STUDIES OF THE CATALYTIC ACTIVITIES AND RESISTANCE TO SULPHUR POISONING OF P-3 NICKEL AND P-3 COBALT BORIDES

BY

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ABSTRACT

The heterogeneous liquid-phase catalytic hydrogenation of alkenes over partially hydrogenated P-3 nickel and P-3 cobalt borides has been investigated. These catalysts of proposed formulae $(Ni_2B)_2.H_3$ and $(Co_2B)_5.H_3$ are more active than the previously studied P-1 and P-2 type nickel borides and high-activity Raney nickel.

P-3 nickel is highly active for hydrogenation of terminal and internal olefins and causes isomerisation of 1-octene to 2-octene. Contrary to this, although P-3 cobalt readily reduces terminal olefins, it only slowly hydrogenates internal olefins and does not cause isomerisation of 1-octene under the reaction conditions studied.

Hydrogenations over P-3 nickel and P-3 cobalt appear to follow a Rideal-Eley type mechanism where one reactant (i.e. alkene) is strongly adsorbed initially to form a substrate-catalyst intermediate followed by reaction with a second non-adsorbed reactant (i.e. molecular gaseous hydrogen). A second mechanism has been suggested for the isomerisation of 1-octene over P-3 nickel and this possibly involves an allylic intermediate.

P-3 nickel, P-3 cobalt, and Raney nickel are highly resistant to poisoning by hydrogen sulphide. For example, P-3 nickel is initially active towards hydrogenation of 1-hexadecene in the presence of even 800 mg/l hydrogen sulphide in the gas phase. The catalyst's resistance is critically dependent, however, on the pressure of hydrogen. These catalysts appear to be more sensitive towards

sulphur poisoning in the form of _n_-butanethiol, although the resistance is still extraordinary. Thus, the catalytic activities of P-3 nickel, P-3 cobalt, and Raney nickel towards hydrogenation of 1-hexadecene only drop to zero in the presence of 52, 90, and 27 mg/l sulphur respectively under the reaction conditions studied, which are fully discussed in this thesis.

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TABLE OF CONTENTS

Page

CHAPTER 1. INTRODUCTION

CHAPTER 2. EXPERIMENTAL

Page

CHAPTER 3. RESULTS

CHAPTER 4. DISCUSSION

CHAPTER 5. APPENDIX

LIST OF FIGURES

Page

LIST OF TABLES

Page

CHAPTER 1

INTRODUCTION

1.1 Introduction to Heterogeneous Catalysis

Catalytic reactions involve a series of steps in which the "catalyst" enters as a reactant in the first step, and appears as a product in the last step (1). The "catalyst" may be an enzyme, a complex in a liquid solution, a gaseous molecule, or a grouping of atoms at the surface of a solid called an "active site". Systems involving the latter type of structure are called heterogeneous catalysts. The "active centre" is the site or group of sites that takes part in the reaction. With this type of catalysis, the solid catalyst can be readily separated from the fluid reaction medium (be it gaseous or liquid).

The "activity" of a catalyst is quantitatively represented by the rate of a particular reaction (1). The "selectivity" of a catalyst is defined as a ratio of rates; that of a desired reaction over the sum of rates of other undesirable reactions (1).

Finely divided metals, supported or unsupported, have been used as catalysts for many industrial heterogeneous reactions, and have generally been considered the most active and useful type of heterogeneous catalyst available. However, during the last twenty-five years, a considerable amount of study has been made of catalytic systems produced by reduction of certain metal salts in aqueous or alcoholic solutions with sodium borohydride under moderate conditions. The resulting "metal boride", in particular those of nickel and cobalt, have received a great deal of attention. The following presents a summary of work that has been reported concerning this field, and will thus introduce the present study.

1.2 Preparation and Activities of Nickel and Cobalt Borides for Use as Liquid-Phase Heterogeneous Catalysts

During World War Two, H. Schlesinger and H.C. Brown (2) found that the reduction of certain transition metal salts (e.g. those of Ni, Co, Mn, Cu, Fe, Pt, Ru, and Rh) with $NaBH_4$, (in air and in aqueous solution), give finely divided precipitates of metal borides. These so-called metal borides (M_2B) are easily prepared under mild conditions (room temperature, atmospheric pressures), and are active catalysts for the hydrolysis of sodium borohydride.

$$NaBH_4 + 2H_2O \xrightarrow[\text{metal boride}]{} NaBO_2 + 4H_2 \qquad \{1\}$$

It has been reported further (3,4) that the reaction of $NaBH_4$ with Ni(II) and Co(II) salts is as follows:

$$2NaBH_4 + NiCl_2\ (CoCl_2) + 4.5H_2O \longrightarrow 0.5Ni_2B\ (Co_2B) + 1.5H_3BO_3 + 6.25H_2 + 2NaCl \qquad \{2\}$$

Following this first study, numerous reports of the preparation of these so-called (see later discussion) nickel and cobalt borides have been made. It is of the utmost importance to note the conditions used for the catalyst preparation as variations in this procedure lead to great differences not only in the chemical properties of the metal borides so produced, but also in their catalytic activities in various reactions.

In 1952, Paul, Buisson and Joseph (5) discussed the preparation of nickel and cobalt borides from the M(II) salts in aqueous solution in air by reduction with sodium or potassium borohydride. The voluminous, black precipitates formed from nickel salts are "non-magnetic", non-pyrophoric, and less soluble in HCl and potassium triiodide than Raney nickel. The B-Ni (Co) content only accounts for 93% of the product, (7-8% B, 84-85% Ni(Co)), and the remainder was thought to be due either to water, or to products formed by partial oxidation of the boride. The ratio of boron to nickel (cobalt) is fairly constant, and these workers proposed the formula for these so-called metal borides as Ni_2B (Co_2B).

In addition, "promoted" metal borides can be prepared by reducing the nickel or cobalt salt in the presence of another metal salt. The added metal salt (chromium sulphate, sodium molybdate, sodium tungstate, ammonium vanadate, or manganese chloride) is reduced to its corresponding metallic state by the metal boride or some intermediate since it is known that $NaBH_4$ itself does not normally cause such a reaction. The catalyst so produced contains approximately 2% of free promoter metal (5). It was believed that since the metal borides have a finely divided form, and since the amount of boron is small compared with nickel or cobalt, the metal borides may be active in reactions in which metallic nickel (i.e. Raney nickel) is commonly used.

The unpromoted nickel boride prepared from nickel chloride or nickel sulphate has an activity inferior to that of Raney nickel for the hydrogenation of safrole, and benzonitrile. However, if nickel acetate is used for the preparation, the catalyst is more active than Raney nickel. Promoted nickel and cobalt borides are found to be more active than the unpromoted ones. The promoter action is believed to be associated with an increase in the catalyst surface area (6).

All unpromoted nickel borides (5) prepared in this manner have inferior activities to Raney nickel for the hydrogenation of furfural.

However, if the nickel boride is prepared in slightly acid medium (pH less than 5), its activity is increased and it also shows greater resistance to fatigue (i.e. catalytic poisoning) than Raney nickel. In all cases, the corresponding cobalt boride is somewhat less active than the nickel boride.

These nickel borides are more active for the hydrogenation of ethylenic groups than for carbonyl functions (7). Unlike the Pd/HCl system, the nickel boride prepared by this method is active for the reduction of β-carbonyl groups (7). The nickel boride prepared by Paul's method (5) is also active for the reduction of cycloalkenes (8).

It is also interesting to note that the analogous cobalt boride, prepared in aqueous solution and in air, catalyzes the reduction by sodium borohydride of nitrate ion to ammonia (9), and can also reduce this substrate, itself, in the absence of an excess of sodium borohydride (10). This cobalt boride was further found to be active for the decomposition of hydrazine to ammonia, and of hydrogen peroxide at 25-65° C (9).

Even more active metal boride catalysts can be readily prepared (11) by reductions of aqueous nickel(II) salts under nitrogen using a two-fold molar excess of sodium borohydride at room temperature and at one atmosphere pressure. The resulting black, granular precipitate is "non-magnetic", non-pyrophoric, and decomposes slowly in HCl (12). Once again, the amounts of Ni and B only account for 91% of the product and the approximate formula Ni_2B and name P-1 Ni were assigned.

P-1 Ni is considerably more active than commercial Raney nickel towards hydrogenation of less active olefins and has much less tendency towards isomerisation of the olefin during hydrogenation (11). The presence of sodium borate, sodium acetate, or sodium hydroxide during catalyst generation has little effect upon the activity of the catalyst for the hydrogenation of 1-octene (12). Generally, P-1 Ni prepared from nickel chloride or nickel sulphate is slightly less active than that prepared from nickel acetate. P-1 Ni prepared from nickel nitrate is too fine to wash by decantation.

The relative times for half hydrogenation of several olefins over P-1 Ni and Raney nickel were found to be in the ratio (12): safrole (1.0:1.0), 1-octene (1.0:1.3), cyclopentene (1.3:2.0), cyclohexene (2.5:3.5), and cyclooctene (2.0:5.5). Substitution of methyl groups for hydrogen atoms alpha to the double bond of terminal olefins produces little change in the rate of hydrogenation over P-1 Ni. Replacing vinyl hydrogen atoms with more alkyl groups causes a great decrease in reaction rate. However, even highly hindered tetra-substituted olefins are reduced over P-1 Ni at

25° C and atmospheric pressure. Cyclic olefins are reduced in the order $C_5 > C_8 > C_6$, and phenyl-substituted olefins are hydrogenated at least as readily as the aliphatic ones. There is no evidence for reduction of the aromatic ring over P-1 Ni under normal conditions (12), but norbornene, which has double bond strain, is readily reduced. In contrast to this, P-1 type cobalt (prepared under hydrogen) hydrogenates phenol, aniline, benzene, toluene, and chlorobenzene to their corresponding cyclohexanes (13). P-1 Ni selectively reduces unconjugated dienes (12). Thus, reduction of 2-methyl-1,5-hexadiene gives 2-methyl-1-hexene (93%) and reduction of 4-vinylcyclohexene gives 4-ethyl-cyclohexene (98%).

P-1 Ni and P-1 Co borides, unpromoted *or* promoted with 2% Pt, Pd, Eu, or Cr reduce selectively soybean oil to mono- and diunsaturated *cis* esters, producing little stearate, and only small amounts (9-10%) of the *trans* isomer at atmospheric pressure (14).

P-1 type nickel borides have also been reported (15) as causing partial dechlorination of DDT (an organochlorine pesticide) in methanol in the presence of an excess of sodium borohydride.

Yet another method (16) of preparation of nickel boride is the reduction of nickel salts in *ethanolic* solution under *hydrogen* with *equimolar* amounts of sodium borohydride. The black, colloidal product is, like P-1 Ni, "non-magnetic" and non-pyrophoric (12, 17). This so-called P-2 Ni was described (17) as being an amorphous mixture with a Ni:B ratio of 2.0 to 2.5:1.0. The catalyst can equally well be prepared under a nitrogen or argon atmosphere (17), although contact with air during reduction of the nickel salt causes a large decrease in catalytic activity. If P-2 Ni is prepared in the presence of high surface area carbon or silica (23% metal loading by weight), no significant change in the catalyst's activity is apparent. This indicates (17) that P-2 Ni has an extremely high state of dispersion. The activity of P-2 Ni is (16) highly sensitive to the structure of the olefin, and is also remarkably free from isomerisation tendencies (i.e. even less than with P-1 Ni). P-2 Ni is very active for reduction of terminal alkenes, but substitution in the alpha position greatly interferes with hydrogenation - presumably by hindrance of substrate adsorption. Thus, the relative rates of hydrogenation over P-2 Ni (17) are 1-octene (1.0), 3-methyl-1-butene (0.23), and 3,3-dimethyl-1-butene (0.07).

Direct substitution of the double bond produces even more drastic results (17). For example, relative rates of hydrogenation are 1-octene (1.0), cis 2-pentene (0.03), 2-methyl-1-pentene (0.004), trans 2-pentene (0.003), 2-methyl-2-pentene (less than 0.001), and 2,3-dimethyl-2-butene (0). Most medium sized ring alkenes are reduced by P-2 Ni although, benzene and , surprisingly, cyclohexene are inert.

P-2 Ni is also (16,17) very selective for the partial hydrogenation of dialkylacetylenes to cis olefins. Thus, under moderate conditions, substituted alkynes are reduced over P-2 Ni to the corresponding alkenes with a cis:trans ratio of 30:1 (18). However, in the presence of ethylenediamine, this same reaction over P-2 Ni leads to the production of nearly pure <u>cis</u> olefin (200:1).

As was found with P-1 Ni, P-2 Ni readily hydrogenates norbornene, and also this strained double bond is selectively reduced in preference to other exocyclic double bonds (19).

P-2 Ni prepared under hydrogen, was also reported (20,21) as being active for the reduction of unsaturated compounds which contain oxygen or nitrogen,at pressures of 30 psi of hydrogen. Similarly, P-2 Ni has been shown (22) to be selective first for reduction of the C-C double bond of α,β unsaturated aldehydes to produce saturated aldehydes, followed by <u>slow</u> reduction of the carbonyl function to yield saturated alcohols. P-2 Ni, unlike several metal catalysts, is not poisoned by amines. The results of the above studies are shown in tables 1.1 (20,21) and 1.2 (22).

A P-2 type cobalt boride, in the presence of an excess of sodium borohydride and at 20—40°C, reduces nitriles, amides, and nitro — compounds to amines (23,24), although sodium borohydride alone does not reduce these functional groups. This reaction occurs in non-hydroxylic solvents (23). The similar nickel boride system was found (25) to reduce selectively the olefinic grouping in unsaturated esters. In other studies concerning the reduction of nitrogen-containing functional groups, a P-2 type cobalt boride prepared from cobalt bromide was found (26,27,28) to reduce nitrosamines, aromatic nitroso compounds, azoxybenzenes, and hydrazobenzenes to azoxybenzenes, azobenzenes, anilines, or diphenylamine . Azobenzene itself is not reduced.

TABLE 1.1

Times of Hydrogenations Over Nickel Boride

Reactant	Time[a]
Diallyl ether	20 min[b]
Allyl alcohol	30 min
2-Butene-1,4-diol (<u>cis</u>)	1 hr
Cinnamyl alcohol (<u>trans</u>)	3 hr
2-Cyclopentene-1,4-diol	30 min
1-Phenyl-2-propenol	8 min
Cinnamaldehyde (<u>trans</u>)	24 hr[c]
5-Hexene-2-one	12 min
Mesityl oxide	6.75 hr
Allyl acetate	16 min
Ethyl cinnamate	2 hr
Cinnamic acid (<u>trans</u>)	d
Maleic acid	1 hr
Allylamine	10 min
Diallylamine	25 min[b]
Acrylamide	8 min
Methacrylamide	15 min
3-Butenenitrile	30 min
2-Butenenitrile	30 min[e]
Cinnamonitrile	16 hr[e]

[a] Time required for the uptake of 1 equiv. of hydrogen, 100 mmole of substrate, 5 mmole of catalyst, 50 ml of solvent. [b] Time required for the uptake of 2 equiv. of hydrogen. [c] Half reaction. [d] No H_2 uptake after 37 hr. [e] 20 mmole of catalyst.

TABLE 1.2

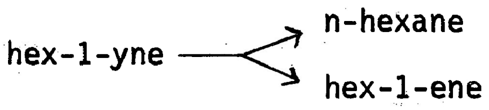
Times of Hydrogenations of Unsaturated and Saturated Aldehydes Over Nickel Boride[a]

Reactant	Product	mmole Ni	Time[b]
Acrolein	Propionaldehyde	5	30 min
Crotonaldehyde	Butyraldehyde	5	8 hr
Crotonaldehyde	Butyraldehyde	20	45 min
Cinnamaldehyde	Hydrocinnamaldehyde	20	1 hr
Tiglaldehyde	2-Methylbutyraldehyde	20	1 hr
Propionaldehyde	1-Propanol	50	15 hr
Butyraldehyde	1-Butanol	50	21 hr
Hydrocinnamaldehyde	3-Phenyl-1-propanol	20	4 hr
2-Methylbutyraldehyde	2-Methyl-1-butanol	20	7.5 hr
Benzaldehyde	Benzyl alcohol	10	48 hr
Furfural	Furfuryl alcohol	5	12 hr

[a] 100 mmole reactant, 30 psi inititial H_2 pressure, ambient temperture, in 50 ml 95% ethanol. [b] Time for uptake of 100 mmole H_2.

Studies (29) of the mechanism of hydrogenation of hex-1-yne over borohydride reduced catalysts have shown two possible pathways.

(1)



(2) hex-1-yne $\longrightarrow$ hex-1-ene $\longrightarrow$ n-hexane

Both P-1 and P-2 Ni boride appear to follow the first mechanism, with direct formation of n-alkane from the alkyne.

Turning to supported catalysts, two studies (30,31) have been made of nickel and cobalt borides of the P-1 or P-2 types supported on silica or alumina although few details were given. In addition, Barnett (32) has shown that nickel or cobalt borides (promoted or unpromoted) supported on charcoal are active for the hydrogenation of aliphatic nitriles in solution at 70°C and two atmospheres of hydrogen pressure. Also, supported Ni and Co borides have been prepared (33) by trapping metal salts in a polymer (crosslinked 2-hydroxyethyl methacrylate) followed by reduction with ethanolic sodium borohydride. These too are catalytically active in alkene hydrogenations.

In addition to the hydrogenations already discussed, P-1 and P-2 Ni and Co borides are also active for dehydrogenations (6), hydrocracking (30,31), hydrodealkylation, and polymerisation (34-38).

In other catalytic applications, nickel boride prepared from nickel sulphate in aqueous solution (39) is more resistant to sintering at 220°C in vacuo than is finely divided nickel prepared from nickel formate. The nickel boride is, therefore, useful for fuel cell anodes since large surface areas can be maintained even at high temperatures (40-45).

In non-catalytic applications, nickel borides have been reported (46-50) to be useful desulphurizing reagents, being more selective than Raney nickel, although yields are generally lower. This was thought by the present author to indicate that nickel boride may be less sensitive to sulphur-compounds (i.e. sulphur poisoning) in hydrogenation reactions than is Raney nickel and this point will be discussed further in later sections of this thesis.

In this connection, nickel borides have been used for desulphurization of thiols, disulphides, sulphides, sulphoxides, (47) and mercaptoles (46), but are inactive towards sulphones (47). Some heterocyclic thiols have been desulphurized by P-1 Ni in aqueous solution at 200°C (49). Reductive desulphurization of S-containing peptides by nickel borides (50), and of ethylenedithioacetals and hemithioacetals (48) have also been reported. No direct studies of sulphur poisoning of the nickel or cobalt boride catalytic hydrogenation systems have been reported.

The above summary covers the studies made of the catalytic activities of P-1 and P-2 type nickel and cobalt borides and similar less active borides prepared earlier. However, still another method for their preparation has been reported recently (51).

Hawthorne et al. (51) prepared nickel and cobalt borides by reduction of metal(II) halides with a three-fold molar excess of sodium borohydride in ethanolic solution under nitrogen. When these borides are heated under reduced pressure, hydrogen is lost between 100° and 800°C. Therefore, on the basis of the amount of hydrogen lost and other data, the formulae proposed for these partially hydrogenated metal borides are $(Ni_2B)_2.H_3$ and $(Co_2B)_5.H_3$ and this author has designated them as P-3′ borides in keeping with the practise of others. It was also noticed that some trapped sodium chloride is present. When dry, the metal borides are ferromagnetic, pyrophoric, amorphous by X-ray diffraction analysis, very soluble in dilute mineral acids, almost insoluble in alkali, and have BET surface areas of 5.3 to 57.8 m^2/g. It was suggested that the hydrogen is held in some clathrate-type lattice of the metal boride, and that it is responsible for at least a part of the catalytic activity of the metal borides. These observations pose interesting questions about the structures and actual compositions of the various so-called borides and this aspect of the subject under review is discussed in the next section.

1.3 Structural Studies of Nickel and Cobalt Borides

No structural studies of the catalytically active nickel or cobalt borides were reported before 1964. It is difficult to determine the chemical composition of the nickel (cobalt) boride as extensive washing with water leads to formation of hydroxides with subsequent "loss" of boron, and insufficient washing leaves behind sodium salts (51).

Studies by Hofer (52) of the nickel boride precipitate, after washing with water, showed that the chemical analysis fitted the formula $Ni_{2.5}B$. X-ray diffraction studies show that at room temperature, the material is amorphous, at 80 °C some nickel metal appears, while at 250 °C the presence of both Ni_3B and Ni (metal) was observed. No compound of formula Ni_2B could be detected. The Ni_3B, which is stable up to 750 °C, is characteristic of the Rundquist and Fruchart structure (or cementite phase) which is prepared by fusion of the elements at 900 °C. Other workers (53, 54, 55) obtained similar X-ray results. Radiocrystallographic studies (56, 57) of the P-1 type nickel catalyst also failed to reveal the presence of any compound of formula Ni_2B.

Thonnart's studies (58) of P-1 Ni at 450 °C show that at this temperature, a new phase having an orthorhombic cell appeared. The boron was thought to be distributed randomly, and would thus perturb the structural organisation of the nickel. Further X-ray studies (59) of P-1 type Ni and Co borides show that the products are amorphous at room temperature, and that the composition of the catalytically active species does not correspond to any exact stoichiometric formula. At 300-500 °C *in vacuo*, X-ray diffraction patterns (59) show the presence of Ni_3B, and sometimes a mixture of Ni (metal) *or* Ni_2B. The electron diffraction patterns (59) of the freshly prepared P-1 Ni and P-1 Co at room temperature are almost identical. The lattice constants are such that the Ni or

Co atoms could not touch each other, and therefore vacancies large enough to accomodate boron and hydrogen atoms or boron-hydrogen pairs or chains could occur. Electron diffraction studies of the heated samples show the formation of the cementite phase. If the cobalt boride is heated, there is a substantial rise in magnetization at 400°C indicating the presence of a new magnetic phase (Co_3B). The nickel boride is ferromagnetic. The products formed upon heating the metal borides have greatly diminished catalytic activity.

In contrast to the above reports, several studies (10,60) have indicated that nickel and cobalt borides, when heated in argon to 400°C, show the presence of nickel metal and $\underline{Ni_2B}$. Additionally, P-1 and P-2 Ni were shown to contain adsorbed hydrogen and water (10,61).

1.4 Gas-Phase Hydrogenations Using Nickel and Cobalt Borides

Although this review and study are concerned primarily with liquid phase catalytic reactions, it is important to note that several studies have been made on the use of nickel and cobalt borides as catalysts in gas-phase alkene hydrogenations.

The first report of this type of reaction using unsupported catalysts was made by Hawthorne et al. (51) in 1974 in which it was also noted that partially hydrogenated P-3 type nickel and cobalt borides are active gas-phase catalysts for methanation of carbon monoxide. Further work in this area has since been reported (62). Thus, metal boride, supported on glass wool, hydrogenates cis

2-butene at one atmosphere pressure of hydrogen. Using 1.22 mole % of the alkene, at 62°C, 50% hydrogenation occurs and at 90°C, quantitative reaction occurs with no isomerisation to trans 2-butene or 1-butene. In contrast, below 200°C, Raney nickel causes significant isomerisation during this reaction. At higher temperatures, above 300°C, hydrogenolysis occurs to yield methane. With temperatures greater than 400°C, the catalyst's activity is lost.

Recently (63) the preparation of the stoichiometrically reproducible $(Co_2B)_{10}RhH_6$ and $(Ni_2B)_{10}RhH_{15}$ by addition of 5 molar % $RhCl_3.3H_2O$ to a 1M solution of Co(II) chloride or Ni(II) chloride in ethanol, followed by addition of a four-fold molar excess of $NaBH_4$ under nitrogen, was reported. These rhodium-promoted catalysts are more stable at high temperatures, and no loss in activity up to 500°C was observed.

Unsupported P-3′ type Ni and Co borides (62), silica supported nickel and cobalt borides (64), and rhodium-promoted P-3′ Ni and P-3′ Co (63) are better methanation catalysts than Raney nickel. With a H_2:CO ratio of 2:1 at 240-340°C and at atmospheric pressure, methane is produced. Nickel and cobalt boride supported on silica gel or alumina are active for the methanation of CO_2 at 360°C (65).

Finally, another gas-phase catalytic study (66) found that vacuum dried nickel boride is about as active as finely divided nickel for the gas-phase decomposition of formic acid.

1.5 Kinetics of Liquid-Phase Heterogeneous Hydrogenations

To lay the groundwork for this author's own studies, it is necessary to consider other aspects of solution phase heterogeneous catalysis. One such aspect is kinetic studies of hydrogenation reactions.

Yao and Emmett (67) proposed the following equation to explain liquid-phase catalytic hydrogenation using metal catalysts.

$$-\frac{dC}{dt} = \frac{abC}{1 + bC} \qquad \{3\}$$

where $-\frac{dC}{dt}$ is the rate of decrease of substrate concentration, _a_ is a mobilization term concerning movement of hydrogen in the system, _b_ is a combination of the true reaction rate constant (k) and modified weight of catalyst used (W), and _C_ is the substrate concentration. Thus, if $bC \gg 1$ (_i.e._ high substrate concentration), then

$$-\frac{dC}{dt} = a \qquad \{4\}$$

and the rate of reaction is dependent only upon the hydrogen concentration. If $bC \ll 1$, then

$$-\frac{dC}{dt} = abC \qquad \{5\}$$

and the rate of reaction is dependent on hydrogen, substrate, and catalyst concentration. The amount of catalyst consistent with the validity of equation {5} depends on the activity of the catalyst towards the substrate. As the amount of catalyst decreases, a range is generally found in which the hydrogen adsorbed in the earlier part of the reaction is proportional to the amount of catalyst while above this range, either equation {4} holds or a situation of mixed kinetics may exist. When the concentration of substrate is high, hydrogen adsorption is linear with time. Therefore, one can assume that the catalyst surface, which has a small area relative to the other reactants, is completely occupied by substrate. It can be further assumed that adsorption of hydrogen and substrate is non-competitive. The initial rate of reaction is given by:

$$-\frac{dC}{dt} = akW\left(\frac{\alpha C_s}{\alpha C_s + \beta C_r}\right) \qquad \{6\}$$

where α and β are the adsorption coefficients of the substrate and the reduced substrate (i.e. product) respectively. It is assumed that the rate of reaction is independent of hydrogen pressure above some particular threshold.

Studies by Maxted and Stone (68) on the hydrogenation of crotonic acid in a series of solvents showed little change in rate. However, Yao and Emmett (67) found a great difference in rate of reduction of nitro-compounds dependent upon the amount of water in the solvent. The solvent could modify the a factor - i.e. hydrogen movement. It could also affect the adsorption coefficient of substrate (or poison), but there has not been a sufficient study of a variety of solvents or of substrates to draw up such a correlation.

Later, Kishida and Teranishi (68,69) reported kinetic studies of the liquid-phase hydrogenation of ketones using Raney nickel and P-1 or P-2 type nickel borides as the catalyst. They found that for the hydrogenation of acetone, the hydrogen, acetone, and solvent were all adsorbed competitively on the catalyst surface. The rate equation was derived on the basis of the Langmuir-Hinshelwood (1) mechanism which proposes that both reactants are chemisorbed on the catalyst before reaction occurs. The adsorption of the three components was thought to be reversible with all three competing for the same surface sites. The fractional surface coverage of each species is dependent on its concentration and on its free energy of adsorption relative to the other species present. If the rate-determining step of the reaction is dependent on the surface reaction between adsorbed acetone and adsorbed hydrogen, then the rate is proportional to the product of the surface coverage of acetone and hydrogen. If the number of molecules in the liquid phase is much greater than the number of molecules in the gas phase, then it can be assumed that the catalyst surface is almost saturated with the three adsorbates during the reaction.

Thus, $$\zeta_{\text{acetone}} + \zeta_{\text{hydrogen}} + \zeta_{\text{solvent}} = 1 \qquad \{7\}$$

where ζ represents the fractional surface coverage.
Altering the liquid phase concentration, and surface coverage, of one component, would result in changing the fractional coverage by either one and/or both of the other adsorbates. The solvent concentration dependence of rate must differ according to the adsorption strength of the solvent used.

Figure 1.1 shows that the rate passes through a maximum peak as the concentration of the substrate is increased. This is characteristic of a Langmuir-Hinshelwood scheme. The position of the maximum depends on the solvent and is related to the adsorption strength of the latter. Saturated hydrocarbons have the least effect upon the rate. Hence their adsorption strength must be small and they do not interfere in the reaction by blocking sites required by substrate and hydrogen. In past years, kinetic studies were generally carried out using such a solvent so that its influence could be disregarded.

Figure 1.2 shows that the adsorption strength of ketones on nickel boride decreases with an increase in the number of alkyl carbon atoms. The amount of hydrogen adsorbed during the reaction was measured as the ketone concentration varied. The coverage of hydrogen decreases with an increase in ketone concentration. The experimental data agrees with the theoretical calculations and, therefore, supports the previously proposed kinetic model for liquid phase hydrogenation of ketones.

