

LIQUID PHASE HYDROFORMYLATION BY ZEOLITE SUPPORTED RHODIUM

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(ABSTRACT)

The purpose of this research was to directly compare the behavior of zeolites containing rhodium with that of homogeneous rhodium species as catalysts for liquid phase hydroformylation of 1-hexene in order to study the effects of zeolite immobilization. NaX zeolite was cation exchanged with several rhodium salts and used as hydroformylation catalysts at 50°C and 125°C in the presence of: triphenylphosphine (PPh₃), dimethylphenylphosphine (PMe₂Ph), and the poison for zeolite surface and solution rhodium: triphenylmethylmercaptan (Ph₃CSH). The results of these experiments were compared with those of several homogeneous catalysts under similar conditions.

It was found that previously reported results of intrazeolitic activity with RhNaX at 50°C were probably incorrect, since, the addition of PMe₂Ph, Ph₃CSH, or both, virtually halted all reactivity of RhNaX.

The catalytic results at 125°C did not conclusively indicate the location of the active rhodium. Thus, intrazeolitic

activity at 125°C may or may not have been observed, and needs further investigation.

Reaction profiles were obtained for several of the catalyst systems, using an automatic sampling system. From these profiles it was found that the addition of excess PMe_2Ph halted isomerization of 1-hexene to 2-hexenes for the zeolite-supported rhodium, and hindered, but did not stop isomerization for the homogeneous catalysts. Also, as expected, it was observed that the homogeneous catalysts reacted to completion faster than the heterogeneous catalyst.

In addition, the effects of such treatments as preheating in air and precarbonylation of the heterogeneous catalysts were studied. Pretreatments had no effect upon the catalysis. Also, no activity was observed from the heterogeneous catalysts at 125°C unless phosphines were present.

Finally, the hydrogenation of 1-hexene was studied. Heterogeneous and homogeneous rhodium catalysts showed hydrogenation activity which was accompanied by isomerization at 60°C and 125°C.

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1.0 INTRODUCTION

In recent decades, many homogeneous catalytic processes have been developed for industrial applications. They tend to be highly selective under relatively mild operating conditions. Reactor temperature control is facilitated for exothermic reactions by heat transport through the solvent. In addition, the chemical reactivity of homogeneous catalysts is easily modified by changing ligands or solvents.¹ Some of the negative aspects of homogeneous catalysis include difficult, costly, and often incomplete separation from products. In addition, relatively low operating temperatures are required to prevent decomposition of the catalyst complex and/or solvent loss. This requirement limits the use of generated heat elsewhere in a plant.

Heterogeneous catalysis offers the obvious advantage over homogeneous catalysis of ease in separation of the catalyst from reactants and products. Also, heterogeneous catalysts are typically able to withstand higher reaction temperatures. However these catalysts also have their drawbacks. For example, reaction rates are generally considerably slower due to mass transfer limitations.

One class of heterogeneous catalysts is based upon transition metal containing zeolites. The zeolite can be size selective to reactant and product molecules due to the fact

that the pore sizes are the same order of magnitude as the molecules. However, the transition metal can reside at different sites on the zeolite, for example, on the surface, or within the pores, and may react differently at each location. Thus, selective poisoning of surface sites may be necessary to achieve size selective reaction behavior.

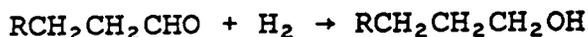
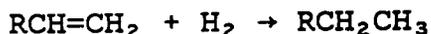
The following section will review some of the literature which is available on the recent advances in hydroformylation and supported rhodium catalysis.

2.0 BACKGROUND ON HYDROFORMYLATION

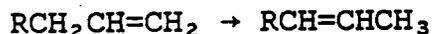
The first industrial hydroformylation took place in 1948, and commercial as well as academic interest in this reaction has increased steadily since that time. Known industrially as the oxo reaction, hydroformylation is the reaction of an alkene with hydrogen and carbon monoxide to form an aldehyde:



A catalyst is required for this reaction to take place and the desired product is the linear aldehyde. Two reactions typically accompany hydroformylation. These are hydrogenation:



and isomerization:



The major hydroformylation process today is butyraldehyde formation from propylene. Currently, the world market for 2-ethylhexanol and butanols derived from butyraldehyde exceeds 6 billion pounds per year.²

Much of the 2-ethylhexanol is converted to phthalate esters for use as plasticizers. Butanol and other short-chain alcohols... are used extensively as solvents.¹

The first generation of catalysts used for promotion of this reaction were simple transition metal carbonyls like $\text{Fe}(\text{CO})_5$ and $\text{Co}_2(\text{CO})_8$. It was first recognized in the mid-50's that rhodium carbonyl catalysts were more active, and could be operated at milder conditions than cobalt.³ However, since the cost of rhodium is approximately 3500 times that of cobalt, and since only 3-4 tons/year of rhodium are produced worldwide, the use of homogeneous rhodium carbonyls has not been feasible. Also, rhodium carbonyl catalysts tend to give mostly branched aldehydes.¹ A current process involving rhodium phosphine catalysts is available, but only for ethylene and propylene hydroformylation. In this process the catalyst remains in a liquid phase while the olefin and products are continuously supplied and removed in the vapor phase. One of these processes will be described later in this section.

2.1 Effect of Phosphine Modification

Many studies have involved the effects of modifying rhodium carbonyl catalysts by displacing one or more carbonyls with ligands such as triphenylphosphine. In general, this type of modification results in increased thermal stability,⁴ a suppression of isomerization,⁴ and an increased selectivity to the straight-chain aldehyde.⁵ ,⁶ On the nega-

tive side, the phosphine can lead to reduced activity;⁴ especially over certain P/Rh ratios which are specific for each system.⁹

Although most phosphine ligands appear to have a beneficial effect on rhodium catalysis, triphenylphosphine appears to be the best choice, as noted by Masters:¹⁰

As far as the nature of the tertiary-phosphine ligand is concerned, of those tested, triphenylphosphine appears to be optimal in terms of reaction rate, selectivity, and also of cost.

It appears that phosphines inhibit isomerization by inhibiting the double bond shift.⁵ Carbon monoxide also appears to have this inhibiting effect. The isomerization rate decreases with increasing CO pressure, and is very low for a CO partial pressure greater than 150 atmospheres.⁵

Increased selectivity to the straight-chain aldehyde by the addition of a trisubstituted phosphite was demonstrated by Pruett and Smith⁷ for a heterogeneous catalyst. In studying the hydroformylation of 1-octene by carbon-supported rhodium, they found an increase in the percentage of normal aldehyde from 31 to 89% with an increase in triphenylphosphite from 0 to 60 grams per 112 grams 1-octene in 200 ml toluene. The reaction environment was mild (90°C and 80-100 psi 1:1 H₂/CO).

2.2 LPO Process

Union Carbide Corp., Davy Powergas Ltd, and Johnson Matthey and Co. Ltd. (U.K.) won the 1977 Kirkpatrick Chemical Engineering Achievement Award² for their process called the Low Pressure Oxo (LPO) process. This process was one of the first to use a rhodium catalyst for hydroformylation of propylene to produce butyraldehyde. Some of the improvements of this process over the old cobalt hydrocarbonyl homogeneous process are summarized in Table 1.

The efficiency of this process is significantly higher than that of conventional oxo processes:

Typical feedstock consumption is 750 kg propylene (94 mole percent), and 740 normal cubic meters of synthesis gas (99 mole percent), per 1,000 kg of n-butyraldehyde. The conventional oxo process, by contrast, is said to consume 930 kg of propylene and 1,200 cubic meters of synthesis gas.²

Energy requirements are low for this process because (1) there is no need to compress the synthesis gas and (2) only minimal distillation is needed. In addition, there is negligible environmental impact because:

The process has only two effluent streams, a liquid containing the minor output of heavy byproducts, and a gas stream. Both can be used as fuel.²

Table 1. Comparison of LPO and Cobalt processes

	LPO	COBALT HYDROXY- CARBONYL	PHOSPHINE- MODIFIED COBALT
n/i	>10:1	3-4:1	6-8:1
Side reactions	low occurrence	high occurrence	high occurrence
Temp.	80-120°C	140-180°C	180-200°C
Pressure psi	200-400	4000-5000	800-1500

Most important for a rhodium-catalyzed process, there is no need for catalyst recycle since this is heterogeneous process (the catalyst is in a homogeneous liquid phase, while the feed propylene and products are gases). However, a catalyst makeup point is incorporated into the process with the claim that "if the catalyst is accidentally deactivated or poisoned, it can be recovered with little loss."²

Other processes incorporating homogeneous liquid-phase rhodium catalysts for the hydroformylation of gaseous propylene have been reported,^{6,11} but an industrially acceptable rhodium-catalyzed process for hydroformylation of higher α -olefins has yet to be developed. This is due to the inability to sufficiently recover rhodium from the product stream.

2.3 Zeolites

Zeolites are hydrated crystalline aluminosilicates containing monovalent or divalent cations which can be reversibly exchanged without destroying the zeolite framework.¹² Zeolite NaX, (a synthetic faujasite) is used in this study, and has the following empirical formula: $\text{Na}_{86}(\text{AlO}_2)_{86}(\text{SiO}_2)_{186} \cdot 264\text{H}_2\text{O}$. Figure 1 shows the NaX structure, where the α cage or supercage diameter is 12.5Å, with

pore openings of 8.1Å. The β cage has a 6.6Å diameter with 2.6Å pore openings.

