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Kinetic Studies of Polymer-Bound Rhodium (I) Hydrogenation Catalyst

Nee-Yin Chou

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Chou,
Nee-Yin
1979

KINETIC STUDIES OF POLYMER-BOUND
RHODIUM (I) HYDROGENATION CATALYST

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Nee-Yin Chou
April 1979

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KINETIC STUDIES OF POLYMER-BOUND
RHODIUM (I) HYDROGENATION CATALYST

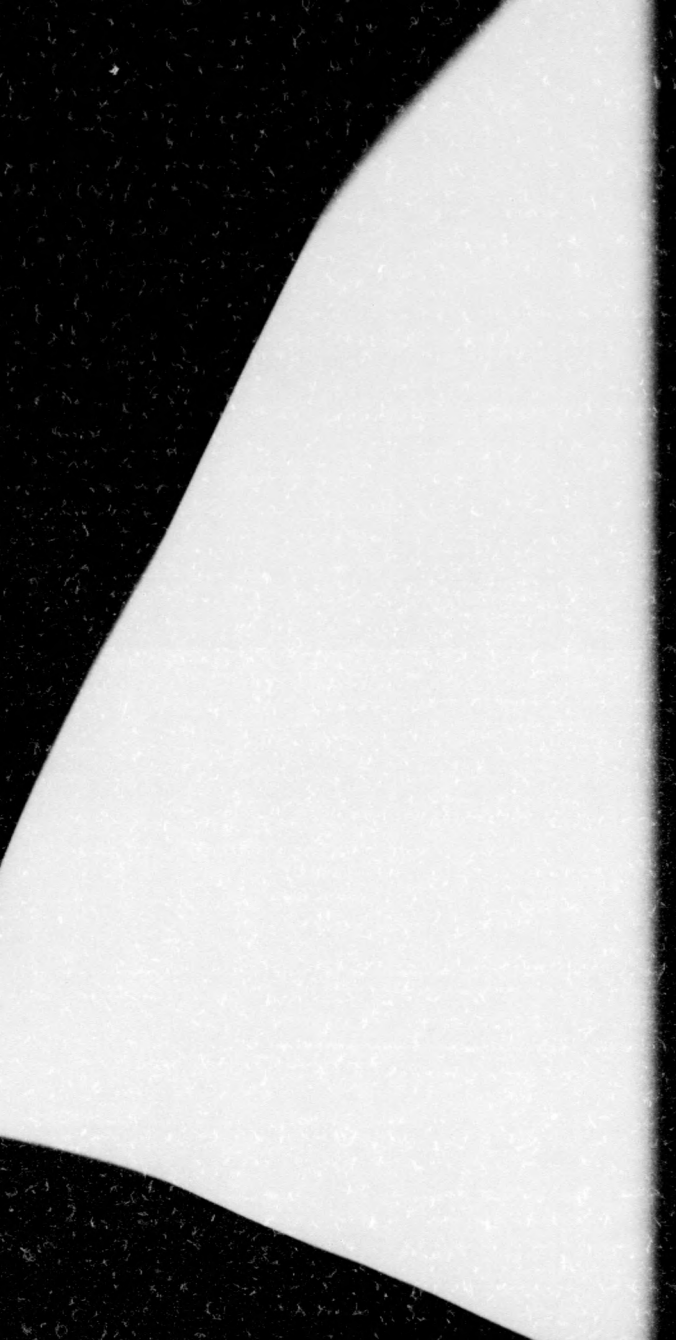
APPROVED 4/10/79 :
(Date)

Norman Holy
Director of Thesis

Earl F. Pearson

John C Craig, Jr.

Elmer Gray
Dean of the Graduate School



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ACKNOWLEDGEMENTS

I wish to express my gratitude to all the faculty members and graduate students of Western Kentucky University for their suggestions and friendship, particularly Dr. E. F. Pearson and Dr. C. C. Wilkins for their scientific insight and unselfish guidance. My special gratitude goes to my research advisor, Dr. N. L. Holy, for his direction, understanding, and unstinted contributions of his time. Finally, another kind of thanks to Mrs. F. Dixon, without whose encouragement this work might never have been completed.

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KINETIC STUDIES OF POLYMER-BOUND
RHODIUM (I) HYDROGENATION CATALYST

Nee-Yin Chou

April 1979

60 pages

Directed by: Norman L. Holy

Department of Chemistry

Western Kentucky University

Abstract

For many years, it has been customary to classify catalysts as homogeneous or heterogeneous. Generally, the former are more active and more selective. But the major disadvantage of the homogeneous catalysts is the need to separate the reaction products and to recover the catalyst, which is often somewhat more expensive than a "classical" heterogeneous catalyst. It has been considered, especially in the last ten years, that there might be advantages in chemically binding a homogeneous catalyst to a solid support.

Polymer-bound, anthranilic acid anchored rhodium (I) catalysts have been prepared. The rate of hydrogenation of cyclohexene has been studied quantitatively, and its dependence on factors such as substrate and catalyst concentration, temperature, and pressure has been determined. A possible mechanism has been proposed. Hydrogen-deuterium exchange has also been studied.

CHAPTER I

INTRODUCTION

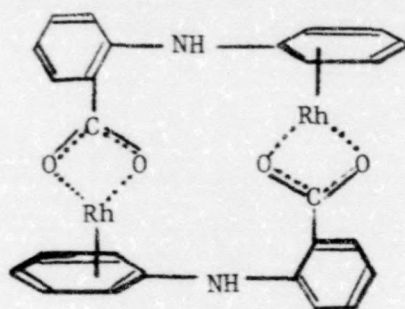
Catalytic reduction of olefins with a polymer-supported rhodium (I) catalyst was first suggested in 1971, by Grubbs and Kroll.¹ They pointed out that making homogeneous transition metal catalysts insoluble by attachment to various polymers can possibly prevent loss of expensive catalytic materials and contamination of reaction products.^{1,2,3,4} Pittman *et al.* indicated that this method also offers the activity of soluble homogeneous catalysts and the ease of recovery of heterogeneous catalysts.^{5,6,7,8} However, Pittman and his coworkers also showed that the requirement of diffusion of the reagents into crosslinked resins can retard reaction rates.^{1,9}

Generally, successful catalytic reduction depends on the right choice of both functional group and polymeric matrix. Two types of polymer support, polystyrene and silica, have been widely studied. Warshawsky concluded that polystyrene, because of its commercial availability in gel, macroreticular,¹⁰ expanded, or isoporous forms, is the polymer of choice.¹¹ Collman and his coworkers² found that 2% divinylbenzene-styrene copolymers are mobile enough to allow ligands attached to polymer beads to act as chelates. It had been proved by Grubbs *et al.*¹² that there is much less chelation, *i.e.* less mobility of the polymer structure, in the 20% crosslinked than in the 2% crosslinked polymer. While most studies have utilized 1-2% crosslinked

polystyrene, there are reports of employment of a wide variety of polystyrene, spanning the range of those having no crosslinking to those over 90% crosslinked.¹³ The more highly crosslinked polymers should provide a more rigid matrix and thereby more effective isolation of functionalized sites.¹⁴ Warshawsky, Kalir, and Patchornik chose highly crosslinked polymer XAD-4 beads to be the solid support.¹¹

Grubbs *et al.* indicated that the choice of ligand to be anchored is usually based on attempts to create environments analogous to those in the most active homogeneous catalysts.^{12, 15-20} Since phosphines are the most general ligands for homogeneous catalytic studies, they have most often been the ligands of choice. But many other types of ligands, *e.g.* amines and carboxylic acids, demonstrate attractive characteristics when bound to polymers.¹³

Avilov, Khidekel and their associates²¹ found that the Rh(I) complex of N-phenyl anthranilic acid (1) displayed exceptional hydrogenation activity with aromatic hydrocarbons.



(1)

Furthermore, the catalyst was not highly oxygen-sensitive and tolerated water.

Holy revealed that since N-phenylanthranilic acid functions as a multidentate ligand it seemed attractive, with respect to catalyst longevity, to prepare a structurally similar polymer-bound catalyst.²⁰ Anchoring N-phenylanthranilic acid to chloromethylated polystyrene did not result in an active catalyst. Later, Holy²² indicated that anchoring anthranilic acid to chloromethylated polystyrene, followed by complexation with Rh(III) and then reduction to Rh(I), led to a hydrogenation catalyst of exceptional activity toward a greater variety of functional groups than is true of any known homogeneous catalyst. He also noted that this hybrid-phase catalyst is highly air-stable and has a high turnover rate (for example, 130 cycles/atom-h for hydrogenation of cyclohexene at room temperature, 30 psig. hydrogen pressure).

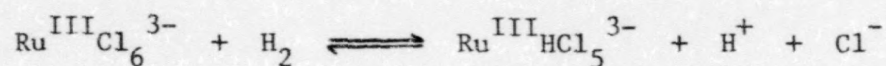
This work has involved kinetic studies of Holy's Rh(I) catalyst.

CHAPTER II

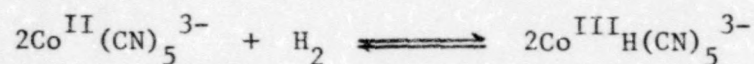
KINETICS OF HOMOGENEOUS HYDROGENATION CATALYSTS

The first documented example of a homogeneous catalytic hydrogenation was reported in 1938 by Calvin,²³ who discovered that in quinoline solution at about 100°C and 1 atm hydrogen cuprous acetate catalyzed the reduction. In 1939, Iguchi²⁴ reported the activation of molecular hydrogen by rhodium (III) complexes, such as $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$, $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, and RhCl_3 . Considerable progress in the understanding of hydrogen activation by transition metal ions and complexes was made by Halpern and other workers between 1955 and 1965.²⁵ Halpern *et al.* noticed that in each case it appears that H_2 is split by the catalyst with the formation of a reactive transition metal hydride complex (which may or may not be detected) as an intermediate. They also suggested three distinct mechanisms by which this can occur. Those are exemplified by the following reactions.

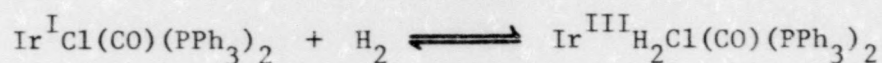
I. HETEROLYTIC SPLITTING²⁶



II. HOMOLYTIC SPLITTING²⁷



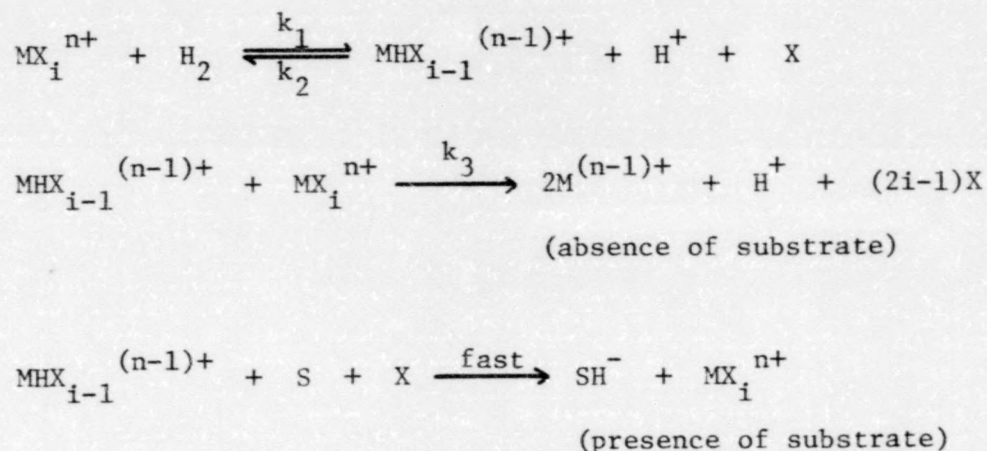
III. DIHYDRIDE FORMATION BY OXIDATIVE ADDITION²⁸



(A) HETEROLYTIC SPLITTING (THROUGH MONOHYDRIDE PATH)

Halpern et al.²⁹ proposed that this mechanism involves basically a substitutional process (replacement of a chloride ligand by a hydride derived from H_2) without change in the formal oxidation number of the metal. In the case of Cu^{2+} , Hg^{2+} , RuCl_6^{3-} , RhCl_6^{3-} , and PdCl_4^{2-} , the general mechanism is given by Martell as follow:³⁰

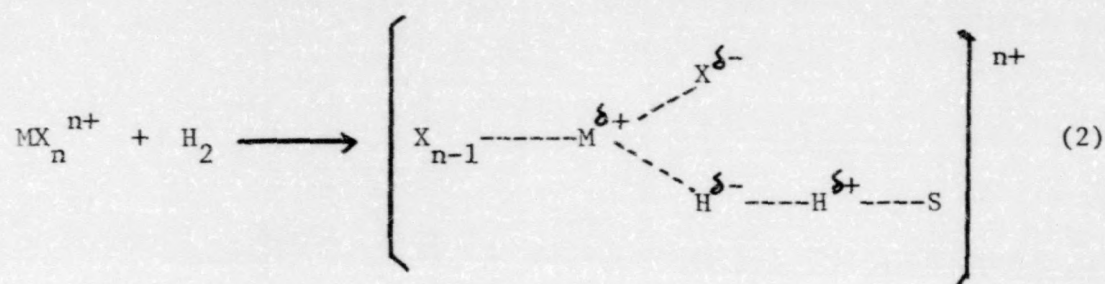
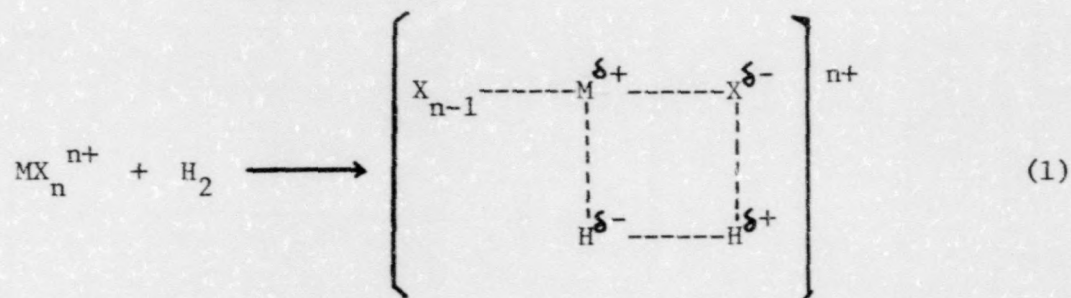
Diagram 1



Halpern indicated that reactivity is governed by the substitution lability of the complex, by the stability of the hydride formed, and by the presence of a suitable base (which may be the solvent or the displaced ligand) to stabilize the released proton.^{29a,b} Martell³⁰ had found that in the case of $\text{Cu}(\text{II})$, the rate increases in the order of the basicity of the

ligand, $\text{H}_2\text{O} < \text{Cl}^- < \text{SO}_4^{2-} < \text{CH}_3\text{COO}^- < \text{CH}_3\text{CH}_2\text{COO}^- < \text{CH}_3(\text{CH}_2)_2\text{COO}^-$.

Halpern proposed two transition states in a disproportionation reaction of the hydrogen molecule,^{29c}



where, X is the ligand and S is the solvent.

He stated that in solvents of low polarity transition state (1) would be favored since it would produce a species of lower dipole moment. In polar solvents and in low-polarity solvents containing an additional basic catalyst, the extended form of the intermediate, transition state (2), would be expected to compete more favorably with (1) and may even predominate.