1.6 Catalyst Poisoning

Catalyst poisoning is a preferential adsorption effect dependent on the formation of abnormally strong bonds between catalyst and poison (70). A compound may be a poison for one catalyst but have no effect on another catalyst depending upon the reaction conditions

Figure 1.1. Solvent Effect on the Rate of Hydrogenation of Acetone Over Raney Nickel at 10°C

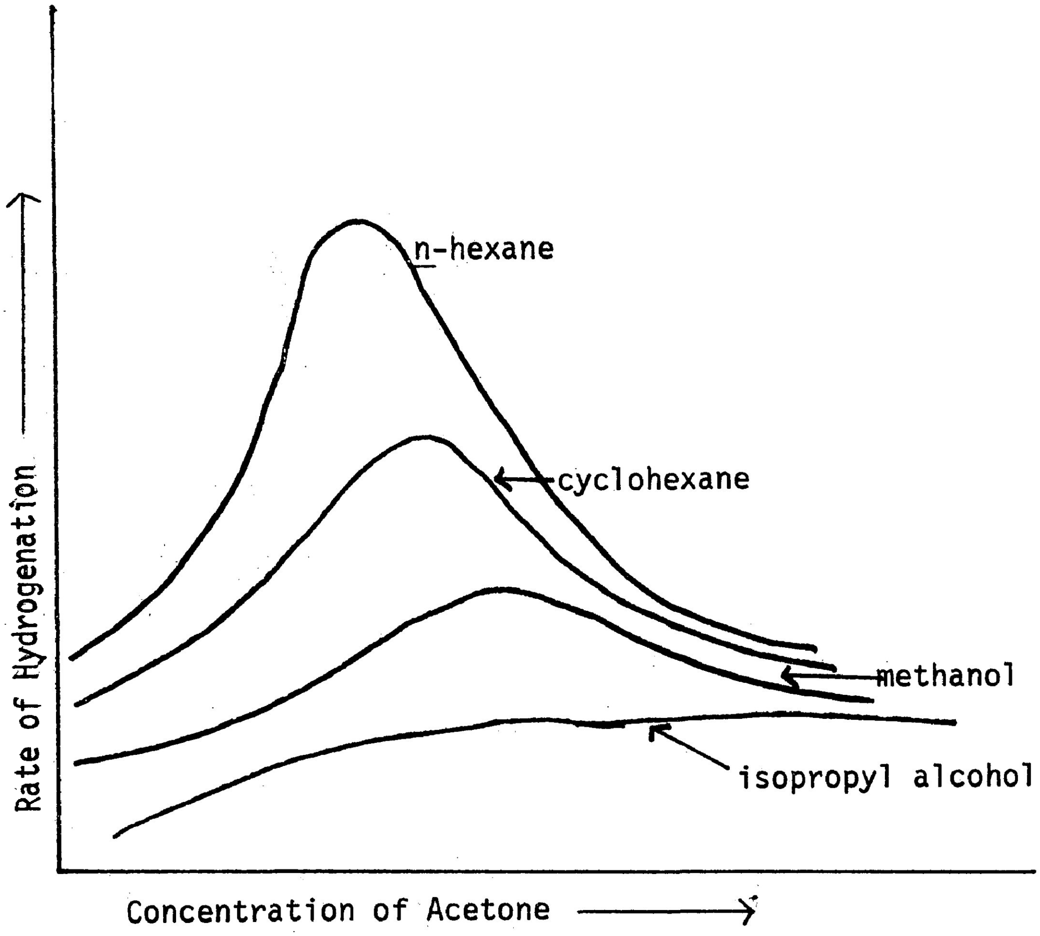
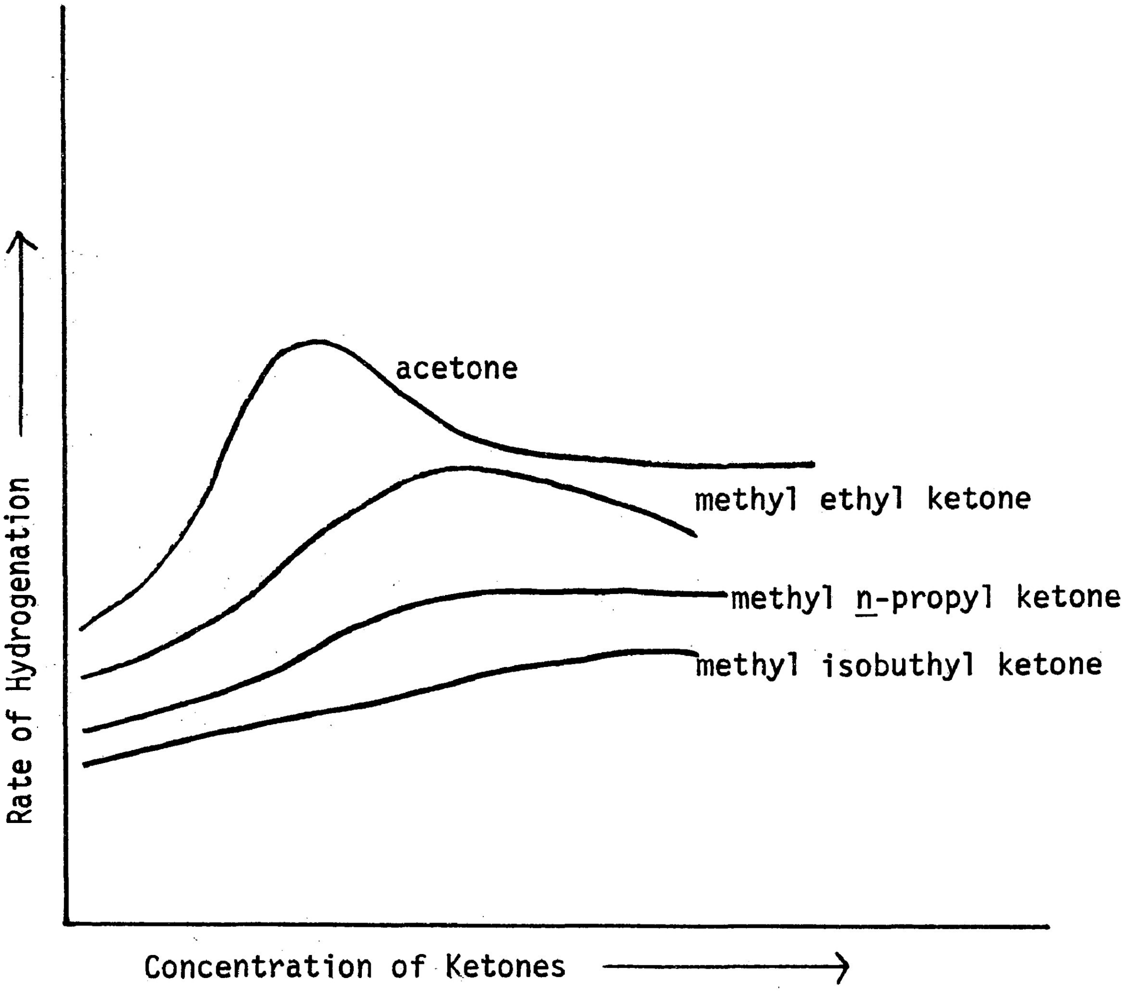


Figure 1.2 Hydrogenation of Various Ketones Over P-2 Nickel Boride in Cyclohexane at 30°C



used. This difference is associated with the relative strength of the catalyst-poison bond formed, and, therefore, the relative lifetime of the adsorbed "poison". If there is a low rate of desorption, there will be an accumulation of the toxic species even if present in small amounts, and, therefore, the reaction will be poisoned. The formation of bonds is dependent on the electronic configuration of the poison. Most poisoning studies have been carried out on Group VIII catalysts (71).

Catalyst poisons can be divided into three broad classes (70):

a) molecules containing elements of groups Vb and/or VIb, *i.e.* N, P, As, Sb, O, S, Te, Se, containing nonbonding electron pairs which can be donated to the vacant or partially vacant *d* orbitals of the metal,

b) compounds which contain toxic metallic ions which have *d* electrons that can be involved in bonding, and,

c) molecules containing multiple bonds (*e.g.* CO) where electrons can pass into metal orbitals to form a bond.

Of interest to this study are poisons which fall into group (a), and in particular those containing sulphur. Such compounds are most frequently encountered in industrial hydrogenations. Toxicity (71) depends on the presence, in the outer valency orbitals of the sulphur atom, free electron pairs which apparently take part in and are necessary for the bond by which the poison is strongly adsorbed on the catalyst surface. If these valency electrons are already involved in stable bonding to other elements, the sulphur compound loses its toxicity and is said to be shielded. Examples of sulphur toxic and non-toxic compounds are listed below.

Toxic (poisons)

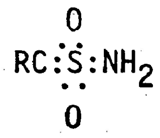
$RC:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:CR$

sulphide

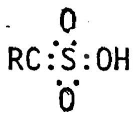
$RC:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:H$

thiol

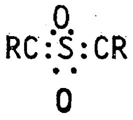
Non-toxic (shielded)


$RC:\overset{O}{\underset{O}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}}}:NH_2$

sulphonamide

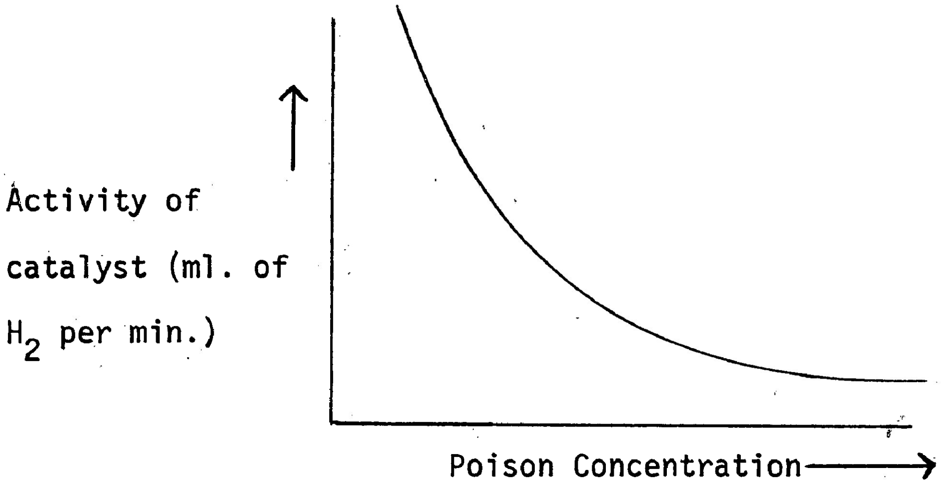

$RC:\overset{O}{\underset{O}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}}}:OH$

sulphonic acid


$RC:\overset{O}{\underset{O}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}}}:CR$

sulphone

Catalytic poisoning curves (70) have been found to have the following form.



This is called an "effective" poisoning curve since the concentration of poison is represented by the amount of poison introduced. The "true" poisoning curve would involve the actual concentration of poison adsorbed on the catalyst, and would have a similar form. It has been found that activity falls approximately linearly with poison content. This continues until a stage is reached at which the greater or at least a substantial part of the activity has been suppressed. There is then an inflection point after which the activity falls less steeply with further increase in poison content. The rate of hydrogen adsorption follows a similar decrease with increased poison concentration.

The above curve can be represented by the following equation proposed by E. Maxted (70).

$$k_c = k_o\ (1 - \alpha' C_i) \qquad \{8\}$$

where k_c is the activity in the presence of a poison of certain concentration equal to C_i, k_o is the activity of the unpoisoned catalyst, and α' is the adsorption coefficient of the poison. This coefficient reflects the effect of each unit of poison and is used to compare relative toxicities of different poisons. The value of α' is represented by the slope of the main linear portion of the graph.

In the presence of a catalyst poison, the Yao and Emmett equation can be extended to include the effect of the poison (72). Thus,

$$\frac{-dC}{dt} = akW \left(\frac{\alpha C_s}{\alpha C_s + \beta C_r + \gamma C_i} \right) \qquad \{9\}$$

This equation can be reduced when the product does not intefere (i.e. when β is small) to give the relationship:

$$\frac{-dC}{dt} = akW\left(\frac{\alpha C_s}{\alpha C_s + \gamma C_i}\right) \tag{10}$$

where γ is the adsorption coefficient of the poison. Since the actual catalyst surface area is not known, the true values of the adsorption coefficients cannot be determined. To overcome this problem, Baltzly (72) proposed the following equation for the case where the catalyst is "half poisoned" - i.e. the rate of hydrogenation is half of that found in the absence of poison. Thus,

$$\frac{-\frac{dC}{dt}'}{-\frac{dC}{dt}} = \frac{k_p'}{k_o'} = 0.5 = \frac{\alpha C_s}{\alpha C_s + \gamma C_i} \tag{11}$$

where k_p' and k_o' are overall apparent reduction rates in the presence and absence of poison respectively. When proper data are available, the ratio of α and γ can be determined and compared for various catalyst-poison systems. If equations {8} and {11} are compared it can be seen that:

$$\frac{\alpha C_s}{\alpha C_s + \gamma C_i} = 1 - \alpha' C_i \tag{12}$$

$$\text{or} \quad \alpha' C_i = \frac{\gamma C_i}{\alpha C_s + \gamma C_i} \tag{13}$$

Both poison and substrate require a set of adjacent unoccupied surface sites for their accomodation. As the concentration of poison on the surface is increased, the number of sets of sufficiently large adjacent surface sites will decrease. This will give a nearly linear plot up to a certain degree of poisoning followed by a sharp curvature <u>or</u> the whole poisoning graph will be curved with the curvature being increased with an increased number of adjacent sites required by each molecule of poison or reactant. This means that in the initial part of the reaction, the activity is proportional to the poison concentration. However, after a time, the number of available sites for the poison is less, and therefore, an increase in poison concentration no longer has the same effect on the reaction rate as there is no more room for the poison to be adsorbed.

The toxic effect of a poison depends on:

a) the size or individual surface coverage factor which controls the number of surface sites of the catalyst obstructively occupied or influenced by each molecule or atom of poison in an adsorbed state, and,

b) the average length of stay of the adsorbed molecule on the surface. The adsorbed lifetime is connected with the partition of the poison between the adsorbed state and the free liquid or gas phase. A plot of concentration of poison adsorbed versus concentration of poison in the system produces the adsorption isotherm which is usually linear.

E. Maxted (70,71,73-79) has done many studies of catalyst poisoning since 1930, and the results of these and others are summarized below.

a) At room temperature, poisoning of catalysts is reversible and under the proper conditions, the poison can be removed - i.e. detoxification occurs (70,71,80). At higher temperatures, however, rearrangement of the adsorbed complex may lead to irreversible poisoning due to formation of a metal sulphide.

b) The toxicity of a sulphur compound per gram of sulphur increases with its molecular size. The molecule is thought of as being anchored by the adsorbed sulphur atom, and the normally non-toxic part of the molecule also acts toxically due to its coverage of the surface. Relative increasing toxicities of several sulphur compounds on nickel are hydrogen sulphide (1.0), carbon disulphide (2.4), thiophene (4.5), and cysteine (5.4).

c) For alkyl thiols and sulphides, toxicity increases with chain length. The rate of increase in toxicity with each additional ($-CH_2$) unit decreases, however, as the chain gets longer. Sulphides which contain two chains are more toxic than the corresponding thiols which only have one chain.

d) For a single sulphur anchor, the chain is free to move, and, therefore, a circle of radius equivalent to the chain length is inhibited. If anchored by sulphur atoms at each end, the area of inhibition is reduced due to restriction of mobility of the chain - e.g. propane-dithiol is considerably less toxic than propanethiol. The presence of an unsaturated bond in the chain apparently does not affect the toxicity since allyl sulfide and n-propyl sulphide have the same toxicity. Branched chain compounds are generally less toxic than a straight chained compound of the same length - e.g. isopropyl sulphide is less toxic than n-propyl sulphide.

e) Toxicity studies of ring compounds show that thiophene is less toxic than β-phenylethylthiol, which in turn is less toxic than thiophenol. The latter has an exocyclic sulphur atom, and a 6-membered ring and has greater coverage than the 5-membered thiophene ring. For β-phenylethylthiol, there is greater removal of the ring from the catalyst surface and less favorable circumstances for adsorption and the molecule is less toxic than thiophenol.

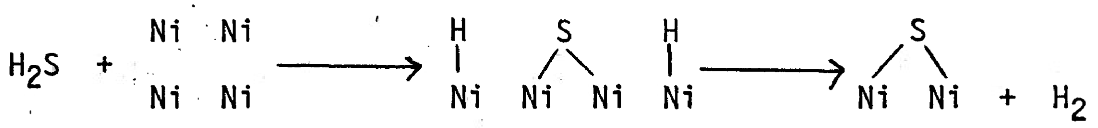
f) The sensitivity of a catalyst is dependent on its degree of subdivision. A coarse grained, relatively inactive catalyst is far more sensitive to poisoning than is a finely divided, highly active catalyst.

g) Maxted and Josephs (74) studied the heats of adsorption of diethyl sulphide and thiophene on platinum and found them to be 65-70 and 33 kcal/mole respectively. The difference in the heats of adsorption was, therefore, equal to approximately 35 kcal /mole. It appears that thiophene loses its resonance structure on adsorption. Similar evidence has been found for the adsorption of benzene.

The adsorption of sulphur compounds on metal catalysts has been studied (81-91) since the early 1960's using magnetic experiments, infra-red spectra of the adsorbed state during the reaction, and deuterium exchange experiments.

The adsorption of hydrogen sulphide on supported nickel catalysts has been carried out in the temperature range from -80° to 645°C. It has generally been agreed that hydrogen sulphide is dissociatively chemisorbed - i.e. the H-S bond breaks on adsorption. This has been supported by the fact than upon evacuation, only hydrogen is removed and also infra-red studies show no H-S stretching frequency for the adsorbed state. At high surface coverage only approximately two-thirds of the total hydrogen brought to the surface in the form of hydrogen sulphide is desorbed (85). Therefore, there must be two types of hydrogen present.

I. Den Besten and P. Selwood (82) proposed that hydrogen sulphide is adsorbed via four chemisorptive bonds.

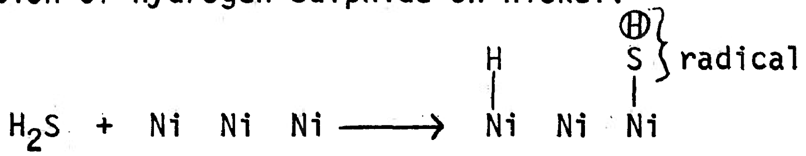


at low coverage at high coverage

If coverage is low, the dissociated hydrogen can be adsorbed on bare sites, but if coverage is high the desorbed hydrogen is forced out into the gas phase as H_2, or is held below the sulphide layer in which case it would not be desorbed on evacuation. However, hydrogen has a limited solubility in nickel at 25°C and, therefore, it would seem unlikely that such a large volume of hydrogen, as that unaccounted for, could be dissolved in the nickel.

Saleh and coworkers (87,91) proposed a different scheme for adsorption of hydrogen sulphide on nickel.

Thus,



$$H_2S + Ni\ \ Ni\ \ Ni \longrightarrow \overset{H}{\overset{|}{Ni}}\ \ Ni\ \ \overset{\overset{\textcircled{H}}{S}}{\overset{|}{Ni}}$$

2nd site blocked by size of S

The atom Ⓗ which is close to the sulphur atom undergoes slow exchange with deuterium - <u>i.e.</u> it is held to the sulphur. The other hydrogen atom which is free from the influence of the sulphur undergoes rapid exchange with deuterium and accounts for hydrogen removed on evacuation.

Others (81,83,84,85,86,88,89,90) provide evidence which supports both ideas, and, therefore, the mechanism of hydrogen sulphide adsorption is still not known for certain. It is known, however, that after the catalyst surface layer is completely covered by dissociated hydrogen sulphide, the formation of bulk sulphide follows.

$$H_2S_{(g)} + Ni_{(s)} \longrightarrow H_{2(g)} + NiS_{(s)} \qquad \{14\}$$

The rate determining step is thought to be diffusion of the Ni^{2+} ion (0.7 $\overset{o}{A}$) through the sulphide layer as it has a smaller radius than the S^{2-} ion (1.75 $\overset{o}{A}$).

Sulphur uptake depends on hydrogen and hydrogen sulphide pressure. The ratio required (84) for bulk sulphide formation is 100 to 1000 times greater than that normally required for poisoning. Hydrogen sulphide must be chemisorbed first. It has also been found that sulphur has a much greater affinity for nickel than does hydrogen.

Further studies (84,86) have been made of the adsorption of other sulphur compounds on nickel surfaces. Carbon disulphide, like hydrogen sulphide, shows no infra-red bands in the adsorbed state and must be dissociatively adsorbed. The infra-red spectra of ethyl mercaptan (C_2H_5SH) shows that the C-C-S skeleton remains intact which means that sulphur must be bound to the surface with resulting cleavage of the S-H bond. Methyl mercaptan (CH_3SH) shows no characteristic infra-red bands in the adsorbed state for the S-H stretch.

In 1966, Leftin and Stern (92) reported that the gas-phase hydrogenation of *cis* 2-butene over a nickel catalyst supported on silica at 105°C is poisoned in fifteen minutes upon addition of a small amount of hydrogen sulphide. The electronic spectrum of the poisoned solid catalyst shows an intense band at 4260 Å and a weak band at 5700 Å, the latter being characteristic of the *d-d* band normally observed in square planar bis(dithioketone) complexes of Ni(II). Such compounds have previously been prepared by reaction of a "suitably substituted acetylenically unsaturated hydrocarbon with metal sulphides under moderate conditions" (92).

This was the first evidence of the presence of a coordination complex in sulphur poisoning of a nickel catalyst.

The only article (93) which discussed poisoning of a nickel boride catalyst appeared in 1973. It reported on the liquid phase (ethanolic) hydrogenation of styrene at 30°C in the presence of phosphorus poisons. The P-2 type nickel catalyst with a BET surface area of 21.8 m^2/g, is more resistant to poisoning than a nickel metal catalyst whose surface area was 13.8 m^2/g. For both catalysts, the relative toxicities of several phosphorus compounds was found to be in the decreasing order of: $PPhCl_2$, $CH_2(SH)CH(SH)CH_2OH$, $P(OCH_3)_3$, and $P(OPh)_3$. The high resistance by nickel boride towards poisoning was attributed to the bonding electrons of the boron atom occupying the vacant d orbitals of the nickel atom, and thus making it difficult for the lone pairs of the inhibitor to coordinate with, and so poison, the nickel boride catalyst.

1.7 Aim of the Present Work

In view of the potential value of the metal borides earlier discussed, a general investigation of alkene hydrogenations catalyzed by these species was undertaken with the following objectives.

a) To compare more thoroughly the activities of the apparently several different "types" of nickel borides, discussed in the earlier part of this review, for a single liquid-phase hydrogenation under identical reaction conditions. This is effectively a study of the effect of the method of catalyst preparation upon the catalyst activity. Particular attention is paid to the recently reported P-3 type catalysts which have received little attention in connection with solution phase hydrogenations.

b) To compare the activities of P-3 nickel boride, cobalt boride, and Raney nickel for several hydrogenation reactions.

c) To study the kinetics of liquid-phase alkene hydrogenations over P-3 nickel and cobalt borides in order to suggest a reaction mechanism for the process, and,

d) quantitatively determine and compare the resistance of nickel and cobalt boride catalysts, and Raney nickel towards poisoning by gaseous and liquid-phase sulphur-compounds. Again, it was hoped that a poisoning mechanism might be established.

CHAPTER 2

EXPERIMENTAL

The experimental work described in this section was carried out by the author between July 1975 and August 1976 in the Department of Chemistry at Lakehead University, Thunder Bay, Ontario, Canada.

2.1 Reagents

Absolute ethanol, USP reagent grade, was obtained from Consolidated Alcohol Ltd. n-Heptane, I.P. grade, supplied by the British Drug Houses Ltd. was degassed with nitrogen and, like all other solvents and liquid reagents mentioned later, was stored under oxygen-free nitrogen in a glove box. Distilled water was used where aqueous solvents were required. Reagent grade ether, from the McArthur Chemical Co. Ltd. was degassed with nitrogen. 1-Hexene, 1-octene, 1-decene, and 1-hexadecene (99%) obtained from the Humphrey Chemical Co. were purified before use by stirring for approximately twelve hours with iron(II) chloride and then the supernatant liquid was heated under reflux over calcium hydride for two to three hours. The purified alkene was distilled and degassed with dry, oxygen-free nitrogen for fifteen to twenty minutes. Benzene (ACS grade) and acetone (ACS grade), obtained from the McArthur Chemical Co. Ltd., cyclohexene from the Aldrich Chemical Co. Inc., and acetonitrile from the Fisher Scientific Co. were purified by heating under reflux over calcium hydride for two to three hours and were then distilled and degassed with oxygen-free nitrogen. Allyl alcohol from the Fisher Scientific Co. was degassed for approximately fifteen minutes with oxygen-free nitrogen. Cis-trans 2-octene (98%) and trans 4-octene (99%) were obtained from the Aldrich Chemical Co. Inc. and were used without further purification. Silver nitrate (99.9%) was obtained from the British Drug Houses Ltd.

The gas-liquid chromatography standards 1-nonene, n-nonane, and n-octane (98%) were obtained from the Polyscience Corp. n-Butanethiol was obtained from the Aldrich Chemical Co. Inc.

Nickel "Catgen" pellets ($NiCl_2.4NaBH_4$), cobalt "Catgen" pellets ($CoCl_2.4NaBH_4$), and sodium borohydride were supplied free of charge by the Ventron Corporation and this donation is gratefully acknowledged. Reagent grade nickel(II) chloride hexahydrate, and nickel(II) acetate hydrate were supplied by the British Drug Houses Ltd. while high activity Raney nickel was purchased from Strem Chemicals Inc.

Nitrogen, certified grade, hydrogen sulphide, chemically pure grade, and hydrogen, UHP containing less than two ppm. oxygen, were obtained from Canadian Liquid Air. A deoxo gas purifier, capable of removing oxygen to less than one ppm., obtained from Canadian Liquid Air, was attached to the hydrogen cylinder.

2.2 Instrumental Techniques

The mass spectra of several liquid samples were recorded on an Hitachi-Perkin-Elmer RMU-7 double focussing mass spectrometer using a liquid inlet system.

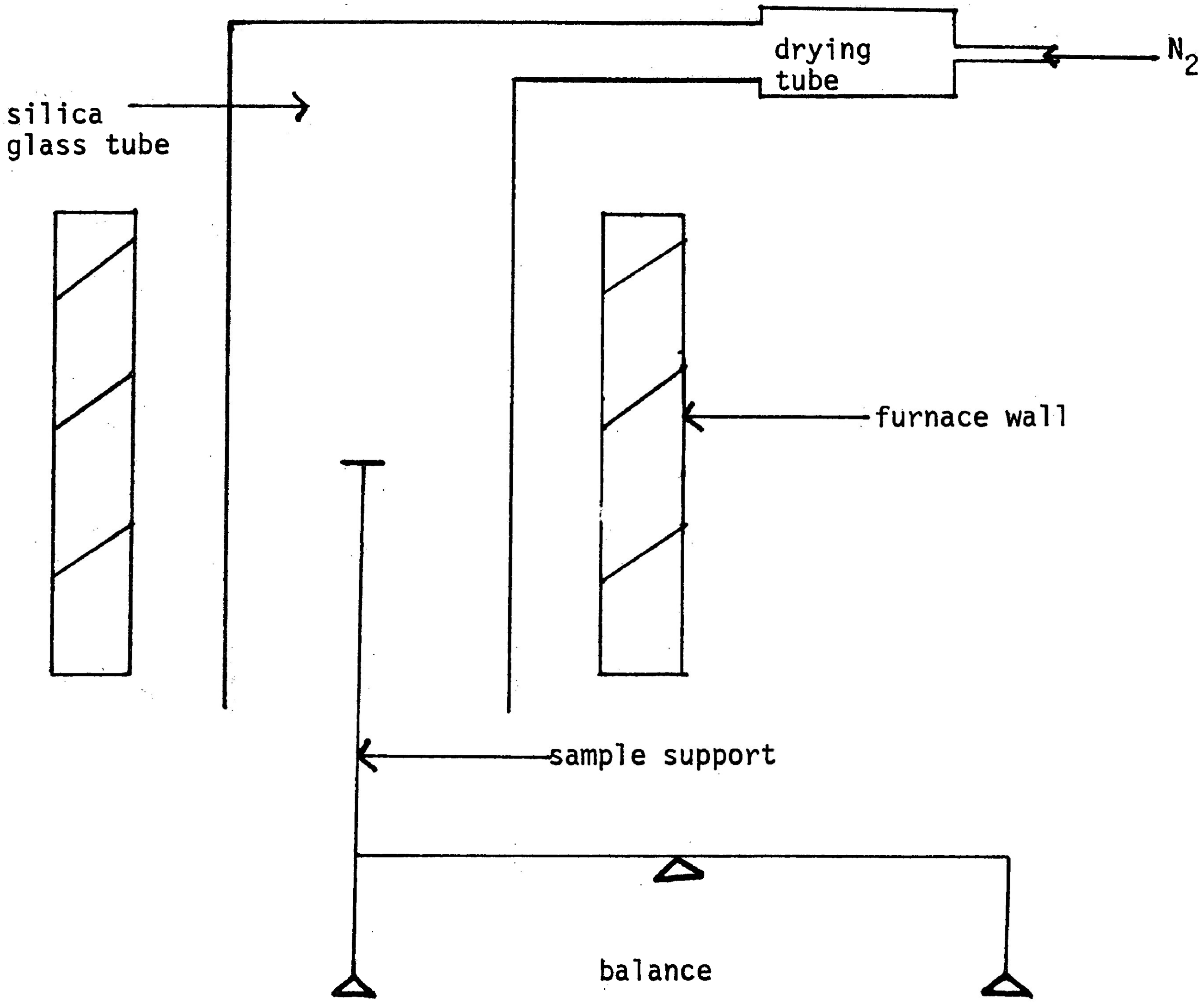
Gas-liquid chromatograms were recorded on a Hewlett-Packard model no. 5750 Research Gas Chromatograph equipped with a thermal conductivity detector. The analytical columns were six feet long stainless steel and were packed with _n_-octane/Porasil C. The carrier gas was helium, which was maintained at a flow rate of 30 ml/min. through the columns. Two microlitre samples were injected using a Hamilton syringe. The analytical columns were temperature programmed from 40° to 135°C at a rate of 2° per minute.

The glove box used was manufactured by Marine and Industrial Plastics Ltd. (model no. 3108). Dry, oxygen-free nitrogen flowed continuously through the box at a rate of approximately 4 ml/min.

A Stanton Redcroft Thermobalance model HT-SF, was used in the dynamic thermogravimetric studies. The temperature was raised from ambient to 1000°C at a heating rate of 7°C/min with a dry nitrogen flow of 230 ml/min (NTP). Buoyancy corrections were determined using dead-burned alumina. A schematic representation of the system is shown in figure 2.1.

In the hydrogen sulphide poisoning experiments, the free sulphide ion concentration in the catalyst-free ethanol solution. was measured indirectly using an Orion Research Ionalyzer, specific ion meter model 94-16A. The instrument was calibrated using a standard 0.100 M silver nitrate solution. Method: The sulphide ion solution was added to a silver ion solution of premeasured concentration with the subsequent formation of the black precipitate silver sulphide. The remaining free silver ion was then measured and the difference between initial and final silver ion concentrations

Figure 2.1. Schematic of Thermobalance Assembly



was directly related to the initial free sulphide ion concentration in the sample.

