·050

TABLE 4.29

N_T Values of Toluene on Platinum Catalysts

t (°C)	% Conversion of Toluene on Pt/Al_2O_3	(N_T)	% Conversion of Toluene on Pt/SiO_2	(N_T)
105°	56·09	7·45	60·00	7·58
135°	78·23	10·39	81·67	10·32
165°	85·03	11·29	88·33	11·16
190°	92·95	12·34	90·00	11·37
215°	89·74	11·92	86·40	10·91
235°	83·33	11·06	70·00	8·84
260°	71·19	9·45	50·00	6·32
290°	27·24	3·62	20·10	2·54
315°	9·26	1·23	11·67	1·47
335°	4·63	0·61	–	–

TABLE 4.30

N_T Values for Toluene on Palladium Catalysts

t (°C)	% Conversion of Toluene on Pd/Al_2O_3	(N_T)	% Conversion of Toluene on Pd/SiO_2	(N_T)
105°	-	-	17·01	0·126
135°	16·67	0·122	27·21	0·201
165°	23·33	0·171	56·12	0·415
190°	25·00	0·183	81·63	0·604
215°	30·00	0·220	83·33	0·616
235°	31·67	0·232	76·53	0·566
260°	23·81	0·174	56·12	0·415
290°	11·90	0·087	25·51	0·189
315°	5·10	0·037	8·50	0·063
335°	-	-	1·70	0·013

4.4.6 Retention of Aromatic Hydrocarbons by Platinum and Palladium Catalysts

The Hydrogenation of aromatic hydrocarbons carried out on platinum and palladium catalysts, allowed information to be obtained regarding the retention of benzene and toluene by the metal catalysts. The retention of the aromatic hydrocarbons was also investigated by microanalysis of the catalysts used, using a Carlo-Erba automatic C.H.N. Analyser. The results obtained with the two methods are in accordance.

4.4.7 Retention of Benzene by Platinum Supported on Silica and Alumina

When adsorption was conducted in hydrogen as carrier gas, greater losses of benzene were observed on platinum catalysts, than those found when helium was used as carrier gas. The results are given in table 4.3.1.

4.4.8 Retention of Toluene by Platinum Catalysts

Loss of toluene was also observed when the experiments were conducted in hydrogen as carrier gas. The retention of toluene decreased as the temperature was raised from 105° to 190°C. Above 190°C no retention by platinum catalysts was obtained from the chromatographic analysis, the total amount of toluene injected onto the catalysts was registered on chromatograms as methylcyclohexane and unreacted toluene. Table 4.32 shows the results obtained for toluene on platinum catalysts.

TABLE 4.31

Adsorption of Benzene on Platinum Catalysts

t (°C)	$\frac{\text{Molecules of Benzene}}{\text{g Catalyst (Pt/Al}_2\text{O}_3\text{)}} \times 10^{-19}$	$\frac{N_{C_6H_6}}{N_{sites}}$	$\frac{\text{Molecules of Benzene}}{\text{g Catalyst (Pt/SiO}_2\text{)}} \times 10^{-19}$	$\frac{N_{C_6H_6}}{N_{sites}}$
105°	7·14	0·795	5·90	0·691
135°	12·30	1·370	13·20	1·546
165°	10·25	1·141	14·90	1·745
190°	10·15	1·130	12·30	1·440
215°	10·56	1·176	13·14	1·539
235°	11·36	1·265	13·95	1·633
260°	10·36	1·154	4·90	0·574
290°	5·86	0·653	4·60	0·539
315°	4·30	0·479	4·00	0·468
335°	1·00	0·111	3·26	0·382

TABLE 4.32

Adsorption of Toluene on Platinum Catalysts

t (°C)	$\frac{\text{Molecules of Toluene}}{\text{g Catalyst (Pt/Al}_2\text{O}_3\text{)}} \times 10^{-19}$	$\frac{N_{C_7H_8}}{\text{Nsites}}$	$\frac{\text{Molecules of Toluene}}{\text{g Catalyst (Pt/SiO}_2\text{)}} \times 10^{-19}$	$\frac{N_{C_7H_8}}{\text{Nsites}}$
105°	4·86	0·541	5·98	0·700
135°	3·28	0·365	4·12	0·482
165°	1·96	0·220	3·10	0·363
190°	-	-	0·96	0·112
215°	-	-	-	-
235°	-	-	-	-
260°	-	-	-	-
290°	-	-	-	-
315°	-	-	-	-
335°	-	-	-	-

Each used catalyst was microanalysed for carbon residues; the following results for benzene and toluene on platinum catalysts were obtained.

Catalyst	$\frac{\text{Benzene Molecules}}{\text{g Catalyst}} \times 10^{-19}$	$\frac{\text{Toluene Molecules}}{\text{g Catalyst}} \times 10^{-19}$
5% Pt/Al_2O_3	3·54	1·22
5% Pt/SiO_2	2·76	1·18

Retention of benzene and toluene was not observed in the studies of hydrogenation of aromatic hydrocarbon on palladium catalysts. Microanalysis of the used palladium catalysts also failed to show any retained hydrocarbonaceous materials. In view of this behaviour, palladium supported on silica was studied in more detail. 10 injections of 1·0 μℓ each, were injected onto a freshly reduced catalyst and the activity of catalyst was studied as function of number of pulses at four different temperatures. The results obtained are shown in figure 4.7. It is observed that, no deactivation of the catalyst occurred after successive pulses of hydrocarbon at 165°, 215°, 260° and 315°C.

4.5 Competitive Hydrogenation of Benzene and Toluene on Platinum and Palladium Catalysts

When a mixture of two or more compounds are hydrogenated,

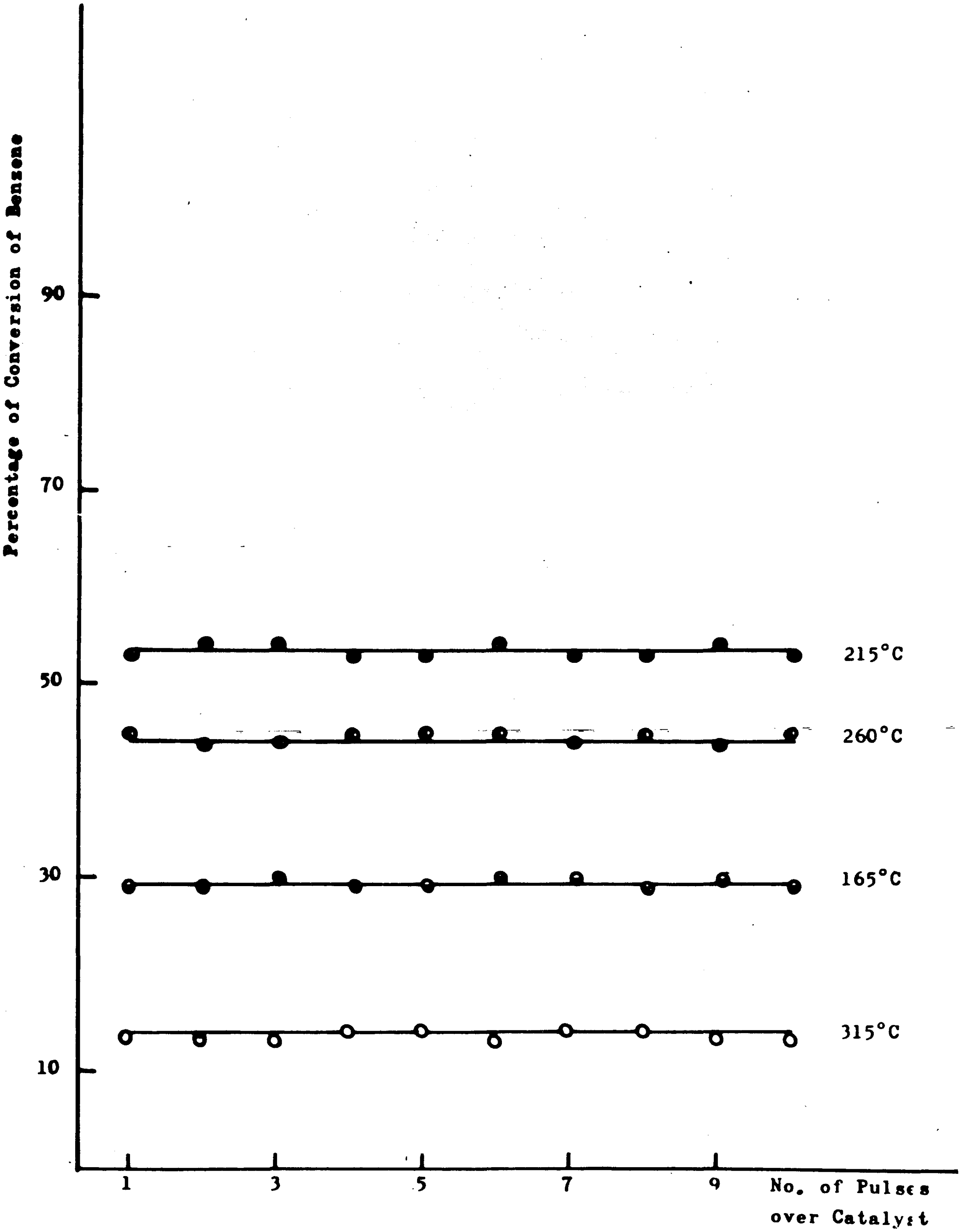


Fig. 4.7 Activity of 0·1g Pd/SiO_2 in Function of Benzene Pulses at Various Temperatures.

the relative rate of reaction of each reflects the preference of the surface for that compound. From such studies, information about the surface-adsorbate interaction can sometimes be deduced. The relative conversion of each compound can be determined by gas chromatographic analysis of the reaction mixture. The competitive hydrogenation of benzene and toluene over platinum and palladium catalysts was examined, in the temperature range of 100° to 335°C in hydrogen at atmospheric pressure. The catalysts were selective for the reactions:

$$\text{Benzene (g)} + 3H_2\ \text{(g)} \xrightleftharpoons{\text{catalyst}} \text{cyclohexane (g)}$$

$$\text{Toluene (g)} + 3H_2\ \text{(g)} \xrightleftharpoons{\text{catalyst}} \text{methylcyclohexane (g)}$$

no other products were observed.