As mentioned above, it is possible to exchange the charge balancing cations. Although there are cations in both the α and β cages, "from the standpoint of catalysis it is important that the catalytic complex be located in the supercages."¹³

2.4 Supported Rhodium Catalysis

Recent studies on heterogenized homogeneous rhodium catalysis have included a wide variety of methods for immobilization as well as a variety of supports. Some of these supports include polymers, such as phosphinated styrene resins,¹⁴ gas-liquid chromatography supports, such as Silocel suspended in methanol,¹⁵ carbon and alumina supports,¹⁶ and zeolites.¹³

Surrel¹⁷ points out that for heterogenized operation in liquid phase the method of attaching a metal complex to a carrier via formation of chemical bonds is to be preferred in general since the dry or supported liquid phase catalysts may easily be destroyed by immersion in solvents or liquid reactants. Mantovani et al.¹³ note of zeolite supported catalysts that "their stability toward drastic experimental

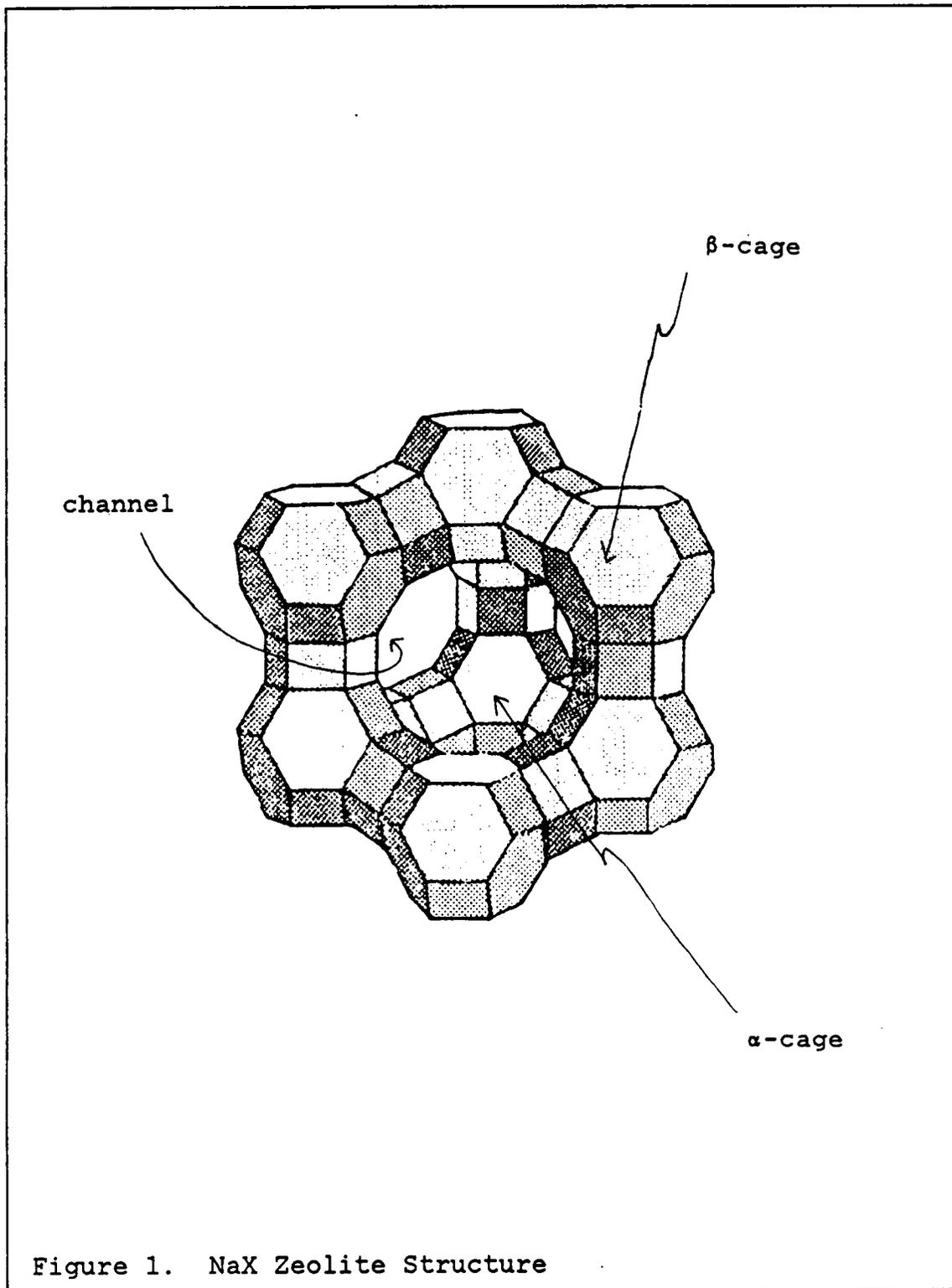


Figure 1. NaX Zeolite Structure

conditions may give them advantages over functionalized polymers."

All heterogeneous processes offer the advantage of easy separation or the use of a continuous, rather than batch processes. Zeolites, however, offer an added advantage of a pore structure capable of providing both additional selectivity as well as increased stability at high temperatures. The selectivity of zeolites can be due to various reasons such as:

1. Limiting the access of certain reactant molecules to the intrazeolitic active sites;^{18, 19}
2. Hindering the desorption of certain products;¹⁹
3. Inhibiting the formation of certain reaction intermediates;¹⁹
4. Change in pore size due to coating by intracrystalline water.¹⁸

It is generally desirable to have supported catalysts with equivalent or higher selectivities than their homogeneous analogues to compensate for the drawback of diffusion limitations. However, this drawback may also be compensated for by

the fact that the support may stabilize catalytic intermediates such that the catalyst can be operated at higher temperatures than their homogeneous counterparts without deactivation.²⁰

One widely studied reaction using rhodium exchanged zeolites is methanol carbonylation. A review of these studies is given by Rode.²¹

2.4.1 Rhodium Supported on Zeolites

Mantovani et al.¹³ report good results for the hydrofomylation of olefins with rhodium carbonyl clusters supported on NaY zeolites. These clusters were formed by the CO reduction of rhodium ions exchanged within the zeolite. For liquid phase hydroformylation of 1-hexene they obtained a selectivity to aldehydes of approximately 95% and an n/b (normal/branched aldehyde) of 1/1.2. Also studied was the effect of reaction temperature and pressure on catalysis. Little differences other than conversion were observed for temperatures ranging from 80 - 130°C and pressures from 50 - 100 atmospheres of 1/1 H₂/CO. Mantovani et al.¹³ claim that this catalyst was found to be stable over several catalytic cycles, although a rhodium loss of about 10% in the first two cycles and another 10% occurred in the following four cycles.

A more recent study on zeolite supported rhodium was performed in this laboratory by Davis et al.²² This study compared several types of both homogeneous and heterogeneous rhodium species for the liquid phase hydroformylation of 1-hexene. The supported catalysts were classified into three

types based on the activity observed. Type I showed solution activity due to the high amount of rhodium eluted into solution. Type II appeared to have surface active sites, and Type III to have intrazeolitic active sites.

Proof of Type I behavior was given by a comparison to the homogeneous catalyst behavior, plus the observation of colored solutions after reaction, and the detection of rhodium in solution by atomic absorption (AA). It should be noted here that the AA method for determining rhodium in the reaction solution was qualitative not quantitative, and that since the time of that study, an accurate method of determining rhodium elution has been found (utilizing UV spectroscopy). The catalysts which exhibited Type I behavior were RhNaY (NaY cation exchanged with $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$ at a 1% rhodium loading), RhNaY (from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, at a 1% loading), and RhCaA (from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ at a 2% loading). The claim by Mantovani et al.¹³ of intrazeolitic activity from RhNaY catalysts was contradicted by the results of Davis et al.²² who show that the observed catalysis was from solution activity by eluted rhodium from RhNaY catalysts.

Type II behavior (surface catalysis) was observed from two supported catalysts: RhNaX (NaX cation exchanged with $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ at a 1.5% rhodium loading) and Rh-silica at a 1.4% rhodium loading. Since the silica has large pores compared to X and Y zeolites, it would be expected to show

surface activity if the rhodium remained bonded to the support. Although rhodium elution was not discussed for these catalysts, they did show different behavior from both the homogeneous and Type I catalysts, but similar to each other. Hence the claim of surface catalysis.

Davis et al.²² claim Type III behavior (intrazeolitic catalysis) from RhNaX (cation exchanged from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ at three different weight loadings of rhodium: 0.8%, 1.0% and 4%). A much lower 1-hexene conversion and selectivity to aldehydes coupled with a high n/b (normal/branched aldehyde) was observed for these catalysts, possibly indicating the diffusion limitations expected for reactions taking place inside the zeolite supercages. Also, rhodium loss was minimal for the first cycle, since the rhodium loading on the catalyst was found to be constant by AA (within experimental error) before and after exposure to reaction conditions, and in addition, the reaction solution was colorless. It should be pointed out that all of the reactions in this study were performed at 50°C and no poison for rhodium in solution was used. Also, as previously mentioned, an adequate technique for the measurement of rhodium in solution had not yet been found, and the traces of rhodium in solution which were "within experimental error" may have been enough to cause the conversions observed from these catalysts. A poison for

soluble rhodium would have quickly shown whether or not the catalysis was intrazeolitic.

Thus, for conclusive proof of intrazeolitic activity, further work must be done with these catalysts utilizing an effective rhodium elution measurement technique, a poison for solution rhodium, and higher temperatures to enhance diffusion. Finally, the effect of phosphine modification, which was only briefly mentioned, but not performed by Davis et al.,²² must be investigated.

3.0 OBJECTIVES

The objective of this investigation was to directly compare the behavior of zeolites containing rhodium with that of homogeneous rhodium species as catalysts for the liquid phase hydroformylation of 1-hexene in order to study the effects of zeolite immobilization. Rhodium carbonyl and rhodium carbonyl phosphine catalyst systems were used in this study.