2.3 Surface Areas

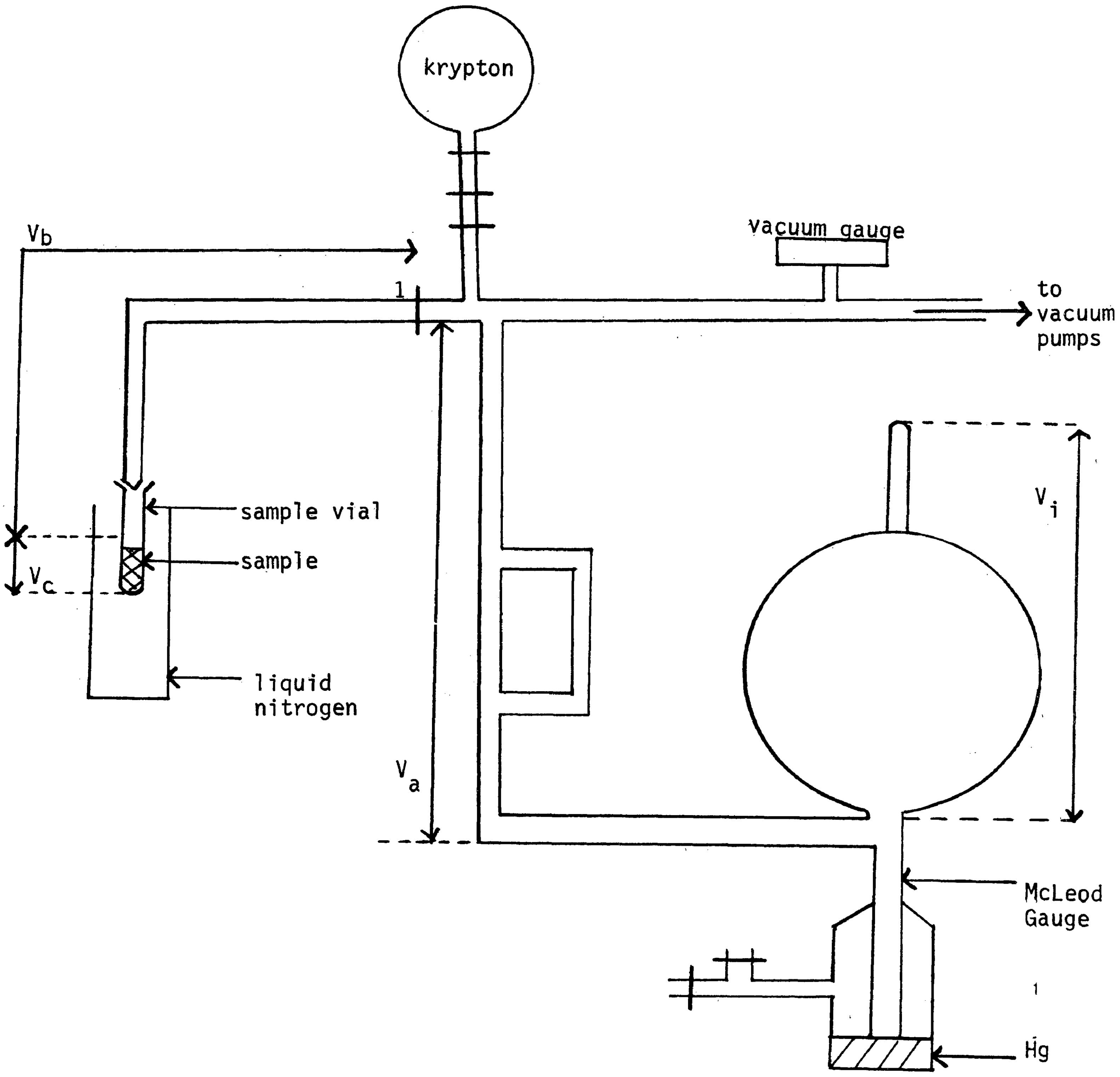
Surface areas were determined by the BET method. The surface area is directly proportional to the quantity of adsorbate that can be accomodated in a completely filled single layer of molecules on the surface of the solid. The number of molecules necessary to form this monolayer can be determined and if the area occupied by each molecule is known, the surface area of the material can be determined. The theory of the method was developed by Brunauer, Emmett, and Teller (BET) (94).

The following equation relating the monolayer volume (V_m) and the saturation pressure of the adsorbate (P_o) to the total volume of gas adsorbed (V_g) at a measured pressure (P) was derived.

$$\frac{P/P_o}{V_g\,(1 - P/P_o)} = \frac{1}{V_m C} + \frac{(C - 1)\,P}{V_m C P} \qquad \{15\}$$

$\underline{C}$ is a constant dependent on the heats of adsorption and liquefaction of the gas. A plot of $\frac{P/P_o}{V_g\,(1 - P/P_o)}$ against P/P_o gives a straight line of slope $\frac{(C - 1)}{V_m C}$ and intercept $1/V_m C$ valid for relative pressures, P/P_o, between 0.05 and 0.35. The apparatus used is shown in figure 2.2 and employs a diffusion pump to bring pressures down to 10^{-4} Torr. The area occupied by one molecule

Figure 2.2. BET Apparatus



of adsorbate, in this case krypton, is taken as 19.5 $\AA^2$.

Each solid sample was evacuated at 10^{-4} Torr for two to three hours before admission of krypton. Krypton was first admitted to sections A and I. The pressure in this space was then measured on the McLeod gauge, range 10^{-2} to 2 mm , and tap (1) was then opened to admit the gas to the sample container which was then immersed in liquid nitrogen. After equilibration was complete (thirty minutes for each addition), the pressure was again measured on the McLeod gauge. The volumes of the dead spaces were found to be:

V_a = 13.6 ml
V_b = 1.65 ml
Vc = 0.7 ml
(volume of sample tube immersed in liquid nitrogen)
V_i = 47.37 ml

The volume of krypton could then be calculated. A typical BET plot found for sample P3A is shown in figure 2.3.

2.4 Hydrogenation Apparatus

The apparatus schematic is shown in figure 2.4. The glass apparatus had a total volume of 310 ml (including the volume of the reaction flask, but not including the volume of liquid phase) when storage bulbs A, B, and C (of volumes 80, 286, and 128 ml respectively) were closed and the system was under reduced pressure (0.01 cm). Note: With a total pressure of 76 cm., this initial gas volume was

Figure 2.3. BET Plot for P-3A Ni

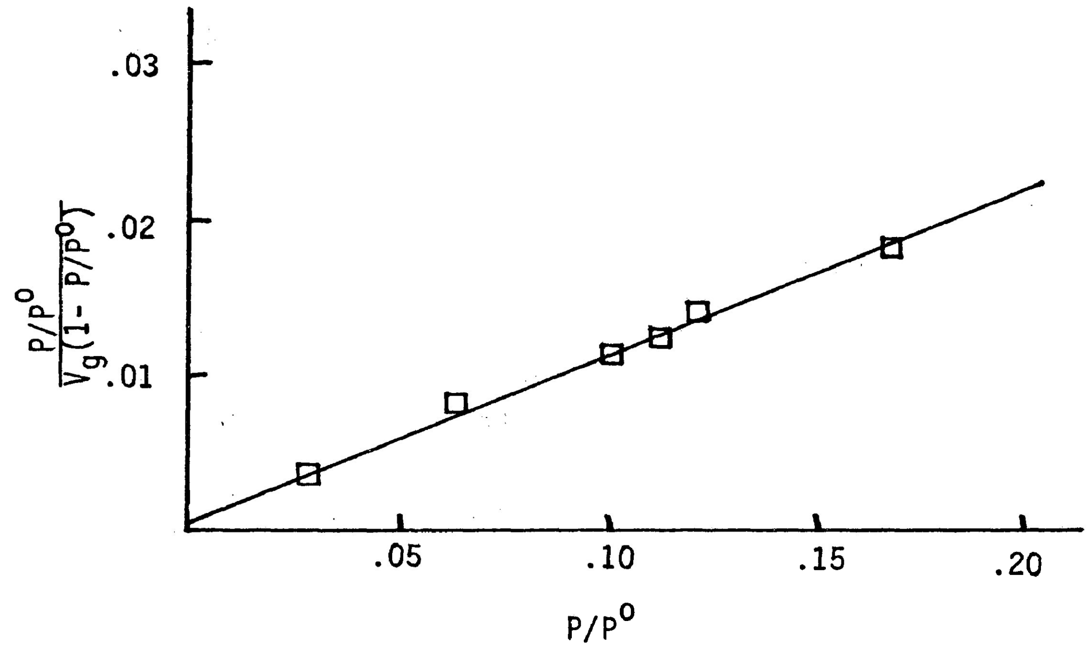
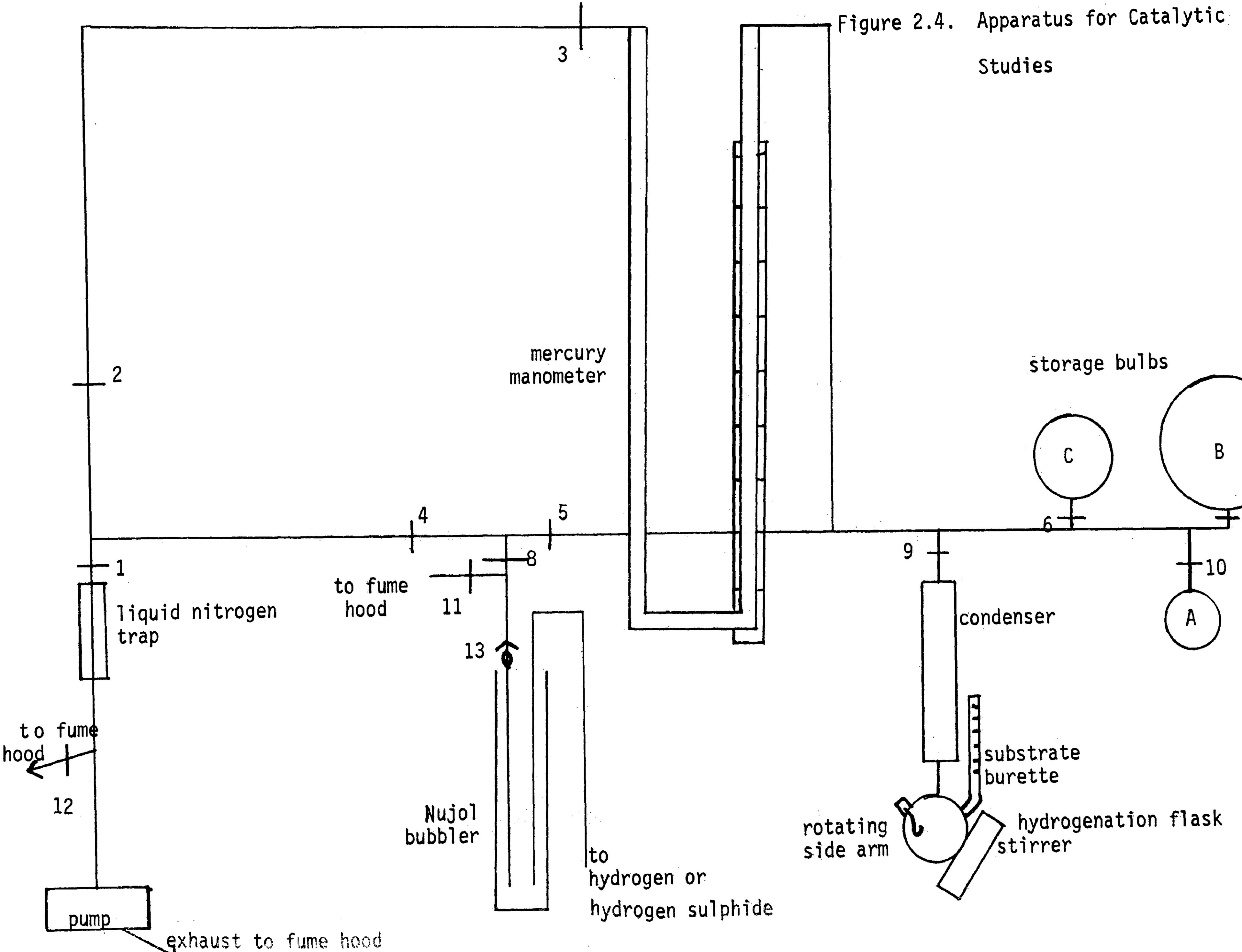


Figure 2.4. Apparatus for Catalytic Studies



329 ml. Unless otherwise noted the total liquid volume was twenty-five ml..

The reaction vessel was a 3-necked, approximately 100 ml., round-bottom flask. One side neck was fitted with a burette (approximately 8 ml), for substrate addition, and the other side neck was fitted with a rotating side arm from which a teflon bucket, containing the catalyst, could be hung and later dropped into the oxygen-free reaction solution. The side of the flask was flattened to enable more efficient stirring at the gas-liquid interface using a one inch magnetic stirrer bar during hydrogen uptake measurements. During the preparation of the catalyst and/or the degassing of the solvent, the mixture was stirred from the bottom of the flask. The flow rates of hydrogen and hydrogen sulphide were followed by passing the gas streams through separate Nujol bubblers which were alternately attached to the vacuum line at point (13) when required. The height of the mercury column in the manometer was measured with a metre rule placed behind the manometer. The reaction temperature was always $21^{\circ}C \pm 3$.

2.5 Catalyst Preparation

2.5.1 Catalyst Preparation and Use for Hydrogenation Rate Measurements

P-3 Ni and P-3 Co

Nickel (cobalt) "Catgen" pellets ($NiCl_2.4NaBH_4$) ($CoCl_2.4NaBH_4$) were ground to a powder. An appropriate amount (usually approximately

0.14 g , 5 X 10^{-4} moles of metal) was weighed in a teflon bucket inside a weighing bottle to prevent water absorption from the air. The bucket was attached to the hydrogenation apparatus and dropped into the oxygen-free (see later discussion) ethanol under a hydrogen atmosphere. Immediate reaction occurred with the production of the black colloidal P-3 Ni (P-3 Co) and subsequent hydrolysis of the excess of sodium borohydride accompanied by evolution of hydrogen. The mixture was stirred for approximately one hour or until hydrogen evolution was complete. The P-3 Ni (P-3 Co) catalyst was prepared freshly *in situ* before each reaction.

Hawthorne's Catalyst (P-3' Ni)

Nickel "Catgen" powder ($NiCl_2.4NaBH_4$) (approximately 0.14 g , 5 X 10^{-4} moles Ni) was added to oxygen-free ethanol (21.4 ml) in the hydrogenation reaction flask in the glove box under a nitrogen atmosphere. The mixture was stirred for approximately one hour until hydrogen evolution had ceased. The mixture was frozen for atmospheric protection and transferred to the hydrogenation apparatus.

P-3" Ni

In one case, the catalyst prepared according to Hawthorne's method was filtered, washed three times with water, and then three times with ethanol, and was finally dried under reduced pressure. In the glove box, the dried catalyst (designated P-3") (0.0261 g , approximately 4 X 10^{-4} moles Ni) was placed in oxygen-free ethanol in the reaction flask, the mixture frozen and the whole transferred to the hydrogenation apparatus.

P-3A Ni

A known amount of powdered nickel "Catgen" ($NiCl_2.4NaBH_4$) (approximately 2.0 g) was added to oxygen-free ethanol (approximately 50 ml) in the glove box under nitrogen and was stirred for approximately one and a half hours. The product (designated P-3') was filtered, but not washed, dried under reduced pressure for approximately six hours, and was stored in the glove box. The dried product (designated P-3A) was weighed and a portion (containing 4-5 X 10^{-4} moles Ni) was added, in the glove box, to oxygen-free ethanol in the reaction flask, the mixture frozen, and the whole was transferred to the hydrogenation apparatus. (In certain noted cases, the P-3A was added to *n*-heptane, or *n*-heptane-ethanol mixtures.) Batches of P3A were not used for more than approximately three or four days.

Raney Nickel

A portion of the water-slurry of high activity Raney nickel was filtered in the glove box under nitrogen, washed twice with ethanol, dried under reduced pressure for approximately twelve hours, and stored in the glove box. A portion of the dried Raney nickel (0.03 g , approximately 5 X 10^{-4} moles Ni) was weighed without exposure to oxygen and was then added to oxygen-free ethanol in the reaction flask. The stoppered flask was transferred to the hydrogenation apparatus. Note: Raney nickel is air stable, when under a solvent.

P-1 Ni

This catalyst was prepared by a method essentially the same as that in the literature (11). In the glove box, under nitrogen, 25 ml of oxygen-free water was added to $NiCl_2.6H_2O$ (0.1001 g , approximately 4.2 X 10^{-4} moles Ni) or $Ni(C_2H_3O_2).4H_2O$ (0.1048 g , approximately 4.2 X 10^{-4} moles Ni) in the hydrogenation reaction flask and the mixture was stirred. A bucket containing $NaBH_4$ (0.0477 g , approximately 12.6 X 10^{-4} moles) was dropped into the stirred solution. The mixture was stirred until hydrogen evolution ceased and the supernatant liquid was clear (approximately one hour). The water was removed by decantation and the black granular precipitate (P-1 Ni) was washed twice with oxygen-free ethanol (approximately twenty-five ml portions). Oxygen-free ethanol (21.4 ml) was added to the P-1 Ni and the mixture was frozen (for protection from air) and the whole was transferred to the hydrogenation apparatus.

P-2 Ni

Again, this catalyst was prepared by a method very similar to that described in the literature (17). $NiCl_2.6H_2O$ (0.1001 g , approximately 4.2 X 10^{-4} moles Ni) or $Ni(C_2H_3O_2).4H_2O$ (0.1048 g , approximately 4.2 X 10^{-4} moles Ni) was dissolved in ethanol (21.4 ml) in the hydrogenation reaction flask. $NaBH_4$ (0.0159 g, approximately 4.2 X 10^{-4} moles) was placed in the teflon bucket and hung in the reaction flask. The ethanol-nickel salt solution was frozen, vacuum pumped, and flushed with hydrogen three times. The mixture was then warmed to room temperature and stirred under hydrogen for approximately one minute. This freezing, pumping and flushing procedure was repeated twice more to ensure hydrogen-oxygen exchange in the solvent. The bucket was then dropped into the oxygen-free solution and the mixture was stirred for approximately one hour until hydrogen evolution ceased. The resulting black colloidal solid was P-2 Ni.

Typical "Normal" Procedure for Carrying Out the Hydrogenation Reaction

Prior to each hydrogenation reaction, the entire system (figure 2.4) up to stopcock (9), including the storage bulbs when used, was pumped under reduced pressure for approximately twenty minutes. Stopcocks (2) and (3) were then closed for the duration of the experiment. The hydrogen line was flushed *via* stopcock (11) for approximately twenty minutes before use.

The oxygen-free substrate was placed in the burette in the glove box under nitrogen. The rotating side arm (in certain cases holding the teflon bucket) and the burette were attached to the reaction flask which contained the solvent (not yet degassed) *or* the frozen solvent-catalyst mixture (oxygen-free) in cases where catalyst preparation was carried out outside the hydrogenation apparatus. The reaction flask was then attached to the condenser and stopcock (9) was opened briefly to remove the majority of the air present by pumping. The solvent was then frozen, if necessary, using liquid nitrogen, and (9) was reopened to pump further. Stopcock (4) was then closed and hydrogen was allowed into the system *via* (8) to a total pressure of approximately sixty cm. Stopcock (8) was then closed and the system was again pumped to low pressure by opening (4). Flushing with hydrogen was repeated twice more. In the presence of hydrogen (approximately sixty cm) the reaction mixture was warmed to room temperature using a water bath and the mixture was stirred for approximately one minute, (five minutes for the P-1 Ni, Raney nickel, P-3', P-3", and P-3A mixtures), to ensure hydrogen-oxygen exchange. For the cases where only solvent was present (i.e. before generation of P-3 Ni, P-3 Co, or P-2 Ni) this freezing, pumping and flushing procedure was repeated twice more. The catalyst was then generated according to the method outlined in section 2.5.1.

In order to add the substrate, the reaction vessel had to be pumped to low pressure (approximately five cm) and stirring was stopped. After addition of substrate, hydrogen was introduced into the apparatus to give a total pressure of approximately 76 cm and the timer and stirrer were started simultaneously. Measurements were made of total pressure readings (from manometer) at thirty second intervals for the first ten minutes of the reaction.

2.5.2 Preparation and Use of Catalysts for Surface Area Measurements

P-3 Ni was prepared according to Hawthorne's method as described in Section 2.5.1 and was dried under reduced pressure to give P-3A.

Raney nickel was prepared according to Section 2.5.1.

P-1 Ni was prepared according to section 2.5.1 and was washed four times with ethanol and then dried under reduced pressure.

P-2 Ni was prepared in the glove box, under nitrogen. A bucket containing $NaBH_4$ (0.318 g, approximately 8.4 X 10^{-4} moles) was added to a stirred solution of $NiCl_2.6H_2O$ (2.002 g, approximately 8.4 X 10^{-4} moles Ni) in oxygen-free ethanol (25 ml). The mixture was stirred for approximately one and a half hours and was then filtered, washed four times with ethanol, and dried under reduced pressure.

Note: In each case the catalyst was placed in the surface area sample vial, weighed without exposure to air, and transferred to the BET apparatus. Surface area measurements were carried out as previously described.

2.5.3 Catalyst Preparation for Thermogravimetric Analysis

2.5.3.1 "Unused" P-3 Ni

P-3 Ni was prepared according to the method outlined in section 2.5.1. The mixture was frozen and taken to the glove box where it was warmed, filtered under nitrogen and washed once with oxygen-free ether. The product (0.0540 g) was used for thermogravimetric analysis. A buoyancy blank of 0.0540 g dead-burned alumina was also done.

2.5.3.2 "Used" P-3 Ni

P-3 Ni was prepared according to the method outlined in section 2.5.1. Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) with a total measured hydrogen uptake of 0.02 moles (0.8 M) was allowed to occur. The reaction mixture was frozen and was taken to the glove box where it was warmed, filtered under nitrogen and washed once with oxygen-free ether. The residual catalyst (0.0314 g) was used for thermogravimetric anaylsis of used catalyst. A buoyancy blank of 0.0314 g dead-burned alumina was also done.

2.5.4 Catalyst Preparation and Use for Gas-Liquid Chromatographic Studies

P-3 Ni and P-3 Co were prepared according to the method outlined in section 2.5.1 and the typical hydrogenation procedure was followed unless otherwise noted in the results section. After a certain measured amount of hydrogen uptake (see results section), the reaction was stopped, and the reaction mixture was centrifuged in air, and the clear supernatant liquid was analyzed by gas-liquid chromatography.

Slight variations in the above procedure were used in several cases. For example, in one set of results (Table 3.22 in the results chapter) the usual amount of substrate was used, but the initial hydrogen gas volume was increased to approximately 1132 ml by opening the 286 ml storage bulb and by replacing the 128 ml storage bulb with a 518 ml bulb. Similarly, for the results displayed in Table 3.23 (next chapter), this larger initial gas volume was also used and, in addition, the substrate concentration was doubled to 1.0 M.

Furthermore, for the results summarized in Table 3.25 (next chapter), the usual amount of substrate was used and the initial gas volume was the usual 330 ml (at a total pressure of 80 cm). However, in this case, n-butanethiol was added with the substrate to give a final sulphur concentration in the solution of 25 mg/l.

2.6 Preparation of n-Butanethiol Standard

n-Butanethiol (0.90 ml) was made up to 200 ml with ethanol in a volumetric flask. This gave a 1,335 mg/l of sulphur stock solution. The n-butanethiol was added to the reaction mixture in one of two ways outlined in the following subsections.

2.6.1 n-Butanethiol Added With Solvent

An appropriate amount of the stock n-butanethiol was added, in the fume-hood, to the ethanol in the reaction flask which was then stoppered and transferred to the hydrogenation apparatus. (The total final liquid volume including solvent, n-butanethiol, and substrate was, as usual, 25 ml. The total apparatus volume under reduced pressure was 310 ml). The catalysts were prepared according to the methods outlined in section 2.5.1. However, n-butanethiol was present during the catalyst generation.

2.6.2 n-Butanethiol Added With Substrate

The alternate, more commonly used, method was addition of the n-butanethiol with the substrate after the catalyst was prepared. The stock solution was degassed by freezing and pumping, and was then taken into the glove box. Solutions of substrate and n-butanethiol were prepared and placed in the burette. The procedure then followed was identical to that described for the typical hydrogenation reaction.

2.7 Typical Hydrogenation Reaction in the Presence of Hydrogen Sulphide

In all cases the catalysts were prepared according to the methods described in Section 2.5.1.

2.7.1 Typical Run

The apparatus, including the storage bulbs, was evacuated up to and including the condenser which was sealed by placing a round-bottom flask on the lower end. The hydrogen sulphide line, Figure 2.4, was flushed with hydrogen sulphide <u>via</u> stopcock (11) for approximately twenty minutes. With stopcocks (2), (3), (4), and (9) closed, (8) was opened to allow hydrogen sulphide into the system to the desired total pressure. The storage bulb(s) was then closed to trap the hydrogen sulphide, stopcock (8) was closed, stopcock (9) was opened and the system was pumped for approximately half an hour <u>via</u> (4) to ensure removal of any traces of hydrogen sulphide in the rest of the system. The hydrogen sulphide line was removed, the hydrogen line attached and the apparatus flushed with hydrogen <u>via</u> (11) for approximately half an hour. The apparatus up to and including the condenser was then filled with hydrogen and then pumped (this process was repeated several times) to ensure removal of residual hydrogen sulphide. The typical hydrogenation procedure was then followed up to and including the addition of the substrate. Then, in the presence of approximately 60 cm total pressure of hydrogen, the hydrogen sulphide storage bulb(s) was opened. More hydrogen was introduced to bring the total pressure of the system to approximately 76 cm. The reaction mixture was then stirred at the gas-liquid interface and pressure readings taken every thirty seconds for ten minutes.

The total gas volumes when the system is under reduced pressure are given in Table 2.1.

TABLE 2.1

Storage bulb open	Total volume of system under reduced pressure (0.01 cm) (ml)
none	310
A (80 ml)	390
A (80 ml), B (286 ml)	676
A (80 ml), B (286 ml), C (128 ml)	804

2.7.2 Variation to Typical Run

A slight variation to this usual procedure was made as noted in Tables 3.6 and 3.7 (next chapter). Before addition of the substrate, and at low hydrogen pressure (approximately 10 cm), the hydrogen sulphide storage bulb(s) was opened and the reaction mixture (containing the catalyst) was stirred in the presence of the hydrogen sulphide for approximately fifteen minutes. Stirring was then stopped, the substrate added and then hydrogen was let in to bring the total gas pressure to approximately 76 cm. Stirring and pressure readings were then started simultaneously.

2.7.3 Variation to Typical Run

Yet another variation in the usual procedure was made in one case (noted in Table 3.6, next chapter). The hydrogen sulphide was present in the system prior to generation of the catalyst P-3 Ni. (The gas phase in this case contained 5 mg/l hydrogen sulphide). The P-3 Ni was then generated in the presence of the hydrogen sulphide (approximately one hour). The system had to be evacuated, thus removing most of the hydrogen sulphide, in order to add the substrate. The subsequent procedure was the same as that discussed for the typical hydrogenation reaction.

2.8 Calculation of the Rate of Hydrogen Uptake

During the hydrogenation, the manometer reading (x), was recorded at thirty second intervals for ten minutes. The actual pressure (P_{total}) is equal to 95.6 - 2x (cm) where the total length of the mercury column is 95.6 cm. (The pressure of hydrogen is the total pressure minus the vapor pressure of the solvent and substrate (in this case approximately 3 cm)). Since the total gas pressure and the total gas volume at any particular time are known, the total number of moles of gas in the system (be it hydrogen or a combination of hydrogen and hydrogen sulphide in certain instances) can be determined. Using the ideal gas law,

$$PV = nRT$$

thus,

$$n = \frac{PV}{RT}$$

where P is the measured total pressure (atm), V is the measured total gas volume (ml), R is the ideal gas constant (82.05 ml atm/^{o}K mole), and T is the measured temperature (^{o}K). Since the initial number of moles of gas present is known, and the number of moles of gas present after a timed interval is known, it is possible to calculate, by difference, the number of moles of gas (i.e. hydrogen) consumed. This would, therefore, give the number of moles of hydrogen consumed in a particular time period by the usual 25 ml liquid reaction mixture volume. To calculate the number of moles of hydrogen consumed per litre of typical reaction mixture volume, this result is multiplied by forty. A plot can be made of hydrogen taken up (M) versus time (minutes). The initial slope of this plot, therefore, gives the initial rate of hydrogen uptake (M/min). The slope is determined at the initial steepest part of the slope which usually lies in the total pressure range of 60 to 75 cm.

This representation of results applies to all subsequent tables and graphs. Thus, the rate symbol (M/min) is defined as "the moles of hydrogen taken up per litre of reaction mixture per minute" and the symbol (M) is defined as the "moles of hydrogen taken up per litre of reaction mixture".

CHAPTER 3

RESULTS

3.1 Introduction

As mentioned in the introduction to this thesis, Hawthorne (51) reported the preparation of partially hydrogenated nickel and cobalt borides of proposed formulae $(Ni_2B)_2.H_3$ and $(Co_2B)_5.H_3$ respectively. These borides (called P-3' borides by this author) were reported as being highly active catalysts for the liquid-phase hydrogenation of unsaturated compounds and the activity of these metal borides was attributed, at least partially, to the presence of "lattice bound" hydrogen. Further investigation of these partially hydrogenated metal borides, which have the potential for being extremely active hydrogenation catalysts of comparable or even greater activity than the common industrial catalyst Raney nickel, was considered by this author to be of considerable industrial importance. This chapter, therefore, presents results obtained in a detailed investigation of the use of these metal borides as hydrogenation catalysts.

The results obtained in some portions of this study were unexpected and not easy to rationalize by themselves. For this reason, little or no discussion of the results is included in this chapter and a detailed discussion and rationalization of all of the information obtained is recorded in a separate chapter of this thesis.