1·0 μl of a mixture 1:1 (v:v), corresponding a molecular ratio of benzene to toluene of 1:0.84; was injected onto a freshly reduced catalyst and the extent of hydrogenation, as a function of temperature of the catalyst, was obtained from the chromatographic analysis. The fraction of benzene and toluene converted to cyclohexane and methylcyclohexane as a function of the temperature are shown in figures 4.8 to 4.11.

Figures 4.8 to 4.11 show that, benzene can be hydrogenated in the presence of toluene to cyclohexane. Again it was observed that the conversion of benzene and toluene increased as the temperature was raised from 100° to 215°C and then decreased as the temperature was raised to 335°C (cf section 4.4). The maximum conversion was observed at

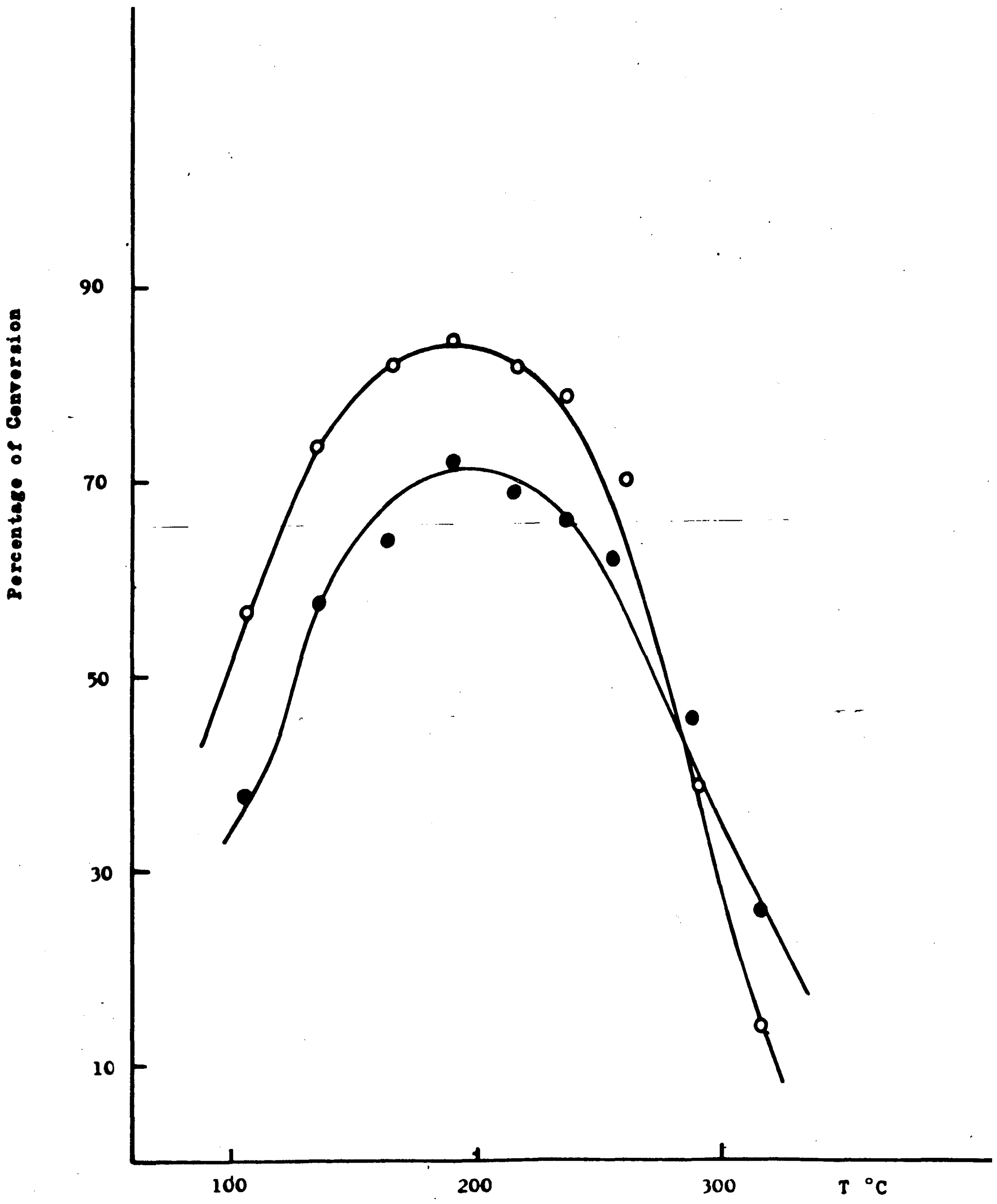


Fig. 4.8 Hydrogenation of a Mixture 1:1 (v:v) of Benzene and Toluene on 0·005g Pt/Al_2O_3 (● = Benzene, O = Toluene)

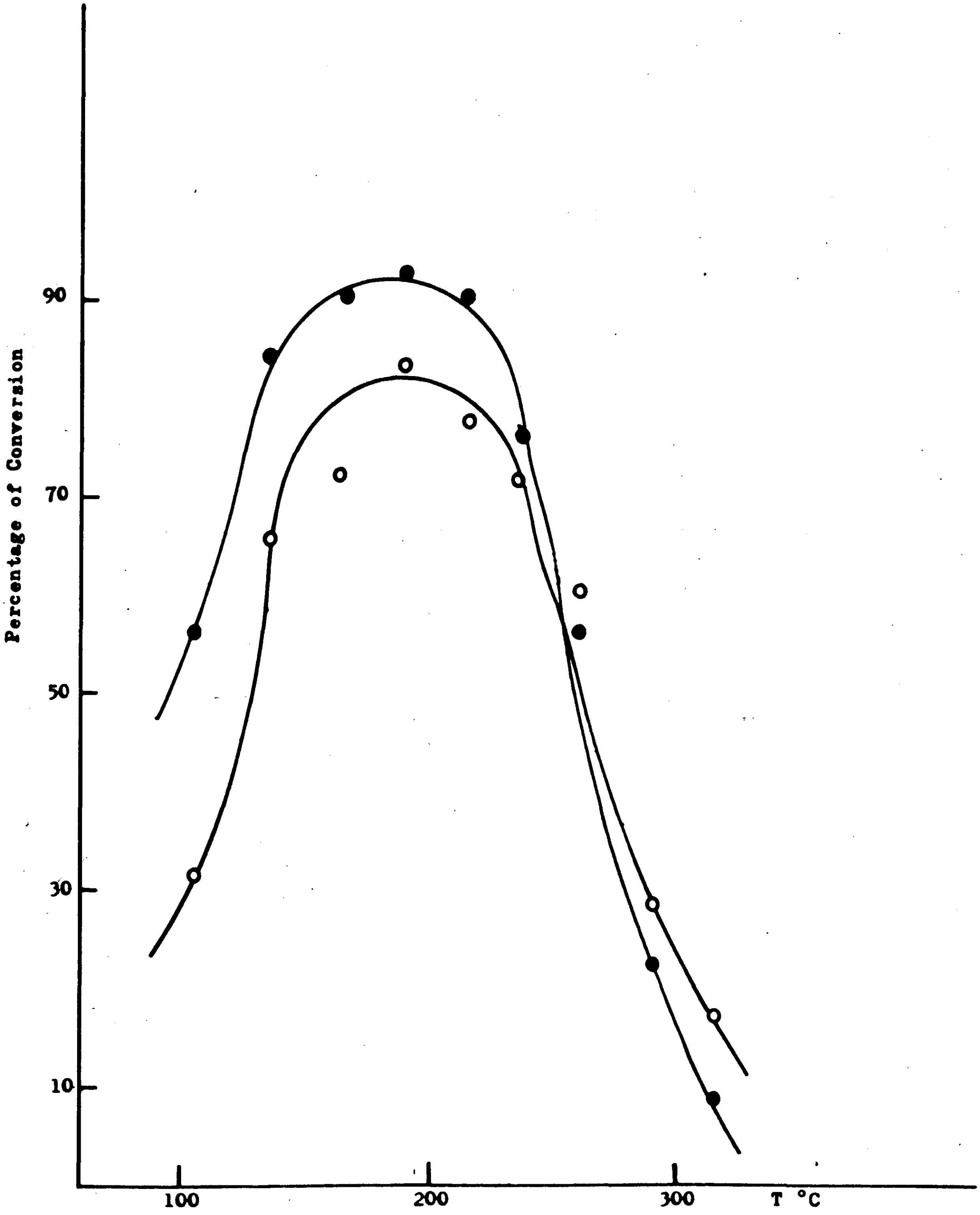


Fig. 4.9 Hydrogenation of a Mixture 1:1 (v:v) of Benzene and Toluene on 0·005g Pt/SiO_2 (O = Benzene, ● Toluene)