A considerable number of catalysts are known to operate by this monohydride path. Laplaca and Ibers³¹ first reported that $\text{HRu}(\text{PPh}_3)_3\text{Cl}_2$ will rapidly hydrogenate 1-heptene and 1-hexyne (1:1 $\text{C}_6\text{H}_6/\text{EtOH}$, 25°C, 1 atm H_2) after heterolytic splitting of H_2 for catalyst activation. Hallman et al.^{32,33}

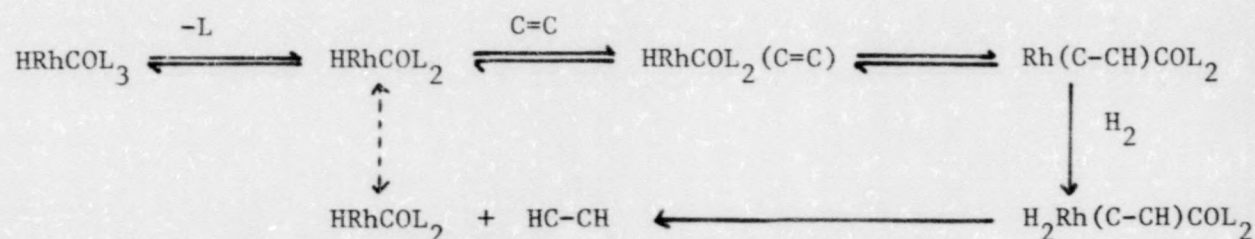
collected extensive data on H_2 uptake rates for various substrates for this catalyst. Jardine and McQuillin³⁴ noted also that the rate controlling step is the coordination of substrate with the metal hydride. Wilkinson *et al.*³⁵ did a kinetic study and found a rate law (with inhibition by excess PPh_3).

$$-d[\text{substrate}]/dt = k[HRu(PPh_3)_3Cl_2][H_2][\text{substrate}]$$

Ogata *et al.*³⁶ reported that the active form of catalyst $[Ru(\pi-C_6H_6)Cl_2]_n$ is presumed to be the monohydride $HRu(C_6H_6)Cl$ since catalysis is speeded by addition of small amounts of base (*e.g.* NEt_3). McQuillin and coworkers³⁷ investigated a very versatile catalyst system of the type $Rhpy_2(\text{amide})(BH_4)Cl_2$ which can reduce several functional groups such as $RhN=NPh$, $PhNO_2$, $PhCH=NPh$, *etc.*, that are not commonly reduced by homogeneous systems. Halpern^{29d,e} found that Rh^{II} in 3M HCl can catalyze hydrogenation of maleic and fumaric acids. Hui and James³⁸ believed that hydrogen activation by heterolytic splitting occurs before, not after, complexation of the substrate in the catalytic path when reducing maleic acid by a similar complex, $Ru(bipy)Cl_4$. They noted in their rate studies that there is an induction period followed by a linear rate of H_2 uptake.

Other catalysts which function by a monohydride pathway include $HCoL_n (n=3,4)$ ³⁹, $trans-HPtL_2X$ ⁴⁰, $IrL_nH_3 (n=2,3)$ ⁴¹, $HIrCl_2L_3$ ⁴², $L_nRh^{III}Cl_3 (n=2,3)$ ⁴³, $ML_2(CO)_3X_2 + SnCl_2 (M=Mo, W)$ ⁴⁴, and $HRh(CO)(PPh_3)_3$ ⁴⁵. The characteristics of the last catalyst have been reviewed by Wilkinson. His group has done extensive work on rate studies of hydrogenation to determine the mechanism.⁴⁶

Diagram 2

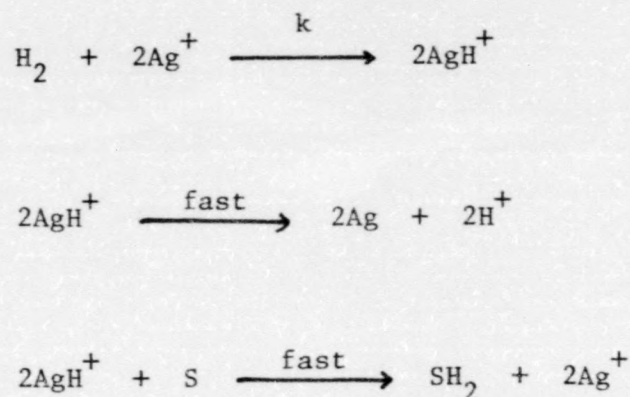


The rate-determining step is olefin displacement of solvent in the coordination sphere.

(B) HOMOLYTIC SPLITTING (THROUGH RADICAL PATH)

The first mechanism for the homolytic splitting of molecular hydrogen by Ag^+ reported by Webster and Halpern, in 1956,⁴⁷ is given in diagram 3,

Diagram 3



where, S = solvent.

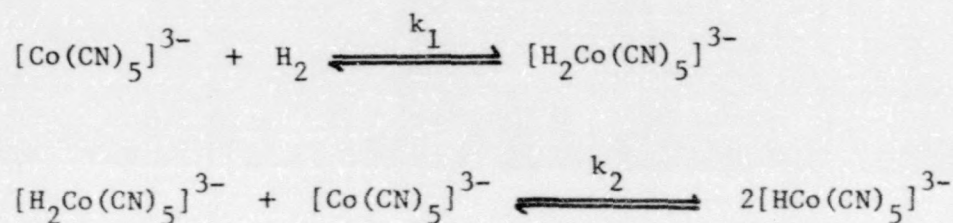
They stated that the reaction follows third-order kinetics, first-order with respect to molecular hydrogen and second-order with respect to silver ion.

Dolcetti⁴⁸ indicated that all catalysts of the radical path type appear to utilize homolytic splitting of the H_2 molecule with conceivably one electron oxidation of the metal. Martell⁴⁹ noted that in several cases,

homolytic splitting of H_2 occurs with cleavage of a metal-metal bond to yield two molecules of metal hydride.

The most widely studied radical type hydrogenation catalyst is $Co(CN)_5^{3-}$.⁵⁰ The absorption of molecular hydrogen by aqueous solutions of pentacyanocobaltate(II) was first observed by Iguchi in 1942.⁵¹ A detailed spectroscopic study by King and Winfield confirmed the formation of $[HCo(CN)_5]^{3-}$ as one of the intermediates when hydrogen is absorbed by $[Co(CN)_5]^{3-}$.⁵² Banks and Pratt⁵³ isolated the hydrido complex as the cesium-sodium salt, $Cs_2Na[HCo(CN)_5]$. King and Winfield suggested the mechanism shown in diagram 4 for the absorption of molecular hydrogen by $[Co(CN)_5]^{3-}$.⁵²

Diagram 4

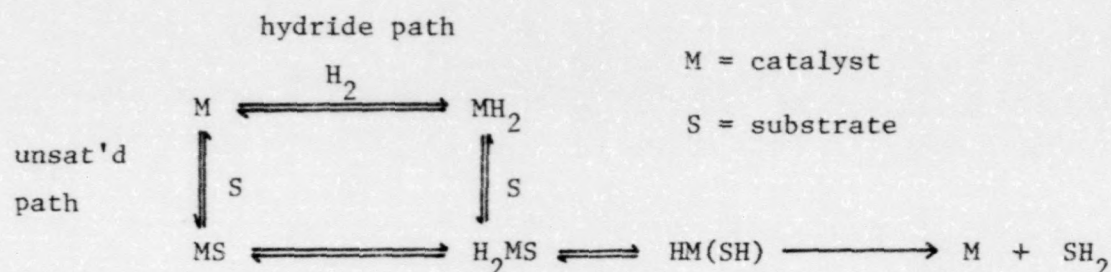


The rate of hydride formation was also third-order kinetics, first order with respect to molecular hydrogen and second order with respect to cobalt concentration. From their detailed kinetic studies of reduction of sorbic and cinnamic acid, Simandi⁵⁴ postulated a two-step radical transfer of $H\cdot$ with sufficient concentration of radical intermediates.

(C) OXIDATIVE ADDITION (THROUGH DIHYDRIDE FORMATION)

A number of hydrogenation catalysts which function by a dihydride pathway (activation of H_2 by oxidative addition to the metal complex) have been discovered. Collman⁵⁵ proposed that the mechanism involves two possible routes, as shown in diagram 5, both of which may be simultaneously operative. Both routes require free coordination sites for addition of H_2 and complexation of substrate.

Diagram 5

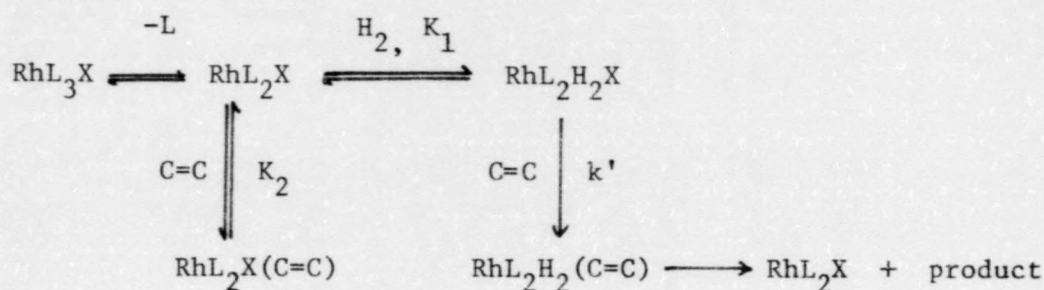


Dolcetti and Hoffman termed one route the "hydride path," the other route the "unsaturated path."⁴⁸ They stated that in most systems, the hydride path is thought to predominate because coordination of substrate (generally an olefin or acetylene) removes a sufficient amount of electron density from the metal by strong π -back-bonding to prevent H_2 from oxidatively adding to the complex to a significant extent.

Osborn's group investigated $ML_2(S)_2^+$ (M = Rh, Ir) type catalysts.⁵⁶ Collman et al.⁵⁷ used nitrosyl type catalysts $M(NO)L_3$ (M = Rh, Ir; L = phosphines) to hydrogenate nonconjugated dienes and alkynes. Frank et al. investigated $M(\text{arene})(CO)_3$ (M = Cr, Mo, W) type catalysts.⁵⁸

Other catalysts which function by this dihydride pathways include trans- $ML_2(CO)X$ ($M = Ir, Rh$),⁵⁹ ML_nX ($M = Ir, Rh; n = 2, 3$).⁶⁰ Wilkinson's group published a great deal of work on general catalytic properties and on the mechanistic behavior of $Rh(PPh_3)_3X$.⁶¹ They concluded that only the "hydride path" is operative and proposed the mechanism below.

Diagram 6



They had shown from their kinetic studies that

$$\text{rate} = \frac{k'[H_2][\text{olefin}][\text{catalyst}]}{1 + K_1[H_2] + K_2[\text{olefin}]}$$

and maximum catalytic activity results for larger k' and smaller K_2 .

Although Wilkinson's general mechanistic scheme is still considered essentially correct, many of its minor points have been questioned. Among these are a determination of the extent of dissociation of the complex RhL_3Cl ⁶² and the possibility of an operative unsaturated path for activation of H_2 .⁶³ Wilkinson's catalyst $Rh(PPh_3)_3Cl$ still remains the most widely used organometallic homogeneous hydrogenation catalyst.

CHAPTER III

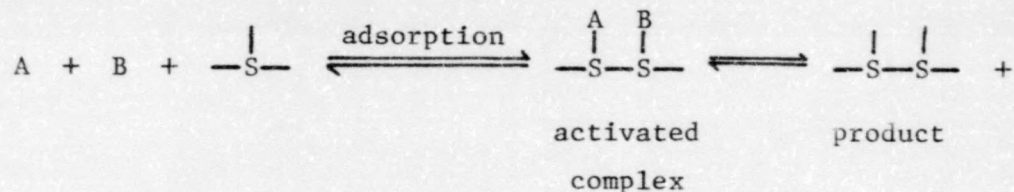
REVIEW OF HETEROGENEOUS CATALYSTS

(A) KINETICS OF "CLASSICAL" HETEROGENEOUS HYDROGENATION CATALYSTS

Heterogeneous catalysts operate through the adsorption of the reactants on the catalyst surface and formation of a chemical bond between reactant and adsorbent. Such adsorption is called chemisorption. In 1918, I. Langmuir⁶⁴ first gave a very straightforward treatment of chemisorption. He proposed two types of mechanism for a reaction between A and B.⁶⁵

Diagram 7

(1) Langmuir-Hinshelwood mechanism



(2) Langmuir-Rideal mechanism



S = surface of catalyst

A considerable amount of kinetic work has been done on the hydrogenation of ethylene on different surfaces since 1922. Quite different behavior was observed under different conditions, and it was found that reaction may occur by either of these mechanisms. Pease's investigation⁶⁶

of the reaction on a copper surface indicated that the ethylene is more strongly adsorbed than the hydrogen and the reaction is consistent with a Langmuir-Hinshelwood mechanism. The rate law is:

$$v = \frac{k[H_2][C_2H_4]}{(1 + K[C_2H_4])^2}$$

But the reaction on a nickel surface⁶⁵ suggested that reaction occurs between a pair of adsorbed hydrogen atoms and a gaseous ethylene molecule and is consistent with a Langmuir-Rideal mechanism. The rate law is:

$$v = \frac{k[H_2][C_2H_4]}{1 + K[C_2H_4]}$$

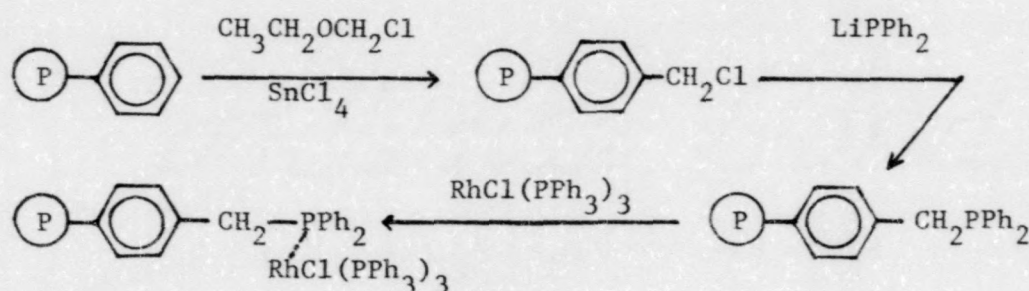
However, the distinction between adsorption of the reactants and formation of an active intermediate is not clear, and in recent years, the point has been emphasized that there could be a great deal of overlap between homogeneous and heterogeneous catalysis.^{9,67}

(B) STUDIES OF "POLYMER-SUPPORTED" CATALYSTS

Polymer attached reagents, particularly transition-metal catalysts, have been demonstrated to have many of the advantages of both heterogeneous and homogeneous analogs.^{1,2,5} The first attempts were made by Bond and his colleagues,⁶⁸ and by Rony.⁶⁹ Bond used rhodium trichloride in ethylene glycol impregnated on to Silocel as a packing for a g.l.c. column, and showed that pent-1-ene was isomerized to pent-2-ene isomers as it passed through the column.⁶⁸ Rony studied the hydroformylation of propylene by $RhCl(CO)(PPh_3)_2$ in butyl benzyl phthalate on granular silica gel.⁶⁹

Grubbs et al. investigated the effect of catalyst loading levels on the hydrogenation rate and the selectivity of the attached catalyst.⁷⁰ They prepared the catalyst by an equilibration technique between a phosphinated styrene-divinylbenzene (DVB) copolymer with a DVB content of about 2%, and the homogeneous Wilkinson's catalyst $\text{RhCl}(\text{PPh}_3)_3$.¹

Diagram 8



It was believed that the rhodium is bound to polymer by more than one phosphine link.^{12, 71, 72} The phosphines are mobile enough on low crosslinked polymer to chelate with a metal center. They loaded rhodium on the polymer at two different levels, and found that the rate of reduction of 1M cyclohexene with the saturated beads ($\text{P/Rh} \approx 5$) is 4.8 times higher than that with the deficient beads ($\text{P/Rh} \approx 10$). They also found that the most active beads are also the most selective on the basis of substrate molecular volumes. For example, the saturated beads, i.e. the more active catalysts, reduce β -pinene 8×10^{-2} times with respect to cyclohexene, whereas, the deficient beads reduce β -pinene 3.5×10^{-1} times as fast as cyclohexene.

Diagram 10 Relative Rate of Reduction

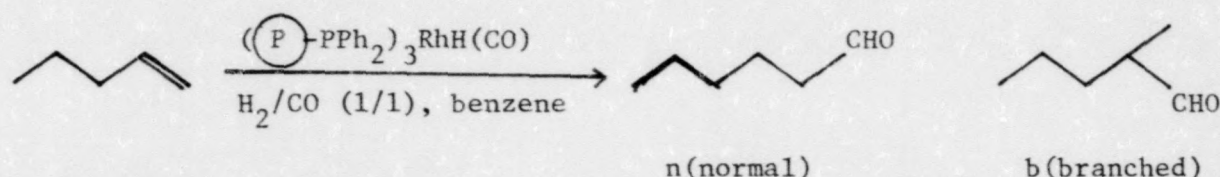
	Saturated Beads	Deficient Beads
Cyclopentene	1.75	1.80
Cyclohexene	1.00	1.00
Cycloheptene	0.805	0.97
Cyclooctene	0.43	0.64
Beta Pinene	0.08	0.35

Thus, the size selectivity of polymer attached catalyst toward substrates of different sizes can be controlled by the loading of the catalyst on the polymer support.⁷⁰ They attributed this decrease in reduction rate to the restriction of the size of the "solvent channels" by the random cross-links in the polymer. Their observations also demonstrated that the major portion of the reductions was taking place inside of the polymer beads.⁷³ A surface reduction reaction would have shown a much lower size specificity for the larger olefins.