3.2 Investigation of Hydrogen Uptake During the Liquid-Phase Hydrogenation of Substrates Over P-3 Nickel and P-3 Cobalt

3.2.1 Liquid-Phase Hydrogenation of Representative Substrates Over P-3 Ni and P-3 Co

The results of preliminary studies carried out by the present author in 1975 (95) are summarized in Table 3.1. The nickel boride designated as P-3 Ni, similar to P-3' prepared by Hawthorne et.al. (51) but prepared in situ under hydrogen, was found to be a highly active catalyst for the liquid-phase hydrogenation of olefins and also has considerable activity towards hydrogenation of carbonyl and nitrile functions. That the hydrogenation is due to catalysis by nickel boride and not by other species present in solution was shown by several observations. First, although sodium borohydride, which is used to generate the metal borides, is known (96) to reduce aldehyde and ketone functional groups under certain conditions, it does not hydrogenate C-C double bonds as other borides do (see first chapter). In these carbonyl reductions, hydrogen is the nucleophile and is transferred with a pair of electrons as the hydride ion $\{\bar{H}:\}$ from the metal to the carbonyl carbon atom. In short, sodium borohydride reduction does not involve the uptake of molecular hydrogen, which does occur in boride catalyzed hydrogenation. Also, at the time that the substrate is added to the suspended metal boride, there would be little or no sodium borohydride left in solution since, as mentioned in the first chapter,

TABLE 3.1

Hydrogenation of Representative Substrates Over Partially Hydrogenated P-3 Nickel Boride[a]

Substrate	{P-3 Ni} (M)[c] (X 10^{-2})	Initial Rate of Hydrogen Uptake[b] (M/min) (X 10^{-2})
1-hexene	3.17	1.09
1-octene	1.64	6.49
1-decene	1.64	6.27
1-hexadecene	1.76	7.40
allyl alcohol	3.29	5.30
acetone	3.29	0.57
acetonitrile	3.29	0.66
cis-trans 2-octene	2.03	4.80
trans 4-octene	2.23	4.10
cyclohexene	3.29	0.00
benzene	3.19	0.00

[a] Hydrogenation of 0.0125 moles substrate (0.5 M) over P-3 Ni in ethanol at 21°C±3. (Initial hydrogen pressure of 76 cm.) [b] Initial rate of hydrogen uptake measured usually in a hydrogen pressure range of 75 to 60 cm Hg with the average rate being calculated from at least two runs. Initial gas volume of 328 ml. Initial liquid volume of 25 ml. [c] The catalyst concentration in this table and for all subsequent data is conveniently, although oversimply, expressed as the number of moles of dispersed nickel present, as determined from starting materials, per litre of liquid-_i.e._ Molar (M). It is realized that since the catalyst is heterogeneous, the reproducibility of measurements of the catalyst concentration in the reaction mixture is dependent on the efficiency of mixing. The catalyst concentration is not expressed in terms of moles of catalyst itself per litre of liquid as determined from starting materials since the exact composition and formula of the nickel boride or cobalt boride under study is not known.

nickel boride catalyzes the hydrolysis of the excess of sodium borohydride. Therefore, it was tentatively concluded that P-3 Ni is the active species for the hydrogenation of acetone and acetonitrile in ethanol solution. Mass spectral analysis of the reaction products listed in Table 3.1 indicates that 1-hexadecene and 1-decene are hydrogenated to their corresponding n-alkanes, and acetone is hydrogenated to 2-propanol.

There still remained the possibility that catalysis is homogeneous because of some soluble nickel species present in solution after generation of the boride. However, these preliminary studies (95) also confirmed that P-3 Ni is a heterogeneous liquid hydrogenation catalyst. Thus, separate activity measurements of the precipitate and supernatant liquid formed in the preparation of 0.033 M P-3 Ni showed that the initial rate of hydrogen uptake for the hydrogenation of 0.5 M 1-octene over the black solid suspended in ethanol was 0.055 M/min while under the same reaction conditions the supernatant liquid was inactive.

In the present study, the activity of the closely related partially hydrogenated cobalt boride, designated as P-3 Co, for liquid-phase hydrogenations of several substrates was also determined for comparison with the activities found for P-3 Ni. Table 3.2 lists these results.

3.2.2 Kinetics of the Liquid-Phase Hydrogenation of 1-Hexadecene Over P-3 Ni and P-3 Co

There have been no reported kinetic studies for the liquid-

TABLE 3.2

Hydrogenation of Representative Olefins Over Partially Hydrogenated P-3 Cobalt Boride[a]

Substrate	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
1-octene	5.00
1-hexadecene	5.57
cis-trans 2-octene	0.20
trans 4-octene	0.50

[a] Hydrogenation of 0.0125 moles substrate (0.5 M) over 4.3 X 10^{-4} moles P-3 Co (0.0171 M) in ethanol. (Initial hydrogen pressure of 76 cm.)

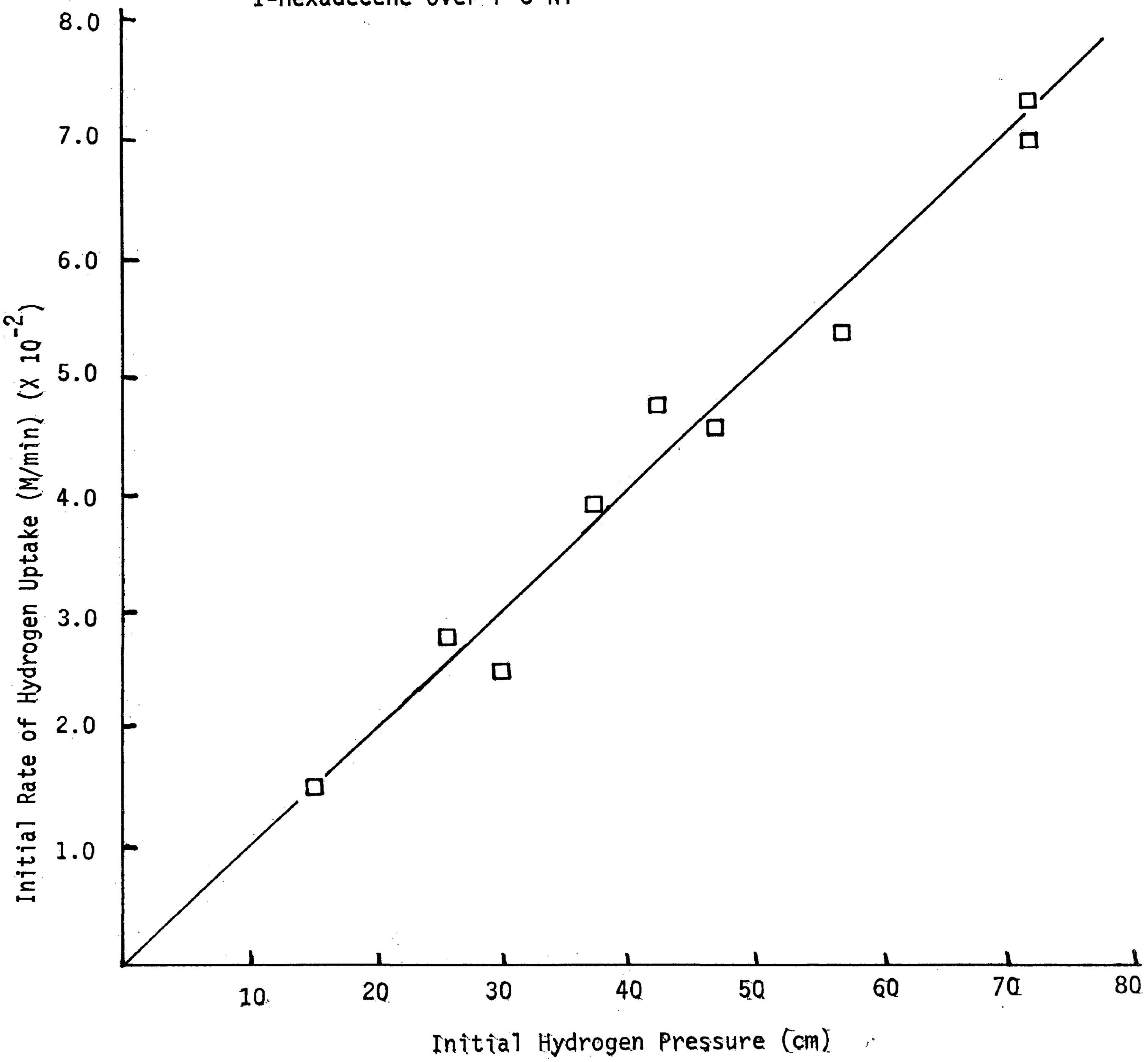
phase hydrogenation of olefins over the partially hydrogenated nickel boride, P-3 Ni. In order to understand the complexities of this heterogeneous hydrogenation over P-3 Ni, and also in an attempt to determine a mechanism for the process, the effect of initial hydrogen pressure, catalyst concentration, and substrate concentration on the initial rate of hydrogen uptake by 1-hexadecene (chosen because of its activity) was investigated. The results are summarized in figures 3.1, 3.2, and 3.3 and are fully recorded in the Appendix.

Similarly, figures 3.4, 3.5, and 3.6 show the results obtained in the study of the effect of the initial hydrogen pressure, catalyst concentration, and substrate concentration on the initial rate of hydrogen uptake in the hydrogenation of 1-hexadecene over P-3 Co. Deductions from these studies and gas chromatographic studies to be described later are discussed in the next chapter of this thesis.

3.2.3 Dependence of the Initial Rate of Hydrogen Uptake in the Liquid-Phase Hydrogenation of Olefins Over Nickel Borides on the Method of Catalyst Preparation

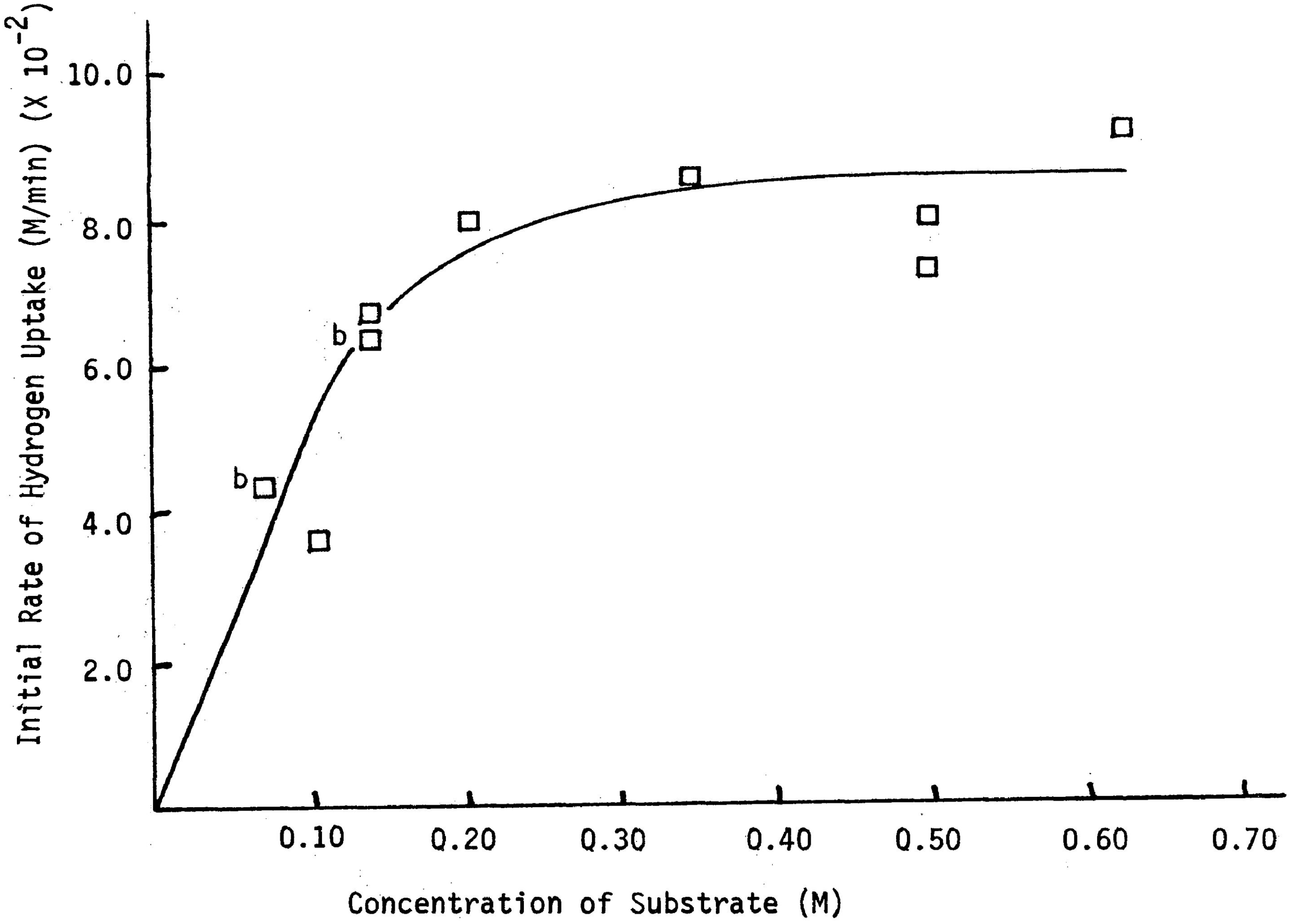
Table 3.3 lists the several preparations,together with references, of nickel boride hydrogenation catalysts which have been reported. Differences in the resulting catalyst activity due to catalyst preparation technique have been recognised by several authors and

Figure 3.1. Effect of Initial Hydrogen Pressure on the Initial Rate of Hydrogen Uptake During the Hydrogenation of 1-Hexadecene Over P-3 Ni[a]



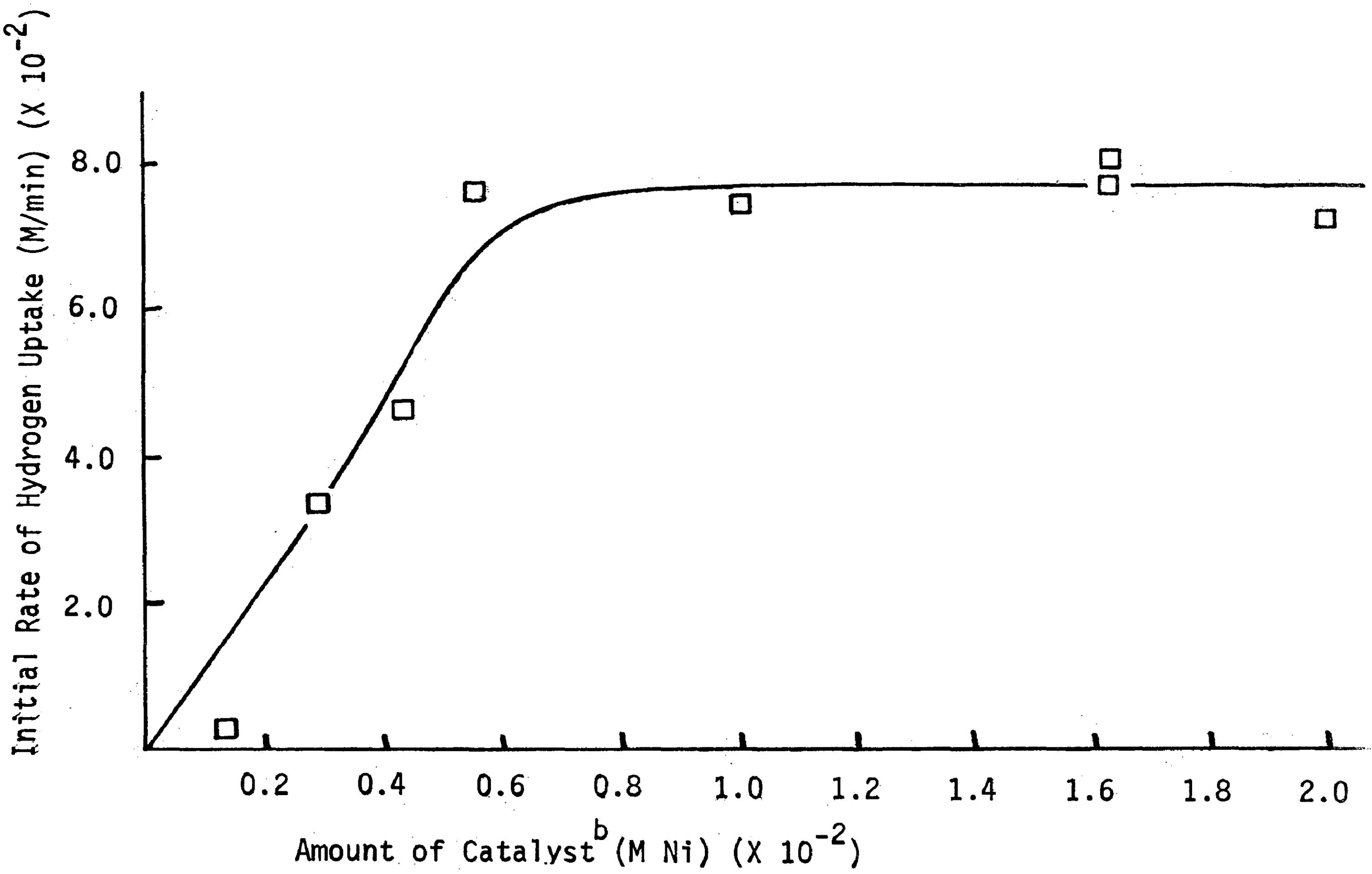
[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 5 X 10^{-4} moles P-3 Ni (0.02 M) in ethanol. Initial gas volume of 328 ml.

Figure 3.2. Effect of Initial Substrate Concentration on the Initial Rate of Hydrogen Uptake During the Hydrogenation of 1-Hexadecene Over P-3 Ni[a]



[a] Hydrogenation of 1-hexadecene over approximately 5 X 10^{-4} moles P-3 Ni (0.02 M) in ethanol. (Initial hydrogen pressure of 72 cm) Initial gas volume of 328 ml. [b] Initial gas volume of 614 ml.

Figure 3.3. Effect of Initial Amount of Catalyst on the Initial Rate of Hydrogen Uptake During Hydrogenation of 1-Hexadecene Over P-3 Ni[a]



[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over P-3 Ni in ethanol. (Initial hydrogen pressure of 72 cm.) [b] Amount of catalyst expressed in terms of moles of Ni (used in preparation) per litre of liquid reaction mixture. Total liquid volume of 25 ml.

Figure 3.4. Effect of Initial Hydrogen Pressure on the Initial Rate of Hydrogen Uptake During Hydrogenation of 1-Hexadecene Over P-3 Co[a]

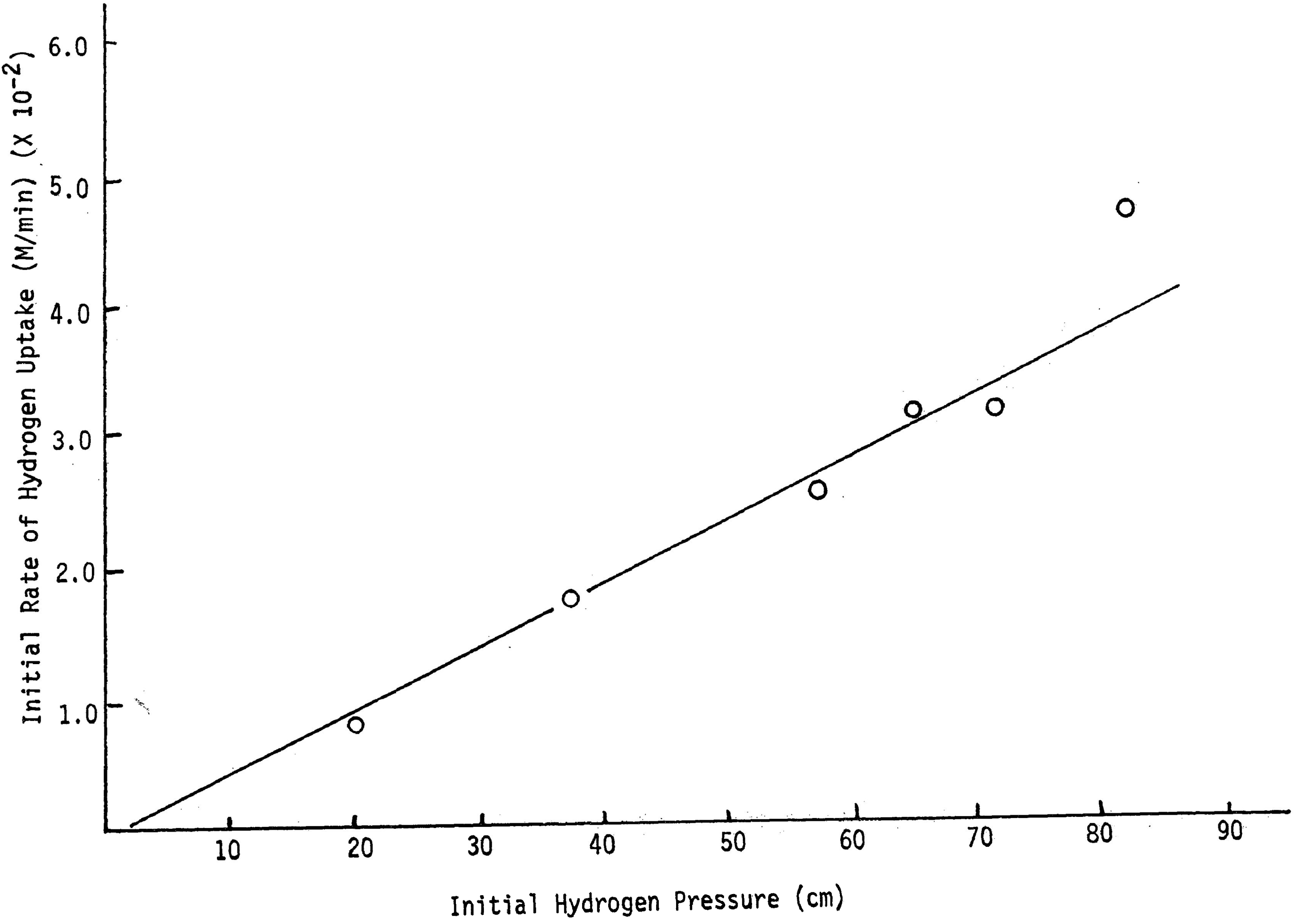
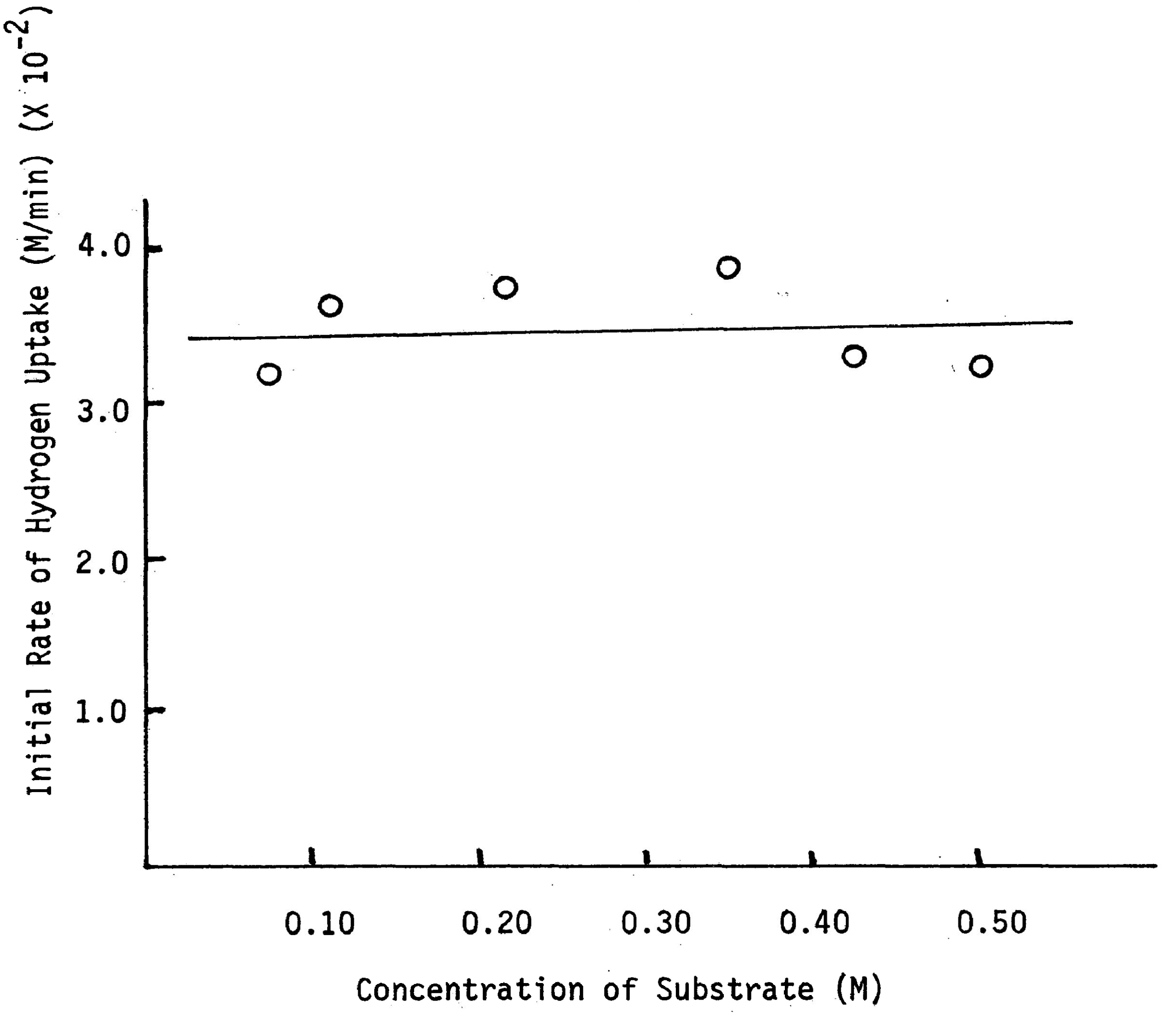


Figure 3.4. (cont.)

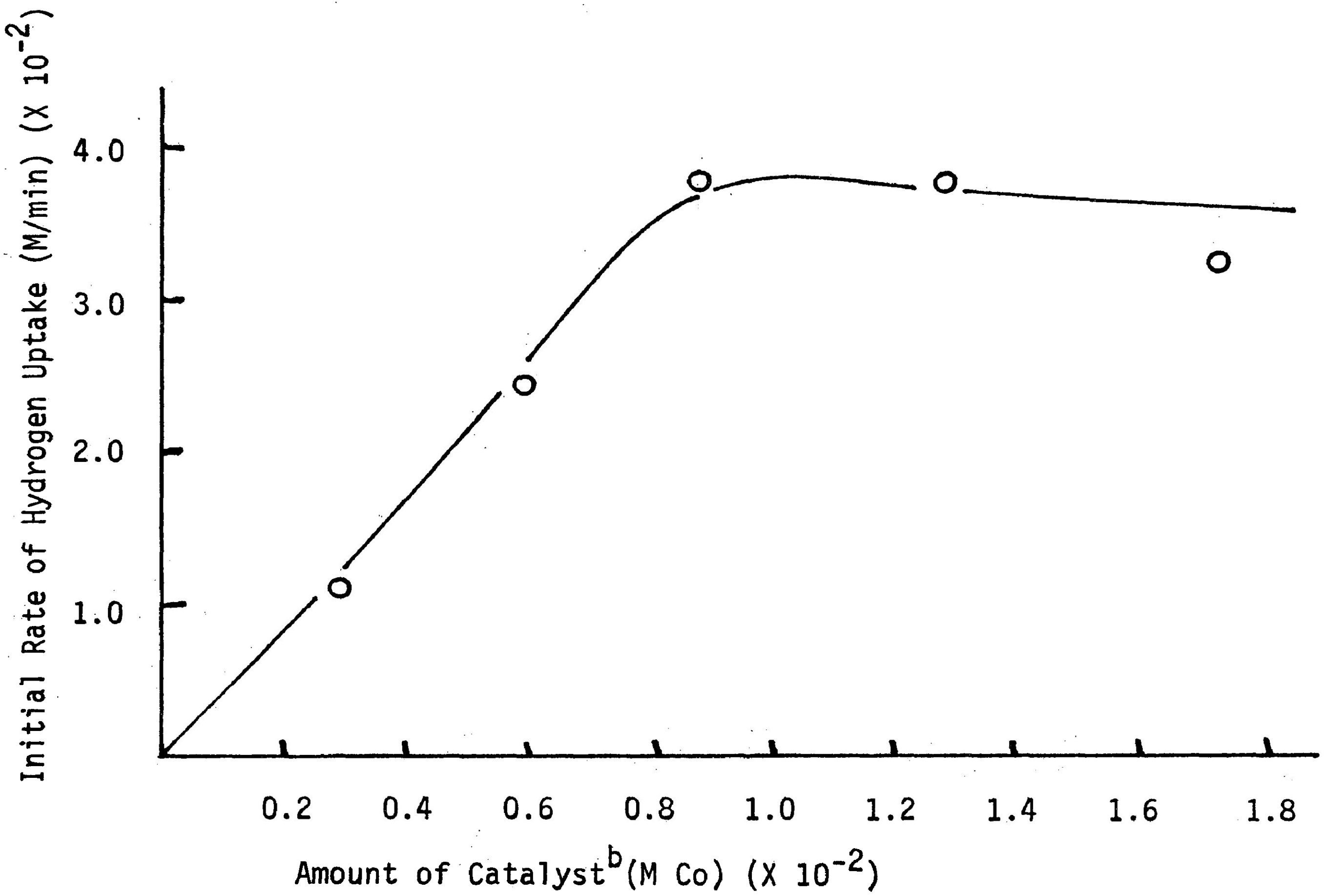
[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 4 X 10^{-4} moles P-3 Co (0.0175 M) in ethanol. Initial gas volume of 328 ml.

Figure 3.5. Effect of Initial Substrate Concentration on the Initial Rate of Hydrogen Uptake During the Hydrogenation of 1-Hexadecene Over P-3 Co[a]



[a] Hydrogenation of 1-hexadecene over approximately 5 X 10^{-4} moles P-3 Co (0.018 M) in ethanol. (Initial hydrogen pressure of 72 cm.) Initial gas volume of 328 ml.

Figure 3.6. Effect of Initial Amount of Catalyst on the Initial Rate of Hydrogen Uptake During Hydrogenation of 1-Hexadecene Over P-3 Co[a]



[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over P-3 Co in ethanol. (Initial hydrogen pressure of 72 cm.) [b] Amount of catalyst expressed in terms of moles of Co (used in preparation) per litre of liquid reaction mixture. Total liquid volume of 25 ml.

TABLE 3.3

Preparation of Several Nickel Borides

Catalyst	Ni(II) Salt Used	Molar Ratio of Ni(II) salt:$NaBH_4$	Solvent	Atmosphere	Proposed Formula	Physical Characteristics	Reference
P-1 Ni	nickel chloride hexahydrate nickel acetate hydrate nickel nitrate nickel sulphate	1:3	H_2O	N_2	Ni_2B	black granular material non-magnetic non-pyrophoric	11,12, 21
P-2 Ni	nickel chloride hexahydrate nickel acetate hydrate nickel nitrate nickel sulphate	(1:2),1:1,(2:1)	EtOH	N_2,H_2,Ar	Ni_2B	nearly colloidal black suspension non-magnetic non-pyrophoric	16,17 20,21
Hawthorne (P-3' Ni)	nickel chloride	1:4	EtOH	N_2	$(Ni_2B)_2.H_3$	ferromagnetic pyrophoric very soluble in dilute mineral acid	51
P-3 Ni	nickel chloride	1:4	EtOH	H_2	$(Ni_2B)_2.H_3$	black colloidal non-pyrophoric	95

both the preparations and the differences have been discussed in some detail in the introductory chapter of this thesis.

Since there are such obvious differences between the catalysts reported earlier, it was considered important to compare the activities of P-1 Ni, P-2 Ni, and Hawthorne's catalyst (a P-3 type boride) with P-3 Ni prepared by this author's method (under hydrogen) in order to determine the preparative conditions necessary to produce the most active and useful nickel boride.