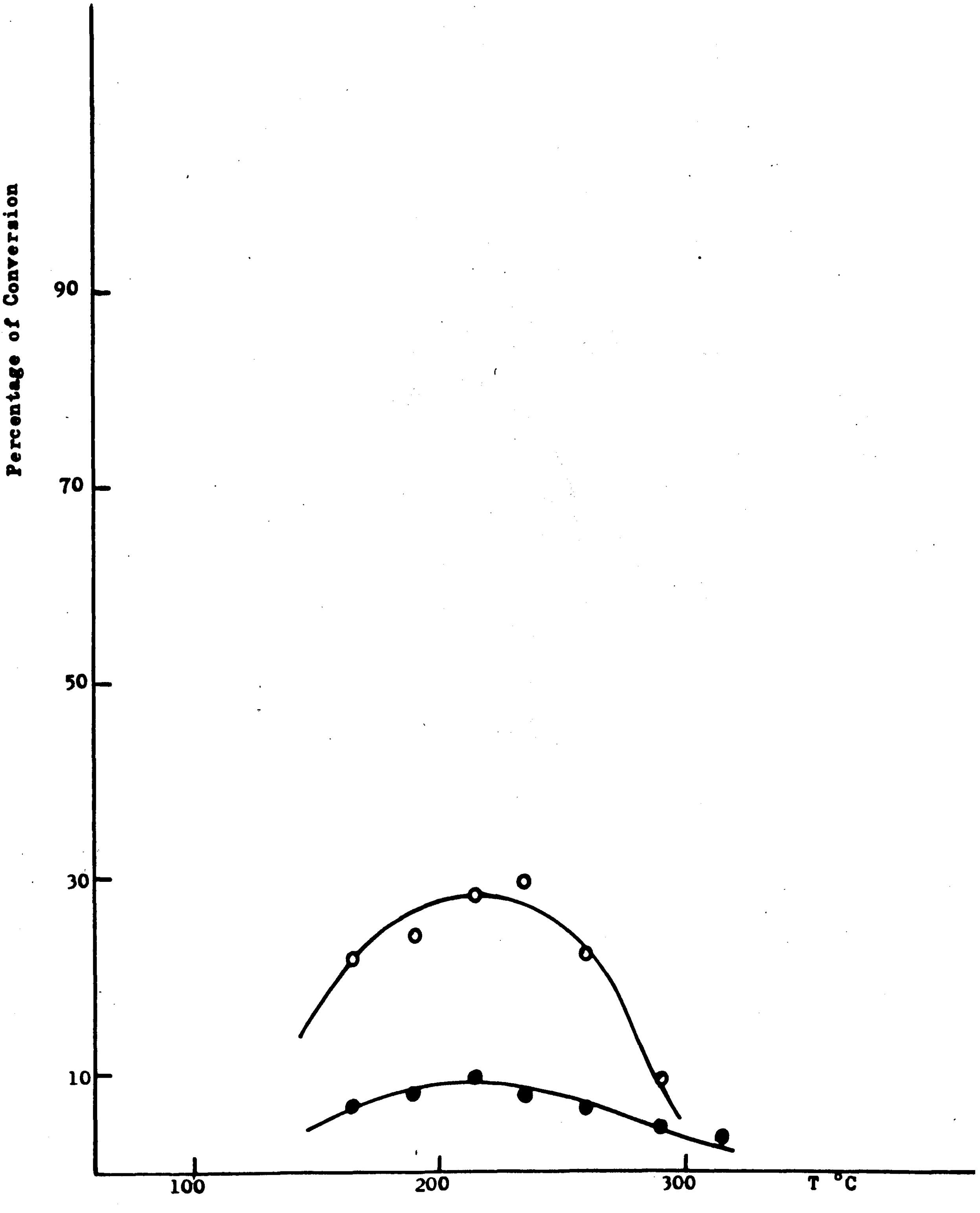


Fig. 4.10 Hydrogenation of a mixture 1:1 (v:v) of Benzene and Toluene on 0·100g Pd/Al_2O_3 (● = Benzene, O = Toluene)

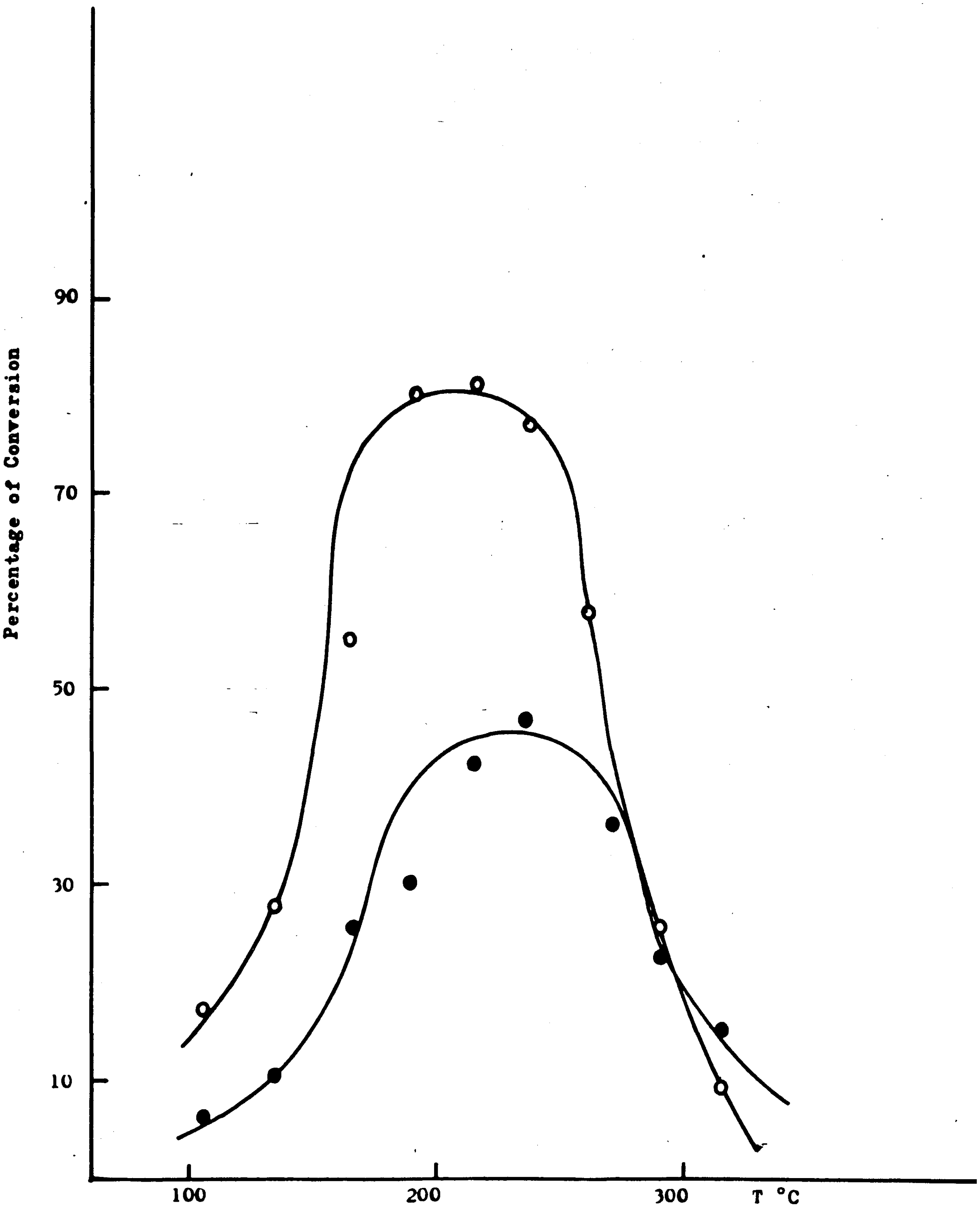


Fig. 4.11 Hydrogenation of a Mixture 1:1 (v:v) of Benzene and Toluene on 0·100g Pd/SiO$_2$ (● - Benzene, O = Toluene)

140°- 230°C in the case of platinum catalysts and between 160° and 250°C with palladium catalysts. It can also be seen that, under the same conditions, the hydrogenation of toluene is greater than that of benzene over the four catalysts examined.