Grubbs et al. also indicated that the rates of hydrogenation of cyclohexene with the polymer-bound Rh(I) catalysts are strongly dependent on the solvent used to swell and suspend the polymer support. The rate decreases with decreasing swelling ratio of the polymer in the solvent (measured as ratio of solvent-equilibrated polymer to dry polymer). The selectivity⁷⁰ of the catalysts toward olefins of different sizes is also dependent on the solvent used. They concluded that, in general, the lower the swelling ratio of the solvent used, the greater the selectivity on the basis of size.

Pittman and Hanes¹⁸ studied the product selectivity of the hydroformylations of 1-pentene catalyzed by $((\text{P})\text{-PPh}_2)_3\text{RhH(CO)}$,

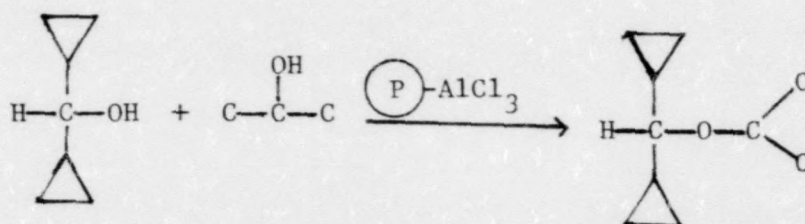
Diagram 11



and compared the n/b selectivity with that catalyzed by Wilkinson's homogeneous hydroformylation catalyst $(PPh_3)_3RhH(CO)$.⁷⁴ They found that, in general, polymer attached catalysts are notably more selective than their homogeneous counterparts at high phosphine loadings and high P/Rh ratios. At low phosphine loadings and lower P/Rh ratios the polymer-attached catalyst's selectivity resembled that of the corresponding homogeneous runs. They attributed this high selectivity partly to an artificially high catalyst-ligand concentration effect within the volume of the swollen resin beads. Since Wilkinson has shown⁷⁴ that the selectivity to linear product increased slightly as the soluble catalyst's concentration increased from 1×10^{-3} to 5×10^{-2} mol l^{-1} . An abnormally high phosphine-rhodium collision rate might occur within polymers having high phosphine loadings and high P/Rh ratios due to close proximity of these groups. They also noticed that at higher temperatures the rate and the n/b selectivity will be increased, due to the higher internal mobility of the resin. This high product selectivity was also observed by other workers.⁷⁰

Neckers and his coworkers⁷⁵ observed that for the reaction of dicyclopentyl carbinol with isopropyl alcohol, much higher product yields (dicyclopentylcarbonyl isopropylether) are obtained with solvents capable of swelling the polymer (1.8% crosslinked $(P-AlCl_3)$). Solvents such as hexane, benzene and carbon disulfide serve to make aluminum chloride more accessible by swelling the polymer.

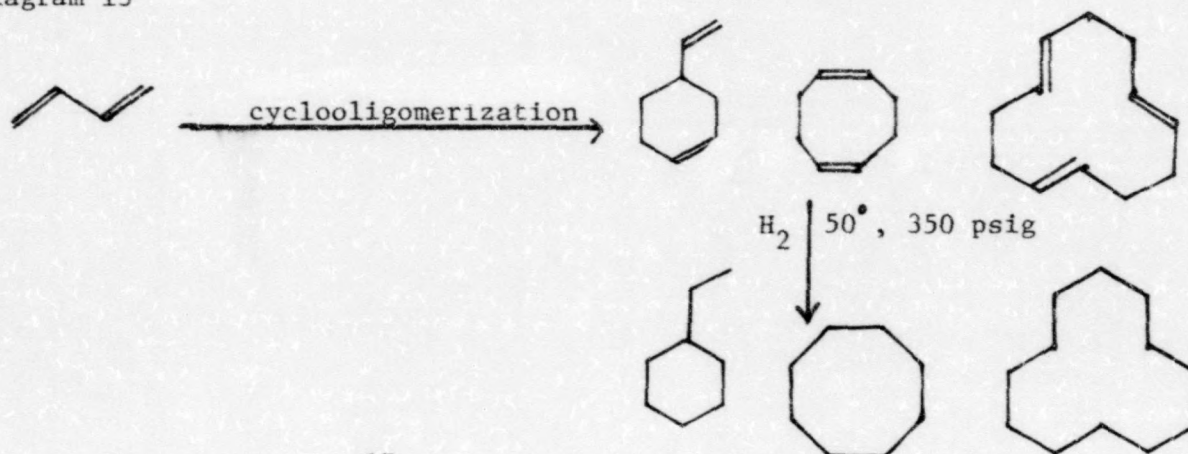
Diagram 12



Regen⁷⁶ reported the use of the spin-labeling technique in examining the mobility of a nitroxide bound to crosslinked polystyrene in the solvent-swelled state.⁷⁷ He found that the choice of swelling solvent has a substantial influence on the physical nature of the resin-bound nitroxide. From the results, he established that those solvents which swell polystyrene matrices the most will allow for the greatest mobility of the substrates bound to them.

Pittman and Smith⁷⁸ established that two catalysts anchored to the same polymer can be used to conduct sequential multi-step organic syntheses such as cyclooligomerization-hydroformylation sequences and cyclooligomerization-hydrogenation sequences. For example, sequential cyclooligomerization of butadiene, followed by hydrogenation to different cycloalkanes, can be accomplished by using a single styrene-DVB resin to which $(PPh_3)_2Ni(CO)_2$ and $(PPh_3)_3RhCl$ had been anchored.

Diagram 13



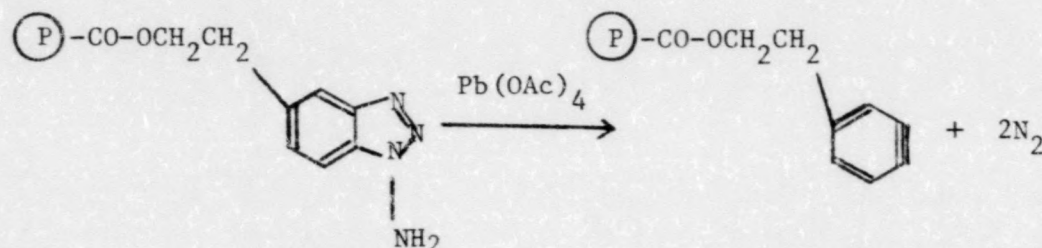
This concept had been applied in enzyme immobilization studies by Mosbach.⁷⁹ He bound both hexokinase and glucose 6-phosphate isomerase to the same polystyrene support and then converted glucose, sequentially, to glucose 1-phosphate and then glucose 6-phosphate. Thus, the product from the first enzymatic reaction became the substrate for the second. Kraus et al.⁸⁰ also studied the mixed ester condensation of two carboxylic acids bound to a common polymer backbone.

Bonds et al.¹⁹ used the polymer to "matrix isolate" one reactive catalytic site from another. They successfully generated polymer anchored titanium metallocenes from anchored biscyclopentadienyl titanium dichloride. Titanium apparently does not undergo dimerization when this method is used, and the effectiveness of the polymer attached titanocene $(\text{P})-(\text{C}_2\text{H}_5)_2\text{TiCl}_2$ as a catalyst for hydrogenation of olefins is enhanced by a factor of 25 to 120 compared to the correspondingly reduced non-attached titanocene dichloride or benzyl titanocene dichloride. They also observed that this attached catalyst shows good pseudo-first-order kinetics under a variety of conditions. They indicated that the major determinant in the rates of reduction with the attached titanocenes is the size of the beads. Grinding the beads increases their activity.

Leznoff et al.⁸⁰ had successfully used insoluble polymer supports (chloromethylated 2% crosslinked DVB-styrene Merrifield copolymer)⁸¹ as monoblocking groups of symmetrical diols,⁸² symmetrical diols,⁸³ and symmetrical diacid chlorides,⁸⁰ and had applied that procedure to the synthesis of insect sex attractants.⁸⁴ This "site-site insulation" phenomenon had also been observed by Mazur et al.⁸⁵ Jayalekshmy and Mazur had found that the ubiquitous dimerization reaction of benzyne is completely suppressed by attachment of this reactive molecule to a

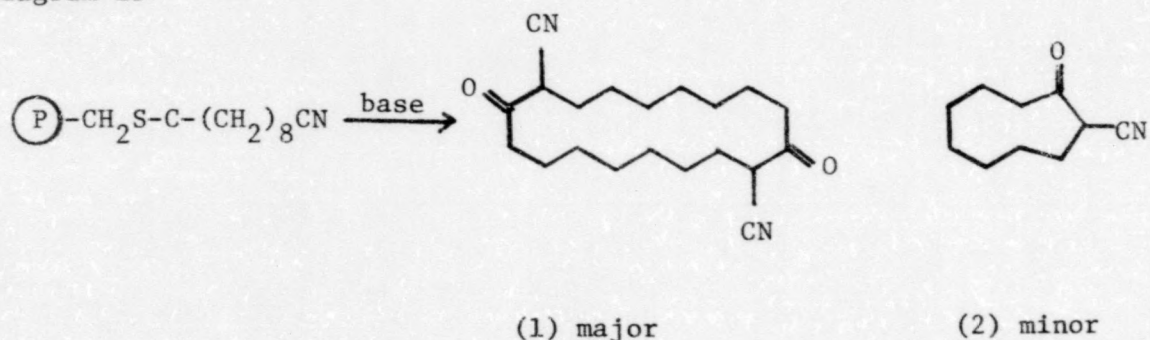
polystyrene resin, causing the solid-phase immobilization of benzyne and thereby extending its lifetime at room temperature to more than a minute.

Diagram 14 Generation of Benzyne



Collman *et al.*² showed "immobilization" of active sites is difficult to achieve with phosphine-substituted polystyrene because of the pronounced tendency of such polymeric ligands to chelate. Rapoport *et al.*¹⁴ made three observations conclusively establishing that intraresin site-site reactions are possible in some solid phase organic syntheses. For example, cyclization of ω -cyanopelargonyl thiol resin ester will give diketodinitrile (1) as major product, and a much smaller quantity of 2-cyanocyclononanone(2).

Diagram 15



From the product observations, it pointed toward the "site-site condensations" as the most straightforward mechanism. Scott et al.⁸⁶ revealed significant site-site interaction on functionalized polystyrene, even at high levels of crosslinking. Crosby and Kato⁸⁷ also observed intraresin reactions by utilizing a polymeric phenylthiomethyl lithium reagent for the homologation of alkyl iodides. They suggested that the mobility of polymer chains will be reduced by increasing the levels of covalent crosslinking (i.e. chloromethylation), by decreasing the swelling capacity of the reaction media,⁷⁶ by lowering reaction temperature and lowering concentrations of polymer-bound functional groups.

Other studies toward polymer-bound catalysts had been made by Reed and his coworkers.⁷² They studied structural effects of crosslinking in polymer-bound Rh(I) catalyst by extended X-ray absorption fine structure (EXAFS) spectroscopy. But the detailed structures of the heterogenized homogeneous catalysts still remain essentially unknown.

CHAPTER IV

EXPERIMENTAL

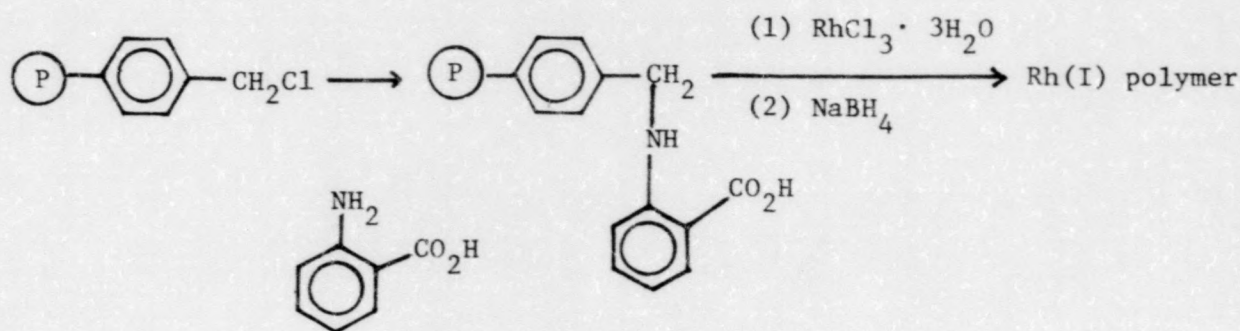
I. Instrumentation

Gas Chromatography measurements were made using a Varian model 3700 Chromatograph with a flame ionization detector, a 2m, OV-17 column, and a Varian aerograph model 20 recorder. Calibrations were made using standard samples. Mass spectra were obtained using a Varian Anaspect model EM 600 mass spectrometer with a Varian model 9176 recorder. Nuclear magnetic resonance spectra were obtained using a Varian A-60A NMR spectrometer. Infrared spectra were recorded on a Perkin-Elmer model 710 infrared spectrophotometer using a thin film between sodium chloride plates if the material was mixed with nujol, or preparing a potassium bromide pellet if the material was mixed with potassium bromide.

II. Materials

Amberlite XAD-4 was a gift of the Rohm and Haas Co. It was obtained as white, hard, insoluble beads. Typical properties of Amberlite XAD-4 are shown in Table I. The Rh(I)-anthranilic acid polymer was prepared according to the procedures of Holy.²²

Diagram 16



He indicated two evidences for nitrogen alkylation: (1) benzyl chloride and anthranilic acid yield the N-alkylated product and (2) infrared studies of the polymer reveal the carbonyl absorption (1690 cm^{-1}) to be more in accordance with a hydrogen-bonding carboxylic acid than an ester. After preparing the catalyst, elemental analyses were performed by Galbraith Laboratories Inc. In one batch the rhodium content was 0.37% (0.036 mequiv/g) and in another it was 0.98% (0.096 mequiv/g). A different hydrogenation rate was observed by different batches of catalysts under the identical conditions. (shown in Fig I). U. S. A. Standard Testing Sieves (A. S. T. M. E-11 specification, Sargent-Welch Scientific Co.) were used to sieve the beads and only the 28-35 mesh beads were used in this study.

Cyclohexene was freed from peroxides by passing it through an activated alumina column, distilling it under nitrogen, and storing it under nitrogen. Deuterated ethanol was prepared by reacting ethanol with sodium metal; then, after removing excess ethanol, deuterium oxide was added and the deuterated ethanol was distilled. From nmr studies it showed about 75% deuterated ethanol was generated. Deuterium D_2 was prepared by reacting deuterium oxide with sodium metal. Hydrogen was used directly from the tank. Other reagent grade chemicals were used without purification.

III. Hydrogenation Apparatus and Procedures

(a) Hydrogenation reactions under atmospheric pressure

A mixture of 5 ml ethanol and 1×10^{-4} mole catalysts (based on rhodium, assuming one rhodium atom per active site) was saturated with hydrogen for half an hour before hydrogenation of cyclohexene took place. The reaction vessel was a 25 ml. 2-neck round bottom flask suspended into water bath. The temperature of the water was controlled by a Haake E52 thermostat (PolyScience-Haake Inc.), and could be maintained to $\pm 0.1^\circ C$. Hydrogen pressure was maintained by the use of a bubbler. A Burrell "Wrist Action" shaker was used to shake the solution. Use of a magnetic stirrer resulted in fragmentation of the beads and a loss of catalyst activity. Small samples were obtained by means of a syringe, and 1 μ l sample solution was injected into the gas chromatograph. The percentage of conversion from cyclohexene to cyclohexane was calculated by measuring the peak height ratio and calibrated with that of the standards. Glass stoppers were used instead of rubber stoppers. The latter caused serious poisoning of the catalyst (shown in Fig II). Parafilm was used to seal the stopper and prevent it from falling into the water bath. Stopcock grease was avoided because it covered the

surface of the beads, contaminated the solution, and eventually deactivated the catalyst.

(b) Hydrogenation reactions under higher pressures

Reactions were carried out in a standard, catalytic apparatus Parr reactor (Parr Instrument Co., model 3911). In a typical run reactor was charged with freshly distilled cyclohexene and catalyst, the system was sealed, purged three times with hydrogen, and then pressurized to the desired pressure. Product was analyzed using gas chromatography.

IV. Catalytic Experiments

(a) Solvent Studies

Holy²² observed that the hydrogenation of cyclohexene is largely independent of solvent (Table II). He attributed this to the high degree of crosslinking of XAD-4 beads. Since swelling is not a major factor in catalyst activity in this case, this small solvent effect is thus related to solvation of reaction intermediates.

(b) Ion Effect Studies

(1) Chloride ion. Potassium chloride, 3.35×10^{-4} mole (0.025g), was put into 6.7ml., 2.5M cyclohexene solution. Increased rate of hydrogenation was observed (shown in Fig III). It will be explained later. After the reaction was terminated, potassium chloride still remained mostly undissolved. It showed only a very insignificant amount of chloride ion was being generated.