The nickel catalysts were prepared according to the previously reported papers, using the molar ratios of reactants, atmospheric conditions, nickel(II) salts, and solvent as underlined in Table 3.3. These preparations are more fully described in Section 2.5.1. It was necessary to prepare all of these nickel catalysts so that comparisons could be carried out using identical reaction conditions. The major difference between the hydrogenation conditions used in this study and those of previous workers in this area is that in the previous studies the hydrogen pressure was kept constant at one atmosphere during the reaction by using a borohydride hydrogenator. The reaction was followed by carrying out gas-liquid chromatography of the reaction mixtures in order to determine the times for 50% and 100% hydrogenation of the substrate.

In the study described in this thesis, the initial pressure of hydrogen was one atmosphere. However, as hydrogen uptake occurred the pressure decreased steadily. The catalyst activities are therefore represented by the initial rate of hydrogen uptake as measured under standard conditions using a mercury manometer and timer.

The catalyst activities can be compared directly from Table 3.4. It should, however, be noted that rate of hydrogen uptake may not be the best measure of the activity of the catalyst in heterogeneous hydrogenations. This will become apparent later and will be discussed in some detail in the next chapter of this thesis.

3.2.4 Effect of Reaction Medium on the Initial Rate of Hydrogen Uptake in the Liquid-Phase Hydrogenation of 1-Hexadecene Over P-3A Ni

In liquid-phase catalytic reactions, the solvent used may have a profound effect on the measured catalyst activity. For example, the solvent itself may block active catalyst sites or may prevent the substrate from reaching such sites due to diffusion, solubility, or steric factors. It is important, therefore, to chose a solvent system which is of least hindrance to the catalytic reaction. P-3 Ni has been shown, as described in the previous section, to be extremely active for the hydrogenation of olefins in ethanol. However, since the substrates being used are only slightly soluble in ethanol, it was of interest to use a non-polar hydrocarbon solvent to determine whether the P-3 Ni is more active in such a solvent. n-Heptane is a frequently used solvent in industrial catalytic reactions, and was chosen here. The P-3 Ni had to be prepared in ethanol under nitrogen, and then filtered, dried, weighed, and finally the product (P-3A Ni) was transferred to the new reaction medium. Table 3.5 lists the results obtained

TABLE 3.4

Hydrogenation of 1-Hexadecene Over Several Heterogeneous Nickel Catalysts[a]

Catalyst	{Ni}[b] (M) (X 10^{-2})	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
P-3 Ni	1.64	7.80
Hawthorne's catalyst (P-3' Ni)	2.50	7.20
P-3A Ni	2.00	3.75[c] 3.85[d]
P-3" Ni	1.60	1.76[e]
P-2 Ni (nickel acetate)	1.68	5.50
P-1 Ni (nickel acetate)	1.68	2.00
P-1 Ni (nickel chloride)	1.68	1.27
P-2 Ni (nickel chloride)	1.68	0.40
Raney nickel	3.05 1.83	2.52[f] 2.17[g]

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over nickel catalysts prepared as described in Section 2.5.1 in ethanol (Initial hydrogen pressure of 76 cm.) [b] Although the catalyst is heterogeneous, the concentration is conveniently expressed as moles of dispersed nickel present per litre of liquid (*i.e.* M) as determined from starting materials. [c] P-3A Ni not stirred under hydrogen, except for flushing, before rate measurements. [d] P-3A Ni stirred in presence of hydrogen for one hour before rate measurements. [e] Hawthorne's catalyst washed with water and dried under reduced pressure before use. [f] Raney nickel not stirred under hydrogen, except for flushing, before rate measurements. [g] Raney nickel stirred in presence of hydrogen for one hour before rate measurements.

TABLE 3.5

Hydrogenation of 1-Hexadecene Over P-3A Ni in Several Solvent Systems[a]

Solvent	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
EtOH	4.11
n-heptane	3.50
1 EtOH: 1 *n*-heptane	3.40
1 EtOH: 5 *n*-heptane	2.10
1-hexadecene[b]	2.40

[a] Hydrogenation of 0.0125 moles (except for last entry in table) 1-hexadecene (0.5 M) over 4.5-5.8 X 10^{-4} moles P-3A Ni (0.018-0.023 M). (Initial hydrogen pressure of 76 cm.) (Initial gas volume of 328 ml.) [b] Initial gas volume of 445 ml and substrate used as solvent.

using several solvent systems. It should be noted that an extra variable has been introduced in that the catalyst used in these experiments (P-3A Ni) is not identical to the P-3 Ni used in the experiments in which ethanol is used as the solvent. It is inevitable that some changes in catalyst composition and activity occur in the work-up procedure leading to P-3A Ni but, nevertheless, the hydrogenation experiments involving solvents other than ethanol are still worth while.

3.3 Investigation of the Poisoning of the Liquid-Phase Hydrogenation of Olefins Over P-3 Ni, P-3 Co, and Raney Nickel by Sulphur

3.3.1 Introduction

Previous studies by Paul and his coworkers (5) have shown that P-1 type Ni exhibits a greater resistance to fatigue than Raney nickel. Russell, et.al. (21) have reported that P-1 Ni and P-2 Ni are active catalysts for the hydrogenation of C-C double bonds even in the presence of amine functional groups. This was in contrast to palladium catalysts which were reported by Maxted (79) as being poisoned by amines. Furthermore, T. Imanaka et.al. (93) reported that P-1 Ni is much more resistant to liquid-phase poisoning by dichlorophenylphosphites, trialkylphosphites, and 2,3-dimercaptopropanol than the nickel metal catalyst used in the hydrogenation of styrene.

These brief studies together with desulphurization studies discussed in the first chapter of this thesis indicate considerable resistance of P-1 Ni and P-2 Ni towards usually catalytically toxic compounds. This is of considerable industrial importance since common catalyst poisons are frequently present in large scale industrial processes. It was therefore of interest to carry these studies further and on a quantitative basis to the apparently very active P-3 Ni and P-3 Co, and to compare their resistance to poisoning to that of high activity Raney nickel.

A common source of catalyst poisons is sulphur-containing compounds. Thus, in the present study, the effects of a gaseous poison, hydrogen sulphide, and a liquid poison, n-butanethiol, were chosen for study.

3.3.2 Effect of the Presence of Hydrogen Sulphide on the Initial Rate of Hydrogen Uptake During Liquid-Phase Hydrogenation of 1-Hexadecene Over P-3 Ni, P-3 Co, and Raney Nickel in Ethanol

The concentration of hydrogen sulphide is expressed as the initial weight of hydrogen sulphide present in the initial gas volume, as this is accurately known. The hydrogen sulphide then diffuses to the reaction interface and possibly into solution. Therefore, before carrying out detailed hydrogenation studies, it was felt desirable to have some idea of how much sulphur is present in solution (ethanol) under various conditions.

In the presence of P-3 Ni or Raney nickel, it was not possible to measure the free sulphide ion concentration in solution using a silver ion electrode because of the reduction of the Ag^+ to silver metal. However, in the absence of the catalyst it was found that;

a) if the initial gas concentration was 30 mg/l H_2S, in a total gas volume of 408 ml, and the ethanol solution (25 ml) was stirred at the gas/liquid interface for 15 minutes in the <u>absence</u> of hydrogen, the solution had a sulphide ion concentration of 47 mg/l (1.17 mg S^{2-}/25 ml liquid) and

b) if the initial gas concentration was 285 mg/l H_2S, in a total gas volume of 408 ml, and the ethanol solution (25 ml) was stirred at the gas/liquid interface for 12 minutes in the <u>presence</u> of hydrogen, the solution had a sulphide ion concentration of 42 mg/l (1.04 mg S^{2-}/25 ml liquid).

Therefore, the presence of hydrogen inhibits hydrogen sulphide from going into solution to the same extent. The effect of hydrogen sulphide poisoning upon hydrogenation of alkenes was studied in the kinetic range where the initial rate of hydrogen uptake is proportional to hydrogen pressure and independent of catalyst and substrate concentration for the hydrogenation of 1-hexadecene over P-3 Ni or P-3 Co in ethanol. The results of these studies are listed in Tables 3.6, 3.7, and 3.8. Relatively low rates of hydrogenation measured for several reactions were probably due to hydrogen sulphide or oxygen (see section 3.3.5) contamination during preparation of P-3 Ni.

TABLE 3.6

Hydrogenation of 1-Hexadecene Over P-3 Ni in Ethanol in the Presence of Hydrogen Sulphide[a]

mg/l H_2S	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})	Hydrogen Uptake in five minutes (M)	Hydrogen Uptake in ten minutes (M)	
0	7.33	0.285	0.390	
14	5.83	0.250	0.360	
30	6.00	0.275	0.350	
30[b]	5.50	0.265	-	
45	6.00	0.275	-	
75	4.00	0.280	-	
187	7.33	0.265	0.270	
187[b]	8.33	0.300	0.320	
300	3.30	0.185	0.265	0.295/0.75 hr
500[c]	5.17	0.185	0.20	0.260/3.0 hr
700[c]	2.92	0.140	0.185	0.260/2.5 hr
800[d]	5.80	0.195	0.215	0.285/2.0 hr
30[e]	5.33	0.32	-	
60[e]	0.00	0.00	-	
5[f]	4.00	0.195	0.285	

TABLE 3.6 (cont.)

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 5.4 X 10^{-4} moles P-3 Ni (0.022 M) in ethanol (total volume 25 ml). (Initial total pressure (P_{H_2} + P_{H_2S}) of 76 cm.) Hydrogen sulphide concentration expressed as mg H_2S per litre of gas phase. (Initial gas volume of 408 ml.) [b] Hydrogenation of 0.025 moles 1-hexadecene (1.0 M). [c] Initial gas volume of 694 ml. [d] Initial gas volume of 822 ml. [e] P-3 Ni stirred in presence of hydrogen sulphide and low partial pressure of hydrogen (less than 10 cm) for fifteen minutes before substrate is added, and then total pressure is increased to 76 cm by introducing hydrogen. [f] P-3 Ni generated for one hour in presence of hydrogen sulphide and hydrogen. Hydrogen sulphide then removed and hydrogenation of 1-hexadecene carried out as usual.

TABLE 3.7

Hydrogenation of 1-Hexadecene Over Raney Nickel in Ethanol in the Presence of Hydrogen Sulphide[a]

mg/l H_2S	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})	Hydrogen Uptake in five minutes (M)	Hydrogen Uptake in ten minutes (M)	
0	2.30	0.135	0.235	
4	2.25	0.110	0.220	0.480/3.0 hr
30	1.93	0.100	0.195	0.280/4.5 hr
60	2.17	0.095	0.165	
300	2.70*	0.140*	0.210	
530[b]	1.22	0.060	0.110	0.230/17 hr
690[b]	1.70	0.080	0.110	0.295/19 hr
694[b]	1.29	0.060	0.110	0.325/32 hr
800[c]	1.29	0.070	0.090	0.340/41 hr
15[d]	1.42	0.065	0.130	
30[d]	0.00	0.000	0.000	0.035/17 hr

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 6.0 X 10^{-4} moles Raney nickel (0.024 M) in ethanol (total volume 25 ml). (Initial total pressure ($P_{H_2} + P_{H_2S}$) of 76 cm.) (Initial gas volume of 408 ml.)

[b] Initial gas volume of 694 ml.

[c] Initial gas volume of 822 ml.

[d] Raney nickel stirred in presence of hydrogen sulphide and low partial pressure of hydrogen (less than 10 cm) for fifteen minutes before substrate is added, and then total pressure is increased to 76 cm by introducing hydrogen.

* Anomalously high.

TABLE 3.8

Hydrogenation of 1-Hexadecene Over P-3 Co in Ethanol in the Presence of Hydrogen Sulphide[a]

mg/l H_2S	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})	Hydrogen Uptake in five minutes (M)	Hydrogen Uptake in ten minutes (M)
0[b]	4.80	0.200	0.315
200[c]	4.30	0.200	0.300

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 4 X 10^{-4} moles P-3 Co (0.016 M) in ethanol(total volume 25 ml). (Initial total pressure (P_{H_2} + P_{H_2S}) of 76 cm.) [b] Initial gas volume of 328 ml. [c] Initial gas volume of 408 ml.

It is quite astonishing to note that for the 700 mg/l H_2S study, the initial hydrogen pressure (approximately 39 cm Hg) is equal to the initial hydrogen sulphide pressure (approximately 39 cm), and for the 800 mg/l H_2S study, the initial hydrogen pressure (approximately 33 cm) is less than the initial hydrogen sulphide pressure (approximately 43 cm). The catalysts are therefore relatively insensitive to hydrogen sulphide poisoning under these conditions although, again, it should be noted that hydrogen uptake is not necessarily a good guide to the rate of alkene hydrogenation. As mentioned before, this point will be discussed later.

It is also important to note that in this study of hydrogen sulphide poisoning, although the initial <u>total</u> gas pressure (76 cm) is constant , the partial pressures of hydrogen and hydrogen sulphide vary. It is surprising therefore to find that at an initial partial pressure of hydrogen of approximately 33 cm, the initial rate of hydrogen uptake is nearly twice as great as that determined in the kinetic study (figure 3.1) for an initial total (<u>i.e.</u> hydrogen) pressure of approximately 33 cm. This seems to indicate that the initial rate of hydrogen uptake in the hydrogenation of alkenes may be dependent on the <u>total</u> initial gas pressure and not just on the hydrogen partial pressure.

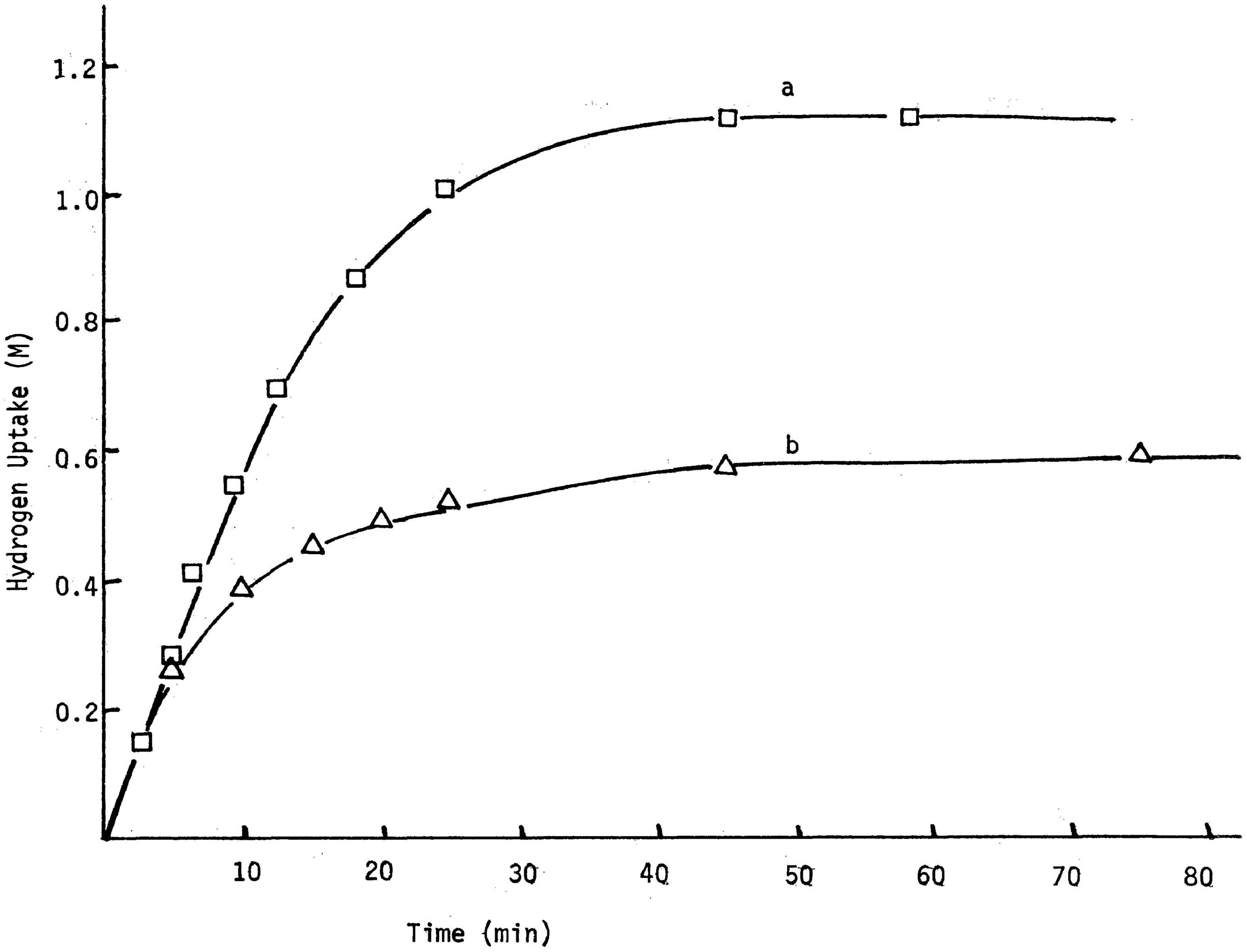
The above results, along with the sulphide ion concentration measurements, indicate that P-3 Ni and Raney nickel are much more sensitive to hydrogen sulphide poisoning at lower hydrogen pressures. To show this more clearly, two nearly identical reactions were carried out. With one, the total pressure was kept at greater than

60 cm, but with the other, although the pressure was adjusted every five minutes, it was allowed to drop considerably below 60 cm before adjustment. Figure 3.7 summarizes the results obtained. Therefore, if the hydrogen pressure drops below a critical level, P-3 Ni, and Raney nickel are irreversibly poisoned by hydrogen sulphide.

3.3.3 Effect of the Presence of n-Butanethiol on the Initial Rate of Hydrogen Uptake During the Liquid-Phase Hydrogenation of Olefins Over P-3 Ni, P-3 Co, and Raney Nickel in Ethanol

In these experiments, a measured volume of liquid n-butanethiol was added to the normal hydrogenation reaction mixture to give a solution of accurately known concentration of sulphur. These results therefore are quantitatively more significant than those found for hydrogen sulphide poisoning studies. n-Butanethiol poisoning was studied in the kinetic range where the rate of hydrogen uptake is proportional to the hydrogen pressure, and is independent of catalyst and substrate concentration for the hydrogenation of 1-hexadecene over P-3 Ni or P-3 Co. The results are presented in Tables 3.9, 3.10, 3.11, and 3.12. The n-butanethiol was added to the reaction mixture in two ways; with the solvent before generation of the catalyst, or with the substrate, after generation of the catalyst. Figures 3.8 and 3.9 show these results graphically. It is seen that the point at which the n-butanethiol is introduced does affect the initial rate of hydrogen uptake. It is interesting to note that curve (b) of figure 3.8 has a similar shape to curve

Figure 3.7. Effect of Hydrogen Pressure on the Degree of Catalyst Poisoning by Hydrogen Sulphide During the Hydrogenation of 1-Hexadecene Over P-3 Ni



[a]Hydrogenation of 0.025 moles 1-hexadecene (1.0 M) over approximately 5 X 10^{-4} moles P-3 Ni (0.02 M) in ethanol in the presence of 30 mg/l hydrogen sulphide. Total pressure (P_{H_2} + P_{H_2S})kept at greater than 60 cm by introducing hydrogen. [b]Same as [a] except that total pressure is increased to approximately 75 cm every five minutes by introducing hydrogen, however, during the reaction the total pressure dropped as low as 45 cm.

TABLE 3.9

Hydrogenation of 1-Octene Over P-3 Ni in Ethanol in the Presence of n-Butanethiol[a]

mg/l Sulphur	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
0.0	5.60 6.70 6.30
13.3	6.70[b] 4.80 4.50
21.3	3.80[b] 5.80[b]
26.7	3.80[b] 3.60
31.9	0.70[b]
40.0	1.70 0.80 0.00
53.3	0.04[b] 0.00

[a] Hydrogenation of 0.0125 moles 1-octene (0.5 M) over approximately 4 X 10^{-4} moles P-3 Ni (0.016 M) in ethanol. (Initial hydrogen pressure of 76 cm.) Concentration of n-butanethiol expressed as mg sulphur per litre of liquid. Initial gas volume of 328 ml. Initial liquid volume of 25 ml. n-Butanethiol added with substrate after generation of P-3 Ni. [b] Same as [a] except n-butanethiol added with solvent before generation of P-3 Ni.

TABLE 3.10

Hydrogenation of 1-Hexadecene Over P-3 Ni in Ethanol in the Presence of *n*-Butanethiol[a]

mg/l Sulphur	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
0.0	7.33
13.3	6.50 6.75
26.6	6.33 4.50
40.0	2.67 3.42
53.3	0.00

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 4 X 10^{-4} moles P-3 Ni (0.016 M) in ethanol. (Initial hydrogen pressure of 76 cm.) Concentration of *n*-butanethiol expressed as mg sulphur per litre of liquid. Initial gas volume of 328 ml. *n*-Butanethiol added with substrate *after* generation of P-3 Ni.

TABLE 3.11

Hydrogenation of 1-Hexadecene Over Raney Nickel in Ethanol in the Presence of n-Butanethiol[a]

mg/l Sulphur	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
0.0	2.83
6.7	1.95
13.3	1.72
27.0	0.09

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over 6.5-9.5 X 10^{-4} moles Raney nickel (0.026-0.038 M) in ethanol. (Initial hydrogen pressure of 76 cm.) Concentration of n-butanethiol expressed as mg sulphur per litre of liquid. Initial gas volume of 328 ml. n-Butanethiol added with substrate after preparation of Raney nickel - ethanol mixture.

TABLE 3.12

Hydrogenation of 1-Hexadecene Over P-3 Co in Ethanol in the Presence of n-Butanethiol[a]

mg/l Sulphur	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
0.0	4.06 5.57
28.0	3.30[b] 4.33
54.0	4.06 4.57
60.0	3.40
65.0	3.25
80.0	1.50
90.0	0.00
108.0	0.00

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 4 X 10^{-4} moles P-3 Co (0.016-0.018 M) in ethanol. (Initial hydrogen pressure of 76 cm.) Concentration of n-butanethiol expressed as mg sulphur per litre of liquid. Initial gas volume of 328 ml. n-Butanethiol added with substrate after generation of P-3 Co.

[b] Same as [a] except n-butanethiol added with solvent before generation of P-3 Co.

Figure 3.8. Effect of the Presence of n-Butanethiol During the Hydrogenation of Olefins Over P-3 Ni and Raney Nickel

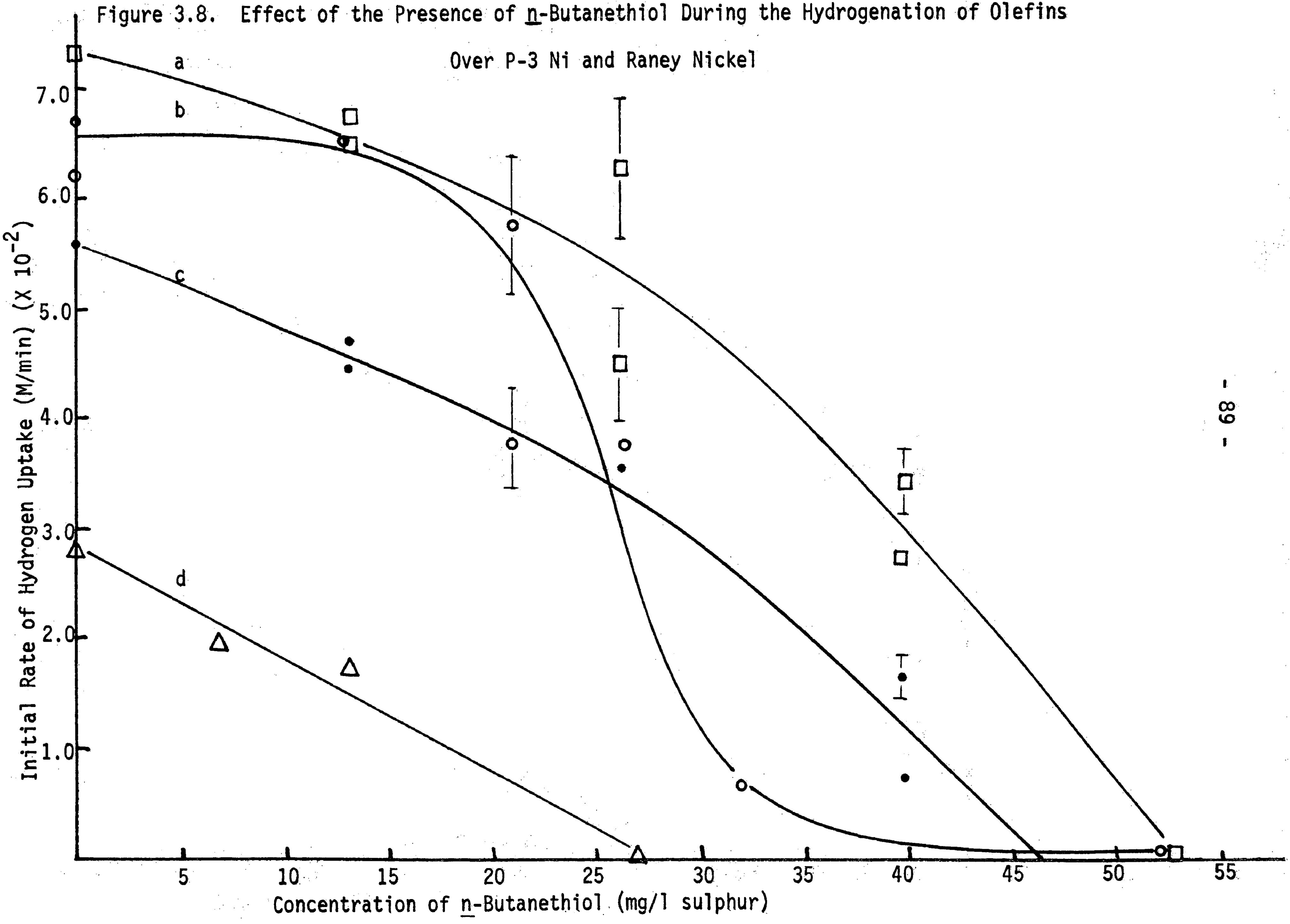


Figure 3.8. (cont.)

[a,□]Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 5 X 10^{-4} moles P-3 Ni (0.02 M) in ethanol. (Initial hydrogen pressure of 76 cm.) Concentration of *n*-butanethiol expressed as mg sulphur per litre of liquid *reaction* volume. *n*-Butanethiol added with substrate *after* generation of the P-3 *Ni*. Initial liquid volume of 25 *ml*. Initial gas volume of 328 ml. [b,○]Same as [a] except using 0.0125 moles 1-octene (0.5 M) and *n-butanethiol* added with solvent *before* generation of P-3 Ni. [c,●]Same as [b] except that *n-butanethiol* added with substrate *after* generation of P-3 Ni. [d,△]Hydrogenation of 0.0125 moles *1-hexadecene* (0.5 M) over 6.5-9.5 X 10^{-4} moles *Raney nickel* (0.026-0.038 M) in ethanol in presence of *n-butanethiol* which is added with substrate *after* preparation of *Raney* nickel.

**Experimental Error

From the three measurements of initial rate of hydrogen uptake for hydrogenation of 1-octene over P-3 Ni in the absence of *n*-butanethiol (*i.e.* 0.056, 0.067, 0.063 M/min) an average minimum experimental error of ±10% was calculated and has been indicated for several points by the use of error bars.

Experimental errors arise from inefficient stirring at the gas-liquid interface during the reaction, slight differences in amount of catalyst used, and possible leakage in the hydrogenation apparatus which would alter the "true" manometer readings. In addition, oxygen contamination during or after generation of the catalyst (see Section 3.3.6) and, in particular for reactions shown in figures 3.8, 3.9, 3.10, and 3.11, contamination by sulphur, due to insufficient "cleaning" of apparatus before the reaction is carried out, are cause for error. From the experimental values obtained and taking into account the error involved, curves which most closely fit the results have been drawn.

It should be noted that the points for curve [b] were experimentally obtained before those for curve [c] and in addition before any poisoning experiments had been carried out on this particular appartus. The latter points, therefore, are possibly lower than the former points partially due to sulphur contamination of the system from these earlier reactions.

Figure 3.9. Effect of the Presence of n-Butanethiol During the Hydrogenation of Olefins Over P-3 Co[a]

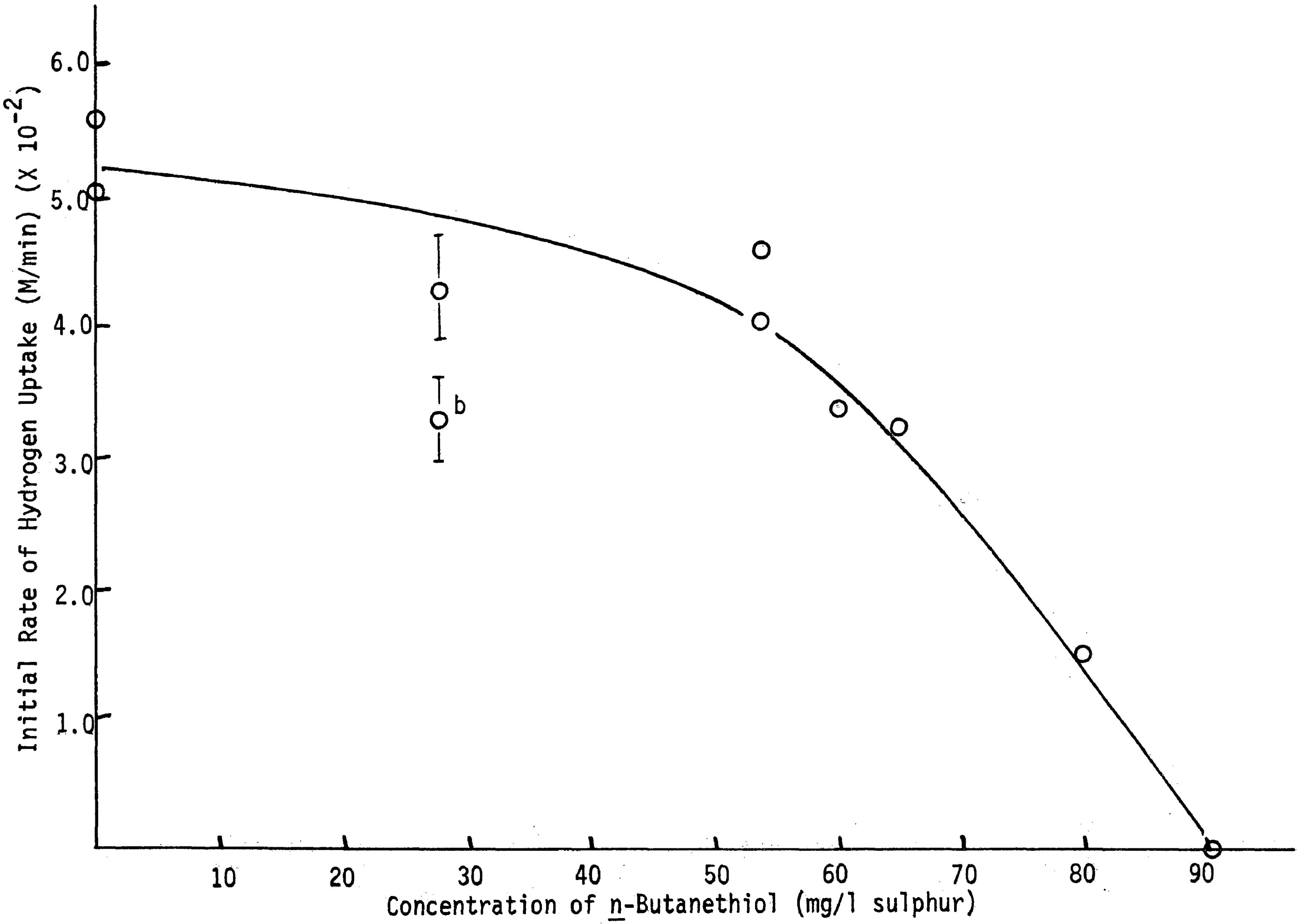


Figure 3.9. (cont.)