4.5.1 The "Turnover Numbers" of Benzene and Toluene in the Competitive Hydrogenation on Pt and Pd Catalysts

The "Turnover Numbers" of benzene and toluene in the competitive hydrogenation of these hydrocarbons, were determined in the temperature range 100° to 335°C under the same conditions as those used in the separate hydrogenations of benzene and toluene. The results may be compared with those shown in section 4.4.5 and, information obtained regarding the preference of the surface for a particular hydrocarbon. The data obtained for benzene and toluene are shown in the tables 4.33 and 4.34.

TABLE 4.33

N_T Values of Benzene and Toluene over Platinum Catalysts

t (°C)	N_T (molecules/sites/sec)			
	Benzene (Pt/Al_2O_3)	Toluene (Pt/Al_2O_3)	Benzene (Pt/SiO_2)	Toluene (Pt/SiO_2)
105°	2·82	3·55	2·51	3·74
135°	4·33	4·62	5·24	5·61
165°	4·79	5·15	5·70	5·98
190°	5·42	5·33	6·61	6·17
215°	5·20	5·15	6·15	5·98
235°	4·98	4·98	5·70	5·05
260°	4·77	4·44	4·79	3·74
290°	3·47	2·45	2·28	1·49
315°	1·95	0·89	1·37	0·56
335°	0·51	–	0·23	–

TABLE 4.34

N_T Values of Benzene and Toluene over Palladium Catalysts

t (°C)	N_T (molecules/sites/sec)			
	Benzene (Pd/Al_2O_3)	Toluene (Pd/Al_2O_3)	Benzene (Pd/SiO_2)	Toluene (Pd/SiO_2)
105°	–	–	0·027	0·063
135°	–	–	0·047	0·104
165°	0·028	0·079	0·113	0·203
190°	0·035	0·087	0·133	0·297
215°	0·043	0·105	0·187	0·300
235°	0·035	0·109	0·207	0·285
260°	0·026	0·080	0·160	0·213
290°	0·018	0·034	0·100	0·095
315°	0·017	–	0·067	0·032
335°	–	–	–	–

CHAPTER FIVE

CHAPTER FIVE

DISCUSSION

The experimental results detailed in chapter four are correlated and discussed with reference to the previous literature. Results from 4.2 (Hydrocarbon Adsorption by the Platinum and Palladium Catalysts), 4.3 (Adsorption of ^{14}C-Benzene by the Catalysts) are discussed together in section 5.1, hydrogenation of aromatic hydrocarbons and competitive hydrogenation of benzene and toluene are discussed in the corresponding sections of the chapter (5.2 and 5.3) and an integrated discussion of benzene adsorption is given at the end of this chapter.

5.1 Hydrocarbon Retention by Platinum and Palladium Catalysts

In the experiments of the section 4.2, the amount of retention of benzene and toluene by platinum and palladium catalysts was measured at four different temperatures, 100°, 150°, 200° and 250°C. In order to obtain significance and precision of the results it was necessary firstly to correlate the data obtained in the characterization of the catalysts and relate these values with the adsorption and hydrogenation of aromatic hydrocarbons.

The results obtained from the physical adsorption of nitrogen shown in table 4.5 indicated that, if the alumina or silica participate in some way in the adsorption or

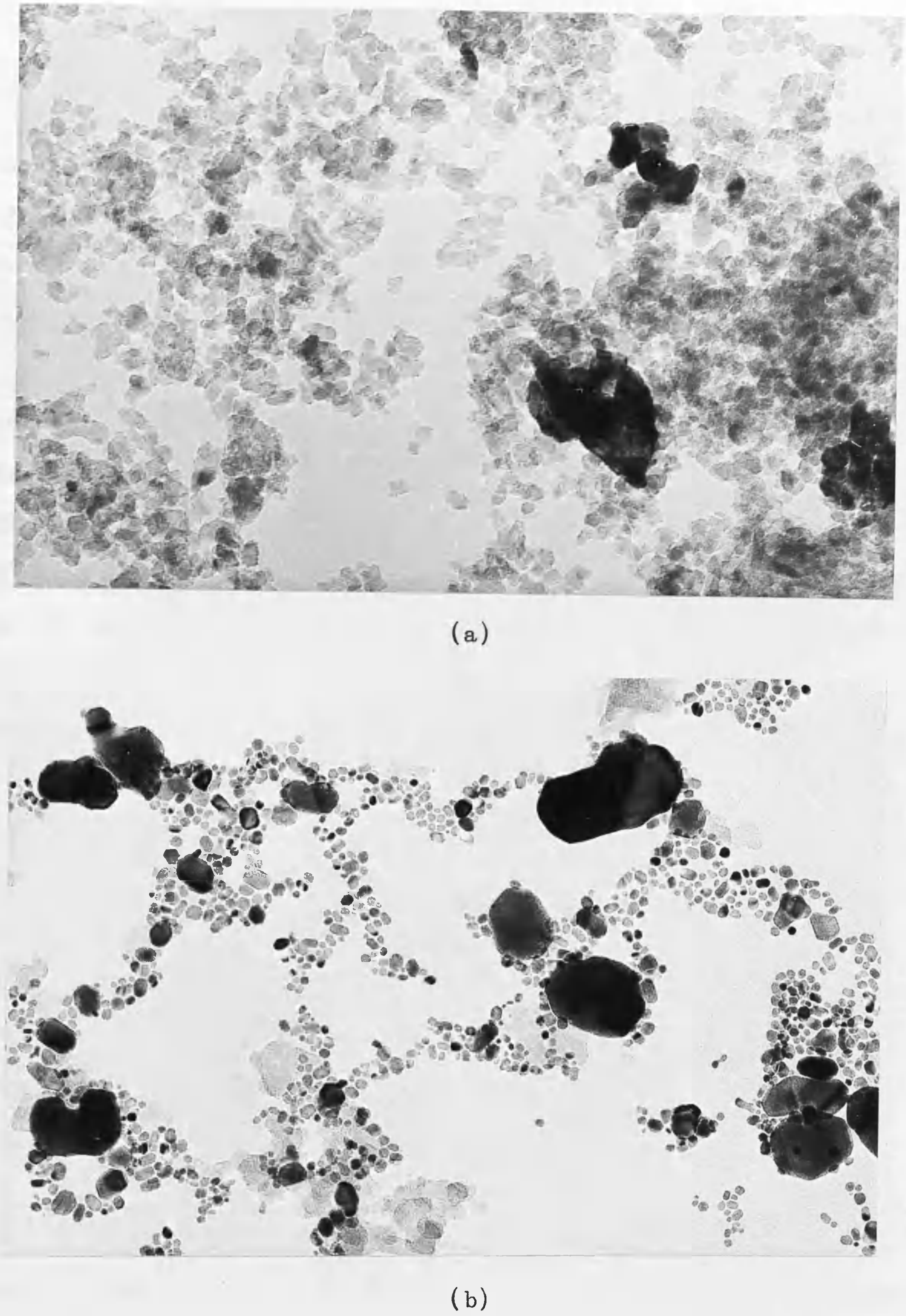


Figure 5.1 Electron Micrographs of (a) 5% Pd/Al_2O_3 and (b) 5% Pd/SiO_2 with magnification x 250,000.

it is clear that the differences in behaviour of the catalysts are associated with some characteristic of the metal, and that the slight differences between the same metal, when supported on silica or on alumina, are possibly due to supported structure and size of hydrocarbon examined.

The adsorption of benzene and toluene on platinum and palladium catalysts was measured in a flow system using helium as carrier gas. Since the measurements were made in a flow system it is necessary to establish whether the results obtained from the first injection represent a true saturation of the surface, or whether further injections of hydrocarbon were necessary before reproducible behaviour was achieved. In order to correlate the observations the catalytic surfaces were normalised with respect to their active site densities. Considering platinum and palladium in dispersed catalysts to expose mainly low index faces (100), (110) and (111), calculations from carbon monoxide adsorption showed that 8.53×10^{18} Pt atoms per g catalyst (Pt/Al_2O_3), $7{\cdot}74 \times 10^{18}$ Pd atoms per g catalyst (Pd/Al_2O_3) and $7{\cdot}66 \times 10^{18}$ Pd atoms per g catalyst (Pd/SiO_2) were exposed.

The injection size ($1{\cdot}0$ µℓ), containing $6{\cdot}77 \times 10^{18}$ molecules of benzene, or in the case of toluene $5{\cdot}67 \times 10^{18}$, was chosen to give a conveniently measurable retention for benzene and toluene. Although in $1{\cdot}0$ µℓ of hydrocarbon there are approximately the same number of hydrocarbon molecules as the number of active sites on the catalyst, hydrocarbon was invariably recovered from the first injection and no more than two injections were necessary in some cases before reproducible behaviour was reached. The percentage hydrocarbon retained by the catalysts, computed from a difference in the peak areas of the calibration and reaction injections, showed good reproducibility in the results.