(2) Hydrogen ion. When 1.7M HCl were present in 2.5M cyclohexene solution, it showed the same reduction rate as that of 0.05M KCl solution (shown in Fig III). When peroxides were present in the substrate, the hydrogenation of cyclohexene without hydrochloric acid occurred after a long period (18 h), whereas, reduction with 0.05M hydrochloric present did not show any induction

period, though the rate was slower than in the absence of HCl (shown in Fig IV).

(3) Acetate ion. Sodium acetate trihydrate, 3.3×10^{-4} mole (0.0456g), was put into 6.7m , 2.5M cyclohexene solution. It showed that acetate ions (0.05M) did not affect the hydrogenation rate (shown in Fig V).

(4) Perchlorate ion. Lithium perchlorate, 3.35×10^{-4} mole (0.0357g), was put into 2.5M cyclohexene solution. It also showed no effect toward hydrogenation of cyclohexene (shown in Fig V).

(c) Substrate Concentration Studies

A typical plot showing the conversion ratio of cyclohexene to cyclohexane against time is shown in Fig VI. The plot of time required for conversion of 1 mmole cyclohexene in 5 ml ethanol solution against different cyclohexene concentrations is shown in Fig VII. Finally, the plot of reciprocal of the rate of cyclohexene consumption after 50% conversion against the reciprocal of different cyclohexene concentrations is shown in Fig VIII. From these results, we assumed that the hydrogenation rate is essentially independent on substrate concentration.

(d) Hydrogen Pressure Studies

The qualitative dependence of the rate on hydrogen pressure can be seen from Fig IX. The reciprocal of the rate of cyclohexene consumption after 50% conversion vs the reciprocal of hydrogen pressure is shown in Fig X. This is not a linear relationship. Thus, assuming Henry's Law was obeyed, the rate of hydrogenation (in mole $l^{-1} \text{ sec}^{-1}$) could be obtained from the plot of log Rate vs log P_{H_2} (shown in Fig XI).

$$\text{Rate} = - \frac{d[C_6H_{10}]}{dt} = 0.38 P_{H_2}^{0.15}$$

where, hydrogen pressure is in atm units.

(e) Catalyst Concentration Studies

The qualitative comparison of the rate of reduction to different catalyst concentrations is shown in Fig XII. A plot of the rate of reduction of cyclohexene vs the number of moles of the catalyst is shown in Fig XIII. The dependence of the rate of reduction (in mole $l^{-1}sec^{-1}$) after 50% conversion on the number of active sites can be obtained from the plot of log Rate against log (number of moles of rhodium) (shown in Fig XIV). Thus,

$$\text{Rate} = - \frac{d[C_6H_{10}]}{dt} = 3.13 \times 10^{-3} (\text{cata.})^{0.43}$$

where, (cata.) is in mole units.

In the absence of catalyst, no hydrogenation occurred even after 2 days.

(f) Temperature Studies

Rates were measured at three temperatures ranging from 21.5°C to 50.0°C. A plot of the ratio of reduction against time consumed is shown in Fig XV. Reaction rates increase at higher temperatures.

V. Deuteration Studies

(a) Deuterated Ethanol

Deuterated ethanol was used as solvent. It was confirmed by nmr spectra that about 75% acidic hydrogen was replaced by deuterium. See Fig XVI. After 60% completion of the reduction, the product was analyzed by mass spectra studies, and was shown in Fig XVII. The strong peak at 84 showed that it is possibly the parent peak of cyclohexane, C_6H_{12} .

(b) Deuterium

Deuterium was generated as described before. Hydrogen was not considered to be present, because of its low content in air (0.5 ppm by volume).

The product was analyzed by mass spectra after 30% hydrogenation, and the result was shown in Fig XVIII. The mass spectra of 74% hydrogenation with H_2 /EtOH is shown in Fig XIX.

Table I

TYPICAL PROPERTIES OF AMBERLITE XAD-4^{*}

Appearance-----	Hard, hydrated opaque beads
Chemical Nature-----	Polystyrene
Nominal Mesh Sizes-----	20 to 50
Surface Area-----	750 square meters/gram
Average Pore Diameter-----	50 angstrom units
Inherent Dipole Moment of	
Functional Groups-----	0.3
Skeletal Density-----	1.08 gram/ml
Degree of Crosslinking-----	Very high
Percentage of Phenyl Groups-Surface, 35%,	
Buried, 65%	

* The data were obtained from Rohm and Haas Co.

Table II

RELATIVE RATE OF HYDROGENATION AS A FUNCTION OF SOLVENT*

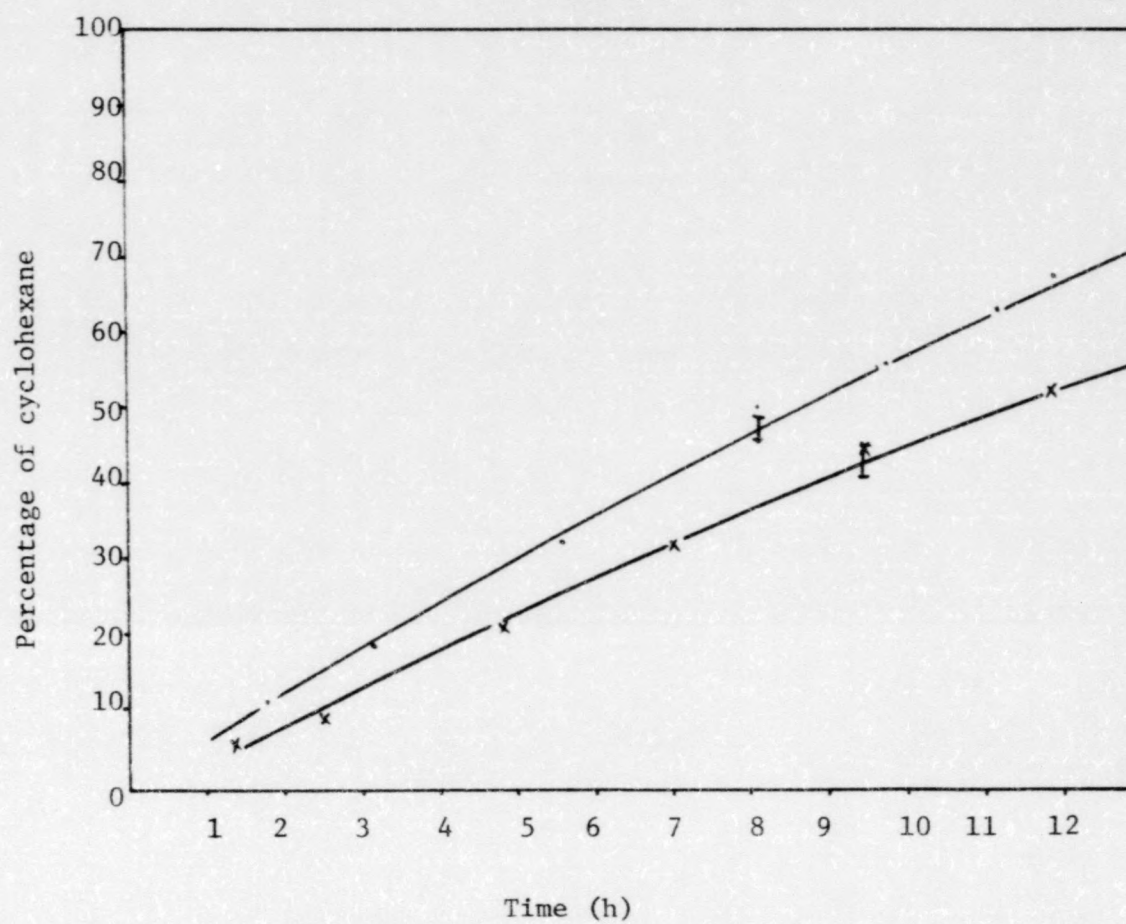
solvent	relative rate
acetonitrile	1.8
dimethylformamide	1.5
ethyl ether	1.0
cyclohexane	1.0

* 20% cyclohexene solutions hydrogenated at room temperature and 50 psig.

N. L. Holy, J. Org. Chem., 44, 236(1979)

Fig I

QUALITATIVE COMPARISON OF THE RATES OF HYDROGENATION
(TWO DIFFERENT BATCHES OF CATALYSTS)

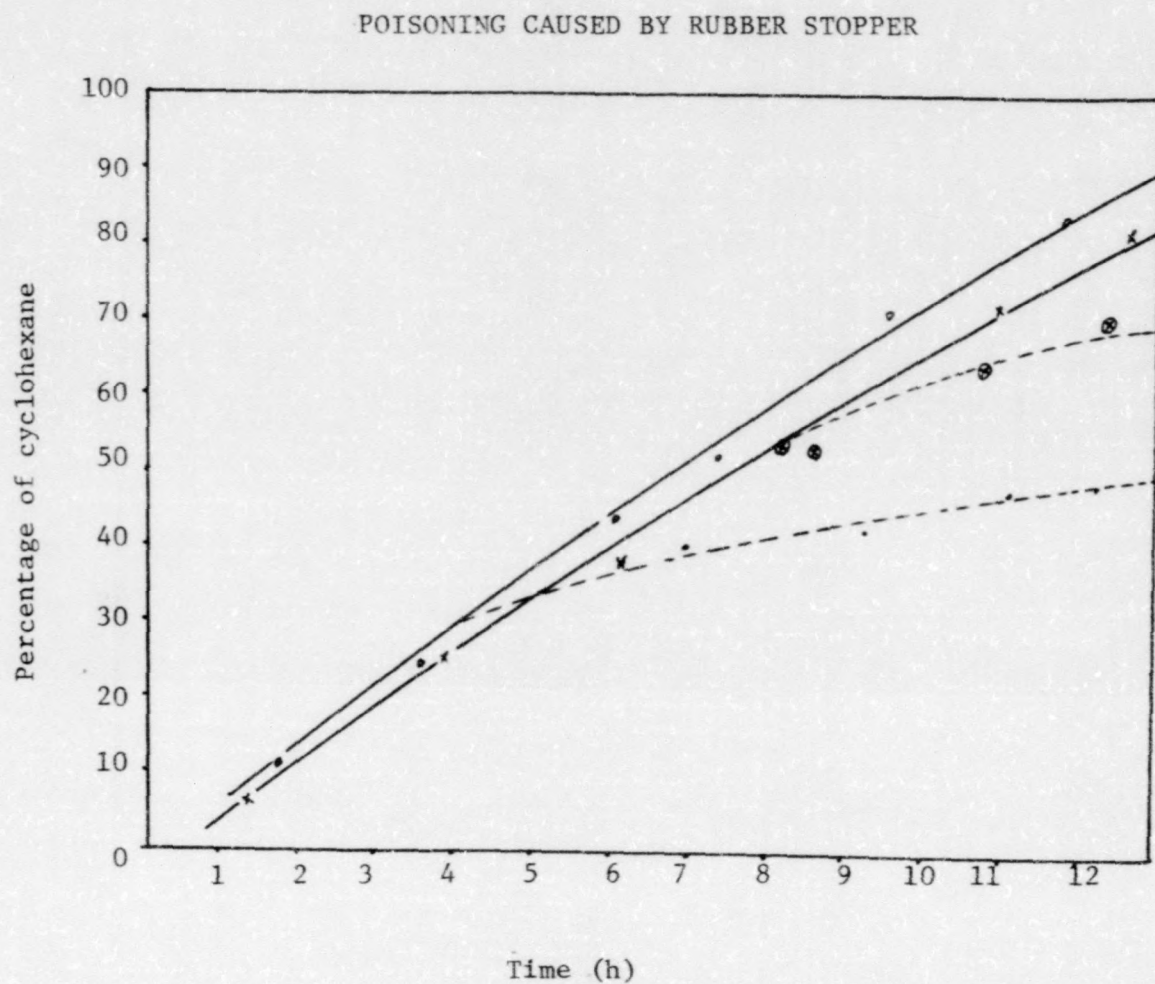


Solvent volume 5 ml with 1.7 ml cyclohexene, 1×10^{-4} moles of catalysts at 21.5°C

* First batch of catalyst, 0.37% Rh content (0.036 mequiv/g)

• Second batch of catalyst, 0.98% Rh content (0.095 mequiv/g)

Fig II



2.5 M cyclohexene, 1×10^{-4} mole catalysts (second batch)

—○— 50°C, using glass stopper

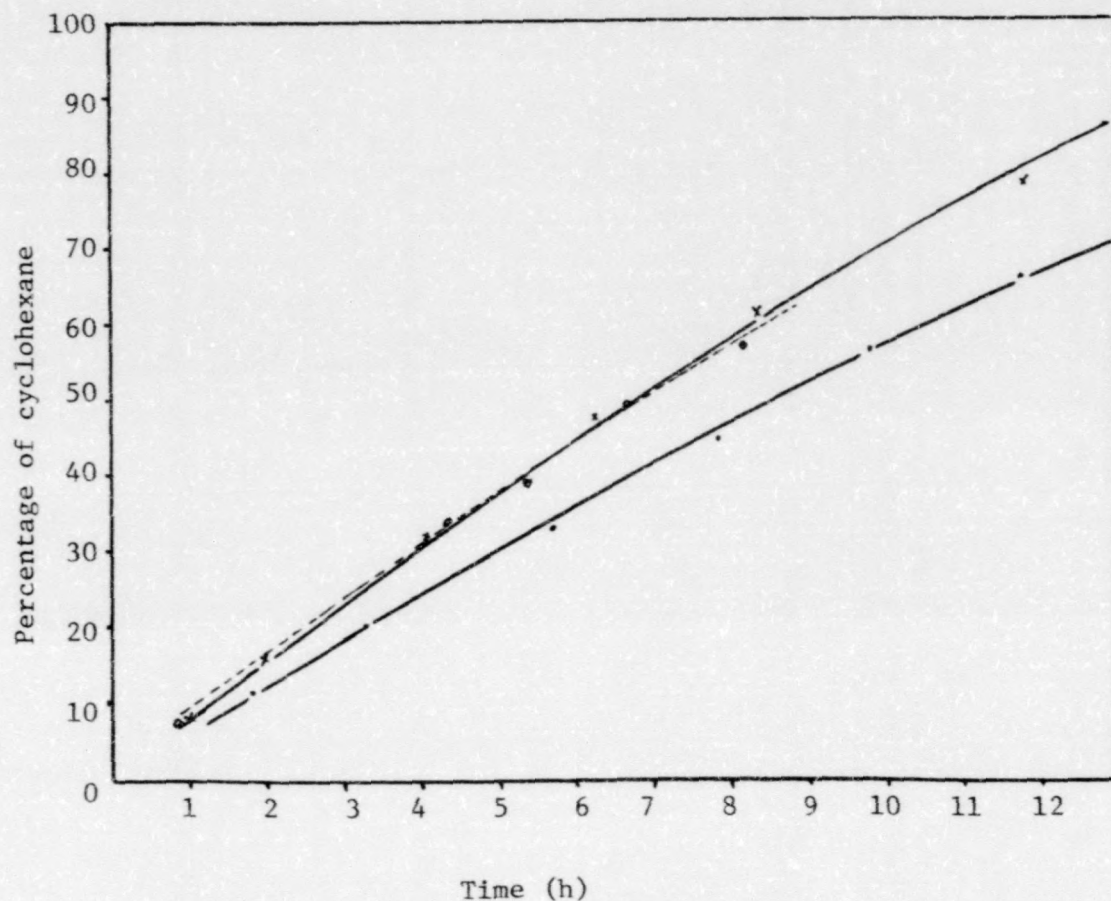
—•— 50°C, using rubber stopper

---*--- 35°C, using glass stopper

---⊗--- 35°C, using rubber stopper

Fig III

QUALITATIVE COMPARISON OF THE RATES OF HYDROGENATION
(ION EFFECT)



Solvent volume 5 ml with 1.7 ml cyclohexene, 1×10^{-4} moles of
second batch catalysts at 21.5°C