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 4 X 10^{-4} moles P-3 Co (0.016-1.018 M) in ethanol. (Initial hydrogen pressure of 76 cm.) Concentration of n-butanethiol expressed as mg sulphur per litre of liquid reaction volume. Initial liquid volume of 25 ml. Initial gas volume of 328 ml. Error bars indicate ± 10% experimental error (see footnote ** of figure 3.8). n-Butanethiol added with substrate after generation of P-3 Co. [b] Same as a except that n-butanethiol added with solvent before generation of P-3 Co.

(a) of figure 3.10(next section). Possibly the n-butanethiol present during the generation of the catalyst blocks "would be" active catalyst sites and in effect reduces the initial catalyst concentration (dispersed amount) for the reaction which is to follow. In this case then, the initial rate of hydrogen uptake would be dependent not only on the initial hydrogen pressure (i.e. as for curve (c) of figure 3.8) but also on the initial amount of catalyst present (i.e. similar to curve (a) of figure 3.10).

It was found that with n-butanethiol, poisoning occurs to a certain extent initially, and that although the rate of hydrogen uptake decreases as the hydrogen pressure decreases, the initial rate of hydrogen uptake can almost be restored by increasing the hydrogen pressure. Therefore, the hydrogen pressure is not critical in maintaining the resistance of the catalyst towards n-butanethiol poisoning in contrast to hydrogen sulphide poisoning.

3.3.4 Effect of the Presence of n-Butanethiol on the Initial Rate of Hydrogen Uptake During Liquid-Phase Hydrogenation of Olefins Over P-3 Ni, P-3 Co, and Raney Nickel in the Kinetic Range Where the Rate of Hydrogen Uptake is Proportional to Hydrogen Pressure, Catalyst Concentration, and Substrate Concentration

In order to see more clearly the effect of sulphur poisoning on the hydrogenation of 1-hexadecene, reactant concentrations were chosen, from the kinetic results, such that this reaction is dependent on hydrogen pressure, substrate concentration, and P-3 Ni concentration (amount of dispersed P-3 Ni).

The results obtained are shown graphically in figures 3.10 and 3.11.

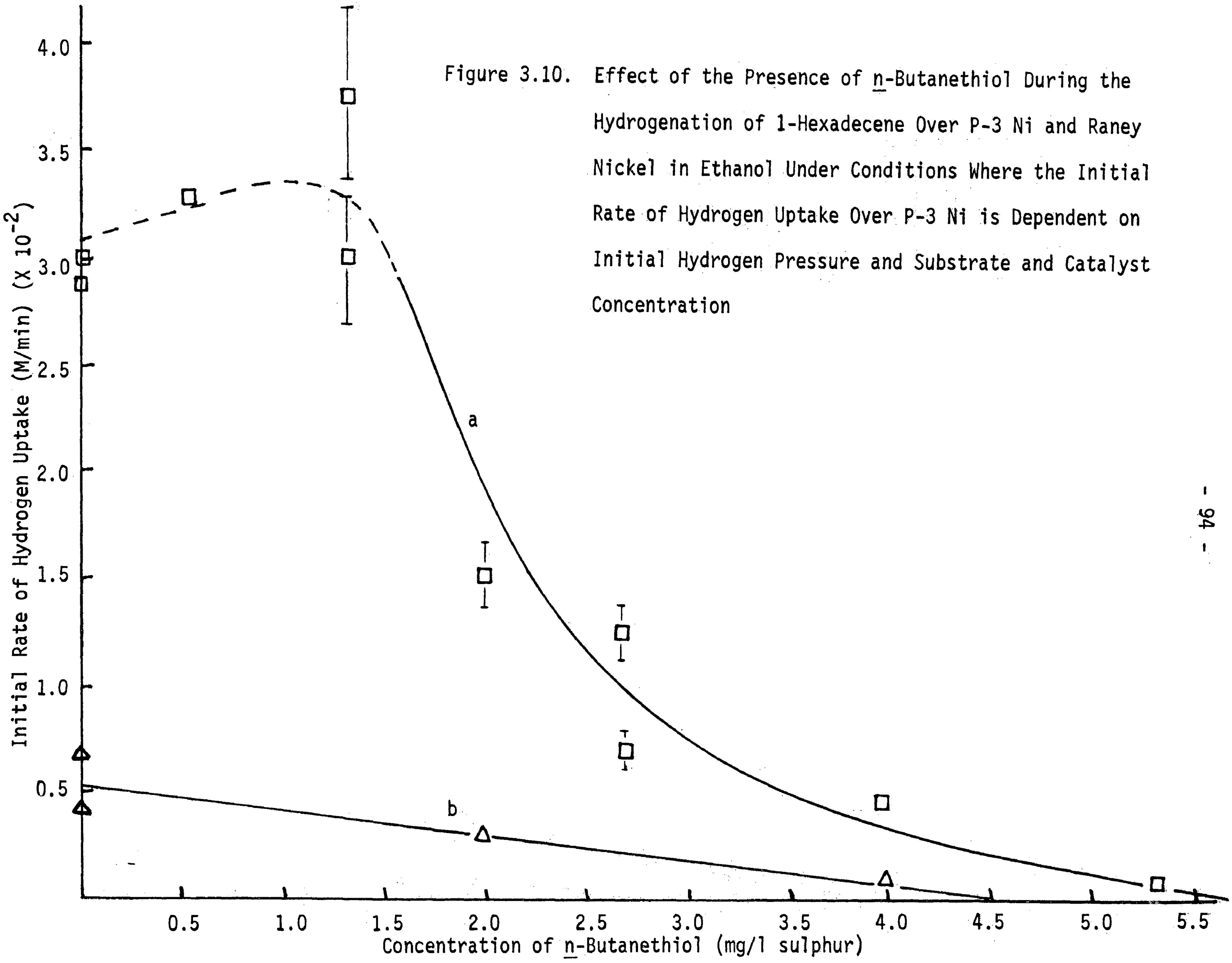
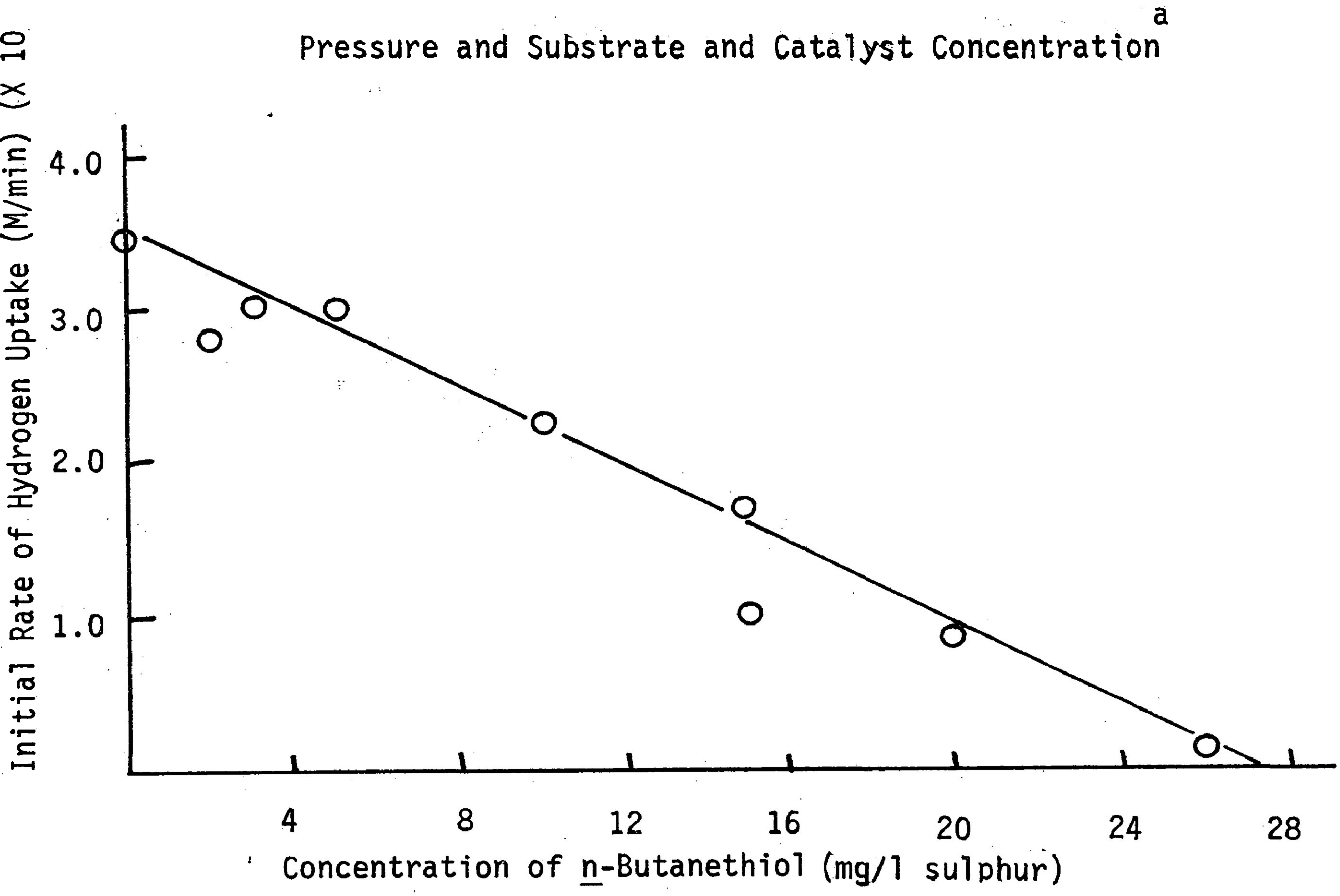


Figure 3.10. Effect of the Presence of n-Butanethiol During the Hydrogenation of 1-Hexadecene Over P-3 Ni and Raney Nickel in Ethanol Under Conditions Where the Initial Rate of Hydrogen Uptake Over P-3 Ni is Dependent on Initial Hydrogen Pressure and Substrate and Catalyst Concentration

Figure 3.10. (cont.)

[a]Hydrogenation of 3.5 X 10^{-3} moles 1-hexadecene (0.139 M) over 1.08 X 10^{-4} moles P-3 Ni (0.0043 M) in ethanol. (Initial hydrogen pressure of 72 cm.) Concentration of n-butanethiol expressed as mg sulphur per litre of liquid reaction volume. Initial liquid volume of 25 ml. Initial gas volume of 328 ml. [b]Same as [a] except hydrogenation is over approximately 1.4 X 10^{-4} moles Raney nickel (0.0052-0.0061 M). Error bars indicate ±10% experimental error (see footnote ** of figure 3.8).

Figure 3.11. Effect of the Presence of n-Butanethiol During the Hydrogenation of 1-Hexadecene Over P-3 Co in Ethanol Under Conditions Where the Initial Rate of Hydrogen Uptake Over P-3 Ni is Dependent on Initial Hydrogen Pressure and Substrate and Catalyst Concentration[a]



[a] Hydrogenation of 3.5 X 10^{-3} moles 1-hexadecene (0.139 M) over 1.08 X 10^{-4} moles P-3 Co (0.0043 M) in ethanol. (Initial hydrogen pressure of 72 cm.) Concentration of n-butanethiol expressed as mg sulphur per litre of liquid reaction volume. Initial liquid volume of 25 ml. Initial gas volume of 328 ml.

3.3.5 Effect of the Presence of Sulphur Poisons on the Initial Rate of Hydrogen Uptake During Liquid-Phase Hydrogenation of 1-Hexadecene Over P-3A Ni and Raney Nickel in *n*-Heptane

It was shown in section 3.2.4 that P-3A Ni is slightly less active for hydrogenation of 1-hexadecene in *n*-heptane than in ethanol, in the absence of catalyst poisons. When discussing catalyst poisoning, it is necessary to realize that the solvent itself may interfere with the poisoning reaction. The resistance of P-3A Ni and Raney nickel towards hydrogen sulphide and *n*-butanethiol was therefore also studied in *n*-heptane. The results are recorded in Tables 3.13, and 3.14. This study was carried out in the kinetic range where the rate of hydrogen uptake in the hydrogenation of 1-hexadecene over P-3 Ni is proportional to the hydrogen pressure and is independent of catalyst and substrate concentration.

The results indicate that both P-3A Ni and Raney nickel lose at least half of their resistance towards poisoning by *n*-butanethiol when the reaction is carried out in *n*-heptane rather than ethanol. However, once again the presence of hydrogen sulphide in the gas phase does not greatly affect the initial rate of hydrogen uptake over either catalyst, although there is a more noticeable decrease in rate when *n*-heptane is used as the solvent than was found for ethanol. Therefore, this suggests that the solvent system does indeed contribute to the catalyst's resistance towards sulphur poisoning, and in this particular case, ethanol has proven to be a more useful solvent than *n*-heptane.

TABLE 3.13

Hydrogenation of 1-Hexadecene Over P-3A Ni in *n*-Heptane Compared with Hydrogenation in Ethanol

Conditions	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
EtOH[a]	4.85
n-heptane[a]	5.10 5.90
n-heptane containing 5 mg/l sulphur (*n*-butanethiol)[b]	2.50 1.90
n-heptane containing 21 mg/l sulphur (*n*-butanethiol)[b]	0.00
n-heptane in presence of 180 mg/l hydrogen sulphide in gas phase[c]	3.30

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 6.6 X 10^{-4} moles P-3A Ni (0.027 M). (Initial hydrogen pressure of 76 cm.) [b] Same as [a] except *n*-butanethiol added with substrate after generation of P-3A Ni. [c] Same as [a] except hydrogen sulphide introduced after addition of substrate and in presence of high partial pressure of hydrogen. Initial gas volume of 408 ml.

TABLE 3.14

Hydrogenation of 1-Hexadecene Over Raney Nickel in _n_-Heptane Compared with Hydrogenation in Ethanol

Conditions	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
EtOH[a]	2.80
_n_-heptane[a]	2.90
_n_-heptane containing 5 mg/l sulphur (_n_-butanethiol)[b]	0.84
_n_-heptane containing 21 mg/l sulphur (_n_-butanethiol)[b]	0.13
_n_-heptane in presence of 30 mg/l hydrogen sulphide in gas phase[c]	2.00
_n_-heptane in presence of 98 mg/l hydrogen sulphide in gas phase[c]	2.20

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over 6.0 X 10^{-4} moles Raney nickel (0.024 _M_). (Initial hydrogen pressure of 76 cm.) [b] Same as [a] except _n_-butanethiol added with substrate after preparation of Raney nickel - solvent mixture. [c] Same as [a] except hydrogen sulphide introduced after addition of substrate and in presence of high partial pressure of hydrogen. Initial gas volume of 408 ml.

3.3.6 Effect of the Presence of Oxygen on the Initial Rate of Hydrogen Uptake During the Liquid-Phase Hydrogenation of 1-Hexadecene Over P-3A Ni

In several non-poisoned reactions, rate measurements of the hydrogenation of 1-hexadecene over P-3 Ni, showed that the catalyst was initially inactive. In one particular case, shown in figure 3.12, it was found that over a period of time under reaction conditions, this inhibition was removed, as shown by a steady increase in the P-3 Ni activity towards hydrogenation of 1-hexadecene. This initial inhibition was thought to be due to the reversible adsorption of oxygen by the catalyst. A study of the effect of exposure of P-3A Ni to oxygen (air) on its resultant activity is listed in Table 3.15.

Apparently, although oxygen is adsorbed on P-3A Ni initially to poison the hydrogenation of alkenes , the forces holding the oxygen to the catalyst sites must be very weak, as the oxygen is displaced by alkene over a period of time, and nearly complete hydrogenation occurs.

3.4 Other Methods of Investigation of the Liquid-Phase Hydrogenation of Olefins Over P-3 Ni and P-3 Co

3.4.1 Surface Areas

Since catalytic activity depends to a considerable degree on surface area, it was felt advisable to compare the surface areas

Figure 3.12. Effect of the Presence of Oxygen During the Hydrogenation of 1-Hexadecene Over P-3 Ni[a]

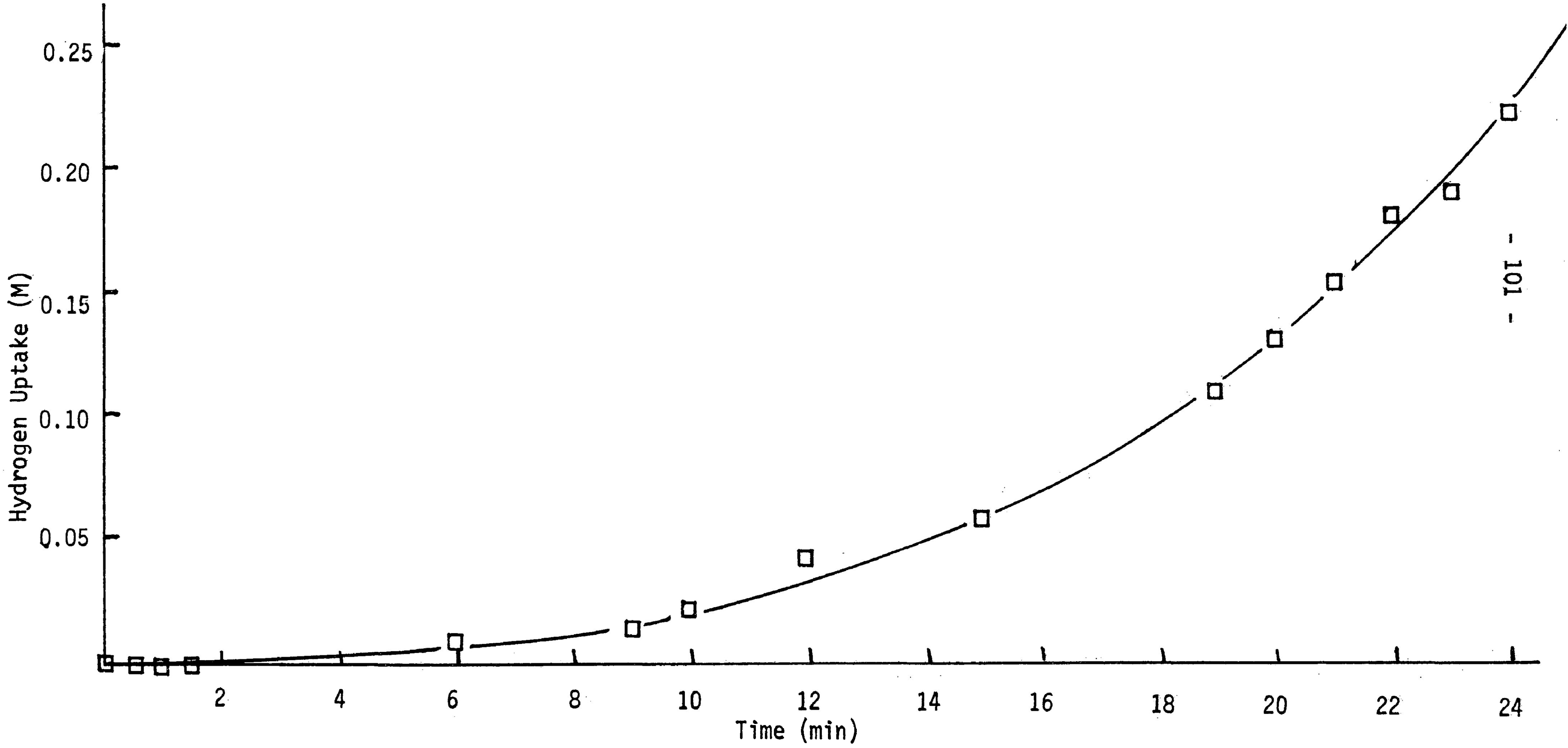


Figure 3.12. (cont)

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 5 X 10^{-4} moles P-3 Ni (0.02 M) in ethanol. (Initial hydrogen pressure of 76 cm.) Initial contamination with oxygen. The typical measured initial rate of hydrogen uptake for this reaction, in the absence of oxygen, is 7.4 X 10^{-2} M/min.

TABLE 3.15

Oxygen Resistance of P-3A Ni in the Hydrogenation of 1-Hexadecene[a]

Conditions	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})	
no air contact	2.82	
mixed in air fifteen minutes	2.83	
mixed in air two days	0.00	0.105 M hydrogen uptake/5 hr 0.460 M hydrogen uptake/28 hr
mixed in air fourteen days	0.00	0.025 M hydrogen uptake/4.25 hr 0.470 M hydrogen uptake/20.25 hr

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over 5.0-7.3 X 10^{-4} moles P-3A Ni (0.020-0.029 M) in ethanol. (Initial hydrogen pressure of 76 cm.)

of the various catalysts used in this study. The surface areas as determined by the BET method are given in Table 3.16. The limits of accuracy of the BET method are generally accepted as ±10% (97) of the measured area. The samples used for surface area measurements were prepared as indicated in the experimental section 2.5.2. It should be remembered that P-3A Ni and P-3 Ni are not identical and measurements of surface area on the former provide only a rough guide to the surface area of the latter prepared *in situ*. It is however, worth noting that although P-3A Ni is apparently more active than Raney nickel, it has a lower surface area.

3.4.2 Study of the Liquid-Phase Hydrogenation of 1-Octene Over P-3 Ni and P-3 Co in Ethanol Using Gas-Liquid Chromatography

During measurements of the hydrogen pressure changes during the hydrogenation of 1-octene or 1-hexadecene over P-3 Ni or P-3 Co, it was found that frequently the amount of hydrogen consumed upon apparent completion of hydrogenation was in excess of the amount expected on the basis that one mole of hydrogen hydrogenates one mole of olefin. Table 3.17 shows that irrespective of the initial catalyst concentration, for every mole of substrate initially present, 1.6 moles of hydrogen are consumed.

It was also found that in the absence of a substrate, hydrogen uptake does not occur for the first hour, *i.e.* in the time period of the initial rate studies discussed earlier. However, if the

TABLE 3.16

BET Surface Areas of Several Nickel Catalysts[a]

Catalyst	Surface Area (m^2/g)
Raney nickel	67 65
P-3A Ni	47
P-1 Ni (nickel chloride hexahydrate)	18 18
P-1 Ni (nickel acetate hydrate)	5
P-2 Ni (nickel chloride hexahydrate)	13 10
P-2 Ni (nickel acetate hydrate)[b]	---

[a] Catalysts prepared according to method outlined in Experimental section 2.5.2. [b] Precipitate in this preparation was too fine to collect for analysis.

TABLE 3.17

Hydrogen Uptake Dependence on Catalyst and/or Substrate Concentration

{P-3 Ni} (M)	{Substrate} (M)	Hydrogen Uptake (M)	Hydrogen Uptake* (M) per mole Substrate
0.02[a]	0.50	0.811	1.62
0.04[b]	0.50	0.807	1.61
0.023[c]	1.79	2.87	1.60

[a] Hydrogenation of 0.0125 moles 1-octene (0.5 M) over approximately 5 X 10^{-4} moles P-3 Ni (0.02 M) in ethanol. (Initial hydrogen pressure of 76 cm.) [b] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 1 X 10^{-3} moles P-3 Ni (0.04 M) in ethanol. [c] Hydrogenation of 0.045 moles 1-octene (1.79 M) over 5.8 X 10^{-4} moles P-3 Ni (0.023 M) in ethanol. *Measured to completion.

P-3 Ni or Raney nickel is left stirring in the presence of hydrogen for a long period of time, a near constant amount of hydrogen is consumed. Results are shown in Table 3.18. This hydrogen uptake, possibly by the catalyst itself, however would not interfere with initial measurements of hydrogen uptake.

In an attempt to explore hydrogen uptake in more detail, gas-liquid chromatographic examination of the reaction mixture was employed. A typical qualitative standard chromatograph indicating retention times is given in figure 3.13. The column effectively separates 1-alkenes from 2-alkenes, and also _cis_ and _trans_ isomers. A typical quantitative standard chromatograph is shown in figure 3.14. The blanks shown here were prepared separately from 1-octene, _n_-octane, and _cis-trans_ 2-octene to give 0.5 M solutions in ethanol. Figure 3.14 is a combination of three individual standard chromatographs. The peak areas for 1-octene, _n_-octane, and _cis-trans_ 2-octene were found to be 7.57, 7.56, and 7.48 cm^2 respectively. This shows that all three components come off the column equally well, and therefore quantitative yields can be measured.

Reaction products contained only 1-octene, _n_-octane , and/or _trans_ and _cis_ 2-octene. The ethanol on this particular column has a larger retention time than all of the products and thus does not interfere with the separation and estimation of the hydrocarbon components.

The gas-liquid chromatography results are summarized in Tables 3.19 through 3.25. All peak areas are standardised and can be directly compared.

TABLE 3.18

Uptake of Hydrogen by the P-3 Ni and Raney Nickel Systems in the Absence of Substrate[a]

{Catalyst} (M)	Hydrogen Uptake (M)
0.0165 P-3 Ni	0.1272 /one week
0.0171 P-3 Ni	0.0076 /70 min 0.1340 /20 hr
0.0221 Raney nickel	0.000 /45 min 0.1268 /17.25 hr

[a] P-3 Ni or Raney nickel stirred in ethanol (25 ml). (Initial hydrogen pressure of 76 cm.)

Figure 3.13. Standard Qualitative Gas-Liquid Chromatograph

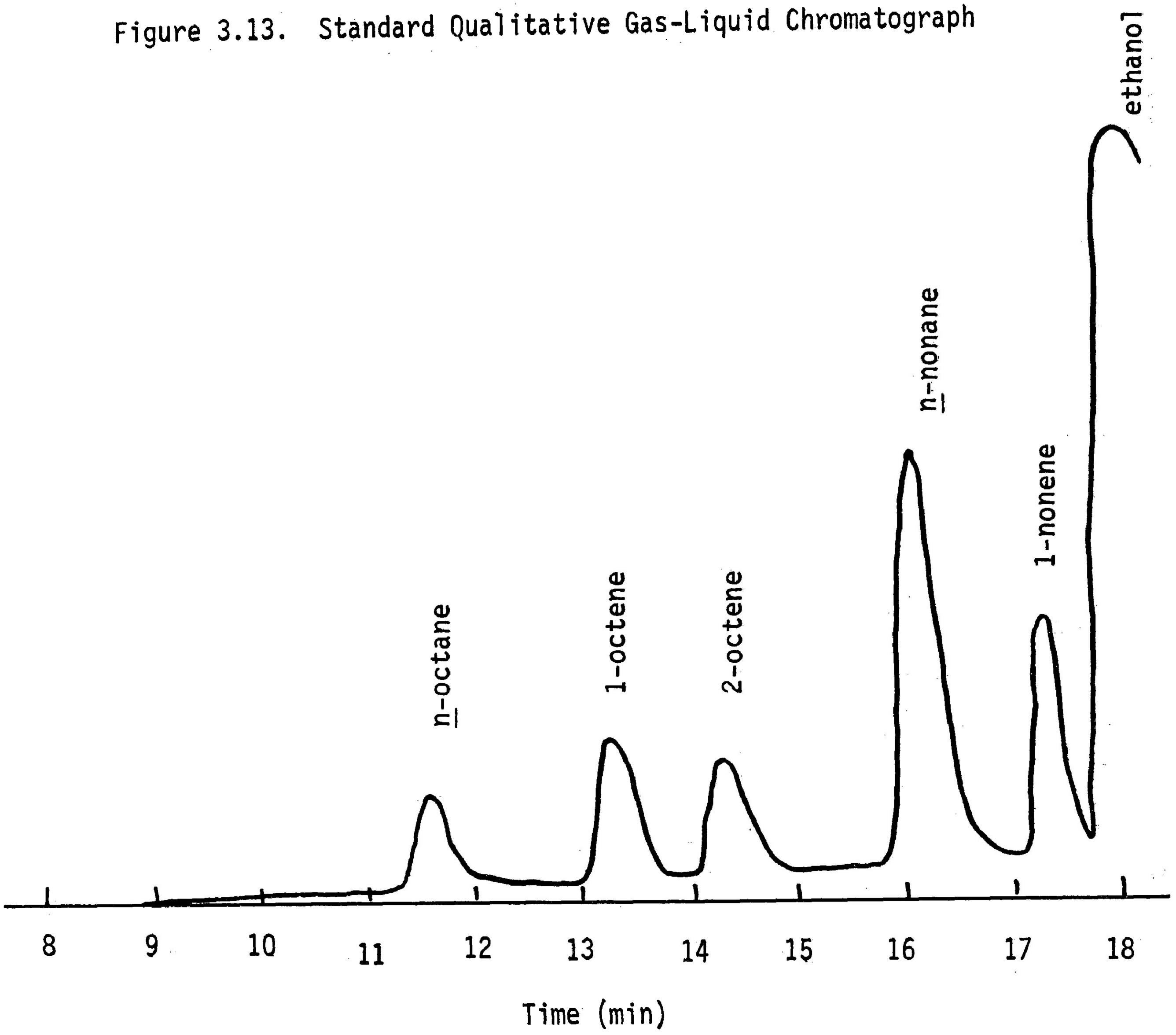
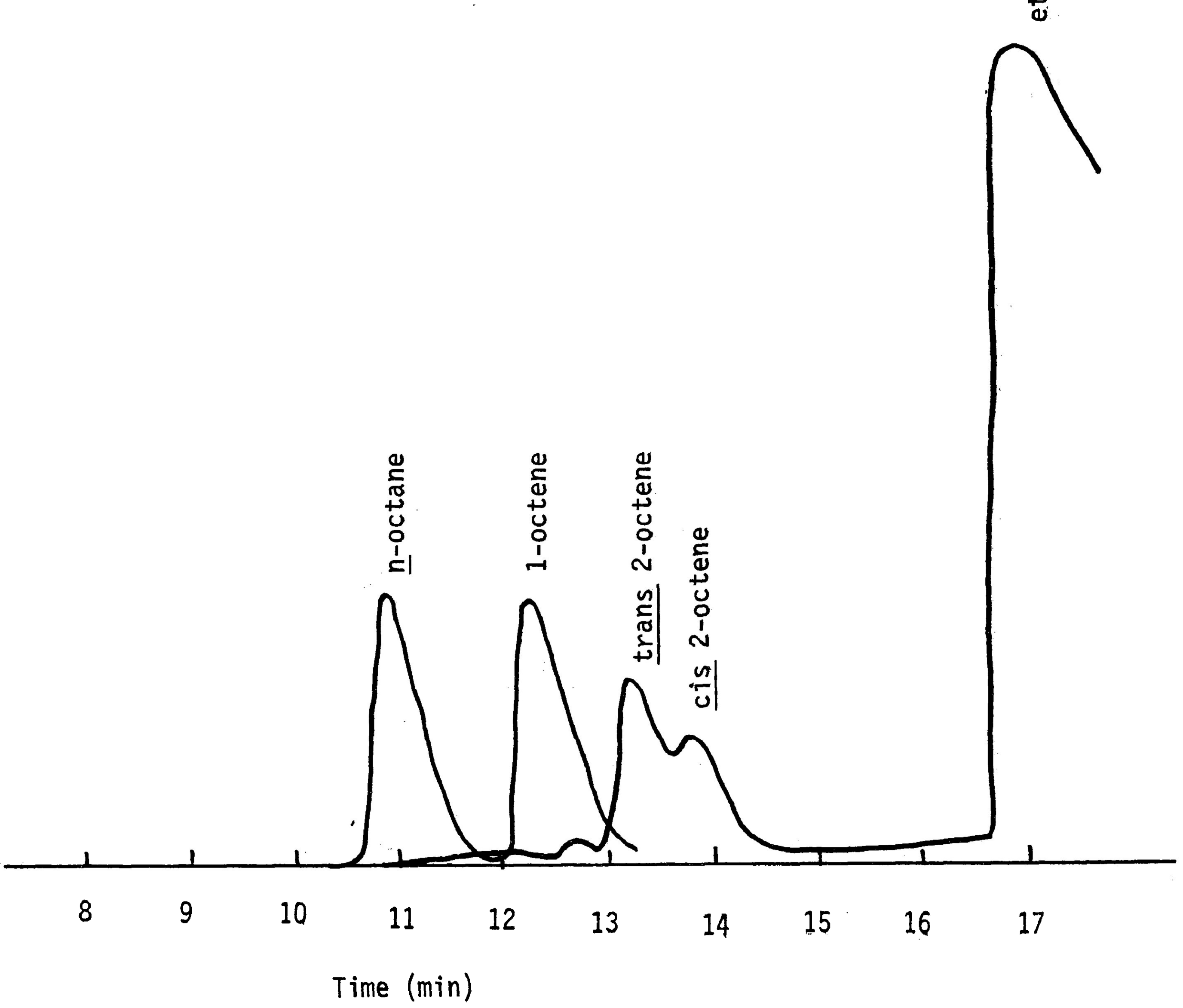


Figure 3.14. Standard Quantitative Gas-Liquid Chromatograph



GAS-CHROMATOGRAPHIC RESULTS

TABLE 3.19

Stirring 0.5 M 1-Octene Over 0.02 M P-3 Ni in Ethanol under Nitrogen for Ten Minutes[a] and Seventeen Hours[b] using an Initial Gas Volume of 328 ml and an Initial Nitrogen Pressure of 77 cm

	Area (Standardised) (cm^2)			% of total as expected from blank[c]		
	n-octane	1-octene	2-octene	*n*-octane	1-octene	2-octene
a	0.00	2.16	0.00	0.0	28.5	0.0
b	0.30	2.00	2.25	4.0	26.4	29.7

[c] 1-Octene blank of 7.57 cm^2.