The data obtained for the adsorption of benzene on 5% Pt/Al_2O_3 at all temperatures studied are shown in table 4.7, it can be seen that, reproducible behaviour was obtained after one injection of benzene. The percentage of each injection retained by Pt/Al_2O_3 is practically constant. In table 4.8 it is also observed that the number of molecules retained by the catalyst did not vary with the temperature, and the ratio of benzene molecules adsorbed to metal sites exposed is less than one, suggesting that one molecule of benzene (area 41 $\mathring{A}^2$) is occupying more than one site. Pitkethly and Goble (74) studied the adsorption of benzene on platinum supported on alumina in the temperature range 26° to 470°C. Evidence was obtained for four types of adsorption of benzene:

(i) a relatively small reversible adsorption (less than 5% of the total) on platinum.

(ii) an irreversible adsorption, independent of benzene pressure, which is constant over considerable ranges of temperature and increases at higher temperature.

(iii) a fast, reversible adsorption on the support below 200°C.

(iv) an additional slow adsorption or reaction associated with the support.

It was also found that 0·22 molecules of benzene were chemisorbed per surface platinum atom on two of the catalysts studied. The authors calculated that for the chemisorption of benzene on perfect face-centred cubic crystallites with the (100) face exposed, the maximum benzene adsorption with Van der Waals spacing (41 Å^2 per molecule) would be 0·185 molecules per surface platinum atom. For adsorption of benzene on the (111) plane, the maximum ratios of benzene to platinum possible on an infinite monolayer with various modes of adsorption are, 0·166 molecules of benzene per surface platinum atom when the adsorption is physical in nature, 0·143 when the molecules are centred over platinum atoms with the carbon atoms in the interstices, and provided no interference between hydrogen atoms, or 0·333 when dehydrogenation or distortion of the molecules occurs to accommodate the carbon skeleton over the interstices. The benzene to platinum ratio of 0·72 observed at high temperature was stated by the authors as possibly due to a different type of adsorption in which one benzene molecule is associated with one atom of platinum. Recently Gland and Somorjai (75), using LEED and work function measurements, studied the chemisorption of benzene on Pt(111) and Pt(100)-(5 x 1) surfaces. A change was observed in the initial surface structure formed when benzene was adsorbed on Pt(111) and simultaneously a variation in the work function occurred. The correlation between the transformation of the benzene surface structure and change in work function suggests that the orientation of the adsorbed benzene molecules changes markedly as a function of increased exposure. The work function change indicates that there is a decrease in the magnitude of the charge transfer between hydrocarbon and metal as the density of the adsorbed layer increases. The authors interpret this effect in the following manner: the increasing density accompanied by a decrease in work function can only be explained by assuming that the area per adsorbed molecule must be decreasing. A model consistent with these criteria is that initial adsorption involves a benzene adsorbed with its ring at some small angle to the surface. The final adsorbed state may involve reoriented benzene molecules adsorbed with their rings at a large angle or perpendicular to the surface. In general, according to the above authors, the benzene to platinum ratio is less than one and the precise value depends on the face and model considered.

On Pd/Al_2O_3 the same phenomena as found with Pt/Al_2O_3 was observed; the retention is practically constant with temperature (see table 4.9 and 4.10). The number of molecules adsorbed on the catalyst surface is constant, within experimental error, and the benzene to palladium ratio is less than one, although the retention of benzene by palladium catalyst was less than Pt/Al_2O_3, indicating that the chemisorption capacity of platinum is greater than palladium.

When palladium was supported on silica, two injections of benzene were necessary before reproducible behaviour was observed. The number of molecules on the catalyst is the same at all temperatures but the retention of benzene is greater in this case than for palladium supported on alumina. It has been seen in section 4.1 that palladium supported on silica and on alumina have similar total surface areas and surface metal areas. Hence, the difference observed in the adsorption of benzene on palladium supported on silica and palladium supported on alumina suggests that, a part of the surface of the metal supported on alumina does not participate in the reaction. It is possible that the very small particles contained in micropores are inaccessible to the rather large hydrocarbon molecules.

When the hydrocarbon was toluene, similar phenomena to those observed with benzene were found. On Pt/Al_2O_3, reproducible behaviour was observed with the second injection, as can be seen in table 4.14, and the number of molecules retained by the catalyst is practically the same in the temperature range between 100° and 250°C as is shown in table 4.15. The ratio of toluene adsorbed to the number of active sites is, as with benzene, less than one, indicating that toluene occupies more than one surface site. When toluene was adsorbed on Pd/Al_2O_3, one injection was necessary to saturate the surface and it was observed that, the amount of toluene retained by the catalyst was less than on Pt/Al_2O_3 under the same conditions. These observations indicate that the adsorption capacity of platinum is greater than palladium for toluene hydrocarbon. In the case of palladium supported on silica, it was found that, the adsorption of toluene was greater than on palladium supported on alumina. At 250°C the hydrogenolysis of toluene was observed on platinum supported on alumina and palladium supported on silica. This phenomena was not observed in the studies of benzene adsorption in the temperature range used. Benzene and methane were the only products of carbon-carbon bond fission observed.

Gland and Somorjai (76) studied the chemisorption of toluene on the (111) and (100) crystal faces of platinum by low energy electron diffraction and work function change measurements at temperatures between 20° and 300°C. After adsorption, reorientation of the molecules in the adsorbed layer formed ordered structures. The diffraction and work function change data indicate that, under the conditions of the experiments, toluene was chemisorbed with the benzene ring parallel to the surface and interacted with the metal surface primarily via formation of a π-bond between the aromatic π-electron and the electron deficient metal surface. This type of interaction results in the large work function changes. The authors also observed that an increase in substrate temperature to 150°C with continued exposure causes disordering of the ordered adsorbate surface structure, while increasing the substrate temperature to 250°-300°C during continued exposure to the vapour molecules results in a decrease in the magnitude of the work function change indicating decomposition of the adsorbed layer.

A comparison with the results obtained for benzene by the same authors (75) indicate some differences in the form of adsorbed benzene and adsorbed toluene on the (111) and (100) crystal faces of platinum, benzene is adsorbed with its ring at some small angle with the surface and which is reoriented towards a large angle or perpendicular as the density of the adsorbed layer is increased, while the adsorption of toluene is with the benzene ring parallel to the metallic surface.

The adsorption of ^{14}C-labelled benzene was studied on the various catalysts in the temperature range 100° to 250°C. In addition to providing a sensitive and powerful method for estimating the extent of chemisorption, the use of the radioactively labelled species also provided a means of examining the reactivity of the adsorbed retained species towards molecular exchange and hydrogenation.

The results obtained from chemical and radiochemical analysis of the reactor eluant, detailed in tables 4.21 and 4.23, show that, at all temperatures studied, no molecular exchange occurred when non-radioactive benzene was admitted to ^{14}C-benzene precovered platinum or palladium surfaces. In each case benzene was recovered but contained no radioactivity. Hydrogen treatment of platinum-alumina or palladium-silica catalysts, previously exposed to ^{14}C-benzene, resulted in the formation of small amounts of radioactive cyclohexane in the temperature range 100° to 200°C. Together these results indicate that the retained benzene is strongly bonded to the surface, largely as a C_6-ring entity, and it may be concluded that the retained species is probably a dissociatively adsorbed species, rather than an associatively bonded species, such as is generally considered to be the reactive adsorbed state in hydrogenation (77). The formation of radioactive cyclohexane resulting from the hydrogen treatment is in general agreement with a large body of information in the literature (36) suggesting that the major product of the removal of the strongly bonded benzene residue is cyclohexane. It is significant that with benzene no cracking products, for example methane, were observed even with prolonged treatment in hydrogen at 250°C.

5.2 The Hydrogenation of Benzene and Toluene

The results obtained for the hydrogenation of benzene and toluene over alumina- and silica-supported platinum and palladium, using hydrogen as the carrier gas, are shown in figures 4.3 - 4.6. From these it can be seen that, over the temperature range 100° to 335°C, the relative specific activities of the metals for each reaction were in the order platinum > palladium. The silica-supported metals were also observed to have a higher specific activity than the corresponding alumina-supported metal for each reaction. Similar observations have been made by Kubicka (49), who reported that for benzene hydrogenation over a variety of alumina- and silica-supported metals, in the temperature range 100° to 235°C, the relative activities were in the order Ru > Pt > Tc ≃ Pd > Re. Amano and Parravano (46) using 0·5% metal-alumina catalysts also reported a benzene hydrogenation activity sequence of Rh > Ru > Pt > Pd; whilst Anderson and Kemball (47) stated that the activity of evaporated platinum films for benzene deuteration was greater than that of evaporated palladium films. The results obtained in the present work are, therefore, in agreement with those reported previously.