4.0 MATERIALS AND METHODS

4.1 Materials

The reagents used for this study were as follows: The 1-hexene was 99+% Aldrich Gold Label, the toluene - 99+% Aldrich Gold Label spectrophotometric grade, the dimethylphenylphosphine - Aldrich 99%, and the triphenylmethyl mercaptan - Aldrich 98%. The triphenylphosphine and NaX zeolite were purchased from Strem Chemical Company. The $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was obtained on loan from Johnson Matthey and the $\text{Rh}_4(\text{CO})_{12}$ was purchased from Tennessee Eastman. The $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ was synthesized by literature methods^{2,3} as were the $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ^{2,4}, and the $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ ^{2,5}. The 1:1 H_2/CO mixture and the pure CO were purchased from AIRCO. For the gas chromatograph, the air was Grade D, the helium, Grade 5, and the hydrogen, Grade Zero 1.0, and these were all purchased from AIRCO. None of the above compounds were purified further before use.

4.2 Equipment

Schematics of the experimental setups may be seen later in this section. The equipment used included the following: a Parr 600 ml pressure reactor with stirrer, a Valco C14WT1

Submicroliter HPLC Injection automatic valve, a Perkin-Elmer Model 900 gas chromatograph with a Hewlett-Packard 3390A integrator and an MMD-1 computer. The solenoid valves were model 2R2HLBG20501, purchased from Skinner Valve and Fitting Corp. The flash arrester was purchased from AIRCO. The porous frit was obtained as a free sample from Mott Metal. The UV spectrophotometer was a Varian-Techtron Model 635, and the UV cells were purchased from Wilmad Glass Co., Inc.

4.3 Cation Exchange Procedure

1.) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$

The amount of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ necessary to give the desired weight % Rh on the zeolite was calculated, and five percent extra was added to allow for incomplete exchange. A solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in water was added dropwise to a 90°C aqueous slurry of NaX zeolite (150-200 ml water per gram zeolite). After the addition, this slurry was stirred at 90°C for 22 hours, then filtered and washed with distilled water. The solid was then dried at 100°C for five hours.

2.) $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ or $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$

The following procedure was used for both exchanges: a solution of the rhodium salt as necessary for the desired weight % Rh plus 5% and NaX zeolite in approximately 200 ml water per gram zeolite was stirred at 50°C for 22 hours. The

solution was then filtered, washed, and dried for five hours as above.

4.4 Reaction Procedure

The procedure for initiating and conducting a typical reaction was as follows (see Fig. 2 for schematic): the appropriate amount of catalyst necessary to produce 0.5 mmole Rh/liter toluene was placed into the reactor vessel along with any other solids needed for the reaction, e.g. the mercaptan and/or triphenylphosphine. Next, the liquid reactant, usually 1-hexene, and the solvent, toluene, were measured and added to the reactor. The reactor was then tightly sealed, and attached to the H₂/CO tank. If dimethylphenylphosphine (PMe₂Ph), an air-sensitive liquid, was to be added, the reactor was flushed several times with 1:1 H₂/CO and the required amount of PMe₂Ph was injected through a septum.

For several experiments in which both PMe₂Ph and the mercaptan were to be added, the necessary amount of catalyst was placed into the reactor vessel along with a portion of the solvent toluene. The remaining toluene (as needed to dissolve the mercaptan) plus the mercaptan and the 1-hexene were measured into a separate container through which gaseous nitrogen was bubbled to de-oxygenate the mixture. After

- 1- VALVE 1
- 2- VALVE 2

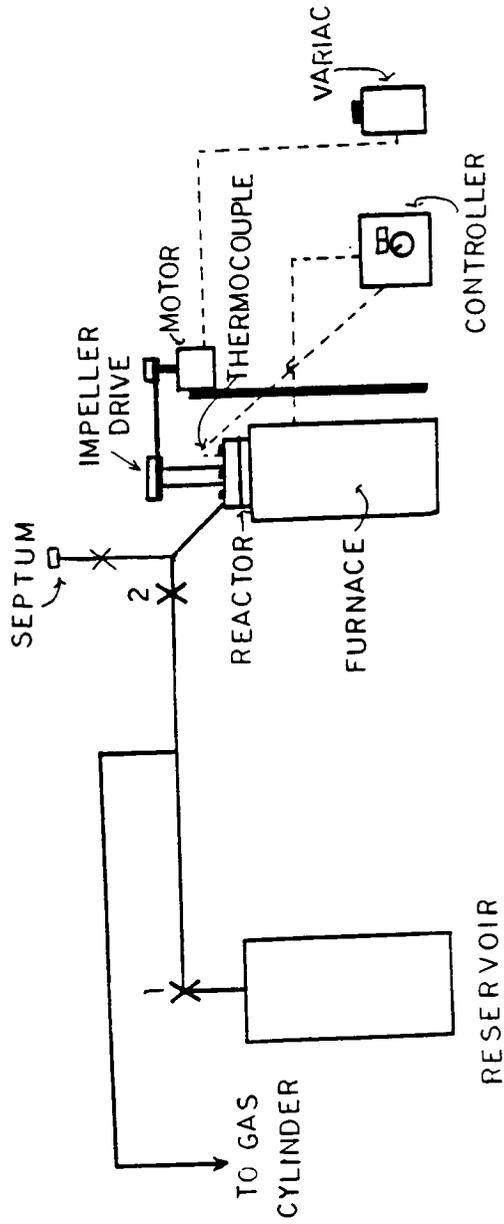


Figure 2. Batch Reactor System (from Rossin²⁶)

flushing the reactor vessel with 1:1 H₂/CO, the PMe₂Ph was injected and stirred with the catalyst/toluene solution for fifteen minutes to promote the formation of a rhodium phosphine complex. At this time the mercaptan/hexene/toluene solution was injected.

Once all of the reagents were added, they were stirred at room temperature under H₂/CO to ensure thorough mixing. At this point, the heater was turned on and a five to ten minute time lag was required to bring the reactor to operating temperature. More H₂/CO was added as necessary to bring the reactor pressure up to 300 psig. The main gas tank was closed off after the reservoir was filled at 300 psig.

After the allotted reaction time, usually 21 hours, the reactor was closed off, detached from the H₂/CO tank and quenched in cold running water for approximately 30 minutes. When cool, the reactor was depressurized and opened for sampling.

For the automatic sampling runs (see Fig. 3 for schematic), the reactor was attached to the gas chromatograph at the same time it was attached to the H₂/CO tank. Due to loss of pressure from sampling, the reservoir was not used for these runs; the main H₂/CO tank was left open. A sampling line terminating in a porous frit was used to obtain liquid samples while preventing solids take-up. Samples were acquired via a timing program (see Appendix A) on an in-line

MMD-1 computer using the Valco automatic sampling valve. A system of solenoid valves before and after the sampling valve were employed to use the pressure in the reactor in order to take samples without a syringe or pump.

4.5 Rhodium Elution Determination

Rhodium elution from the cation-exchanged zeolite was measured as follows: 0.1 g of sodium chloride was added to a porcelain evaporating dish with 10 ml of concentrated hydrochloric acid. The filtered reaction solution, either whole or in part, was added to this solution while heating (somewhere close to, but below the mixture boiling point) with stirring to evaporate the toluene. Additional portions of solution were added as evaporation occurred. Once evaporated to near dryness (solution may evaporate dry or may form a tar-like mass), the residue was heated over a bunsen burner for 15 to 30 minutes. Care was taken to burn off any dark-colored char that formed on the initial heating. At this time, 1.0 g potassium pyrosulfate was added and melted into the residue over the flame. After cooling, the solid was dissolved in 20 ml of warm concentrated hydrochloric acid (or the whole mixture may be heated lightly while adding cold hydrochloric acid). Once the solid was dissolved, 10 ml of 1N SnCl_2 in 1-2N HCl solution were added. This solution was