TABLE 3.20

Stirring 0.5 M *cis-trans* 2-Octene Over 0.02 M P-3 Ni in Ethanol under Nitrogen for Ten Minutes[a] and Seventeen Hours[b] using an Initial Gas Volume of 328 ml

	Area (Standardised) (cm^2)				% of total as expected from blank[c]		
	n-octane	1-octene	2-octene		*n*-octane	1-octene	2-octene
			trans	*cis*			
a	0.00	0.00	2.10	1.20	0.0	0.0	43.9
b	0.00	0.00	3.05	2.20	0.0	0.0	70.5

[c] 2-Octene blank of 7.49 cm^2 (*trans* 4.3 cm^2, *cis* 3.19 cm^2).

TABLE 3.21

Hydrogenation of 0.5 M 1-Octene Over 0.02 M P-3 Ni in Ethanol using an Initial Gas Volume of 328 ml

Hydrogen Uptake (M)	Area (Standardised) (cm^2)			% of total as expected from blank[a]		
	_n_-octane	1-octene	2-octene	_n_-octane	1-octene	2-octene
0.125	0.47	1.90	0.47	6.2	25.1	6.2
0.250	1.17	1.44	0.86	15.5	19.0	11.4
0.375	2.44	0.00	1.93	32.2	0.0	25.5
0.500	4.99	0.00	1.84	65.9	0.0	24.3
0.625[b]	4.68	0.00	1.23	61.8	0.0	16.3
0.750	5.05	0.00	0.00	66.7	0.0	0.0
0.820	4.32	0.00	0.00	57.1	0.0	0.0

[a] 1-Octene blank of 7.57 cm^2. [b] After uptake of 0.5 M hydrogen, the hydrogen pressure was very low (approximately 10 cm) and, therefore, more hydrogen was introduced to the system at this point to bring the total pressure to 80 cm. Note: Initial hydrogen pressure of 77 cm.

TABLE 3.22

Hydrogenation of 0.5 M 1-Octene Over 0.02 M P-3 Ni in Ethanol using an Initial Gas Volume of 1132 ml

Hydrogen Uptake (M)	Area (Standardised) (cm^2)			% of total as expected from blank[a]		
	n-octane	1-octene	2-octene	*n*-octane	1-octene	2-octene
0.125	1.19	1.69	0.93	15.7	22.3	12.3
0.250	2.42	0.37	1.28	32.0	4.9	16.9
0.500	4.89	0.00	0.00	64.6	0.0	0.0

[a] 1-Octene blank of 7.57 cm^2.

TABLE 3.23

Hydrogenation of 1.0 M 1-Octene Over 0.02 M P-3 Ni in Ethanol using an Initial Gas Volume of 1132 ml

Hydrogen Uptake (M)	Area (Standardised) (cm^2)			% of total as expected from blank[a]		
	n-octane	1-octene	2-octene	*n*-octane	1-octene	2-octene
1.000	12.97	0.17	1.86	85.7	1.1	12.3

[a] 1-Octene blank of 7.57 cm^2.

TABLE 3.24

Hydrogenation of 0.5 M 1-Octene Over 0.02 M P-3 Co in Ethanol using an Initial Gas Volume of 328 ml

Hydrogen Uptake (M)	Area (Standardised) (cm^2)			% of total as expected from blank[a]		
	n-octane	1-octene	2-octene	*n*-octane	1-octene	2-octene
0.125	0.66	3.29	0.00	8.7	43.4	0.0
0.250	1.21	2.08	0.00	16.0	27.5	0.0
0.500	2.41	0.99	0.00	31.8	13.1	0.0
0.625	2.42	0.30	0.00	32.0	4.0	0.0

[a] 1-Octene blank of 7.57 cm^2.

TABLE 3.25

Hydrogenation of 0.5 M 1-Octene Over 0.02 M P-3 Ni or P-3 Co in Ethanol using an Initial Gas Volume of 328 ml, and in the Presence of 25 mg/l Sulphur in the Form of *n*-Butanethiol[a]

Hydrogen Uptake (M)	Area (Standardised) (cm^2)			% of total as expected from blank[b]		
	n-octane	1-octene	2-octene	*n*-octane	1-octene	2-octene
0.125[c]	1.02	4.03	trace	13.5	53.2	---
0.250[c]	1.00	1.67	0.50	13.2	22.1	6.6
0.500[c]	2.50	0.00	1.22	33.0	0.0	16.1
0.250[d]	1.76	3.47	0.00	23.3	45.8	0.0

[a] *n*-Butanethiol added with substrate *after* catalyst is generated. [b] 1-Octene blank of 7.57 cm^2. [c] P-3 Ni catalyst. [d] P-3 Co catalyst.

These results can briefly be summarized as follows:

a) the measured hydrogen uptake does not correspond directly to the formation of n-octane over P-3 Ni or P-3 Co and under normal conditions complete hydrogenation of 1-octene to n-octane does not occur,

b) 1-octene is strongly adsorbed initially on P-3 Ni,

c) in the presence or absence of hydrogen, 1-octene is isomerised to a mixture of cis and trans 2-octene over P-3 Ni, although the reverse reaction does not noticeably occur,

d) isomerisation of 1-octene to 2-octene does not occur over P-3 Co, and

e) the presence of n-butanethiol inhibits the initial production of 2-octene over P-3 Ni.

3.4.3 Thermogravimetric Analysis

An additional method of investigation was followed to help determine where the excess of hydrogen taken up during the hydrogenation of olefins over P-3 Ni was going. If the catalyst itself was incorporating more hydrogen into its lattice during the hydrogenation, then it was proposed that since the amount of hydrogen at the end of the reaction contained in the "used" P-3 Ni would be greater than before the reaction, i.e. by following the weight loss of P-3 Ni with increasing temperature, the "used" P-3 Ni should lose more weight than "unused" P-3 Ni as the extra hydrogen is given off. Figure 3.15 shows the results of this study.

3.5 Conclusion

The foregoing account contains many unexpected results which, for lack of complete information, could not be discussed in the appropriate subsection. However, the sum total of these results provides considerable information which may be used in formulating a mechanism for the hydrogenation of 1-alkenes over P-3 borides. This discussion is therefore recorded separately in the next chapter.

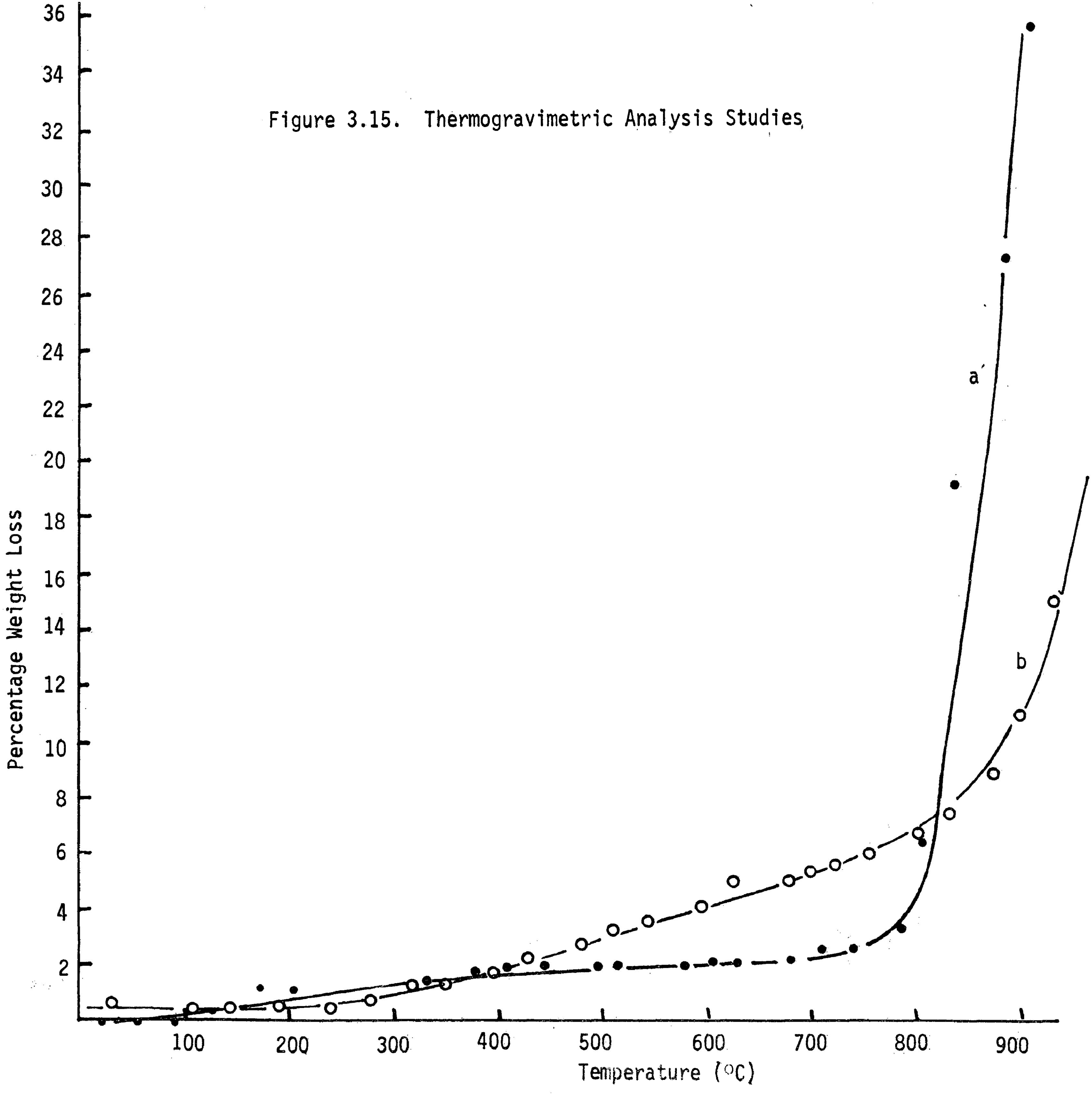


Figure 3.15. Thermogravimetric Analysis Studies

Figure 3.15. (cont)

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 5 X 10^{-4} moles P-3 Ni (0.02 M) in ethanol with a total hydrogen uptake of 0.82 M. The "used" P-3 Ni was filtered under nitrogen, washed with ether, weighed, and transferred to apparatus for analysis.(See experimental Section 2.5.3.2.). [b] 5 X 10^{-4} moles P-3 Ni (0.02 M) was prepared *in situ* in ethanol and the "unused" P-3 Ni was filtered under nitrogen, washed with ether, weighed, and transferred to apparatus for analysis. (See experimental Section 2.5.3.1.).

CHAPTER 4

DISCUSSION

4.1 Introduction

From the results reported in the previous chapter, a number of significant deductions can be made. These include the establishment of a probable kinetic rate law for the hydrogenation of alkenes, deductions regarding the relative activities of the various metal borides and Raney nickel reported in this thesis and the literature, conclusions regarding the degree of resistance of P-3 Ni and Co borides towards sulphur poisoning and establishment of a possible mechanism for the hydrogenation process. These points are discussed more fully in the following sections.

4.2 Summary of the Hydrogenation Study

4.2.1 Kinetics of Hydrogenation of Alkenes by P-3 Ni and P-3 Co

The hydrogenation results in the absence of poisoning agents presented in Chapter 3 may be summarised as follows:

a) At a given catalyst and substrate concentration the initial rate of hydrogen uptake is a linear function of the hydrogen pressure.

b) Under the conditions normally used in the kinetic experiments, the initial rate of hydrogen uptake is independent of both catalyst and substrate concentrations; any effect of the latter is only observed at relatively low concentrations.

c) Under the conditions normally used in the kinetic experiments the initial rate of hydrogen uptake is approximately 1.7 times faster with P-3 Ni than with P-3 Co, the comparison being based on the same concentration (dispersed amount) of the metal.

A number of reactions of a similar type to that in the present work have been described in terms of Langmuir-Hinshelwood kinetics (68) and these will be mentioned again later. The model assumes that both reactants are adsorbed on the catalyst surface and the rate-determining step in the process is the surface reaction. In such circumstances the rate of reaction $(-\frac{dC}{dt})$ is given by,

$$-\frac{dC}{dt} = \frac{k\, K_a K_b C_a C_b}{(1 + K_a C_a + K_b C_b)^2} \qquad \{16\}$$

where k is the rate constant for the reaction, C_a and C_b are the concentrations of the reactants and K_a and K_b are repsectively the adsorption equilibrium constants. In terms of the present work the concentration of one of the reactants, the hydrogen, has been measured in terms of pressure in the gas phase. If we assume that the hydrogen used in the reaction arrives at the catalyst surface via the solution, then its concentration, designated C_b, can be approximated by

$$C_b = \alpha P_{H_2} \qquad \{17\}$$

where α is a constant, essentially the solubility constant at the particular temperature. However, with the rapid agitation of the reaction there is the possibility that the hydrogen is transferred to the catalyst directly from the gaseous phase. In this case

$$C_b = P_{H_2} \tag{18}$$

would apply. In either event, C_b is proportional to the hydrogen pressure. Equation {16} can be re-written as

$$\frac{-dC}{dt} = \frac{k\, K_{alk} K'_{H_2} C_{alk} P_{H_2}}{(1 + K_{alk}C_{alk} + K'_{H_2}P_{H_2})^2} \tag{19}$$

where K_{alk} and C_{alk} refer to the alkene.

The chromatography results indicate that the alkene is strongly adsorbed on the catalyst and in these circumstances,

$$K_{alk}C_{alk} \gg 1 + K'_{H_2}P_{H_2} \tag{20}$$

Hence equation {19} becomes

$$\frac{-dC}{dt} = k\ \frac{K'_{H_2}P_{H_2}}{K_{alk}C_{alk}} = k''\ \frac{P_{H_2}}{C_{alk}} \tag{21}$$

The rate is therefore directly proportional to hydrogen pressure as is observed experimentally but is inversely proportional to the alkene concentration which has not been found to be the case under normal conditions in the present study. Additionally, the model as given above assumes non-dissociative adsorption of hydrogen.

An alternative approach is to consider the reaction in terms of a Rideal-Eley mechanism (98). This model assumes that the reaction is between an adsorbed reactant and another non-adsorbed (or physically adsorbed) reactant. In the terminology given earlier the rate equation would be

$$\frac{-dC}{dt} = \frac{k\ K_{alk}c_{alk}P_{H2}}{(1 + K_{alk}C_{alk})} \tag{22}$$

With the assumption of strong adsorption of alkene as used previously, equation {22} becomes

$$\frac{-dC}{dt} = kP_{H_2} \tag{23}$$

Equation {23} is consistent with the observed kinetics. Moreover equation {22} would explain the deviations observed at low substrate concentrations. If the hydrogen pressure is constant equation {22} becomes

$$\frac{-dC}{dt} = \frac{k'\ K_{alk}C_{alk}}{(1 + K_{alk}C_{alk})} \tag{24}$$

At low substrate concentrations, $(1 + K_{alk}C_{alk})$ would approach unity and equation {24} becomes

$$-\frac{dC}{dt} = k'K_{alk}C_{alk} \qquad \{25\}$$

and hence rate is dependent on substrate concentration as is observed in the present study. It is important to note however that although the present results are consistent with a Rideal-Eley mechanism. it is not proof that this mechanism is the operative one in this reaction.

The results of this present study then are apparently in marked contrast to those found by Brown (17) where it was suggested that hydrogenation of terminal olefins over P-2 Ni proceeds by a process which is first-order in substrate indicating a weak adsorption of the alkene on the P-2 Ni surface. Also Kishida and coworkers (69) interpreted the hydrogenation of ketones over nickel boride in terms of the Langmuir-Hinshelwood mechanism with the assumption that the catalyst surface is fully covered with both adsorbed hydrogen and adsorbed ketone during the reaction. This again, is in contrast to the Rideal-Eley mechanism proposed in the present study for the hydrogenation of alkenes over P-3 Ni boride.

It is of interest to note that kinetic studies by Tverdovskii and Tupitsyn (57) of the hydration of $PhNO_2$ using nickel boride (Paul's type (5)) or skeletal nickel, led these authors to conclude that the properties of the active surfaces on both catalysts are the same.

4.2.2 Comparison of the Rate of Hydrogen Uptake During Hydrogenation of Substrates Over the Several Metal Borides Studied

In addition to the results recorded in the previous chapter, several other observations and deductions have been made and these are discussed in this and subsequent sections.

The catalysts are compared on the basis of the activity measured for a certain initial number of moles of metal used in the preparation of the catalyst. Table 4.1 compares the "normalized" catalyst activities on the basis that the rate of hydrogen uptake during the hydrogenation of 1-hexadecene over P-3 Ni is arbitarily assigned the value of unity. Again, because more hydrogen than is required for hydrogenation is taken up during hydrogenations with P-3 Ni, this type of comparison is a little superficial. This point will be discussed later.

Under similar reaction conditions, partially hydrogenated P-3 Ni has been shown to be three times more active in terms of rate of hydrogen uptake than high activity Raney nickel, five times more active than P-1 Ni prepared from either nickel acetate or nickel chloride, and is 1.4 and 20 times more active than P-2 Ni prepared from nickel acetate or nickel chloride respectively. P-3 Ni has similar activity to Hawthorne's catalyst (P-3') as long as the latter is not washed with water and/or dried. The activity of the dried catalyst (P-3A) for hydrogenation of 1-hexadecene cannot be

TABLE 4.1

Hydrogenation of 1-Hexadecene Over Several Heterogeneous Nickel Catalysts[a]

Catalyst	Relative Initial Rate of Hydrogen Uptake[b]
P-3 Ni	1.00
Hawthorne's catalyst (P-3' Ni)	0.92
P-3A Ni	0.48
P-3" Ni	0.21
P-2 Ni (nickel acetate)	0.71
P-1 Ni (nickel acetate)	0.26
P-1 Ni (nickel chloride)	0.16
P-2 Ni (nickel chloride)	0.05
Raney nickel	0.30

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over several nickel catalysts (see Table 3.4 for amount of catalyst used) in ethanol. (Initial hydrogen pressure of 76 cm.) [b] Rates have been normalised by taking the initial rate of hydrogen uptake for 1-hexadecene over P-3 Ni catalyst as unity.

increased by stirring the catalyst under hydrogen for one hour prior to the reaction. Therefore, the preparative method required to produce the most active nickel boride for hydrogenation of 1-hexadecene, so far studied, is to add a mixture of nickel chloride and sodium borohydride in the molar ratio of 1:4 to oxygen-free ethanol under hydrogen or nitrogen, and stir until hydrogen evolution is complete. The black, colloidal precipitate so produced is the partially hydrogenated P-3 Ni boride of proposed formula $(Ni_2B)_2.H_3$.

This catalyst is slightly more active if the reaction is carried out in ethanol rather than in n-heptane. The initial rate of hydrogen uptake during hydrogenation of terminal alkenes over P-3 Ni was found to be strongly chain length dependent and to increase in the order (Table 4.2):

1-hexene $\lll$ 1-octene $\approx$ 1-decene $<$ 1-hexadecene

Similarly for P-3 Co the relative order is (Table 4.3):

1-octene $<$ 1-hexadecene

This is somewhat similar to the order found for P-1 Ni (12) although the relative ratios of reaction rates are quite different. Thus, the order of initial rates of hydrogen uptake over P-1 Ni is:

1-pentene (1.0) $<$ 1-hexene (1.3) $\approx$ 1-octene (1.3) $>$ 1-dodecene (1.0)

P-3 Ni is inactive towards reduction of cyclohexene as had been previously found by Brown (16,17) for P-2 Ni. However, P-1 Ni is active for this hydrogenation (11,12) in addition to that of other cycloalkenes and the order of rates of reaction is:

1-octene $>$ cyclopentene $>$ cyclohexene $\approx$ cyclooctene

TABLE 4.2

Hydrogenation of Representative Substrates Over Partially Hydrogenated P-3 Nickel Boride[a]

Substrate	Relative Initial Rate of Hydrogen Uptake[b]
1-hexene	0.15
1-octene	0.88
1-decene	0.85
1-hexadecene	1.00
allyl alcohol	0.72
acetone	0.08
acetonitrile	0.09
cis-_trans_ 2-octene	0.65
trans 2-octene	0.55
benzene	0.00
cyclohexene	0.00

[a] Hydrogenation of 0.0125 moles substrate (0.5 M) over P-3 Ni (see Table 3.1 for amount of catalyst used) in ethanol. (Initial hydrogen pressure of 76 cm.) [b] Rates have been normalised by taking the initial rate of hydrogen uptake for 1-hexadecene over P-3 Ni as unity.

TABLE 4.3

Hydrogenation of Representative Olefins Over Partially Hydrogenated P-3 Cobalt Boride[a]

Substrate	Relative Initial Rate of Hydrogen Uptake [b]
1-octene	0.68
1-hexadecene	0.75
cis-trans 2-octene	0.03
trans 4-octene	0.07

[a] Hydrogenation of 0.0125 moles substrate (0.5 M) over 4.3 X 10^{-4} moles P-3 Co (0.0171 M) in ethanol. (Initial hydrogen pressure of 76 cm.) [b] Rates have been normalised by taking the initial rate of hydrogen uptake for 1-hexadecene over P-3 Ni as unity.

This present study has shown that P-3 Ni is also very active for the hydrogenation of internal olefins. The relative rates of hydrogen uptake are:

1-octene (1.0) > *cis-trans* 2-octene (0.74) > *trans* 4-octene (0.63)

P-3 Co, however, is much more selective and the relative rates of hydrogen uptake are:

1-octene (1.0) ≫ *trans* 4-octene (0.1) > *cis-trans* 2-octene (0.04)

Brown (16,17) reported that P-2 Ni is very selective towards the hydrogenation of terminal olefins and some relative rates of hydrogenation are:

1-pentene (1.0) ≫ *cis* 2-pentene (0.075) > *trans* 2-pentene (0.025)

This difference between P-3 Ni and P-3 Co is also indicated by the gas-liquid chromatographic studies. Thus, under normal conditions, P-3 Ni causes rapid isomerisation of approximately 25% of the initial 1-octene to *cis* and *trans* 2-octene whereas the P-3 Co system shows no evidence of isomerisation of the 1-octene during the hydrogenation process. In this connection, Brown (11,12,17) reported that gas-liquid chromatographic analysis of the reaction mixture during hydrogenation of 1-pentene over Raney nickel, P-1 Ni, and P-2 Ni show a maximum degree of isomerisation of 1-pentene to *trans* and *cis* 2-pentene of 24%, 12,5%, and 2.8% respectively. Therefore, P-3 Ni seems to have greater isomerisation tendencies than either P-1 Ni or P-2 Ni if these results can be directly compared given the somewhat different hydrogenation conditions mentioned in the previous chapter.

It seems that although the P-3 Co is slightly less active than P-3 Ni, it appears to be more selective and the alkene hydrogenation product is free from undesirable isomerisation side products.

This study has also shown that P-3 Ni is an active catalyst for the reduction of carbonyl and nitrile functional groups. It was earlier reported (20) that once C-C double bonds are hydrogenated over P-2 Ni, the slower reduction of the C-O bond of the carbonyl function occurs. Reduction of the C-N bond of nitriles has been reported to occur over P-1 Ni, P-2 Ni, and P-2 Co (21,23) to yield primary amines although the catalyst is more selective than the corresponding metal catalyst, and normally C-C double bonds are more susceptible to hydrogenation than C-N triple bonds.

P-3 Ni, like P-1 Ni (12), is inactive towards reduction of the aromatic ring system of benzene.

4.23 Surface Areas

Although Raney nickel is less active than P-3 Ni, it has a larger surface area when both are in a dried state (Table 3.16). However, in an ethanol mixture, P-3 Ni is in a highly dispersed state and the surface area under these conditions is probably much greater than that measured. It has already been shown that the dried catalyst P-3A Ni is considerably less active than the P-3 Ni prepared in situ, and therefore the two are probably quite different in composition and/or structure.

Gas-liquid chromatographic data show that within a very short reaction time, 0.375 M substrate is adsorbed on 0.02 M P-3 Ni. This is a huge amount of substrate to be adsorbed relative to the amount of catalyst present and suggests a much greater surface area than that measured for P-3A Ni. P-1 Ni and P-2 Ni have much smaller surface areas than even P-3A Ni which is consistent with their lower activities.

4.3 Summary of Poisoning Study

This study has shown, surprisingly, that under the reaction conditions described earlier, P-3 Ni, P-3 Co, and Raney nickel are extremely resistant to sulphur poisoning (Tables 3.6, 3.7, and 3.8). Even in the presence of 800 mg/l hydrogen sulphide in the gas phase, the initial rate of hydrogen uptake during hydrogenation of 1-hexadecene only decreases by approximately 20% (relative to the unpoisoned reaction) with P-3 Ni and by 46% with Raney nickel. This decrease is probably mainly due to the lower initial partial pressure of hydrogen itself since the kinetic study shows that the initial rate of hydrogen uptake is dependent on the initial hydrogen pressure. It is important to note, however, that although the initial rate of hydrogen uptake is considerable, the total amount of hydrogen taken up in the first ten minutes of the reaction decreases with an increase in initial partial pressure of hydrogen sulphide. Thus, in the presence of 800 mg/l hydrogen sulphide, only 55% of the normal hydrogen uptake over P-3 Ni occurs in the first ten minutes of reaction, and only 38% of the normal hydrogen uptake over Raney nickel occurs in the first ten minutes. Also, if the catalyst is stirred in the presence of hydrogen sulphide and the absence of hydrogen for only fifteen minutes, the P-3 Ni is totally and irreversibly poisoned by only 60 mg/l of hydrogen sulphide. Raney nickel is similarly irreversibly poisoned by 30 mg/l of hydrogen sulphide.

These results show that the resistance of these catalysts towards gaseous hydrogen sulphide poisoning is critically dependent upon the partial pressure of hydrogen. By keeping the hydrogen partial pressure high (greater than 60 cm) as shown in figure 3.7, complete hydrogenation can be obtained in the presence of 30 mg/l hydrogen sulphide. There is probably competition between hydrogen sulphide and hydrogen for the catalyst sites and, when present in larger amounts, the hydrogen can prevent the hydrogen sulphide from reaching or remaining on the surface for a sufficient time to poison the catalyst's active sites.

P-3 Co is also very resistant to hydrogen sulphide poisoning and in the presence of 200 mg/l hydrogen sulphide, the initial rate of hydrogen uptake, and the total amount of hydrogen consumed in the first ten minutes of reaction is similar to that occurring in the unpoisoned reaction.

Therefore, in a dynamic industrial system where reactant concentrations, including hydrogen, are kept high the effect of even considerable concentrations of hydrogen sulphide in the gas phase on the initial rate of hydrogen uptake and on the overall hydrogen uptake should be very low.

Thus, both P-3 Ni and P-3 Co have been shown not only to be more active than high activity Raney nickel, but also more resistant to poisoning by hydrogen sulphide.