The effect of temperature upon the rate of hydrogenation of benzene and toluene can also be seen in figures 4.3 - 4.6. It was observed that, not unexpectedly, the extent of hydrogenation of the aromatic hydrocarbon increased as the temperature was increased from 100°C to around 220°C. However, as the temperature was further increased to 335°C, the extent of hydrogenation progressively decreased. Well-defined activity maxima were obtained, with all the catalysts examined, in the region 140° to 220°C.

Similar behaviour has been observed previously with nickel catalysts by Germain et al. (42), Nicolai et al. (39) and van Meerten et al. (44). In these studies the reaction rate was stated to reach a maximum at around 180°C. Activity maxima were also reported by Kubicka (49) for benzene hydrogenation over a variety of metals; the phenomenon may also be observed in the data of Taylor (48). Whilst the activity maxima have been qualitatively ascribed as due to poisoning (39) or to a decrease in reactant adsorption (42), no firm mechanistic explanation has been proposed.

The maxima in the activity-temperature curves could arise from catalyst poisoning, since it might be expected that higher temperatures would favour the formation of surface residues. However, sets of successive measurements made with increasing and decreasing temperature cycles yielded similar results, with no hysteresis effects, thus showing that no irreversible catalyst deactivation occurred at the higher temperatures. Moreover, when the activity of 0·1g of palladium-silica catalysts was examined as a function of the number of pulses passed at four different temperatures (figure 4.7), within experimental error no deactivation was observed. Further, in the reaction of benzene and toluene with hydrogen over both platinum and palladium catalysts, the only observed products were cyclohexane and methylcyclohexane respectively. No cracking products were detected in the reactor eluant showing that, in the temperature range under consideration, neither platinum nor palladium exhibited activity for the hydrogenolysis of benzene or toluene. For these reasons catalyst poisoning is concluded to be unimportant in determining the activity patterns of the catalysts under investigation.

Approach to thermodynamic equilibrium conversion could give rise to limitations in the reaction rate. In table 5.1 are shown values for the equilibrium constant calculated according to the data of Janz (78), together with experimental values at similar temperatures.

TABLE 5.1

Thermodynamics of the Reaction $C_6H_6 + 3H_2 \rightleftharpoons C_6H_{12}$

Temperature (°C)	K (calculated)	K^1 (observed)
127°	$6{\cdot}9 \times 10^7$	2·64
227°	186	2·32
265°	4·9	1·54
277°	1·0	0·40

Even at high temperature the dehydrogenation of cyclohexane played no part in our experiments as was shown from a study of the hydrogenation of mixtures of ^{14}C-benzene and unlabelled cyclohexane. The results are shown in table 5.2.

TABLE 5.2

Hydrogenation of Benzene on 0·005g Pt/Al_2O_3

Benzene Specific Activity 2×10^3 counts per μl

t (°C)	Benzene Unreacted Counts per μl of Benzene Injected Sole.	(%)	Benzene Unreacted Counts per μl of Benzene Injected with Cyclohexane	(%)
105°	1153·85	(57·69)	1141·03	(57·05)
165°	428·57	(21·43)	442·86	(22·14)
190°	283·33	(14·17)	266·67	(13·33)
250°	333·33	(16·67)	333·33	(16·67)
320°	1678·57	(83·93)	1642·86	(82·14)

From these results it can be seen that the presence of cyclohexane in the mixture had no effect upon the specific activity of the benzene; the specific activity of the unreacted benzene at each temperature, when it was injected alone and when it was injected with cyclohexane, is practically constant, indicating that cyclohexane dehydrogenation does not occur to any appreciable extent under the experimental conditions used in the present studies. Consequently, the activity-temperature profiles are not a result of the thermodynamics of the reaction system, but probably have their origins in kinetic factors associated with the reaction.

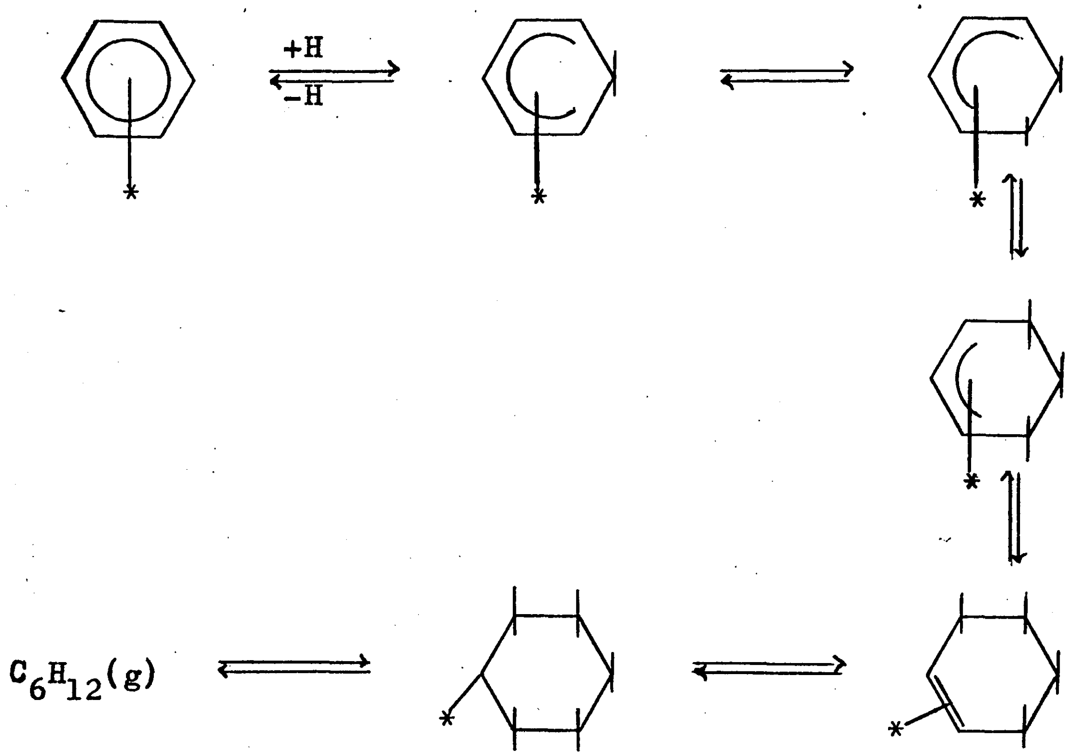
In earlier studies of benzene hydrogenation by Germain et al. (42), Kubicka (49) and van Meerten et al. (44), it has been suggested that the possible cause of the maximum in the rate-temperature curve is a diminution in the surface coverages of the catalyst by benzene and hydrogen at elevated temperature, although an unequivocal explanation has not been given. The vast, but fragmentary, kinetic evidence from the literature is conflicting and does not allow the deduction of any definitive conclusion about the route whereby adsorbed benzene undergoes hydrogenation.

A possible explanation of the shape of the activity-temperature curves is that, as the temperature is raised, the surface metal-hydrogen bond becomes progressively weaker. Thus, increasing temperature favours the hydrogenation of adsorbed benzene, until a certain temperature is reached at which the amount of chemisorbed hydrogen becomes sufficiently low that the reaction rate becomes limited by the hydrogen availability. In consequence, beyond this temperature, the rate of hydrogenation will progressively decrease with further increase in temperature. However, in the absence of full kinetic data at the various temperatures studied, it is not possible to estimate either the temperature at which the maximum is expected or the magnitude of the effect. A similar argument may be applied to the hydrocarbon surface coverage. Considering the fate of an adsorbed hydrocarbon molecule, it may either under hydrogenation or desorption. Since both of these processes are activated, both will increase with increasing temperature and, in consequence, the lifetime of the adsorbed hydrocarbon, which will depend upon the activation energies of the two processes, will decrease with increasing temperature. If, as has been observed with unsaturated aliphatic hydrocarbons (79), the activation energy for desorption is greater than that for hydrogenation, it would be expected that at a certain temperature the hydrocarbon desorption would become the predominant process and, beyond this temperature, the rate of hydrogenation would decrease with further increase in temperature.

The experimental results presented in Section 4.3 showed a lack of reactivity of pre-adsorbed ^{14}C-benzene on a "hydrogen-free" platinum or palladium surface towards hydrogenation, subsequent upon the addition of hydrogen to the catalyst. These results suggest, as was concluded in the previous section, that the adsorption of benzene on a "clean" surface results in the formation of a strongly bound, possibly dissociatively adsorbed, species, which is not the species responsible for hydrogenation.

When the hydrogenation reaction was examined using hydrogen as carrier gas, a completely different behaviour was observed in the reactivity of benzene, values of around 80% in the conversion of benzene on platinum catalysts were obtained. These observations indicate that benzene active for hydrogenation is possibly adsorbed associatively. Together the results indicate that if the hydrocarbon is adsorbed first on the catalyst there is no, or a very small interaction with hydrogen in the temperature range examined. However, if hydrogen is first adsorbed it inhibits dissociation of benzene, but is available for interaction leading to hydrogenation. Martin and Imelik (28), in their magnetization measurements, found a similar behaviour when benzene or hydrogen is adsorbed first on a nickel catalyst. These authors concluded that hydrogen acts as a protective film between the metal surface and benzene, thereby preventing the hydrocarbon cracking.