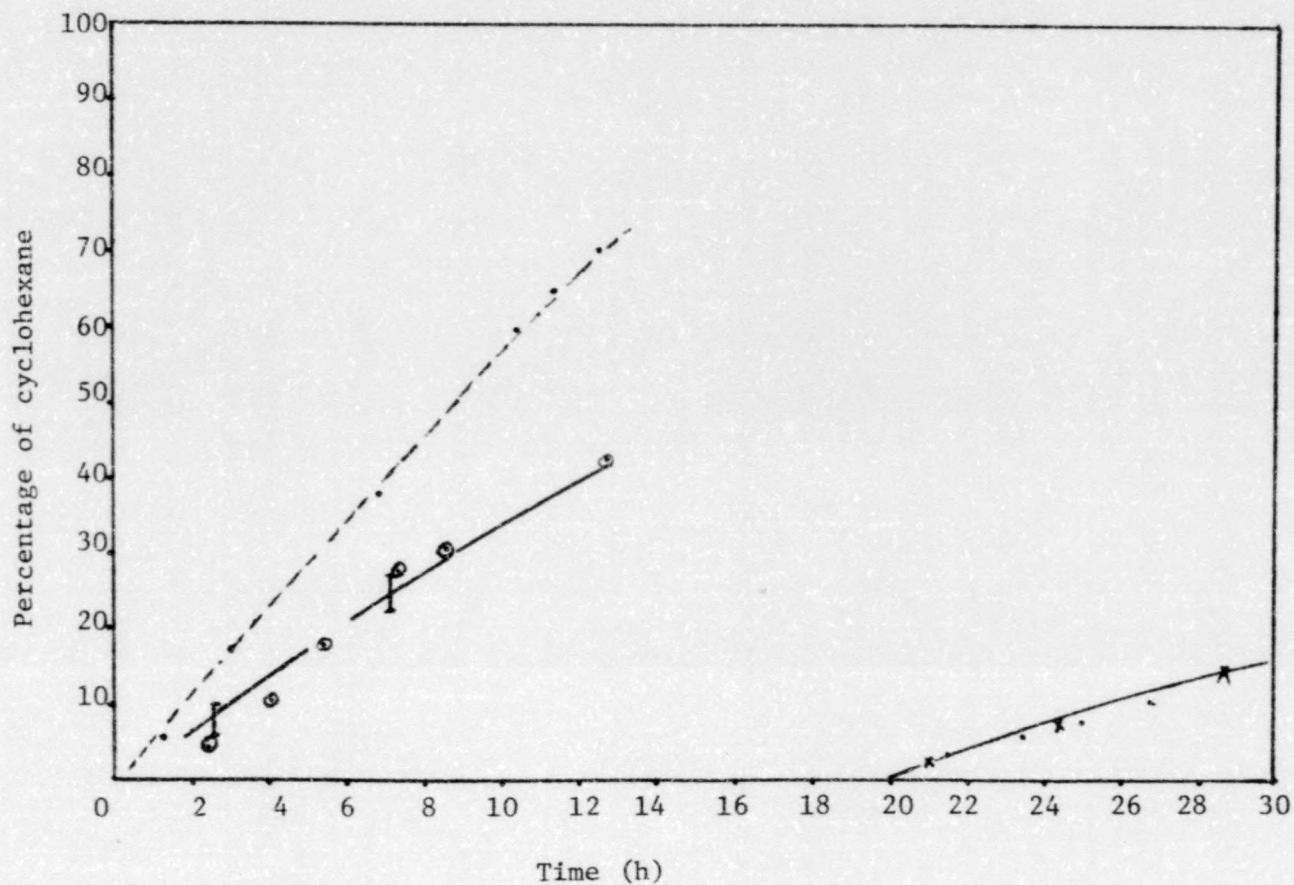
• No other chemicals were added.

* 0.05 M potassium chloride

o 1.7 M hydrochloric acid

Fig IV

QUALITATIVE COMPARISON OF THE RATES OF HYDROGENATION
(PEROXIDES EFFECT)



Solvent volume 5 ml. with 1.7 ml. cyclohexene, 1×10^{-4} moles of catalysts,
21.5°C

● 0.05M HCl

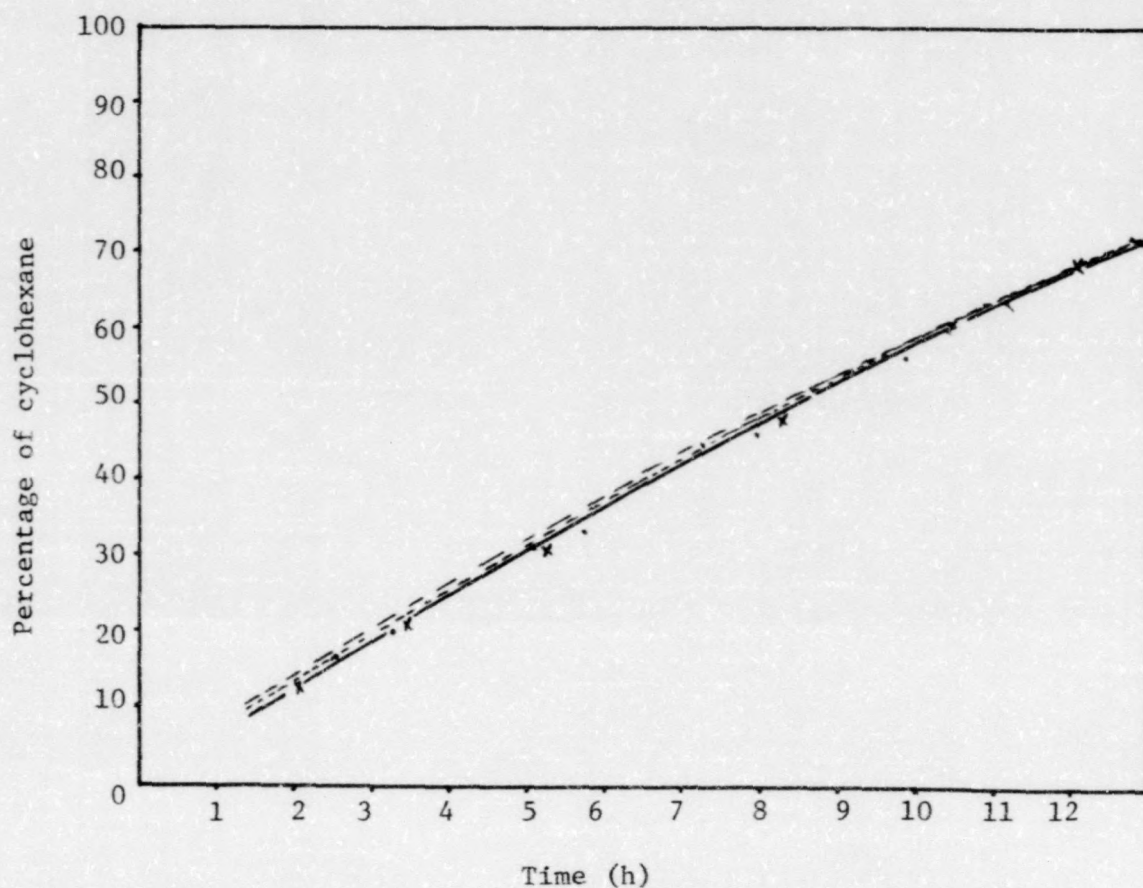
• 0.05 moles of LiClO₄ were added.

* No other chemicals were added.

— — — Purified cyclohexene

Fig V

QUALITATIVE COMPARISON OF THE RATES OF HYDROGENATION
(ION EFFECT)



Solvent volume 5 ml with 1.7 ml cyclohexene, 1×10^{-4} moles of
second batch catalysts at 21.5°C

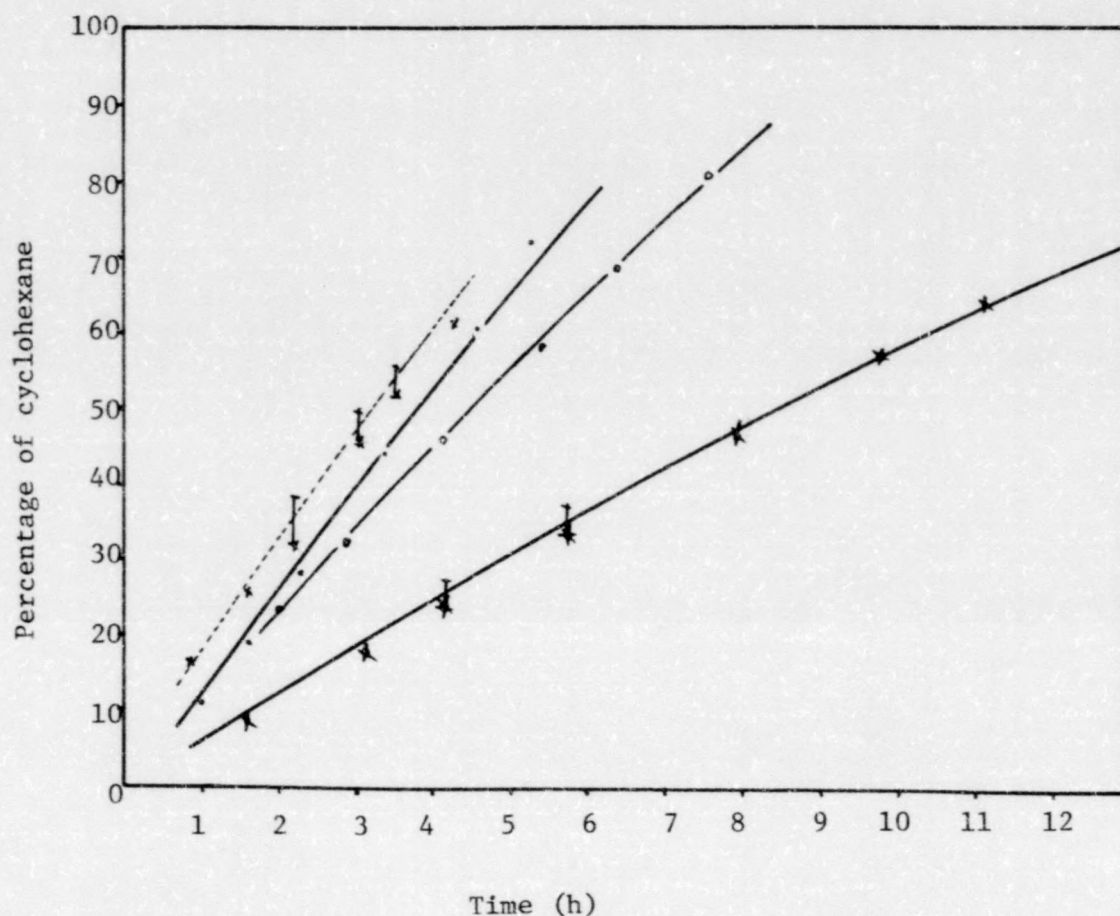
————— No other chemicals were added.

----- 0.05 M lithium perchlorate

---*---*--- 0.05 M sodium acetate

Fig VI

QUALITATIVE COMPARISON OF THE RATES OF HYDROGENATION
(SUBSTRATE CONCENTRATION DEPENDENCE)



Solvent volume 5 ml with 1×10^{-4} moles of second batch catalysts,
at 21.5°C

- *— 2.5 M cyclohexene
- °— 1.0 M cyclohexene
- - * - - 0.75 M cyclohexene
- . . - . 0.50 M cyclohexene

Fig VII

TIME REQUIRED FOR CONVERSION OF 1 mMOL CYCLOHEXENE IN 5ML.
ETHANOL SOLUTION AT 21.5°C VS CYCLOHEXENE CONCENTRATIONS

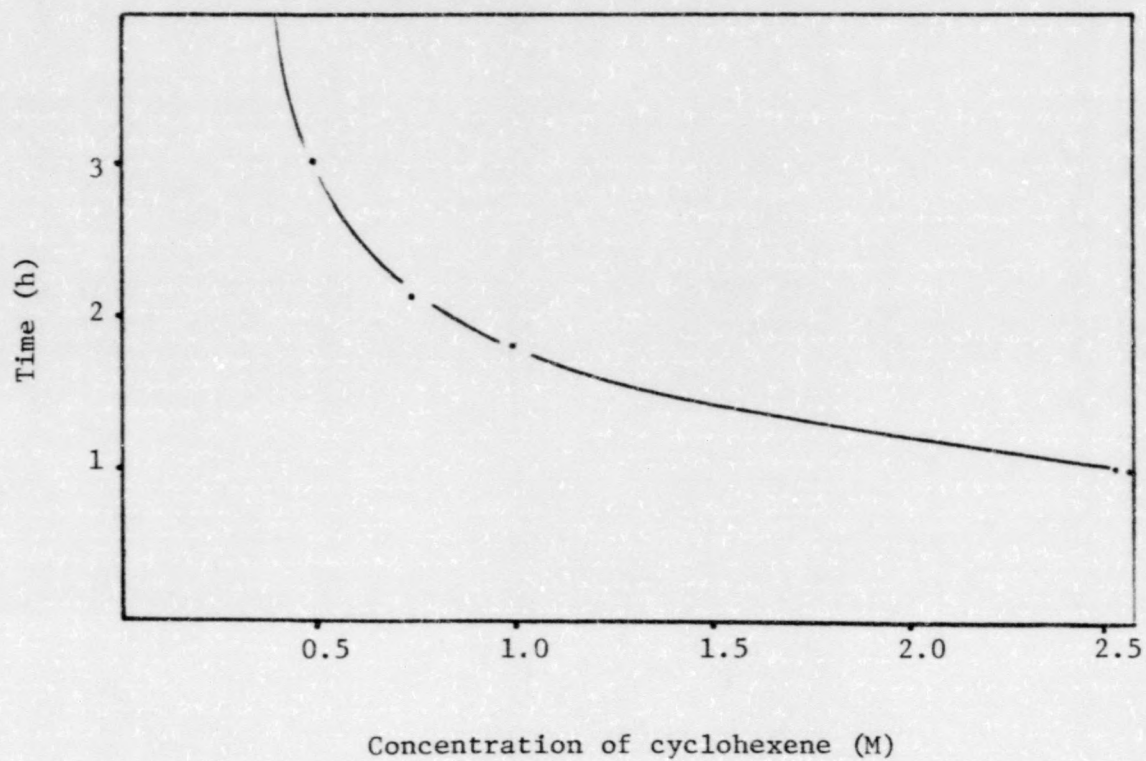
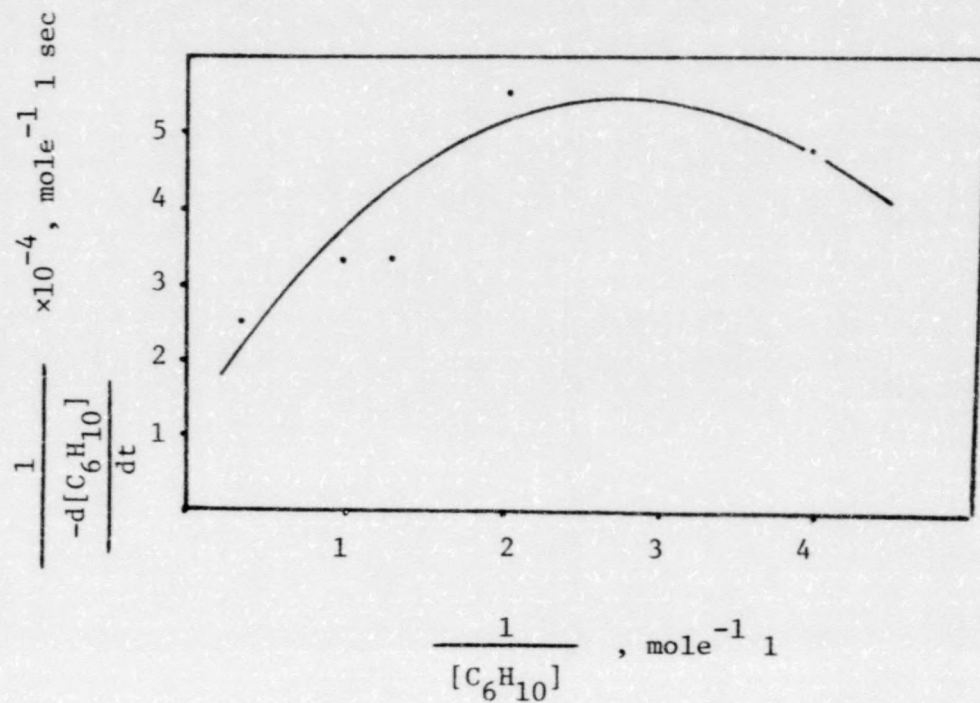