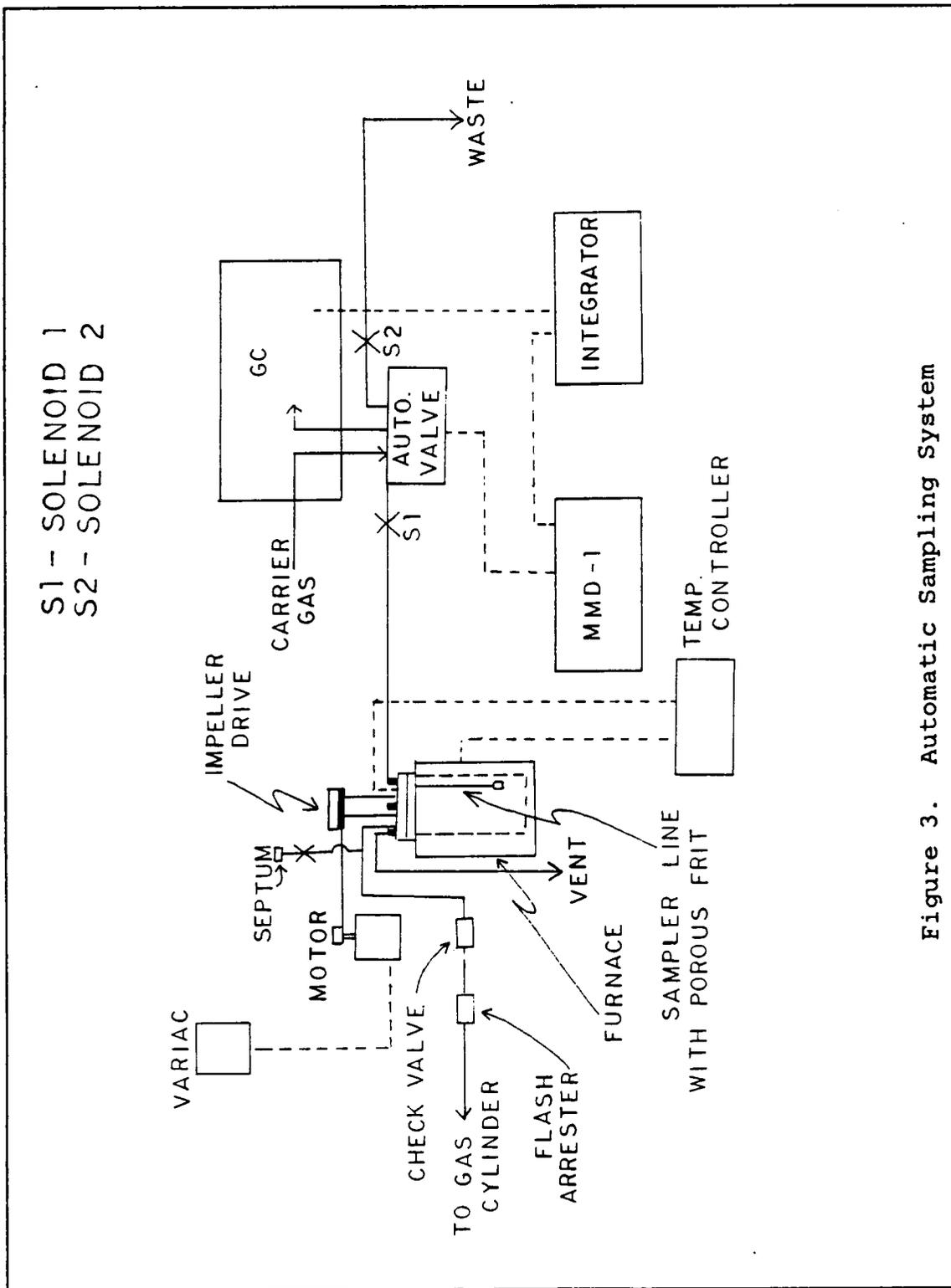


Figure 3. Automatic Sampling System

heated under agitation for 30 minutes, after which a reddish color (indicative of rhodium) was visible. The solution was then removed from the hot plate, and an additional 5 ml of SnCl_2 solution were added. This solution was then poured into a 50 ml volumetric flask and brought to level with 1-2N HCl solution.

The amount of rhodium in the final solution was measured using a UV spectrophotometer. The wavelength, λ , was set at 475 nm and the machine was zeroed using the SnCl_2 solution. The initial calibration of the spectrophotometer was performed using known concentrations of rhodium²⁶. The calibration provided the correlation that $2.78(-4)$ times the %T reading gave the rhodium content in units of moles rhodium/liter. This value was used to determine the total number of moles of rhodium eluted, which was used to calculate moles rhodium per initial volume of toluene. This last value was used to determine the percent of initial rhodium eluted.

5.0 EXPERIMENTAL RESULTS

Throughout this section, the headings on the tables presenting experimental data will be those outlined in Table 2.

5.1 Hydroformylation Results

The 1-hexene hydroformylation reaction was studied at 50°C using two heterogeneous and one homogeneous catalyst. The heterogeneous catalysts were the cation-exchanged products of $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ with zeolite NaX at a 1% rhodium loading and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ also with NaX at both 1% and 3% rhodium loadings. The homogeneous catalyst was $\text{HRh}(\text{CO})(\text{PPh}_3)_3$.

All of the reactions were batch, lasting 21 hours at 300 psig of 50/50 H_2/CO . The reaction solution was stirred constantly for this time. The catalyst was at an approximate concentration of 0.5 mmole Rh/liter toluene in a 1M solution of 1-hexene in toluene. The effects of the following components were studied: (1) triphenylphosphine (PPh_3), (2) dimethylphenylphosphine (PMe_2Ph), and (3) triphenylmethyl mercaptan (Ph_3CSH). It should be noted here that both PPh_3 and Ph_3CSH are too large to fit inside the zeolite supercage, whereas PMe_2Ph is small enough to penetrate the pore system.

Table 2. Table Notation

%RH.....	Approximate wt% rhodium loading on zeolite
TEMP.....	Temperature, centigrade
PHOS.....	Type of phosphine used; number indicates moles phosphine/mole rhodium
PPh ₃	Triphenylphosphine
PMe ₂ Ph.....	Dimethylphenylphosphine
P(t-Bu) ₃ ...	Tri-tertbutylphosphine
Ph ₃ CSH.....	Triphenylmethylmercaptan
CONV.....	% Conversion of 1-hexene to products
SEL.....	Selectivity: ratio of aldehydes to total products
N/B.....	Ratio of normal aldehydes to branched aldehydes
HEPT.....	Mole% heptanal in final solution
2-MET HEX..	Mole % 2-methylhexanal in final solution
2-ETH PENT.	Mole % 2-ethylpentanal in final solution
TIME.....	Reaction time
1-HEX.....	Mole % 1-hexene left in final solution
T-2.....	Mole % trans-2-hexene in final solution
C-2.....	Mole % cis-2-hexene in final solution
RH ELUTION.	Moles rhodium in solution; % of initial rhodium eluted
NM.....	Not measured

The hydroformylation runs at 125°C were performed in the same manner as those at 50°C. The heterogeneous catalysts studied at this temperature were again the cation-exchange products of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with NaX at 3% and 0.5% rhodium loadings and also $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ with NaX at a 1% loading. Two homogeneous catalysts were studied at this temperature: $\text{Rh}_4(\text{CO})_{12}$ and $\text{HRh}(\text{CO})(\text{PPh}_3)_3$.

5.1.1 50°C Hydroformylation by RhNaX

Table 3 shows the results for 50°C hydroformylation with RhNaX cation exchanged from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ at one and three weight percent rhodium loadings.

It can be seen in Table 3 that the addition of PPh_3 significantly changed the selectivity without hindering the amount of eluted rhodium, while the addition of the mercaptan inhibited virtually all reactivity in addition to decreasing the amount of rhodium detected in solution. High loadings of mercaptan with low or zero loadings of phosphines were also studied at this temperature in order to compare to results presented later in this section. No conversion was observed for these runs.

Table 3. Hydroformylation by RhNaX at 50°C

%RH	PHOS	PH ₃ CSH	CONV	SEL	N/B	HEPT.	2-MET HEX.	2-EIH PENT.	RH ELUTION
1	NO	NO	8.93	0.33	2.86	2.17	0.76	0.0	6(-7); 1%
1	20 PPh ₃	NO	8.73	1.00	2.80	6.43	2.30	0.0	4(-7); 0.5%
1	20 PMe ₂ Ph	NO	0.40	0.85	-	0.34	0.0	0.0	0.0; 0.0%
3	NO	NO	84.89	0.33	2.68	20.47	7.63	0.0	4.5(-6); 6%
3	20 PPh ₃	NO	18.11	1.00	2.88	13.44	4.67	0.0	4(-6); 6%
3	20 PMe ₂ Ph	NO	1.36	1.00	1.12	0.72	0.64	0.0	3(-6); 5%
3	NO	20	0.95	1.00	0.07	0.06	0.67	0.22	1(-6); 2%
0.1*	NO	60	0.0	-	-	-	-	-	NM
0.1*	10 PMe ₂ Ph	60	0.0	-	-	-	-	-	NM

* 0.05 mmole Rh/1 toluene (rather than 0.5 mmole/1)

5.1.2 50°C Hydroformylation by $(\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O})\text{NaX}$

Table 4 shows the 50°C hydroformylation results for RhNaX cation exchanged from $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ (except where otherwise noted) at a one weight percent rhodium loading.

From Table 4 it can be seen that the results using $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{NaX}$ and $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{NaX}$ were similar to those for RhNaX from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. The conversion was much higher without phosphines or mercaptan for this catalyst, but in the absence of PMe_2Ph or mercaptan, there was little or no conversion.

5.1.3 50°C Hydroformylation by $\text{HRh}(\text{CO})(\text{PPh}_3)_3$

The homogeneous catalyst $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ was studied at 50°C in the presence of the 20 moles mercaptan/mole rhodium to ensure that the mercaptan was in fact acting as a rhodium poison in solution. Less than one per cent conversion was observed for a 21 hour run, indicating that the mercaptan was an effective solution rhodium poison at this temperature.

Table 4. Hydroformylation by $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{NaX}$ at 50°C

%RH	PHOS	PH_3CSH	CONV	SEL	N/B	HEPT	2-MET HEX	2-ETH PENT	RH ELUTION
1	NO	NO	99.49	0.68	1.03	34.22	26.62	6.51	1(-5); 10%
1	20 PPh_3	NO	99.53	0.79	2.44	54.11	21.39	0.80	1(-5); 15%
1	20 PMe_2Ph	NO	0.0		-	0.0	0.0	0.0	2(-6); 2%
1 *	NO	NO	99.64	0.67	1.21	36.69	25.15	5.22	2(-5); 20%
1* ¹	NO	20	6.29	-	-	0.0	0.0	0.0	NM
1 ²	NO	NO	99.02	0.47	1.96	30.56	14.4	1.21	2(-5); 25%
1 ²	20 PMe_2Ph	NO	2.71	0.98	2.44	1.88	0.77	0.0	3(-6); 5%

* Catalyst heated to 315°C in an oven for 19 hours prior to reaction

¹ Product was nearly all hexane

² RhNaX cation exchanged from $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

5.1.4 125°C Hydroformylation by RhNaX

The 125° results for $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ exchanged with NaX at 3 and 0.5 weight percent rhodium loadings are given in Table 5.

Table 5 shows that for given loadings of PMe_2Ph and Ph_3CSH , a 3% RhNaX is much more reactive than an 0.5% RhNaX catalyst. It also shows that with 20 PMe_2Ph and no mercaptan, there is a higher conversion and selectivity, but a lower n/b than for a run with 20 PMe_2Ph plus 20 mercaptan. The addition of mercaptan with no PMe_2Ph showed little reactivity, while high loadings of PMe_2Ph with mercaptan gave very high conversion and selectivity but a lower n/b than the earlier runs with 20 PMe_2Ph and 20 Ph_3CSH . Finally, loadings of 10 or 20 PMe_2Ph with 60 Ph_3CSH showed very little conversion, and precarbonylation for 24 hours had little effect.