The results of the hydrogenation of aromatic hydrocarbons are consistent with the view that during hydrogenation most of the catalytic surface is covered with hydrogen and the benzene ring acts as a donor of electrons and forms a π-complex with the catalytic surface. This complex is then successively hydrogenated by adsorbed hydrogen atoms. The mechanism of hydrogenation is thought to be as proposed by Rooney and Webb (77) and is shown in the scheme below:



Mechanism for Benzene Hydrogenation.

From the results shown in tables 4.27 - 4.30 and figures 5.2 and 5.3, it can be seen that, under similar experimental conditions, the extent of hydrogenation of toluene was, over each of the four catalysts studied, greater than that of benzene. These observations are in contrast with previous reports (22, 80) that increased alkyl substitution reduces the relative rate of hydrogenation. Such decreases have been interpreted (22) as being a consequence of an increase in the strength of adsorption of the hydrocarbon through the electron-releasing effects of the alkyl substituents, although Gland and Somorjai (76), from LEED and work function measurements, have concluded that the substituents in the benzene ring only affect the ordering of the hydrocarbon overlayers; they have no effect upon the strength of adsorption, which is similar for each substituted benzene. Volter et al. (80) interpreted their observations that, over cobalt and rhodium catalysts, the extent of adsorption increased with alkyl substitution of the ring, although the rate of hydrogenation decreased, in terms of steric effects. They suggested that the alkyl benzenes undergo activated adsorption in such a manner that the methyl groups tend to be oriented away from the surface and their presence retards the approach of hydrogen to the benzene nucleus from the gas phase. These authors did not, however, consider the possibility of the effects of saturating the catalyst surface with hydrogen before the hydrocarbon adsorption, as is the case in the present studies.

It is of interest to note that the maximum in the activity-temperature curves (figures 5.2 and 5.3), for a particular catalyst, occurs at a slightly lower temperature for toluene than for benzene. This may be interpreted as showing that, on hydrogen precovered surfaces, the toluene is more weakly adsorbed than benzene and, in consequence, is more easily hydrogenated. Such a conclusion is also consistent with the observation, noted above, that the

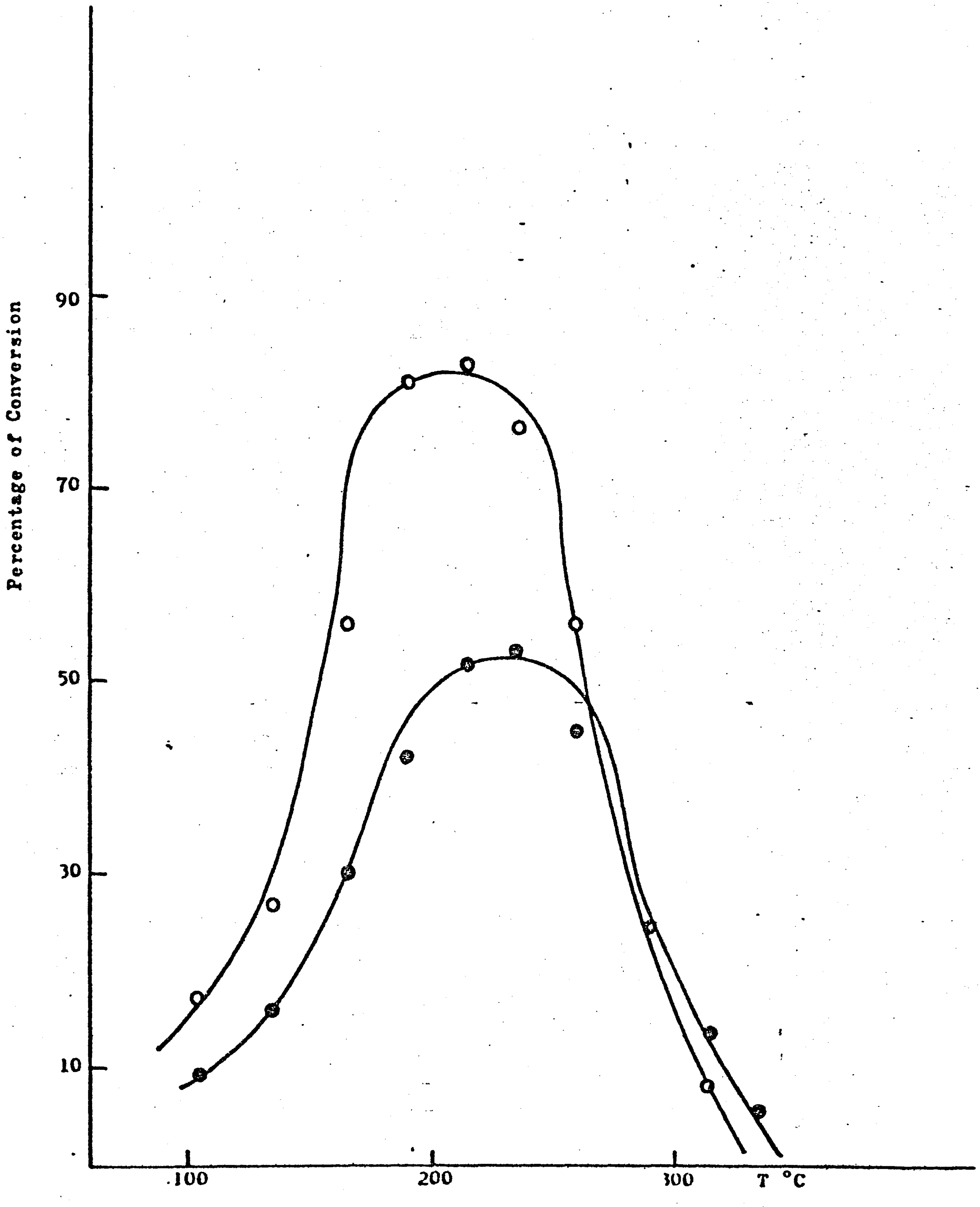


Fig. 5.2 Hydrogenation of Benzene and Toluene on 0·100g Pd/SiO_2 (● Benzene, O Toluene).

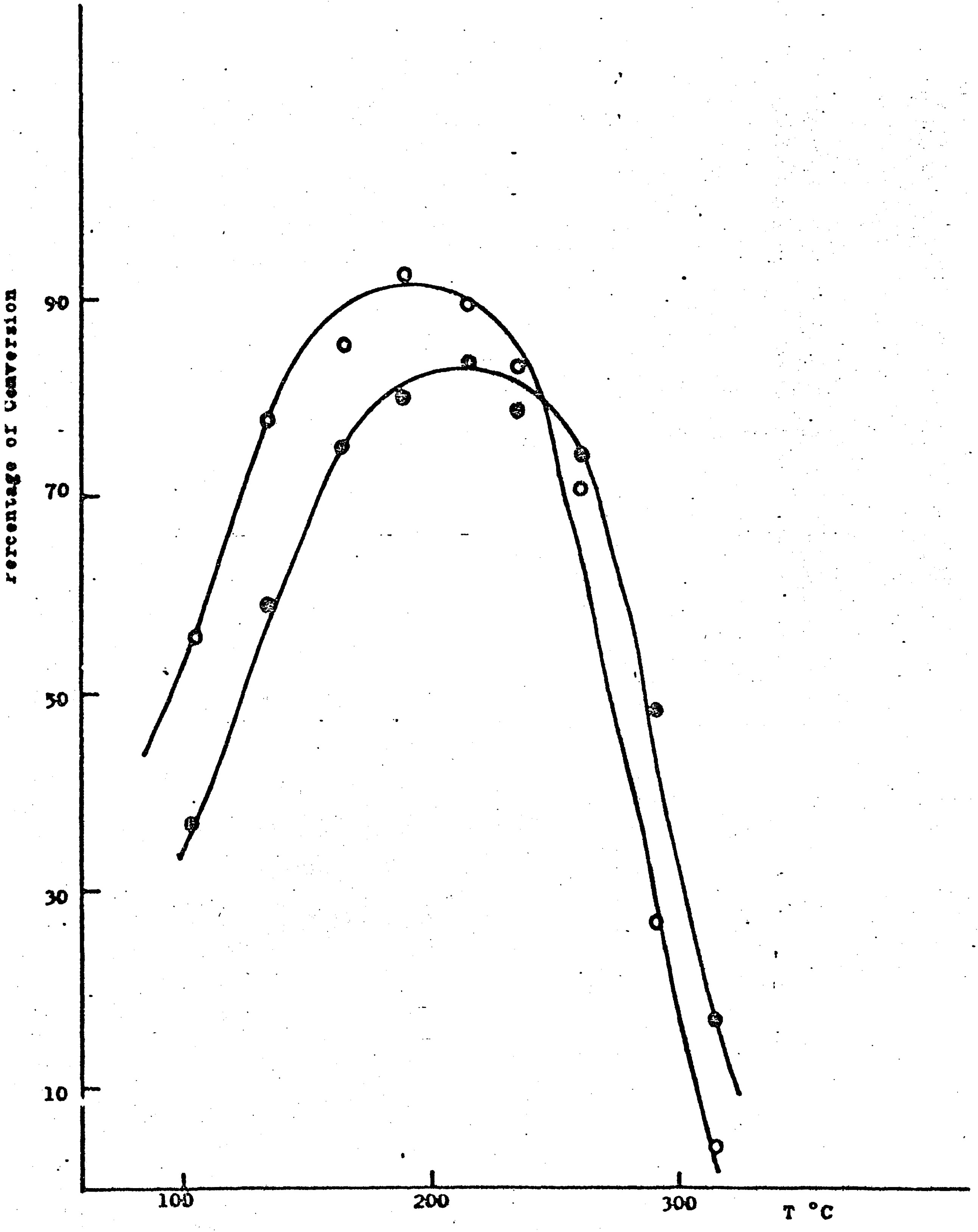


Fig. 5.3 Hydrogenation of Benzene and Toluene on 0·005g Pt/Al_2O_3 (● Benzene, O Toluene).

extent of retention of toluene, under hydrogenation conditions, was less than that observed with benzene.