Fig VIII

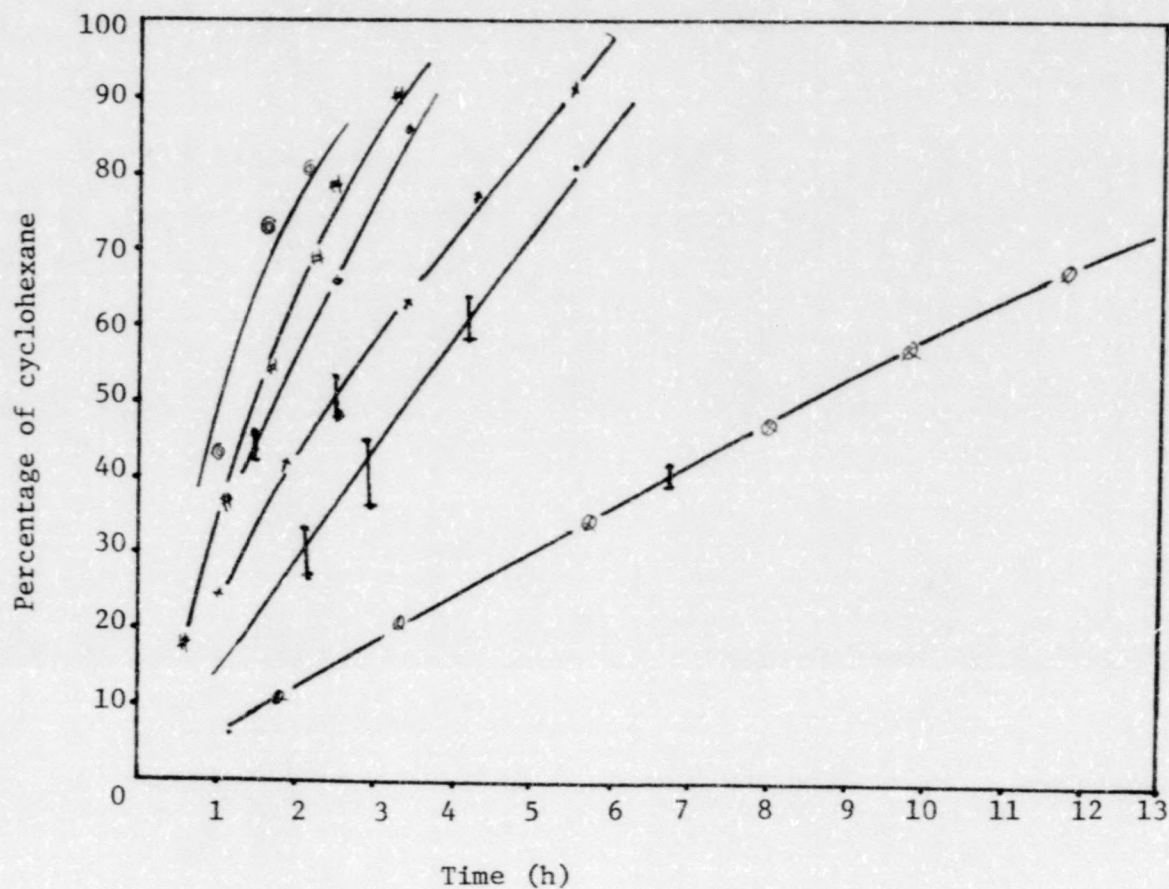
THE RECIPROCAL OF THE RATE OF CYCLOHEXENE CONSUMPTION AFTER
50% CONVERSION VS THE RECIPROCAL OF CYCLOHEXENE CONCENTRATION



Solvent volume 5 ml. with 1×10^{-4} moles of catalysts, 21.5°C

Fig X

QUALITATIVE COMPARISON OF THE RATES OF HYDROGENATION
(HYDROGENATION PRESSURE DEPENDENCE)

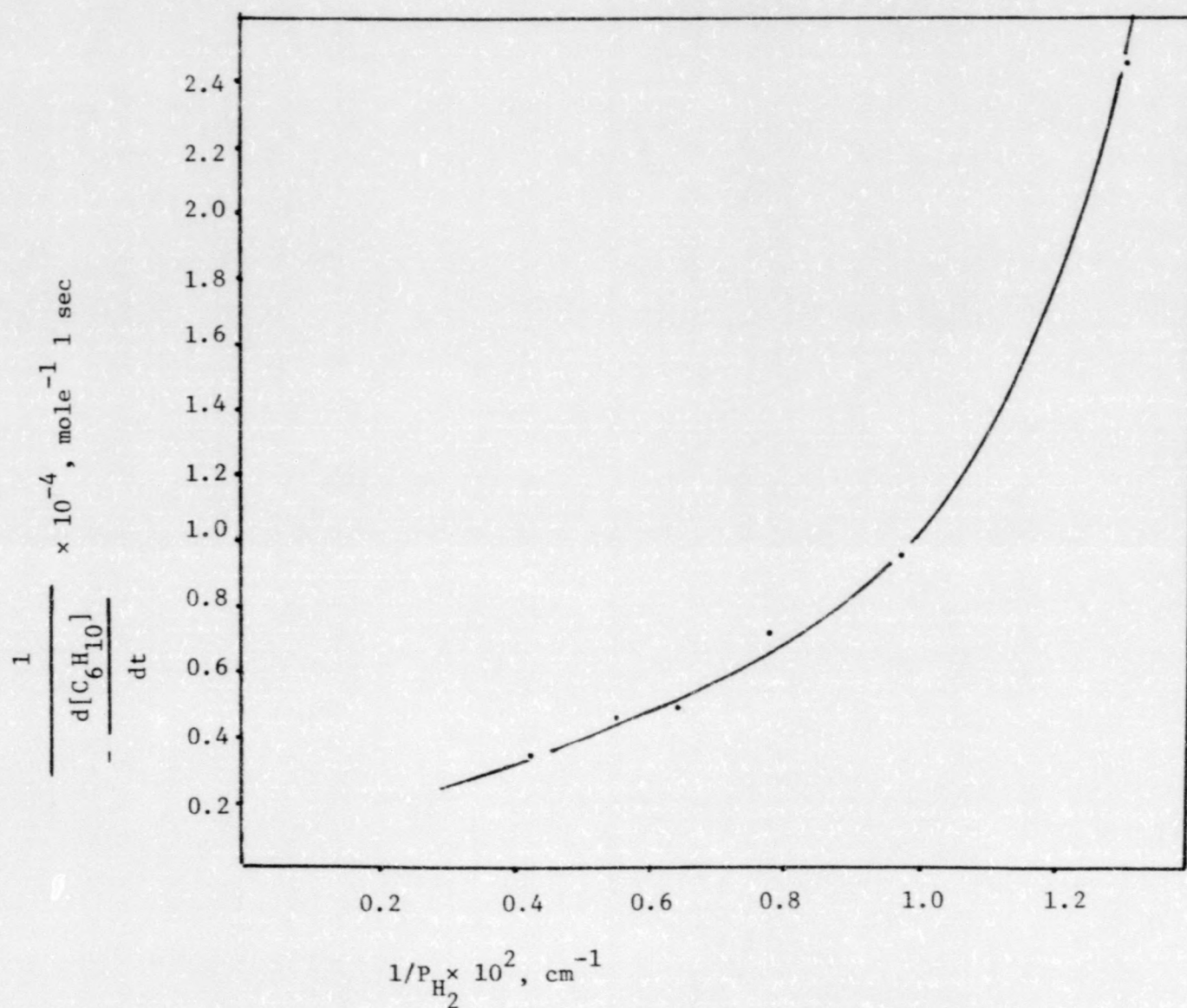


Solvent volume 20 ml. with 6.8 ml. cyclohexene, 4×10^{-4} moles of second batch catalysts, at 25.5°C

- 1.00 atm hydrogen pressure
- 1.34 atm hydrogen pressure
- * 1.68 atm hydrogen pressure
- 2.02 atm hydrogen pressure
- # 2.36 atm hydrogen pressure
- @ 3.04 atm hydrogen pressure

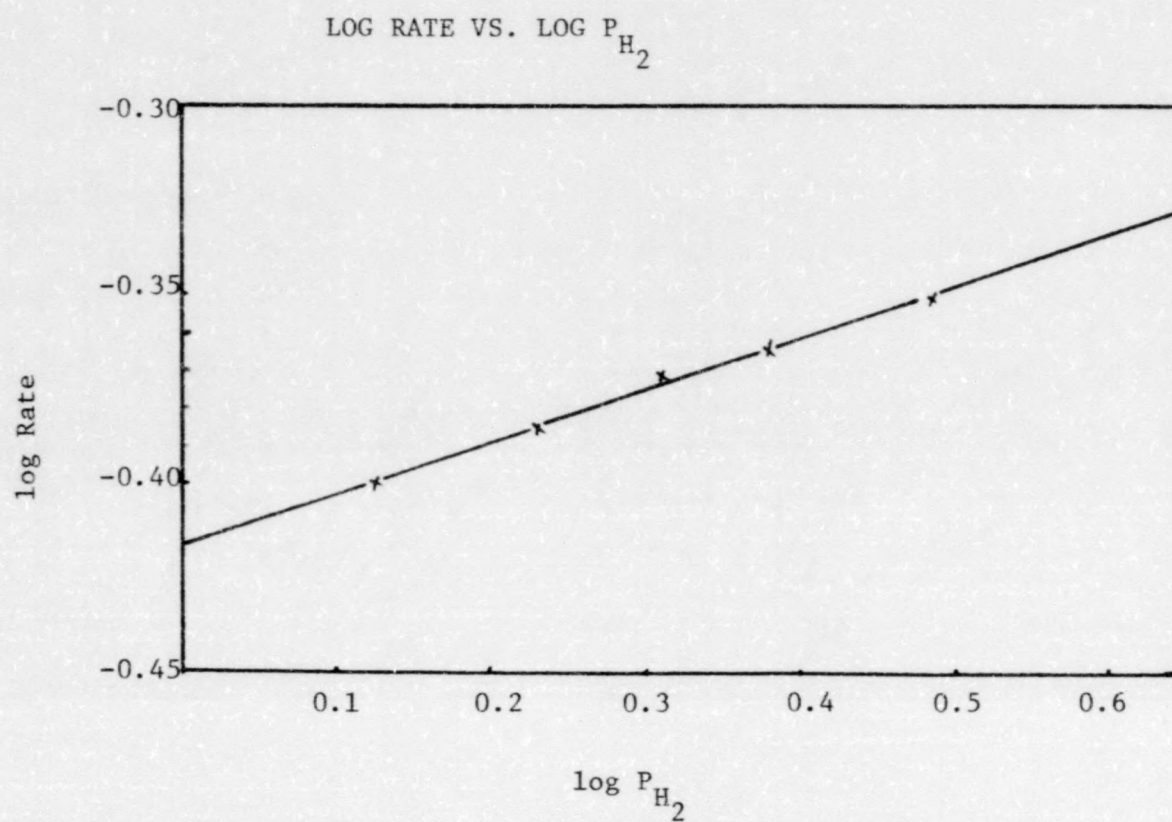
Fig X

THE RECIPROCAL OF THE RATE OF CYCLOHEXENE CONSUMPTION AFTER 50%
CONVERSION VS THE RECIPROCAL OF THE HYDROGEN PRESSURE



Solvent volume 20 ml. with 6.8 ml. cyclohexene, 4×10^{-4} moles of
catalysts, at 25.5°C

Fig XI



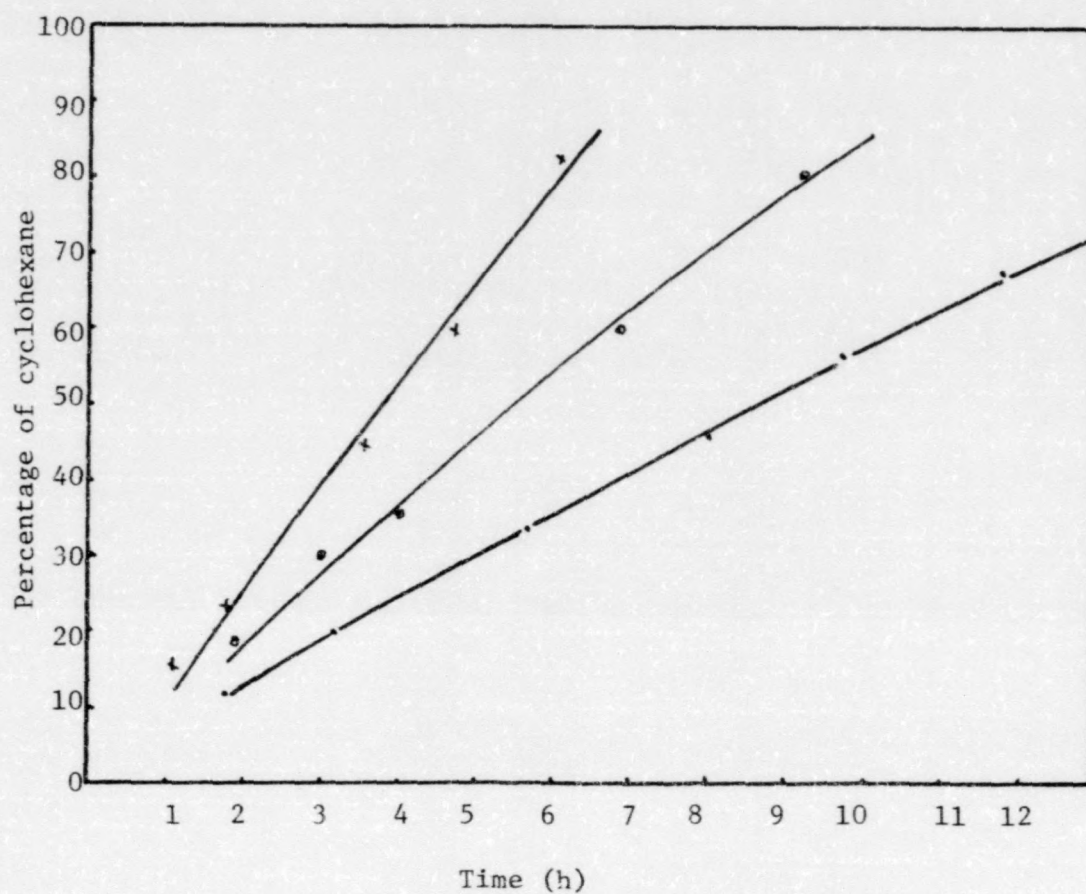
$$\text{Rate} = - \frac{d[C_6H_{10}]}{dt} \quad (\text{in mole l}^{-1} \text{ sec}^{-1})$$

P_{H_2} is in atm units

Solvent volume 20 ml with 6.8 ml cyclohexene, 4×10^{-4} moles of second batch catalysts, 25.5°C

Fig XII

QUALITATIVE COMPARISON OF THE RATES OF HYDROGENATION
(CATALYSTS AMOUNT DEPENDENCE)