5.1.5 125°C Hydroformylation by $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{NaX}$

The results of hydroformylation studies with RhNaX cation exchanged from $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ are shown in Table 6 and are similar in form to the previously discussed RhNaX experiments.

Table 5. Hydroformylation by RhNaX at 125°C

%RH	PHOS	PH ₃ CSH	CONV	SEL	N/B	HEPT.	2-MET HEX.	2-ETH PENT.	RH ELUTION
3	20 PMe ₂ Ph	NO	99.27	0.93	2.41	65.0	26.65	0.35	1(-5); 19%
3	20 PMe ₂ Ph	NO	100.0	0.97	2.17	66.58	29.27	1.45	1.6(-5); 21
3	20 PMe ₂ Ph	20	74.9	0.76	3.75	44.81	11.83	0.11	1.5(-5); 20
3	20 PMe ₂ Ph	20	50.21	0.84	4.21	34.02	8.08	0.0	9.6(-6); 12
0.5*	20 PMe ₂ Ph	20	1.68	0.45	1.42	0.44	0.16	0.15	1(-6); 1%
3	100 PMe ₂ Ph	20	100.0	0.998	3.02	74.98	24.71	0.12	NM
3 ¹	NO	20	0.44	0.95	0.1	0.04	0.16	0.22	2(-7); 0.3%
3 ¹	100 PMe ₂ Ph	20	99.46	1.0	2.78	73.22	26.06	0.18	2(-5); 29%
3	10 PMe ₂ Ph	60	3.78	0.70	0.0	0.0	0.0	2.66	NM
3 ¹	20 FMe ₂ Ph	60	1.90	0.56	0.02	0.02	0.22	0.82	NM

* Concentration of 0.05 mmol Rh/1 toluene in reactor

¹ Precarbonylated 24 hours prior to exposure to reaction environment.

Table 6. Hydroformylation by $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{NaX}$ at 125°C

%RH	TEMP	PHOS	PH_3CSH	CONV	SEL	N/B	HEPT	2-MET HEX	2-ETH PENT	RH ELUTION
1	125	NO	20	0.21	1.0	0.05	0.01	0.21	0.0	NM
1	125	50 PMe_2Ph	20	100	0.98	2.16	66.87	29.2	1.72	NM

From Table 6, it can be seen that the results using $(\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O})\text{NaX}$ were similar for comparable experimental conditions to those for RhNaX (Table 5). There was very high conversion, selectivity, and n/b in the presence of large amounts of PMe_2Ph and mercaptan, and virtually no conversion in the presence of mercaptan alone.

5.1.6 125°C Hydroformylation by $\text{Rh}_4(\text{CO})_{12}$

Results of the homogeneous hydroformylation by $\text{Rh}_4(\text{CO})_{12}$ at 125°C are given in Table 7 (all runs were 21 hours unless indicated by *).

As shown in Table 7, the addition of PPh_3 improved n/b while lowering the selectivity. High loadings of PMe_2Ph greatly improved both selectivity and n/b, however, the addition of mercaptan with this high PMe_2Ph loading did not poison the catalyst. A ratio of 6/1 mercaptan to PMe_2Ph was found to be necessary to stop reactivity at this temperature. No conversion was observed from a run with Ph_3CSH , indicating that in the absence of phosphine, Ph_3CSH is an effective rhodium poison at this temperature.

Table 7 Hydroformylation by $\text{Rh}_4(\text{CO})_{12}$
at 125°C

PHOS	PH_3CSH	CONV	SEL	N/B	HEPT	2-MET HEX	2-ETH PENT
NO	NO	99.44	0.80	1.02	40.29	30.42	9.18
32 PPh_3	NO	99.51	0.75	1.34	42.6	25.14	6.61
100 PMe_2Ph	NO	100	1.0	2.82	73.82	25.87	0.31
100 PMe_2Ph	20	100	1.0	2.74	73.3	26.44	0.27
NO *	20	0.0					
32 PMe_2Ph *	20	9.34	1.0	2.59	6.68	2.65	0.0
20 PMe_2Ph *	20	7.99	0.74	3.3	4.62	1.28	0.0
20 PMe_2Ph	82.14	0.74	3.77	47.82	12.6	0.09	
10 PMe_2Ph *	60	0.0					
10 PMe_2Ph	60	0.0					
20 PMe_2Ph	60	1.34	0.67	0.40	0.26	0.49	0.15

* 1.5 hour runs

5.1.7 125°C Hydroformylation by $\text{HRh}(\text{CO})(\text{PPh}_3)_3$

Homogeneous hydroformylation results using $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ at 125°C are given in Table 8.

Although this catalyst was not studied with the high loadings of phosphine and mercaptan, it can be seen from Table 8 that with even a low loading of phosphine in the presence of mercaptan, the rhodium was not poisoned at this temperature. Also, for a run with no phosphine and 20 moles mercaptan/mole rhodium there was a 1% conversion in 21 hours, which may just have been GC background. Therefore, these results show that for this homogeneous catalyst as well, mercaptan is an effective solution rhodium poison at 125°C in the absence of phosphine.

From the early results with both types of heterogeneous catalysts, good conversions, selectivities, and n/b values were observed while using very high amounts of dimethylphenylphosphine (PMe_2Ph) in the presence of the mercaptan. However, for $\text{Rh}_4(\text{CO})_{12}$ at similar conditions of phosphine and mercaptan, there was also a very high conversion, indicating that at these conditions, the mercaptan was not poisoning the rhodium. There was also conversion with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ at low loadings of phosphine with mercaptan. Finally, it was shown that the amounts of phosphine and

Table 8. Hydroformylation by $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ at 125°C

PHOS	PH_3CSH	CONV	SEL	N/B	HEPT	2-MET HEX	2-ETH PENT
20 PPh_3	NO	99.57	0.78	1.29	43.91	27.18	6.93
20 PPh_3	20	5.36	0.69	2.90	2.76	0.95	0.0
100 PPh_3	NO	99.98	0.96	1.20	52.51	33.36	10.09
NO	20	1.06	1.33	0.37	0.13	0.18	0.04

mercaptan required to poison homogeneous activity yielded little or no heterogeneous activity.

5.2 Hydrogenation of 1-Hexene

Hydrogenation studies were performed using 0.1M 1-hexene in toluene and 0.1% RhNaX (from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) at 125°C and 60°C. Since this catalyst had a low rhodium loading, the rhodium concentration in the reactor was 0.03 mmol/l toluene. All reactions were batch, lasting from 15 to 24 hours at 300 psi of pure H_2 . Comparison studies with the homogeneous catalyst $\text{Rh}_4(\text{CO})_{12}$ were also performed at these temperatures, however, since such a high proportion of the homogeneous catalysts is rhodium, only a small amount can be used in the reactor. Therefore, for the homogeneous runs, a rhodium concentration of 0.5 mmol/l toluene was used.

5.2.1 Heterogeneous Hydrogenation by RhNaX

Table 9 shows the results of heterogeneous hydrogenation by RhNaX cation exchanged from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ at an 0.1% rhodium loading. Large excesses of PPh_3 and Ph_3CSH had to be used here since the amount of rhodium was small. For relatively small amounts in terms of actual weight, the ratios of PPh_3

Table 9. Hydrogenation by RhNaX (from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$)

TEMP	PHOS	PH_3CSH	TIME	1-HEX	HEXANE	T-2	C-2
125	PPh_3	NO	15:15	43.74	25.54	19.70	11.02
125	PPh_3	YES	22:25	97.05	0.0	1.18	1.77
125	NO	YES	22:00	98.08	0.0	0.77	1.15
125	NO	YES	22:00	100.0			
60	PPh_3	NO	24:00	80.99	19.01	0.0	0.0
60 *	PPh_3	YES	24:00	68.54	18.27	8.55	4.64

* Continuation of the previous run with mercaptan added

and Ph_3CSH used were approximately 210 and 640 moles/mole rhodium, respectively.

From this table it can be seen that at 125°C the addition of mercaptan was found to stop all hydrogenation and nearly all isomerization with or without PPh_3 present. At 60°C , there was hydrogenation but no isomerization in the presence of PPh_3 , and there was isomerization but no further hydrogenation when Ph_3CSH was added to the reaction mixture.

5.2.2 Homogeneous Hydrogenation

Table 10 shows the hydrogenation results using $\text{Rh}_4(\text{CO})_{12}$ at 60°C and 125°C .

From this table it can be seen that at both temperatures there was a high conversion to both hydrogenation and isomerization products in the presence of PPh_3 . Very little hydrogenation, but significant isomerization was observed using $\text{P}(\text{t-Bu})_3$.

5.3 Reaction Profiles

Reaction profiles for the two homogeneous catalysts $\text{Rh}_4(\text{CO})_{12}$ and $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ as well as the heterogeneous catalyst RhNaX (cation exchanged from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) were studied using the automatic sampling system described earlier

Table 10. Hydrogenation by $\text{Rh}_4(\text{CO})_{12}$

TEMP	PHOS	PH_3CSH	TIME	1-HEX	HEXANE	T-2	C-2
125	32 PPh_3	NO	22:00	0.48	55.70	34.32	8.92
60	32 PPh_3	NO	22:00	0.16	56.61	33.43	9.80
60	32 $\text{P}(t\text{-Bu})_3$	NO	22:00	0.60	1.51	75.97	21.92

in the Materials and Methods section. These reactions were carried out in the same manner and under the same conditions as the batch hydroformylation reactions except that samples were automatically taken and analyzed by the GC at specified time intervals.