P-3 Ni, P-3 Co, and Raney nickel are also extremely resistant to poisoning by n-butanethiol present in the reaction mixture. For the hydrogenation of 1-octene and 1-hexadecene over P-3 Ni, the plots of initial rate of hydrogen uptake vs. mg/l (ppm) sulphur (figure 3.8) show curves (a and c) whose slopes are small initially but fall off more rapidly with increasing n-butanethiol concentration to approximately zero hydrogen uptake at 46.0 and 52.0 mg/l sulphur respectively. It would appear then that P-3 Ni is not only more active towards hydrogenation of 1-hexadecene than 1-octene, but the former reaction is also more resistant to sulphur poisoning by liquid-phase organosulphur contaminants. A similar plot for Raney nickel, figure 3.8, shows a linear decrease in initial rate of hydrogen uptake with increasing n-butanethiol concentration falling to zero hydrogen uptake at 27 mg/l sulphur. In short, high activity Raney nickel is not only much less active than P-3 Ni (one-third the activity at 0 mg/l sulphur),but is also much less resistant to n-butanethiol poisoning.

Although P-3 Co is slightly less active for hydrogenation of

1-hexadecene as compared with P-3 Ni, figure 3.9 shows that the initial rate of hydrogen uptake of this reaction is virtually unaffected by the 50 mg/l sulphur (as n-butanethiol) which poisons completely and irreversibly the reaction over P-3 Ni. For higher concentrations of n-butanethiol, the rate of hydrogen uptake decreases steadily, falling to zero uptake at 90 mg/l sulphur. For both P-3 Co and P-3 Ni, the resistances towards n-butanethiol poisoning are dependent on whether the catalyst is generated in the presence or absence of this sulphur poison. Gas-liquid chromatographic analyses of the product mixture at various stages in the reaction indicate that the presence of n-butanethiol hinders the initial adsorption of substrate by P-3 Ni and P-3 Co which would be expected since the poison blocks catalyst sites. In the case of P-3 Ni, the presence of n-butanethiol also suppresses the initial formation of 2-octene. The poison appears to affect isomerization sites in preference to hydrogenation sites.

More quantitatively meaningful studies were also made in the range where the initial rate of hydrogen uptake during hydrogenation of 1-hexadecene over P-3 Ni is dependent on hydrogen pressure, catalyst concentration, and substrate concentration. Under these conditions P-3 Ni, P-3 Co, and Raney nickel are all much less resistant to n-butanethiol poisoning. In the absence of catalyst poison, P-3 Ni and P-3 Co have approximately the same activities, however Raney nickel is 80% less active than either of the P-3 systems.

Figures 3.10 and 3.11 show that the initial rates of hydrogen uptake during hydrogenation of 1-hexadecene over P-3 Ni and Raney nickel drop to about zero at approximately 5.5 and 4.5 mg/l sulphur respectively (in form of n-butanethiol), but it should be noted that, although the initial rate of hydrogen uptake is very slow, even at 11 mg/l sulphur P-3 Ni is still active for "complete" hydrogenation of the substrate. For hydrogenation over P-3 Co, the initial rate of hydrogen uptake drops to zero at 26.5 mg/l sulphur. As in the previously discussed hydrogenations, P-3 Co has shown its superior resistance to sulphur poisoning.

A report by R. Baltzly (72) discussed the reaction kinetics of poisoning of liquid-phase hydrogenations in the concentration dependent region. A convenient method of comparing the relative resistance of several catalysts towards poisoning is through a ratio of the adsorption coefficient of the catalyst poison (γ) to the adsorption coefficient of the substrate (α) (as discussed earlier in the introduction chapter). From figures 3.10 and 3.11, it is possible to determine the amount of sulphur necessary to reduce the initial rate of hydrogen uptake by one-half. Table 4.4 shows these results for poisoning with n-butanethiol. The ratios of γ/α clearly show that the strengths of adsorption of n-butanethiol on P-3 Ni and Raney nickel are very similar, however, as expected, n-butanethiol is far less strongly held on P-3 Co.

The present study also shows that P-3 Ni and Raney nickel are far less resistant to sulphur poisoning by hydrogen sulphide or n-butanethiol when the reaction is carried out in n-heptane rather

TABLE 4.4

γ/α Ratios for Poisoning of P-3 Ni, P-3 Co, and Raney Nickel by *n*-Butanethiol

Catalyst	{1-Hexadecene} (M)	Half Initial Rate (M/min)	{Sulphur} at Half Initial Rate (M)	γ/α
P-3 Ni	0.139	1.56×10^{-2}	6.7×10^{-5}	2.07×10^{3}
Raney Nickel	0.139	0.29×10^{-2}	6.3×10^{-5}	2.20×10^{3}
P-3 Co	0.139	1.73×10^{-2}	42.0×10^{-5}	0.33×10^{3}

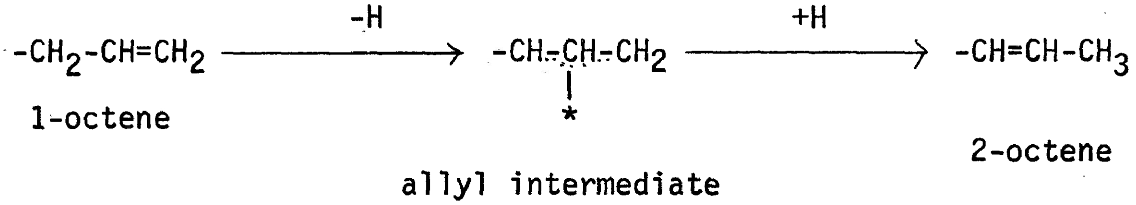
than in ethanol (Tables 3.13 and 3.14). In terms of both catalyst activity and catalyst resistance to sulphur poisoning, ethanol is the better solvent system. It appears that the solvent polarity has a great effect on the catalyst's resistance to sulphur poisoning.

4.4 Summary of Quantitative Hydrogenation Studies

Returning to unpoisoned hydrogenations in the context of gas-liquid chromatographic studies of the hydrogenation mixture at various stages, investigation of the reaction mixture during hydrogenation of 1-octene over P-3 Ni presented several interesting results. In the absence of hydrogen, within ten minutes, 0.36 M of 1-octene is strongly adsorbed by the catalyst indicating an enormous catalyst surface area, much greater than that measured for the derivative P-3A Ni. Only 0.14 M substrate remains in the solution. After being allowed to stand at room temperature for seventeen hours, the reaction mixture contains a small amount of _n_-octane (0.02 M), still approximately the same amount of 1-octene (0.132 M), and a considerable amount of 2-octene (0.149 M) thus leaving 0.199 M 1-octene unaccounted for but probably adsorbed on the catalyst.

It appears that since the 1-octene concentration in the mixture remains constant, the sites used for isomerisation of 1-octene to 2-octene are not recoverable - _i.e._ after isomerisation they are inactive and do not take up more 1-octene from solution.

There are at least two possibilities for the isomerisation reaction intermediate; (1) an allyl type of system , or, (2) an alkyl type of system. The former type involves the formation of a chemisorptive bond (with alkyl C-H cleavage) between the catalyst and the π-bonding system of the alkene, whereas the latter requires the uptake of hydrogen to form a partially hydrogenated intermediate. However, in this present study, it was found that the total amount of isomerisation which occurs over P-3 Ni in the absence or presence of hydrogen is the same. This seems consistent with an "allyl" reaction intermediate for isomerisation as shown below.

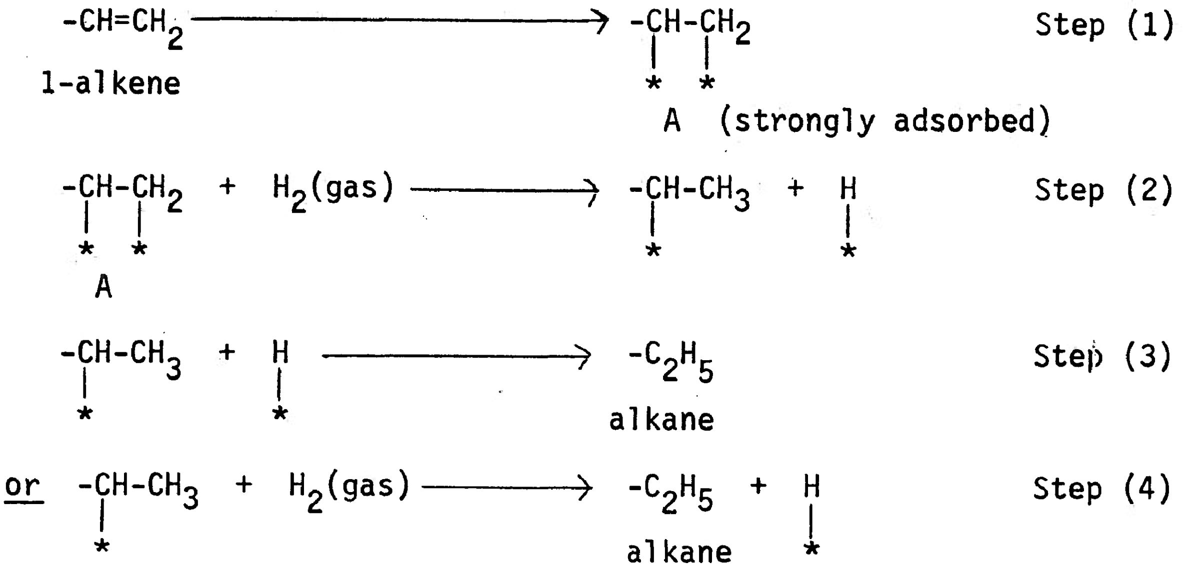


$$-CH_2-CH{=}CH_2 \xrightarrow{-H} -CH\cdots\underset{*}{\underset{|}{CH}}\cdots CH_2 \xrightarrow{+H} -CH{=}CH-CH_3$$

It should also be noted that if the starting substrate is 2-octene and this is stirred in the absence of hydrogen, <u>no</u> isomerisation to 1-octene occurs, thus indicating that the reverse reaction is much more difficult. Evidence for this also comes from the analyses of the reaction at various stages in the presence of hydrogen which show no evidence that the 2-octene formed reacts further.

If, therefore, the P-3 Ni used (0.02 M) is capable of producing 0.12-0.15 M 2-octene which does not react further, and also if initially there is 0.5 M 1-octene present, then the maximum amount of *n*-octane that could be produced is 0.35-0.38 M. Table 3.21 shows that this indeed is the maximum amount of *n*-octane produced under the conditions used for these hydrogenations. Furthermore, if the same amount of P-3 Ni is used, but there is initially 1.0 M 1-octene present, then one would expect the maximum amount of n-octane produced to be 0.85-0.88 M. Table 3.23 shows that actually 0.86 M n-octane was measured. It would appear that the sites used for isomerisation are different from those used for hydrogenation and that the former may be nickel metal sites.

The evidence presented earlier has shown that the catalyst only "takes up" hydrogen in addition to that used for hydrogenation of the 1-alkene within a reasonable time (less than one hour) when the substrate is present. No such uptake occurs in the absence of alkene. This suggests that the formation of a substrate-catalyst intermediate must be the first step in the hydrogenation. The following scheme is therefore suggested.



$$\underset{\text{1-alkene}}{-\mathrm{CH{=}CH_2}} \longrightarrow \underset{\text{A (strongly adsorbed)}}{-\underset{*}{\mathrm{CH}}-\underset{*}{\mathrm{CH_2}}} \qquad \text{Step (1)}$$

$$\underset{\text{A}}{-\underset{*}{\mathrm{CH}}-\underset{*}{\mathrm{CH_2}}} + \mathrm{H_2(gas)} \longrightarrow -\underset{*}{\mathrm{CH}}-\mathrm{CH_3} + \underset{*}{\mathrm{H}} \qquad \text{Step (2)}$$

$$-\underset{*}{\mathrm{CH}}-\mathrm{CH_3} + \underset{*}{\mathrm{H}} \longrightarrow \underset{\text{alkane}}{-\mathrm{C_2H_5}} \qquad \text{Step (3)}$$

$$\underline{\text{or}}\quad -\underset{*}{\mathrm{CH}}-\mathrm{CH_3} + \mathrm{H_2(gas)} \longrightarrow \underset{\text{alkane}}{-\mathrm{C_2H_5}} + \underset{*}{\mathrm{H}} \qquad \text{Step (4)}$$

As long as 1-octene is present in solution, the concentration of A will remain fairly constant, and step (2) will be rate-determining.

The rate of reaction (r) is given by;

$$r = k_1 \{A_s\} P_{H_2} \qquad \{26\}$$

$$= k_2 P_{H_2} \quad \text{when } \{A_s\} \text{ is constant} \qquad \{27\}$$

where A_s is the surface concentration of A.

This would mean that at high substrate concentrations, the rate of reaction would only be dependent on the hydrogen pressure since hydrogen is taken directly from the gas phase. This indeed was observed in the kinetic study. If the concentration of hydrogen is large as compared to the amount required to hydrogenate the substrate present, then steps (2) and (4) would be predominant and thus two moles of hydrogen would be taken up presumably directly from the gas phase for every mole of n̲-octane formed. If the concentration of H_2(gas) markedly decreases, then the slower step (3) could occur. It follows that further production of n̲-octane could occur without further uptake of gaseous hydrogen. This step would be slow since, at this time, the sites holding these activated species would probably be quite far apart and one species would have to diffuse close to the other in order for a reaction to occur. These hydrogen atoms would be strongly chemisorbed through a bond-like attachment. In order to remove such atoms it would require sufficient energy to break this bond and in so doing it would be possible for the hydrogen to react chemically with free boron. If this assumption is true, it would be expected that since there would be no such hydrogen atoms adsorbed initially (but numerous such species at the end of the reaction) the major difference between "used" and "unused" catalyst would be in the presence of these strongly adsorbed hydrogen species in the former. Thermogravimetric studies indeed indicate that the only distictive difference between "used" and "unused" P-3 Ni, is that the former exhibits a much greater weight loss above 800°C than does the latter.

Numerous cases studied in the present investigation have shown that more than one mole of hydrogen is taken up per mole of substrate initially present. This is in direct contrast to a report by Brown (17) which stated that using P-2 Ni, the total hydrogen uptake is within ±2% of that theoretically calculated. Before this author's ideas on the hydrogenation mechanism had been clarified, several experiments were done in this present study in order to try to determine for what this additional hydrogen was being used. Table 3.17 shows that there are 1.6 moles of hydrogen taken up for every mole of substrate present initially. This indicates that the substrate itself is likely the factor that determines the amount of hydrogen consumed and this would be in agreement with the mechanism for hydrogenation proposed above.

It was originally thought that possibly the catalyst "took up" hydrogen during the reaction through some kind of surface conditioning by the alkene. However, it was found that doubling the amount of catalyst present has no effect on the total hydrogen uptake. In the absence of substrate, however, there is significant hydrogen uptake, but this only occurs over a very long period of time. It was also thought that possibly the extra hydrogen taken up is being used in the catalytic reaction of cracking of the saturated or unsaturated hydrocarbons. However, gas-chromatographic analysis of the reaction liquid, and mass spectral analysis of the gaseous product show no evidence of smaller than expected hydrocarbons. All of this information is consistent with the mechanism proposed above.

4.5 Conclusions

This research project has clearly shown that partially hydrogenated P-3 nickel boride is an extremely active heterogeneous liquid-phase catalyst for the hydrogenation of terminal alkenes, having superior activity to all previously studied liquid-phase nickel boride catalysts, and also to high activity Raney nickel. P-3 Ni is also, surprisingly, highly active towards the hydrogenation of internal olefins, and is noticeably active for reduction of carbonyl and nitrile functions.

Kinetic studies and gas-liquid chromatographic measurements of the reaction mixture have led to the proposal of two reaction schemes, one for hydrogenation and the other for isomerisation over P-3 Ni.

The hydrogenation of 1-alkenes over P-3 Ni have been shown to have great resistance towards poisoning by either gaseous or liquid sulphur poisons.

The closely related partially hydrogenated P-3 cobalt boride has also been shown to be an extremely active liquid-phase catalyst for hydrogenation of terminal akenes with activity comparable to P-3 Ni. It is however, much more selective than P-3 Ni being only slightly active towards hydrogenation of internal olefins. Furthermore, hydrogenation of terminal alkenes over P-3 Co is not accompanied by isomerisation. P-3 Co was also shown to have even greater resistance to sulphur poisoning that P-3 Ni.

It appears, therefore, from this present study, that although P-3 Ni is an excellent hydrogenation catalyst in comparison with Raney nickel and other nickel borides, P-3 Co may be even more useful industrially since the hydrogenation is not accompanied by undesirable side reactions such as isomerisation, and its sulphur resistance is incredible.

4.6 Added Note

Since the preparation of this thesis, a very recent article has been published by Thomson and Webb (99) regarding the proposal of a new mechanism for catalytic hydrogenation of olefins on metals. The model suggests that some portion of olefin is irreversibly adsorbed on the metal surface to form an "active centre" M-C_xH_y. Hydrogenation then occurs via transfer of hydrogen from this adsorbed hydrocarbon to an adsorbed olefin. Therefore,the metal itself is not the most important species involved and thus this theory explains why metals having different chemical properties have similar catalytic activity for hydrogenation of olefins.

The above mechanism, like the one proposed by this author, involves the formation of a substrate-metal intermediate before hydrogen is involved. Therefore, as is observed in this present study, no hydrogen uptake occurs, within normal reaction time, in the absence of substrate. The formation of the intermediate proposed by Thomson and Webb would involve loss of a hydrogen atom(s) and, therefore, would probably be an allylic-type species such as the one this author proposed would be required for isomerisation, i.e. addition of hydrogen at a different C atom would lead to the formation of 2-alkene from 1-alkene.

Thomson and Webb are not very explicit on the role of hydrogen in their mechanism i.e. whether the hydrogen transferred is atomic hydrogen from the adsorbed hydrocarbon or molecular hydrogen from the atmosphere. One method that could be used to understand this problem is to label the alkene (to be adsorbed initially) with deuterium. Therefore, if the adsorbed hydrocarbon transfers its own hydrogen to another adsorbed alkene then the saturated product will be labelled.

4.7 Suggestions for Future Work

This study has presented a considerable amount of quantitative material and has clearly compared P-3 Ni and P-3 Co borides with previously studied nickel borides and Raney nickel. However, the study has also brought up several points which require further study outside of this present work. Heterogeneous catalytic reactions are known to be very complex, and it is therefore not unusual in this case to come up against these barriers to our present understanding.

The following discussion lists some further work which should be carried out in order to have a more comprehensive understanding of hydrogenations over metal borides.

a) The major question which has arisen out of this present study is that of how much of the hydrogen taken up actually goes towards hydrogenation of the substrate, and whether further hydrogen is taken up by the catalyst itself. On the other hand, is some hydrogen used for other unnoticed reactions? In addition, since the catalyst is known to contain hydrogen, i.e. the proposed formula is $(Ni_2B)_2.H_3$, it is also of interest to know if this catalyst hydrogen is used up during the hydrogenation and then replaced by added gaseous hydrogen. A study could be made of P-3 Ni boride prepared from deuterated borohydride to attempt to further clarify this problem.

b) The present study has shown that the initial concentrations of reactants in addition to the reaction gas volume have a profound effect upon the initial rate of hydrogen uptake and in the amount of product actually formed. A more complete study should be made of the P-3 Ni and P-3 Co hydrogenation catalyst systems in order to determine the ideal conditions - i.e. the conditions for the maximum rate of reaction, product formation, and selectivity for the minimum amount of reactants and side reactions.

c) This study has thoroughly investigated the effect of two sulphur poisons on the P-3 Ni, P-3 Co, and Raney nickel systems under certain reaction conditions. However, if these catalysts were to be used industrially, it would be beneficial to study the effect of other catalyst poisons and to determine the γ/α ratios for comparison. It would also be advantageous to study the effect of other solvent systems.

d) Gas-liquid chromatographic studies showed that a certain amount of 2-octene is formed during the reaction of 1-octene over P-3 Ni. This product, however, disappears from the reaction mixture upon further hydrogen uptake without appearing as n-octane. It would therefore, be of interest to study further this problem to determine whether the 2-octene is readsorbed by the catalyst, or if it polymerises and becomes adsorbed on the catalyst surface. In this connection, it was found in the present study that mass spectra of such a reaction mixture indicate the presence of a peak at mass greater than that required for C_8 systems and this may suggest polymerisation.

CHAPTER 5

APPENDIX

5.1 Introduction

The following tables provide supplemental data for several figures shown in the previous sections.

A complete list of data corresponding to results indicated in Table 3.16 (*i.e.* surface areas) is also included in this section.

TABLE 5.1 (for Figure 3.1)

Effect of Initial Hydrogen Pressure on the Initial Rate of Hydrogen Uptake During the Hydrogenation of 1-Hexadecene Over P-3 Ni[a]

Initial Hydrogen Pressure (cm)	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
17.0	1.50
25.6	2.80
30.0	2.60
37.0	3.92
42.6	4.75
47.0	4.60
57.0	5.36
72.0	7.00 7.33

---

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 5 X 10^{-4} moles P-3 Ni (0.02 M) in ethanol. Initial gas volume of 328 ml.

TABLE 5.2 (for Figure 3.2)

Effect of Initial Substrate Concentration on the Initial Rate of Hydrogen Uptake During the Hydrogenation of 1-Hexadecene Over P-3 Ni[a]

Initial Concentration of Substrate (M)	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
0.070	4.43[b]
0.096	3.67
0.140	6.40[b] 6.75
0.210	8.00
0.350	8.60
0.500	7.33 8.00
0.630	9.13

[a] Hydrogenation of 1-hexadecene over approximately 5 X 10^{-4} moles P-3 Ni (0.02 M) in ethanol. (Initial hydrogen pressure of 72 cm.) Initial gas volume of 328 ml. [b] Initial gas volume of 614 ml.

TABLE 5.3 (for Figure 3.3)

Effect of Initial Amount of Catalyst on the Initial Rate of Hydrogen Uptake During Hydrogenation of 1-Hexadecene Over P-3 Ni[a]

Initial Amount of Catalyst[b] (M Ni) ($\times 10^{-2}$)	Initial Rate of Hydrogen Uptake (M/min) ($\times 10^{-2}$)
0.13	0.28
0.27	3.38
0.42	4.67
0.55	7.70
1.06	7.50
1.64	8.00 7.80
2.00	7.33

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over P-3 Ni in ethanol. (Initial hydrogen pressure of 72 cm.) [b] Amount of catalyst expressed in terms of moles of Ni (used in preparation) per litre of liquid reaction mixture. Total liquid volume of 25 ml.

TABLE 5.4 (for Figure 3.4)

Effect of Initial Hydrogen Pressure on the Initial Rate of Hydrogen Uptake During the Hydrogenation of 1-Hexadecene Over P-3 Co[a]

Initial Hydrogen Pressure (cm)	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
20.0	0.90
37.0	1.81
57.0	2.56
65.0	3.25
72.0	3.25
82.0	4.75

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over approximately 4 X 10^{-4} moles P-3 Co (0.0175 M) in ethanol. Initial gas volume of 328 ml.

TABLE 5.5 (for Figure 3.5)

Effect of Initial Substrate Concentration on the Initial Rate of Hydrogen Uptake During the Hydrogenation of 1-Hexadecene Over P-3 Co[a]

Initial Concentration of Substrate (M)	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
0.075	3.20
0.104	3.63
0.210	3.80
0.350	3.90
0.420	3.29
0.500	3.25

[a] Hydrogenation of 1-hexadecene over approximately 5 X 10^{-4} moles P-3 Co (0.018 M) in ethanol. (Initial hydrogen pressure of 72 cm.) Initial gas volume of 328 ml.

TABLE 5.6 (for Figure 3.6)

Effect of Initial Amount of Catalyst on the Initial Rate of Hydrogen Uptake During Hydrogenation of 1-Hexadecene Over P-3 Co[a]

Initial Amount of Catalyst[b] (M Co) (X 10^{-2})	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
0.29	1.14
0.58	2.40
0.88	3.80
1.27	3.70
1.74	3.30

[a] Hydrogenation of 0.0125 moles 1-hexadecene (0.5 M) over P-3 Co in ethanol. (Initial hydrogen pressure of 72 cm.) [b] Amount of catalyst expressed in terms of moles of Co(used in preparation) per litre of liquid reaction mixture. Total liquid volume of 25 ml.

TABLE 5.7 (for Figure 3.7)

Effect of Hydrogen Pressure on the Degree of Catalyst Poisoning by Hydrogen Sulphide During the Hydrogenation of 1-Hexadecene Over P-3 Ni

Time (min)	Total Hydrogen Uptake (M)
[a]	
0.0	0.0
2.5	0.157
4.5	0.286
6.5	0.415
9.0	0.553
12.5	0.701
18.0	0.867
24.5	1.023
58.5	1.115
20.0 hr	1.298
[b]	
0.0	0.000
5.0	0.265
10.0	0.394
15.0	0.459
20.0	0.500
25.0	0.524
45.0	0.580
75.0	0.589
120.0	0.589

[a] Hydrogenation of 0.025 moles 1-hexadecene (1.0 M) over approximately 5×10^{-4} moles P-3 Ni (0.02 M) in ethanol in the presence of 30 mg/l hydrogen sulphide. Total pressure ($P_{H_2} + P_{H_2S}$) kept at greater than 60 cm by introducing hydrogen. [b] Same as [a] except that total pressure is increased to approximately 75 cm every five minutes by introducing hydrogen.

TABLE 5.8 (for Figure 3.10)

Effect of the Presence of n-Butanethiol During the Hydrogenation of 1-Hexadecene Over P-3 Ni and Raney Nickel in Ethanol Under Conditions Where the Initial Rate of Hydrogen Uptake Over P-3 Ni is Dependent on Initial Hydrogen Pressure and Substrate and Catalyst Concentration

Concentration of n-Butanethiol (mg/l sulphur)	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
0.000[a]	3.00 2.90
0.530[a]	3.30
1.325[a]	3.75 3.00
2.000[a]	1.50
2.700[a]	0.70 1.25
4.000[a]	0.50
5.300[a]	----
0.000[b]	0.45 0.67
2.000[b]	0.33
4.000[b]	0.11

[a] Hydrogenation of 3.5 X 10^{-3} moles 1-hexadecene (0.139 M) over 1.08 X 10^{-4} moles P-3 Ni (0.0043 M) in ethanol. (Initial hydrogen pressure of 72 cm.) Concentration of n-butanethiol expressed as mg sulphur per litre of liquid reaction volume. Initial liquid volume of 25 ml. Initial gas volume of 328 ml. [b] Same as [a] except hydrogenation is over approximately 1.4 X 10^{-4} moles Raney nickel (0.0052-0.0061 M).

TABLE 5.9 (for Figure 3.11)

Effect of Presence of n-Butanethiol During the Hydrogenation of 1-Hexadecene Over P-3 Co in Ethanol Under Conditions Where the Initial Rate of Hydrogen Uptake Over P-3 Ni is Dependent on Initial Hydrogen Pressure and Substrate and Catalyst Concentration[a]

Concentration of n-Butanethiol (mg/l sulphur)	Initial Rate of Hydrogen Uptake (M/min) (X 10^{-2})
0.00	3.50
2.00	2.79
3.00	3.00
5.00	3.00
10.00	2.25
15.00	1.02 1.67
20.00	0.88
25.00	0.12

[a] Hydrogenation of 3.5 X 10^{-3} moles 1-hexadecene (0.139 M) over 1.08 X 10^{-4} moles P-3 Co (0.0043 M) in ethanol. (Initial hydrogen pressure of 72 cm.) Concentration of n-butanethiol expressed as mg sulphur per litre of liquid reaction volume. Initial liquid volume of 25 ml. Initial gas volume of 328 ml.

TABLE 5.10

BET Surface Area Data for Raney Nickel

P/P_o	$\frac{P/P_o}{V_g(1 - P/P_o)}$
[a] 0.00131	0.00041
0.02200	0.00300
0.13000	0.01310
0.15900	0.01540
0.22400	0.02060
[b] 0.00640	0.00113
0.11300	0.01070
0.13950	0.01288
0.18990	0.01680

[a] 0.0280 g sample of Raney nickel. [b] 0.0169 g sample of Raney nickel.
Note: P_o = 1.754 mm Hg.

TABLE 5.11

BET Surface Area Data for P-3A Nickel

P/P_o	$\frac{P/P_o}{V_g(1 - P/P_o)}$
0.02705	0.00446
0.06342	0.00843
0.10090	0.01160
0.11300	0.01259
0.12162	0.01430
0.16925	0.01860

[a] 0.0177 g sample of P-3A nickel.

TABLE 5.12

BET Surface Area Data for P-1 Nickel[a]

P/P_o	$\frac{P/P_o}{V_g(1 - P/P_o)}$
[b] 0.0969	0.0330
0.1469	0.0465
0.2860	0.0856
[c] 0.0069	0.0062
0.0802	0.0278
0.2240	0.0699
0.3790	0.1260
0.4020	0.1389

[a] P-1 Ni prepared from nickel chloride. [b] 0.0093 g sample of P-1 Ni. [c] 0.0047 g sample of P-1 Ni.

TABLE 5.13

BET Surface Area Data for P-1 Nickel[a]

P/P_o	$\frac{P/P_o}{V_g(1 - P/P_o)}$
0.0648	0.0973
0.1641	0.1990
0.2480	0.2880

[a] P-1 Ni prepared from nickel acetate. 0.0152 g sample used.

TABLE 5.14

BET Surface Area Data for P-2 Nickel[a]

P/P_o	$\frac{P/P_o}{V_g(1 - P/P_o)}$
[b] 0.0854	0.0679
0.1612	0.1098
0.2180	0.1335
[c] 0.0663	0.3115
0.1446	0.0617
0.1796	0.0760

[a] P-2 Ni prepared from nickel chloride. [b] 0.0203 g sample of P-2 Ni.
[c] 0.0086 g sample of P-2 Ni.

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*Note: In the final proof reading of this thesis, it was observed that references (39) and (66) were the same. Since this did not disrupt the context of this thesis, and so as not to cause further ambiguities, the numbering was left as is.

Corrigendum

Recent studies by this author, subsequent to the completion of this thesis, indicate that hydrogenation of 1-hexene (0.5 M) over P-3 nickel boride (0.02 M) in ethanol under the normal reaction conditions proceed at an initial rate of hydrogen uptake of approximately 7.3×10^{-2} M/min. This is considerably larger than the rate for this particular reaction reported in Table 3.1 i.e. 1.09×10^{-2} M/min. and indicates that the rate of hydrogen uptake during hydrogenation of terminal alkenes over P-3 Ni may not be significantly dependent on chain length as was suggested in this thesis. It should be noted that this latter result was taken from a preliminary study done prior to the other work presented in this thesis.