Solvent volume 5 ml. with 1.7 ml. cyclohexene, at 21.5°C

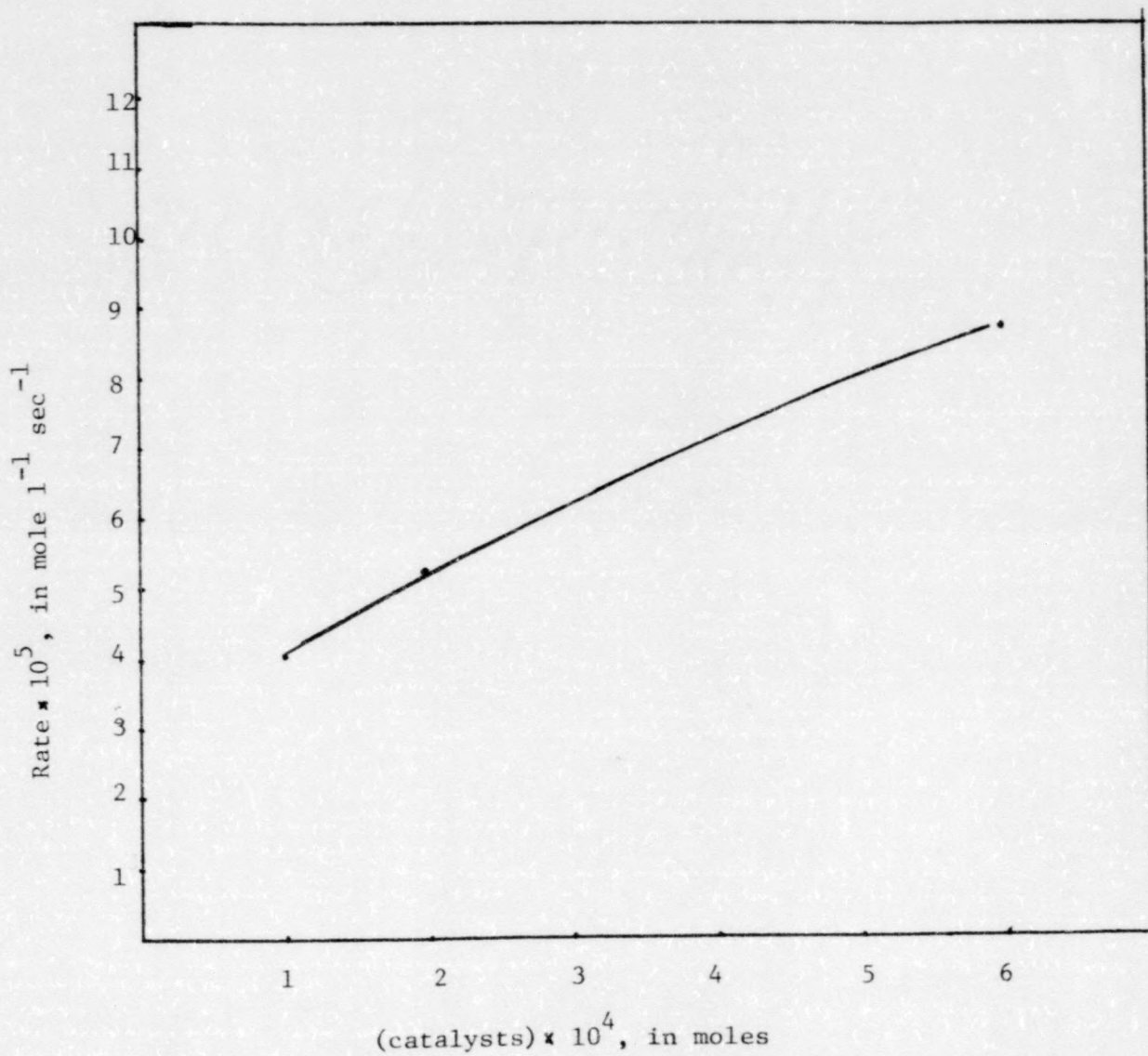
1×10^{-4} moles of catalysts

2×10^{-4} moles of catalysts

6×10^{-4} moles of catalysts

Fig XIII

THE RATE OF REDUCTION OF CYCLOHEXENE VS. THE NUMBER OF MOLES OF THE CATALYST

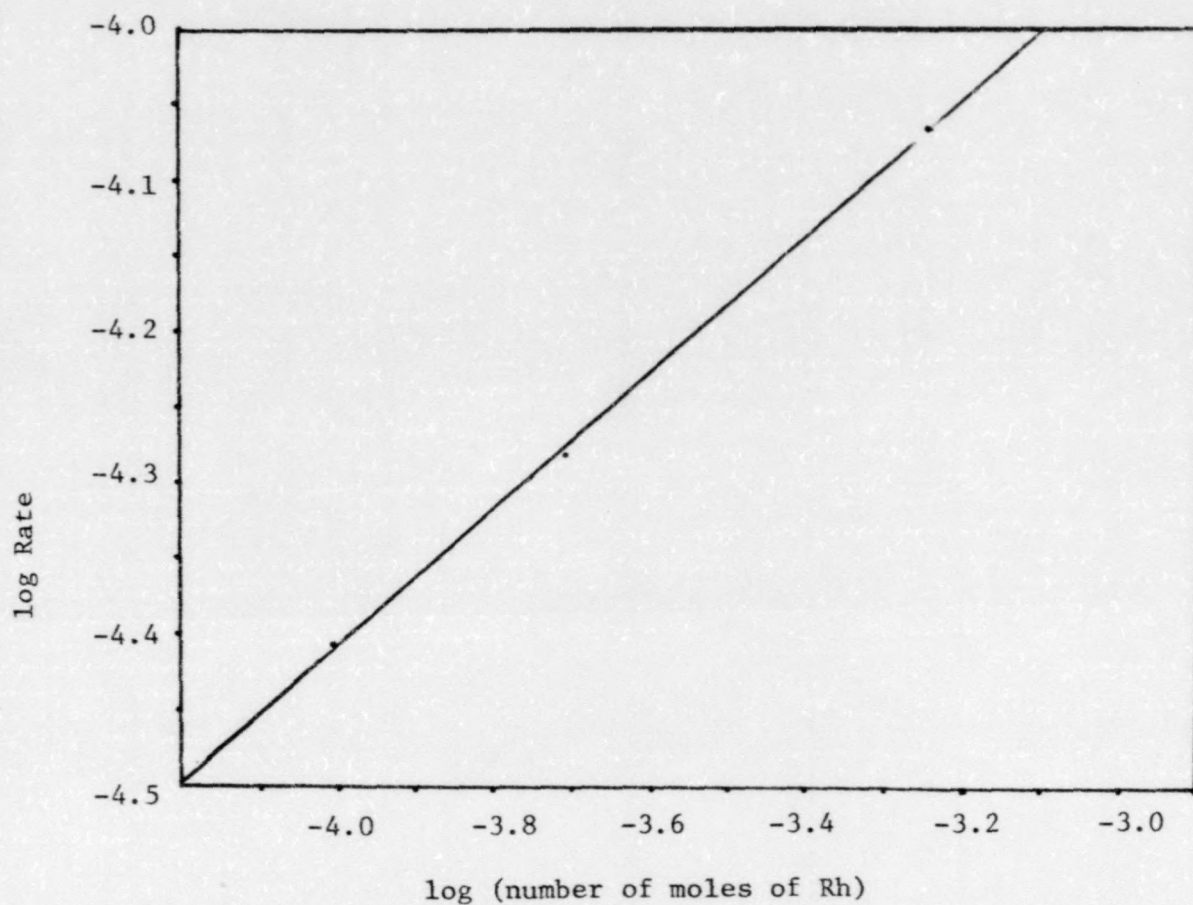


$$\text{Rate} = - \frac{d[\text{C}_6\text{H}_{10}]}{dt}, \text{ (in mole } l^{-1} \text{ sec}^{-1})$$

Solvent volume 5 ml with 1.7 ml C_6H_{10} , at 21.5°C

Fig XIV

LOG RATE VS LOG (NUMBER OF MOLES OF EHODIUM)

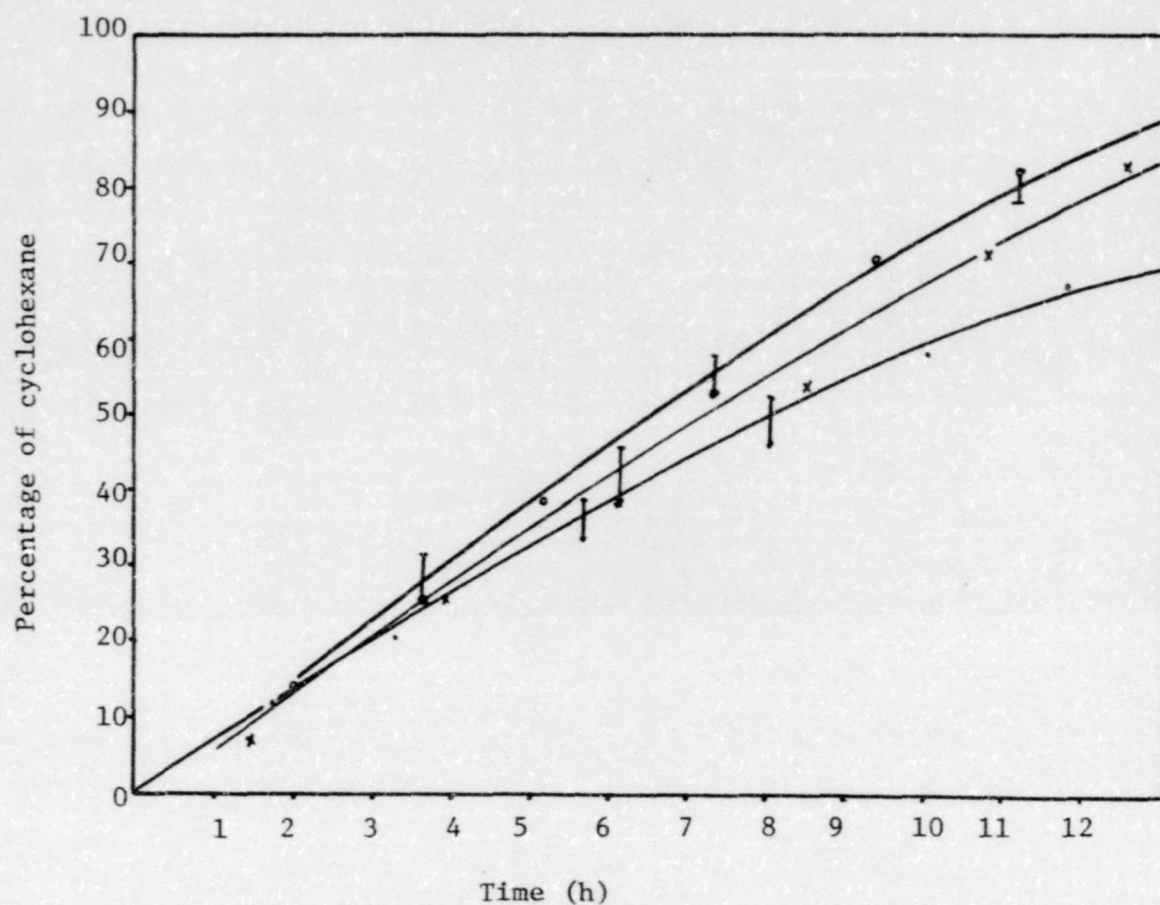


$$\text{Rate} = - \frac{d[\text{C}_6\text{H}_{10}]}{dt} \quad (\text{in mole l}^{-1} \text{ sec}^{-1})$$

Solvent volume 5 ml. with 1.7 ml. cyclohexene, 1×10^{-4} moles
of catalysts, 21.5°C

Fig XV

QUALITATIVE COMPARISON OF THE RATES OF HYDROGENATION
(TEMPERATURE DEPENDENCE)



Solvent volume 5 ml with 1.7 ml cyclohexene, 1×10^{-4} moles
of catalysts

----- 21.5°C

---*--- 35.0°C

-----o----- 50.5°C

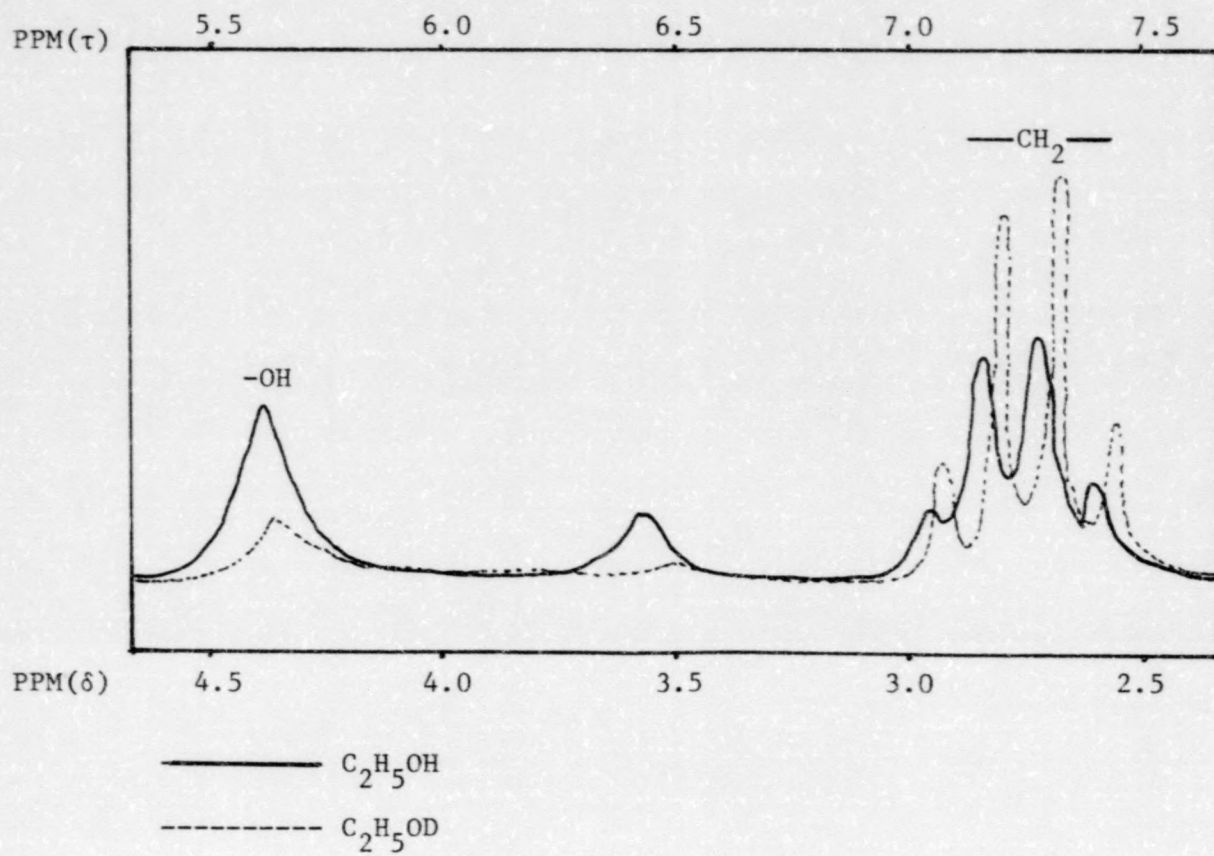
NMR SPECTRA OF C_2H_5OH AND C_2H_5OD 

Fig XVII

MASS SPECTRA OF 60% HYDROGENATION SOLUTION
($\text{C}_2\text{H}_5\text{OD}$ AS SOLVENT)

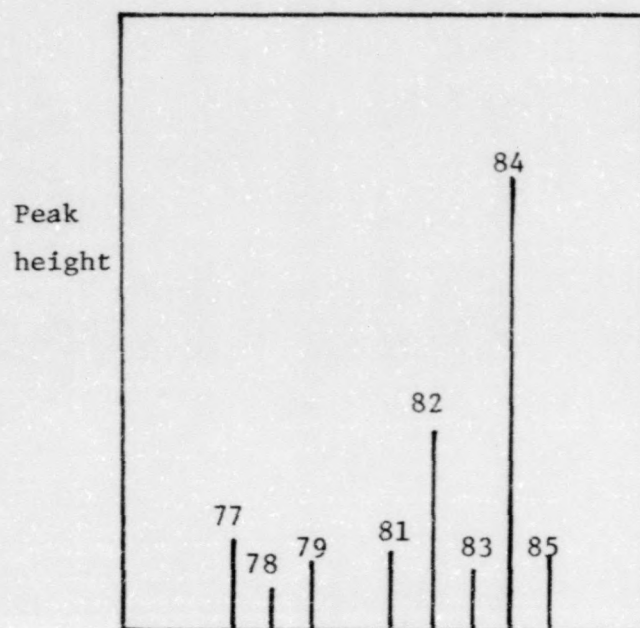


Fig XVIII

MASS SPECTRA OF 30% HYDROGENATION SOLUTION
(DEUTERIUM AND ETHYL ALCOHOL WERE USED)

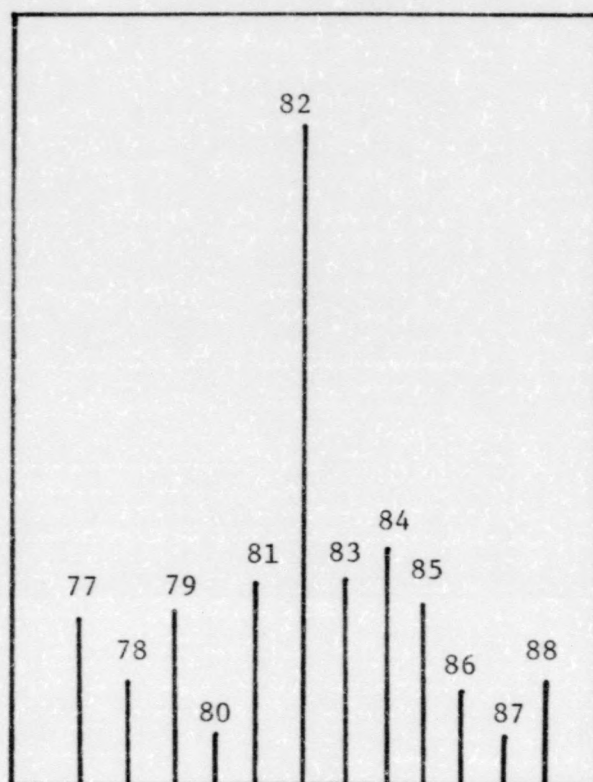
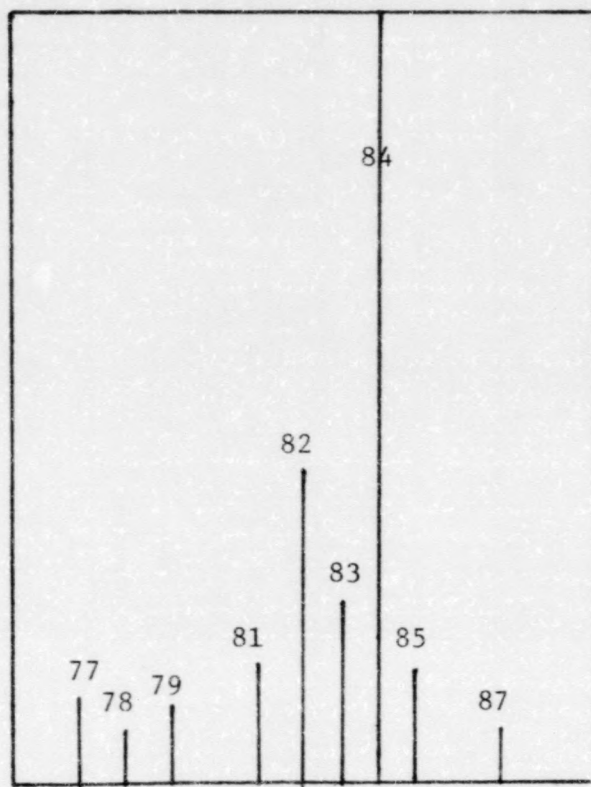


Fig XIX

MASS SPECTRA OF 74% HYDROGENATION SOLUTION
(HYDROGEN AND ETHYL ALCOHOL WERE USED)



The peak height at 84 is off scale.