5.3.1 Reaction profiles with $\text{Rh}_4(\text{CO})_{12}$

Figures 4 and 5 show the reaction profiles of reactants and products as a function of time for hydroformylation at 125°C using $\text{Rh}_4(\text{CO})_{12}$ with and without PMe_2Ph , respectively. Figure 6 shows conversion, selectivity, and n/b as a function of time for these two runs.

It can be seen in these figures that there is virtually no change in product composition after about 8 hours. The PMe_2Ph seemed to arrest much of the initial isomerization and gives a higher overall yield of heptanal along with an increase in reaction rate. Notice the lower selectivity and n/b for the catalyst system not modified by phosphine, as well as the fact that in both cases, n/b decreases with time.

5.3.2 Reaction Profiles with RhNaX (from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$)

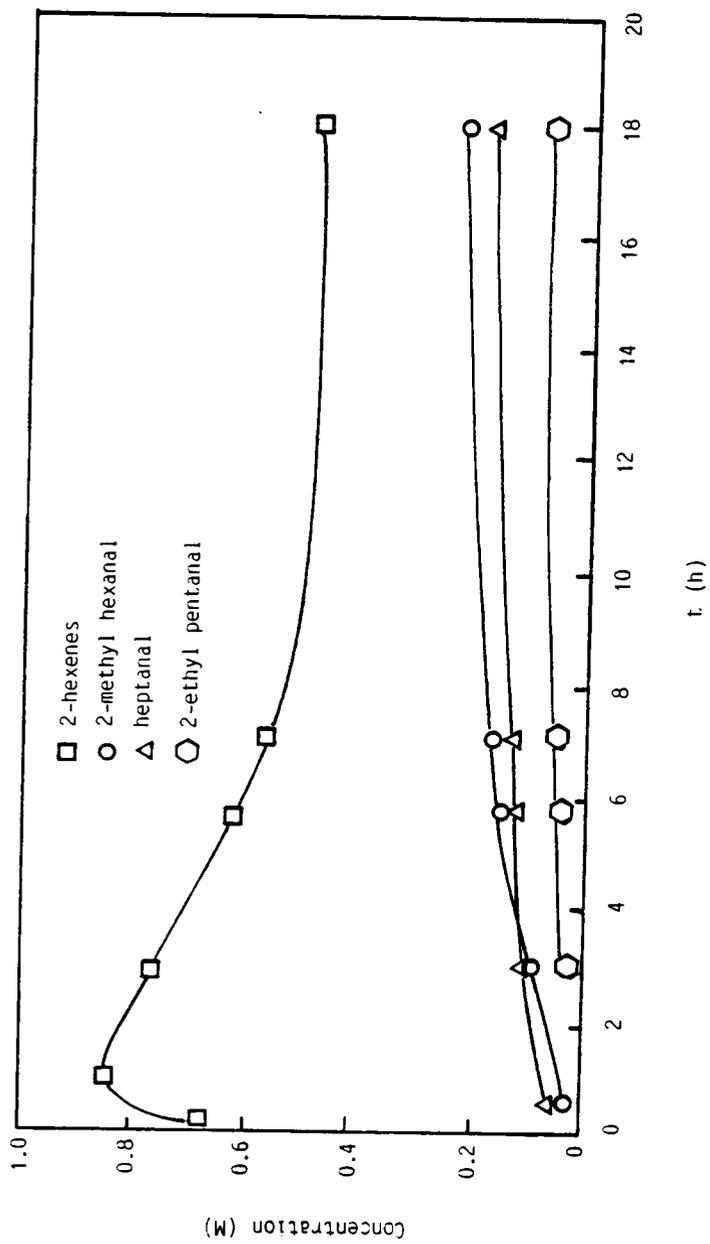


Figure 4. $Rh_4(CO)_{12}$: Reaction Profile at 125°C

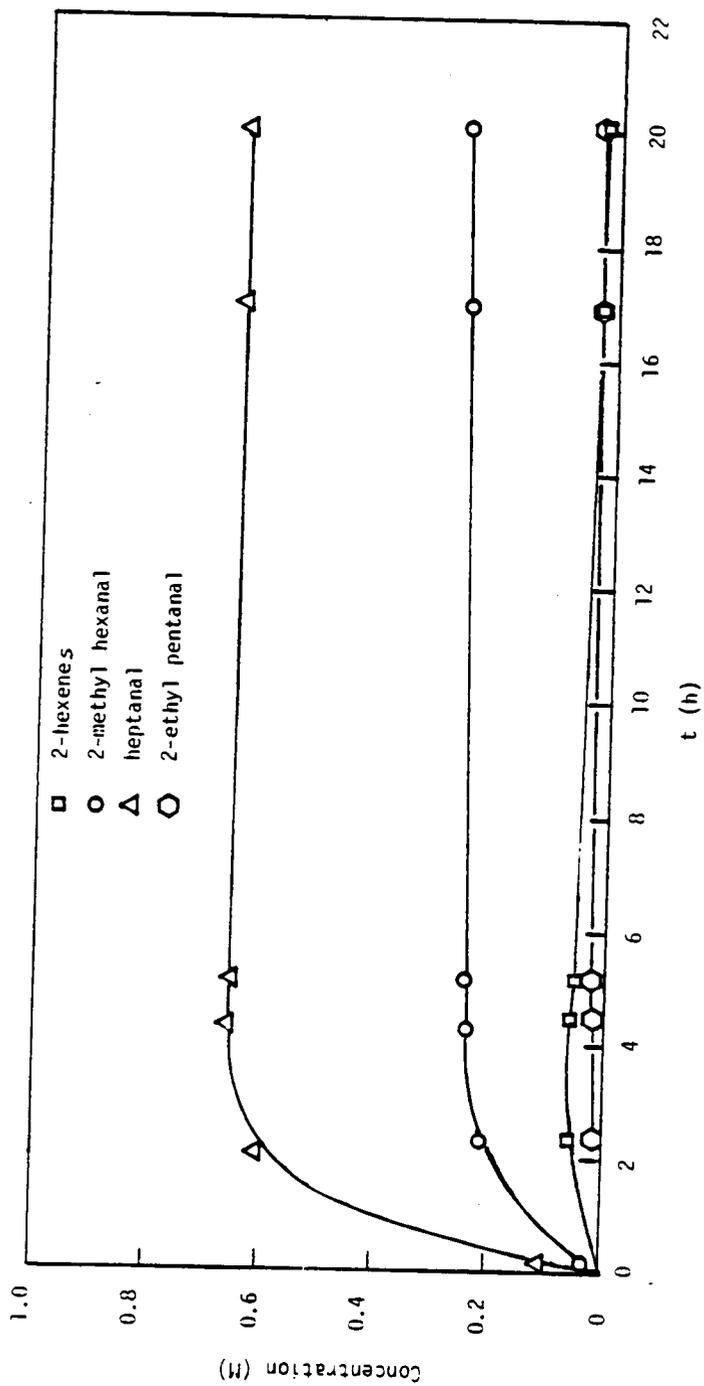


Figure 5. $\text{Rh}_4(\text{CO})_{12}$: Reaction Profile at 125°C with FMe_2Ph

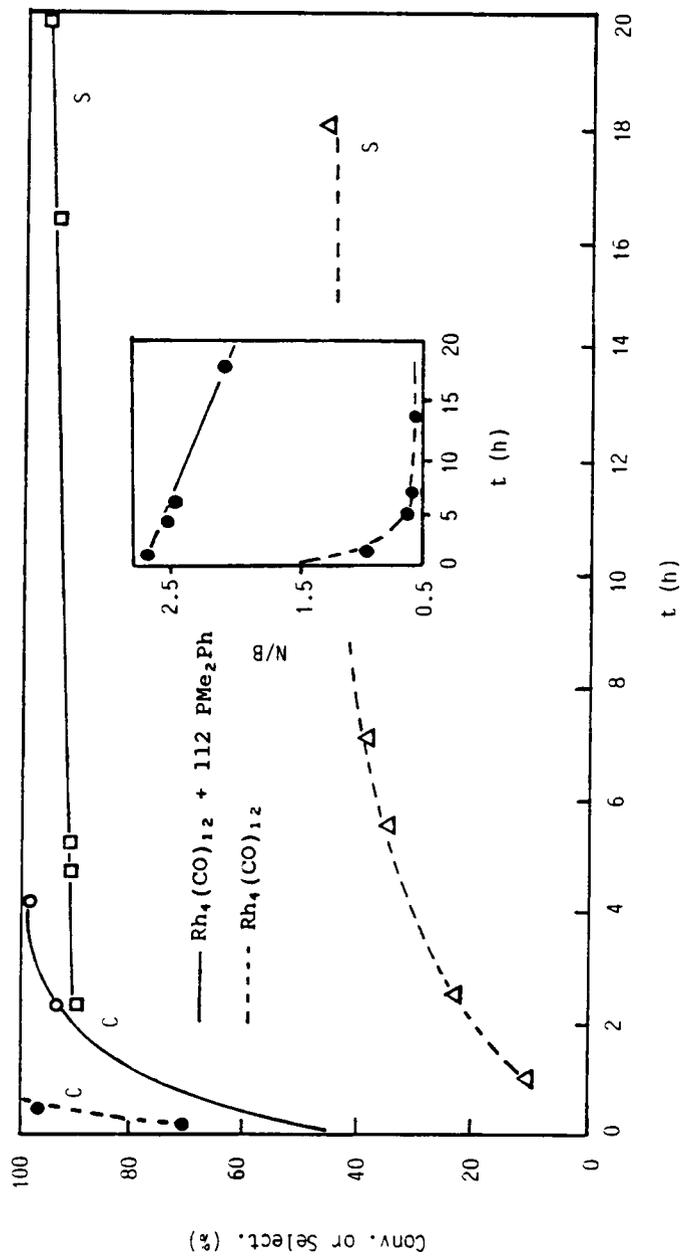


Figure 6. $\text{Rh}_4(\text{CO})_{12}$: Conversion (C), Selectivity (S), and n/b at 125°C

Figure 7 shows the reaction profile and Figure 8 shows the conversion, selectivity, and n/b at 125°C as a function of time for RhNaX cation exchanged from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in the presence of 100 moles PMe_2Ph /mole rhodium and 20 moles Ph_3CSH /mole toluene. An automatic sampling run for RhNaX with 20 moles Ph_3CSH /mole rhodium and no PMe_2Ph was performed, with no conversion observed in 24 hours.