5.3 Competitive Catalytic Hydrogenation of Benzene and Toluene

The results obtained for the competitive catalytic hydrogenation of benzene and toluene on platinum and palladium supported over alumina and silica, using hydrogen as carrier gas, are shown in figures 4.8 - 4.11. From these it can be seen that, the hydrogenation of the mixture 1:1 (v:v) of benzene and toluene pass through a maxima in the same range of temperature as those found in the separate hydrogenations of benzene and toluene. Although benzene can be hydrogenated in the presence of toluene to cyclohexane, the hydrogenation of benzene is about 5% less than when it is separately hydrogenated. These results suggest that benzene and toluene are hydrogenated on the same kind of active sites, and that the toluene inhibits to some extent the hydrogenation of benzene. In earlier studies of the competitive hydrogenation of alkylbenzenes in liquid phase (52), it has been suggested that the relative reduction rate depends upon the steric interference caused by methyl substituents preventing ready attack of the hydrogen on the benzene nucleus or by steric interference of the methyl group with the activated catalyst surface. This latter type of hindrance should be reflected in the relative ease of adsorption of various alkylbenzenes on the active portion of the catalyst surface.

As the steric hindrance is increased the ease of adsorption should decrease.

It has also been found by Rader and Smith (81) that the relative ease of adsorption does not necessarily parallel the relative rates of reduction of the individual hydrocarbons. The authors pointed out that the relative ease of adsorption is a thermodynamic effect, which is determined by the relative stability of chemisorbed nucleus, while the relative reduction rate is a kinetic effect which is determined by the relative stability of the transition state of the rate-determining step. Changes in nuclear substitution may or may not affect the relative stability of the chemisorbed species and the transition state in the same direction.

In figures 4.8 to 4.11 it can also be seen that, the hydrogenation of toluene is greater than benzene over all the catalysts studied. This was interpreted, as was mentioned in section 5.2, by considering that, on hydrogen precovered surfaces, the toluene is more weakly adsorbed than benzene and, in consequence, is more easily hydrogenated.

The turnover numbers for benzene and toluene from a mixture of 1·0μℓ, containing 0·5μℓ of benzene and 0·5μℓ of toluene, are shown in tables 4.33-4.34. From these it can be seen that, the relative specific activity of platinum for each hydrocarbon was greater than that shown by palladium catalysts, confirming the order of activities found in the case of the separate hydrogenation of benzene and toluene.

In general, according to the results obtained and shown in chapter four, it can be concluded that both platinum and palladium show a chemisorption capacity and specific activity for the adsorption and hydrogenation of aromatic hydrocarbons, at all temperatures examined, in the order platinum > palladium.

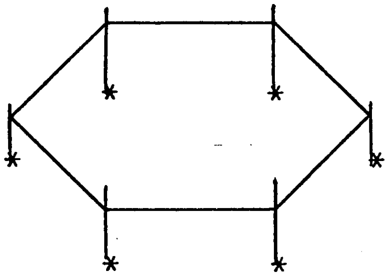
Evidence was obtained for different types of adsorption of benzene. The adsorption of benzene in the helium flow system has proved to be the adsorption of a species inactive in hydrogenation and molecular exchange. In the present study the stream of helium passed continuously over the catalyst previously exposed to hydrocarbon adsorption and no desorption of these species was observed in the chromatographic analysis. These observations suggest that benzene and toluene are adsorbed irreversibly over the catalytic surface and are not removable by flushing with helium during the course of the experiments (considering the helium treatment as equivalent to evacuation). This irreversible adsorption was confirmed by the lack of reactivity of the residues of benzene found in the studies of labelled hydrocarbon. The species responsible for the irreversible adsorption is stable at all temperatures examined and is independent of the number of pulses over the catalyst, after the reproducible behaviour has been reached. This adsorption is evidently associated with the metal; separate experiments confirmed that benzene or toluene was not retained by alumina or silica, pretreated in the same way as the catalyst, under the experimental conditions used in the present work.

The complete lack of reactivity of benzene towards molecular exchange and hydrogen treatment, suggests that the residue is not present as a reactive form of chemisorbed benzene, which is considered to be an associatively bonded species, and as was concluded in the previous section, this type of adsorption is possibly a dissociatively bonded species.

The effect of the temperature on chemisorption seems not only to increase the extent of the dissociative adsorption but, to some degree, to cause C-C bond rupture as was the case with toluene at 250°C, when small amounts of methane and benzene were obtained. Martin and Imelik (27, 28) have found that, in the case of benzene adsorption, the bonds formed between nickel and the substrate increase as the temperature is raised, reaching about 25 bonds at 150°C. This indicates an extensive fragmentation at this temperature.

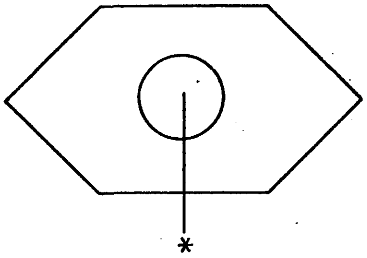
Chemical analysis of the product obtained in the regeneration of the catalytic surface at 350°C by hydrogen treatment resulted in the recovery of small amounts of cyclohexane. More controlled treatment, however, of residues on nickel (36) and platinum (74) has indicated that the catalysts were not poisoned by benzene in the reaction with this substrate.

When the adsorption of benzene was examined in the hydrogen flow system, a reactive adsorbed state of benzene was observed. This type of active benzene in hydrogenation is probably an associatively bonded species. Although much debate exists as to the nature of the hydrocarbon-metal bonding in the associatively adsorbed state, it seems that the aromatic ring is adsorbed flat on the surface, either by six σ-bonds (with loss of resonance energy) as (A) or by a π-bond (with retention of resonance energy) as (B) (82).



(A)

or



(B)

In the present studies, benzene is thought to be adsorbed on hydrogen-precovered surfaces as a π-complex with the benzene ring acting as a donor of electrons. Recently, Sheppard et al. (83), using the sensitive interferometry technique, have reported I.R. evidence for the existence of both a 1,2-di-σ-bonded and a π-bonded species when ethylene is chemisorbed on <u>hydrogen-precovered</u> silica-supported palladium and platinum catalysts. These workers also observed that both species are readily hydrogenated from the surface, with the π-complex being the more reactive species.

Difference in the behaviour of the hydrocarbons seems to be influenced mainly by the medium where the experiments are conducted. Thus, for example, in helium, the dissociative adsorption of the hydrocarbons and the hydrogenolysis of toluene at 250°C were found, while in hydrogen, the associative adsorption of benzene and toluene, and the absence of hydrogenolysis phenomena in the temperature range 100°-335°C, were observed. It was also seen that, the number of toluene molecules retained by the catalysts in hydrogen environment was less than in the case of helium carrier gas. The same phenomena were found in the case of benzene on palladium catalysts. From these observations, it may be concluded that the role of helium is to clean the metallic surface and then favour the dissociative adsorption and hydrogenolysis reaction, while hydrogen acts as a cover of the catalytic surface, reducing the direct interaction of "foreign" atoms or molecules with the metal, but favouring the hydrogenation of hydrocarbons.

5.4 Future Work

Although, from the results quoted in this thesis, a general picture of the adsorption and reactivity of aromatic hydrocarbons has been obtained, much work still remains. In particular the competitive hydrogenation of pairs of aromatic hydrocarbons, such as benzene and toluene or toluene and ethylbenzene, over a variety of transition metal catalysts would be informative in that it would permit an evaluation of the relative importance of steric and electronic effects in the adsorption and hydrogenation processes.

Examination of the detailed reaction kinetics in the region of the activity-temperature maxima would also be of interest from the standpoint of identifying the parameters which determine this phenomenon.

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