CHAPTER V

DISCUSSION

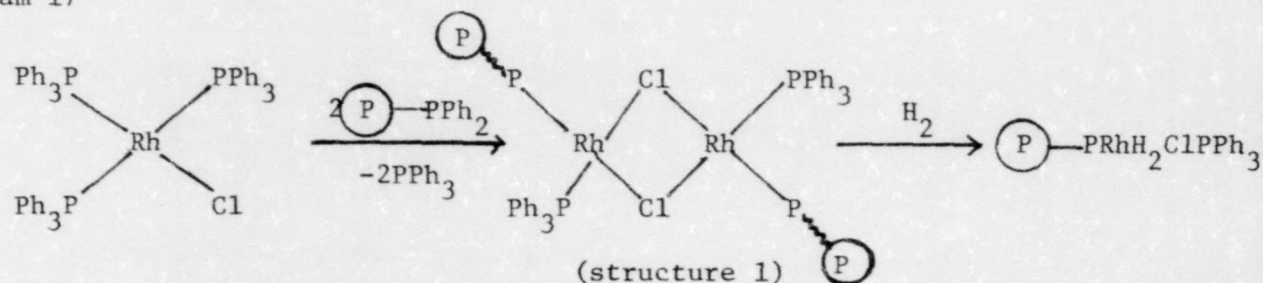
The objectives of this work were to determine the response of the polymer supported catalyst to such things as pressure changes, temperature, concentration, and to determine, if possible, the kinetic dependency and mechanism of hydrogenation. Each of the factors is considered individually.

(1) Kato et al.⁸⁷ determined that higher degrees of crosslinking of the polymer support would decrease or block the effect of "solvent channel" inside the catalysts. Since the solid support of our catalyst, XAD-4, is very high crosslinked (Table I), the hydrogenation was considered to occur on the surface of the beads.^{22,88} Fig I shows that the more active catalyst is the one with higher rhodium content. Infrared studies have been performed on carbonylated catalysts as one means of determining the nature of the catalyst structure. It was considered that by carbonylating the beads it would be possible to have some measure of the uniformity of environments about rhodium. That is, if the infrared spectrum revealed a very narrow CO absorption, a uniform nature would be indicated. If, on the other hand, a broad band or several bands were detected, it would establish that a range of rhodium environments was extant. However, all attempts to detect CO were unsuccessful and because the carbonyl absorption of anthranilic acid was very weak, it may be that the amount of CO taken up by the beads was too low to be detected.

(2) The mechanism of catalytic hydrogenation of unsaturated substrates is generally regarded as one involving three steps: (i) hydrogen activation, (ii) substrate activation, (iii) hydrogen transfer. Polymer-bound Rh(I)

catalysts (structure 1) were proposed by Kincaid *et al*⁷² to activate hydrogen via an oxidative addition path.

Diagram 17

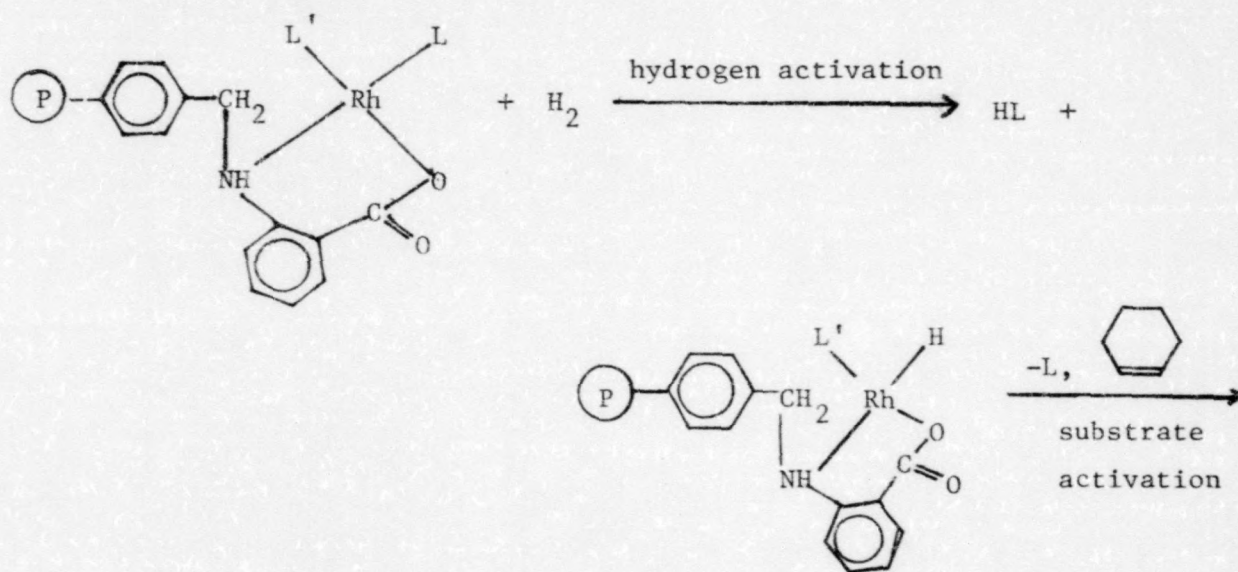


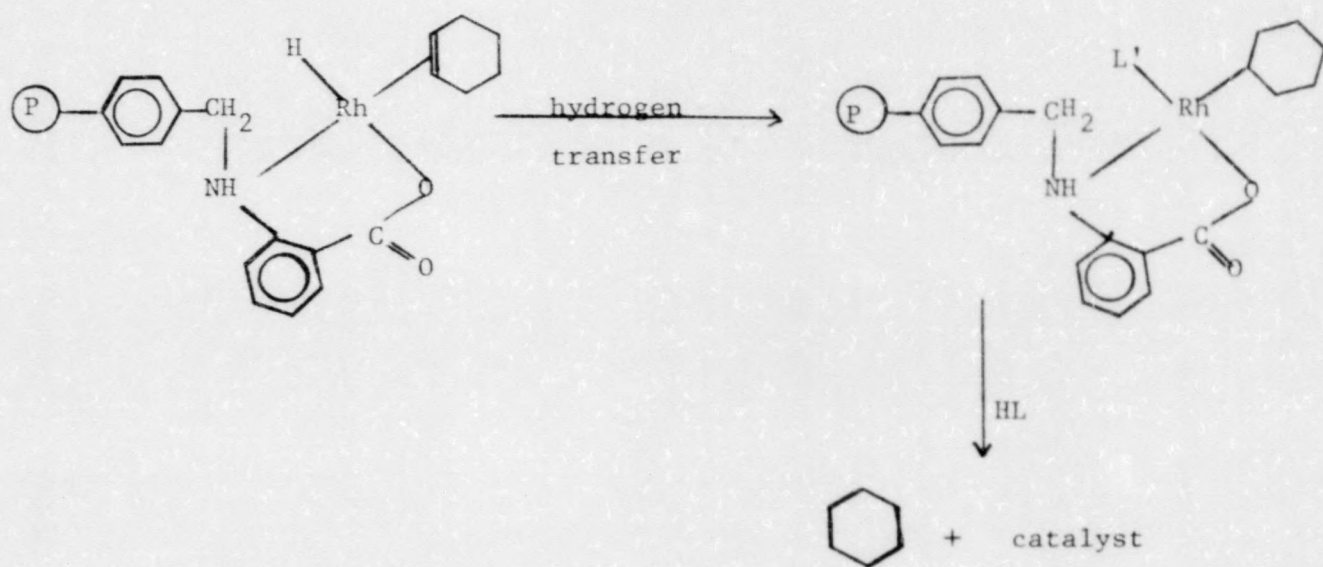
With highly crosslinked XAD-4 beads the likelihood of dimers (structure 1) is extremely low.

Homogeneous rhodium compounds achieve their catalytic activities by either heterolytic splitting of hydrogen or oxidative addition of hydrogen. The two mechanisms have been considered for our catalyst.

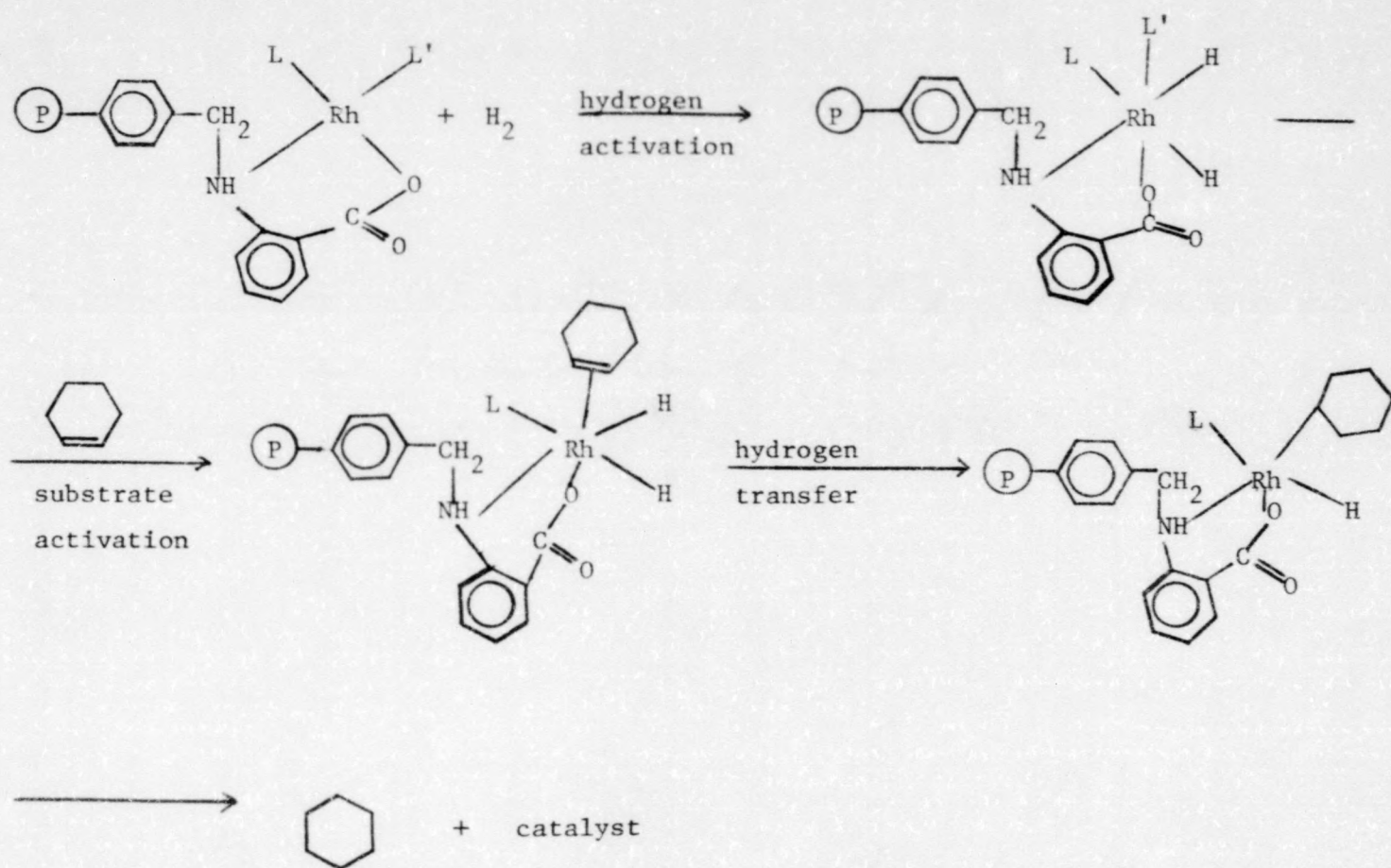
Diagram 18

(I) Heterolytic Splitting





(II) Oxidative Addition



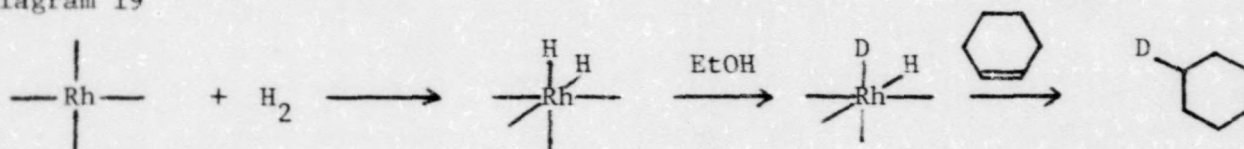
The first mechanism is not likely to be accepted due to the following reasons: (a) The rate of hydrogenation did not increase when additional acetate ions were present (Fig V). It revealed that: (i) mechanism I is not likely since hydrogen chloride was not formed during hydrogen activation step. If the hydrogen activation step was the slow step and one in which there was an equilibrium, addition of acetate would increase the concentration of the intermediate rhodium hydride and correspondingly increase the rate of reaction. If the hydrogen transfer step was rate-determining, acetate should slow the reaction rate because of a lower concentration of EtOH_2^+ . The strongest acid present would be $-\text{CO}_2\text{H}$ in uncomplexed anthranilic acid units, but in view of the location of the catalyst at the bead surface, interaction with the solution seems likely. Therefore, if the heterolytic mechanism was operative it would seem likely that either an increase or decrease in rate should occur when acetate is added. Or, (ii) mechanism I is possible, but hydrogen activation or hydrogen transfer is not the rate-determining step.

(b) The rate did not decrease when additional potassium chloride or hydrogen chloride were present (Fig III). On the contrary, it was increased, and this is interpreted to be further confirmation that the rate of reaction is pH independent, at least under the conditions tested. The rate is dependent, however, upon the concentrations of chloride ion and this effect is not simply a "salt" effect since LiClO_4 does not give a corresponding increase in rate (Fig V). It is apparent that chloride is changing the ligand structure of one or more of the rhodium species during the course of hydrogenation, but a precise interpretation of the effect is not possible.

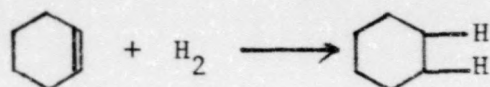
(c) From the mass spectra of the deuteration studies, it appeared (Fig XVII and XIX) that the peak height ratio of 85 peak to 84 peak when hydrogenation was carried out with H_2/EtOD (Fig XVII) is much greater than that

with H_2/EtOH (Fig XIX). The higher ratio of 85 peak to 84 peak in Fig XVII can be explained by either of two mechanisms. One of these is that the reaction proceeds by the heterolytic process and that the increased abundance of the 85 peak represents formation of monodeuterocyclohexane. A second possible explanation is that exchange with the solvent occurs.

Diagram 19



This solvent exchange has also occurred in homogeneous catalysts⁸⁹. Since the 84 peak (Fig XVII) is the largest, so the main reaction is:

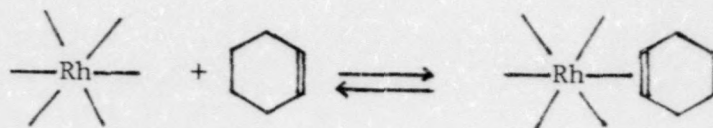


i.e. there is no exchange.

When deuterium D_2 was used instead of hydrogen, the spectra becomes more complicated (Fig XVIII). The detailed discussion needs more definitive mass spectrometry.

(3) Reaction temperature (Fig XV), hydrogen pressure (Fig IX), and the amount of catalyst present (Fig XII) only have very small influence on the rate of hydrogenation of cyclohexene. Reduction rate is considerably higher than Nicholson's polymer-bound rhodium cluster catalyst.⁹⁰ From the substrate concentration studies we assumed that the rate of hydrogenation is essentially independent of the substrate concentration (Fig VI and VIII). However, the time required for the conversion of 1 mmole cyclohexene decreases with increasing cyclohexene concentration, and finally approaches an asymptotic value (Fig VII). This can be explained by the following equilibration.

Diagram 20



The greater number of cyclohexene molecules would have higher collision frequency with the active sites on the catalyst, thus, less time would be needed to convert 1 mmole of cyclohexene.

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