Similar to the $\text{Rh}_4(\text{CO})_{12}$ results, RhNaX in the presence of PMe_2Ph showed minimal formation of 2-hexenes (see Fig. 7). Notice that the heterogeneous catalyst required a longer reaction time - more than 15 hours before near complete conversion was reached (as compared to 8 hours for the homogeneous case). Selectivity was 100% to aldehydes almost immediately and remained at this level for over 20 hours.

5.3.3 Reaction profiles with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$

Figure 9 shows the reaction profile and Figure 10 shows the conversion, selectivity, and n/b at 125°C as a function of time for $\text{HRh}(\text{CO})(\text{PPh}_3)_3$

The addition of PPh_3 with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ did not appear to halt conversion to 2-hexenes as did PMe_2Ph with $\text{Rh}_4(\text{CO})_{12}$ as shown above. Notice the similar behavior for the two

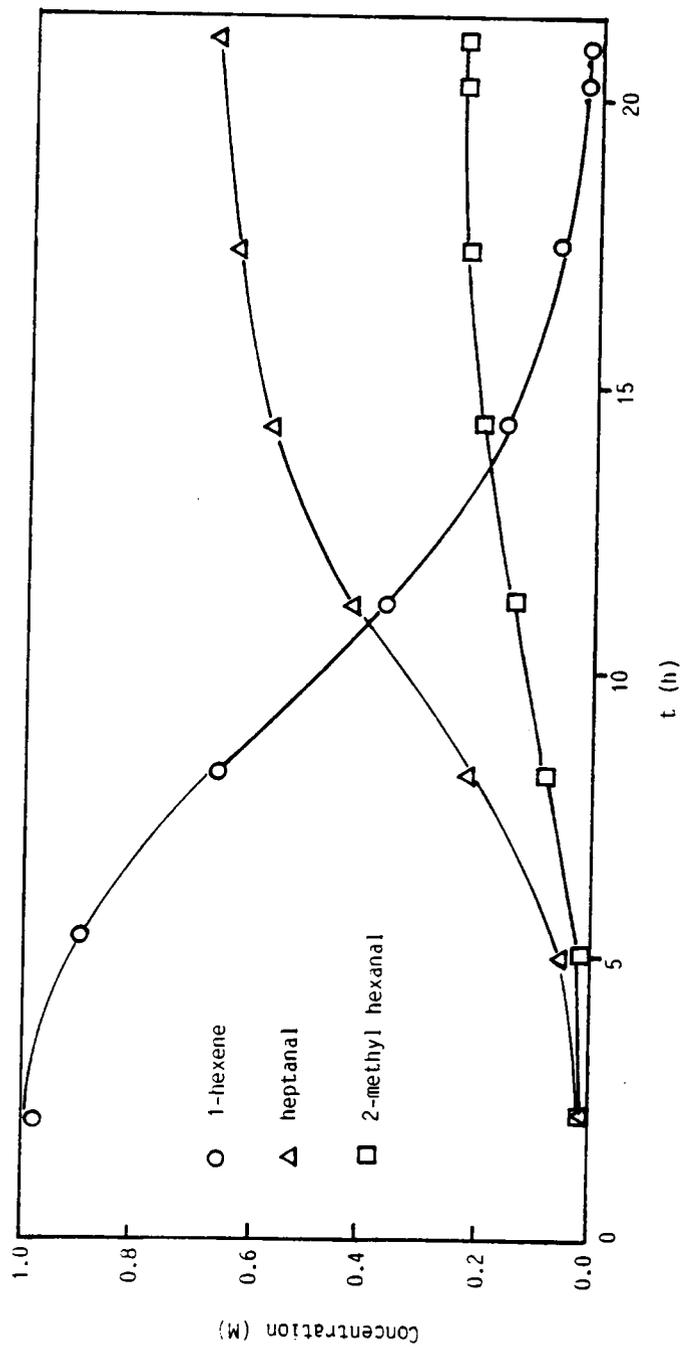


Figure 7. RhNaX: Reaction Profile at 125°C

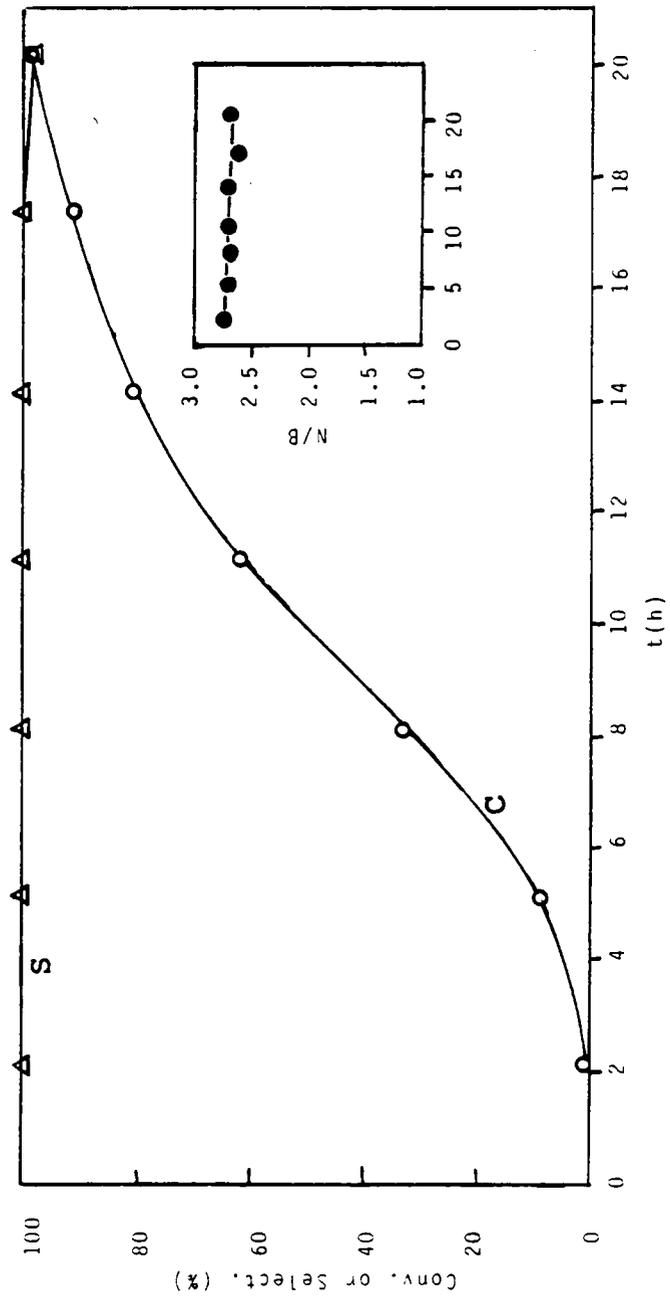


Figure 8. RhNaX: Conversion (C), Selectivity (S), and n/b at 125°C

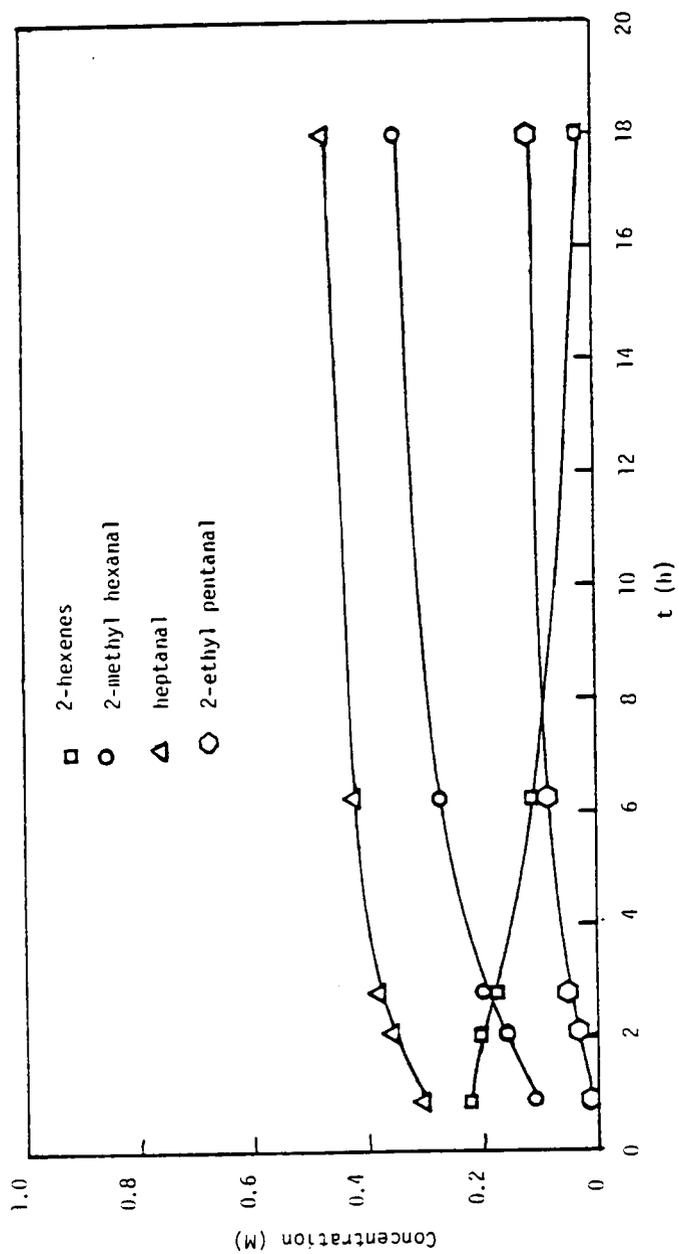


Figure 9. $\text{HRh}(\text{CO})(\text{PPh}_3)_3$: Reaction Profile at 125°C

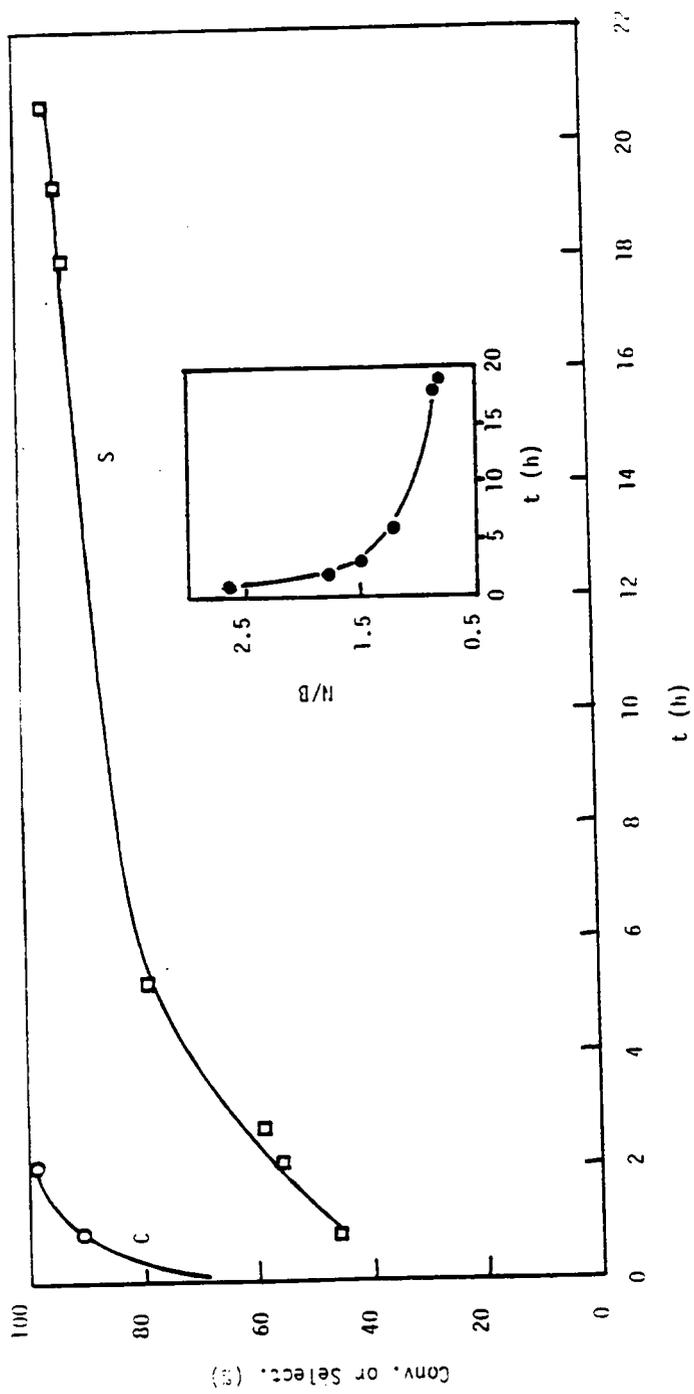


Figure 10. $\text{HRh(CO)(PPh}_3)_3$: Conversion (C), Selectivity (S), and n/b at 125°C

homogeneous catalysts (Figures 6 and 10) in terms of n/b reduction with time, and the relatively slow rate of increase for selectivity as compared to conversion in the presence of phosphine.

6.0 DISCUSSION

6.1 Location of Rhodium

Shannon et al.²⁷ studied the location of rhodium after the exchange of several rhodium salts with several types of zeolites. His work with NaY will be compared with the NaX exchanges performed for this study, since the two zeolites have the same structure. The exchange procedures used during this study were virtually identical to Shannon et al. For the exchange of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ with NaY, Shannon et al. used approximately twice as much water and a temperature of 80°C rather than the 50°C used here. The differences between Shannon et al. and this work for the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ exchange were that here, the rhodium salt was dissolved in water and added dropwise to the zeolite slurry, and the total amount of water was again only about one-half that used by Shannon et al. The similarity of techniques makes it likely that results of rhodium location analyses will be similar. Shannon et al. found that most if not all the rhodium associated with the zeolites for both of the exchanges described above could be found inside the zeolite. They note that for the exchange with $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, the rhodium probably entered the zeolite as a mixture of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$, and that for the exchange with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, the rhodium prob-

ably entered the zeolite as a mixture of $[\text{Rh}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$. It is likely that in the NaX exchanges performed for this study, the rhodium was also inside the zeolite, and in the form of the cations named above.

6.2 Zeolite Crystallinity at Reaction Conditions

The X-ray results shown in Figures 11, 12, and 13 are for the RhNaX cation exchanged from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ at 0.1% rhodium loading. Figure 11 shows the as exchanged catalyst which has been taken to the boiling point of a 1-hexene and toluene mixture for approximately one hour in order to adsorb 1-hexene and toluene and act as a control against the reaction materials. Figures 12 and 13 are for the same catalyst which had been reacted at 125°C under typical batch reactor conditions with dimethylphenylphosphine, and with both the phosphine and triphenylmethylmercaptan; respectively. These figures show no loss of the zeolite crystallinity upon reaction.

6.3 50°C Hydroformylation

Triphenylmethylmercaptan was expected to play an important role in this research as a poison for rhodium in solution and on the surface of the zeolite since it is too large to fit

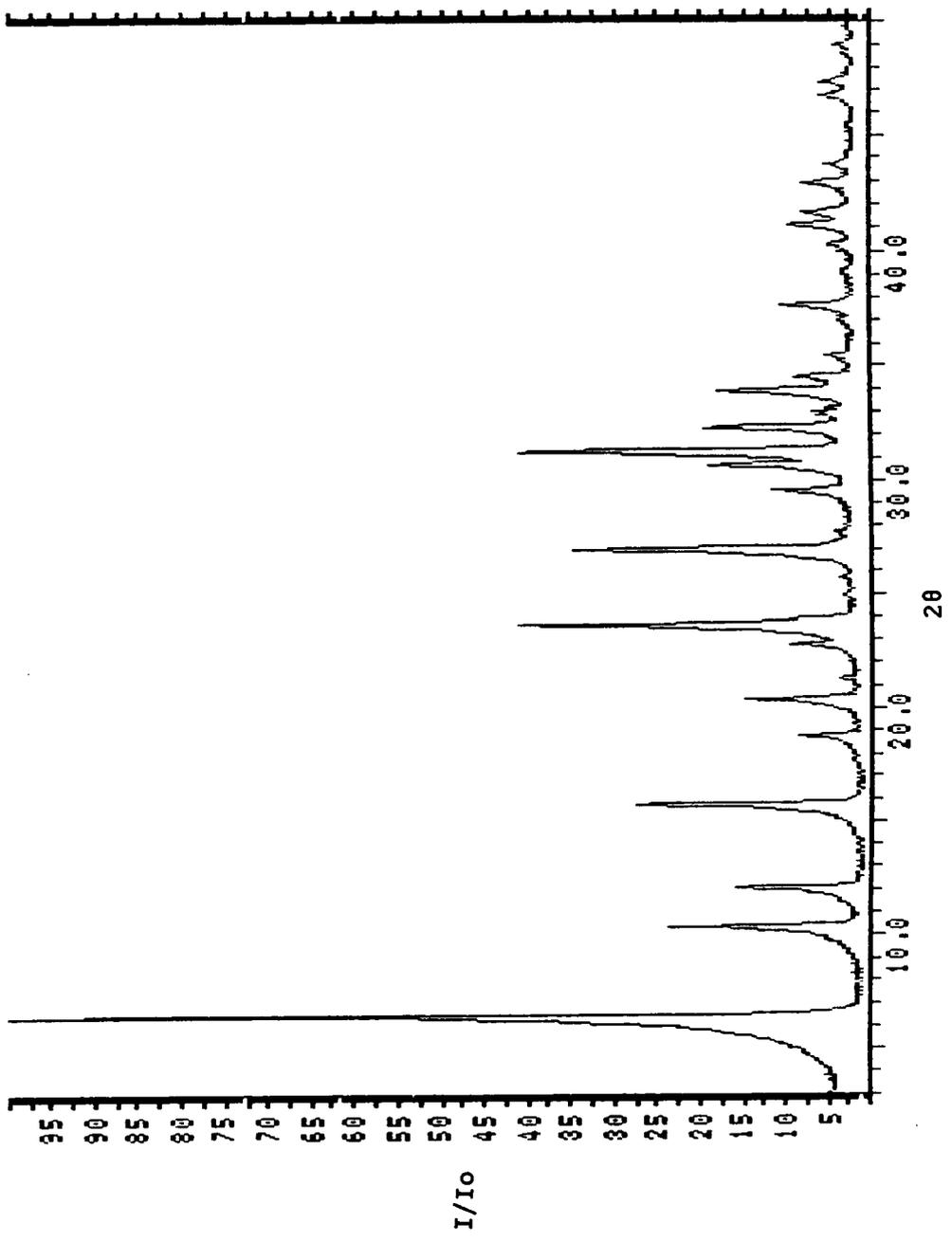


Figure 11. X-ray Spectrum for RhNaX

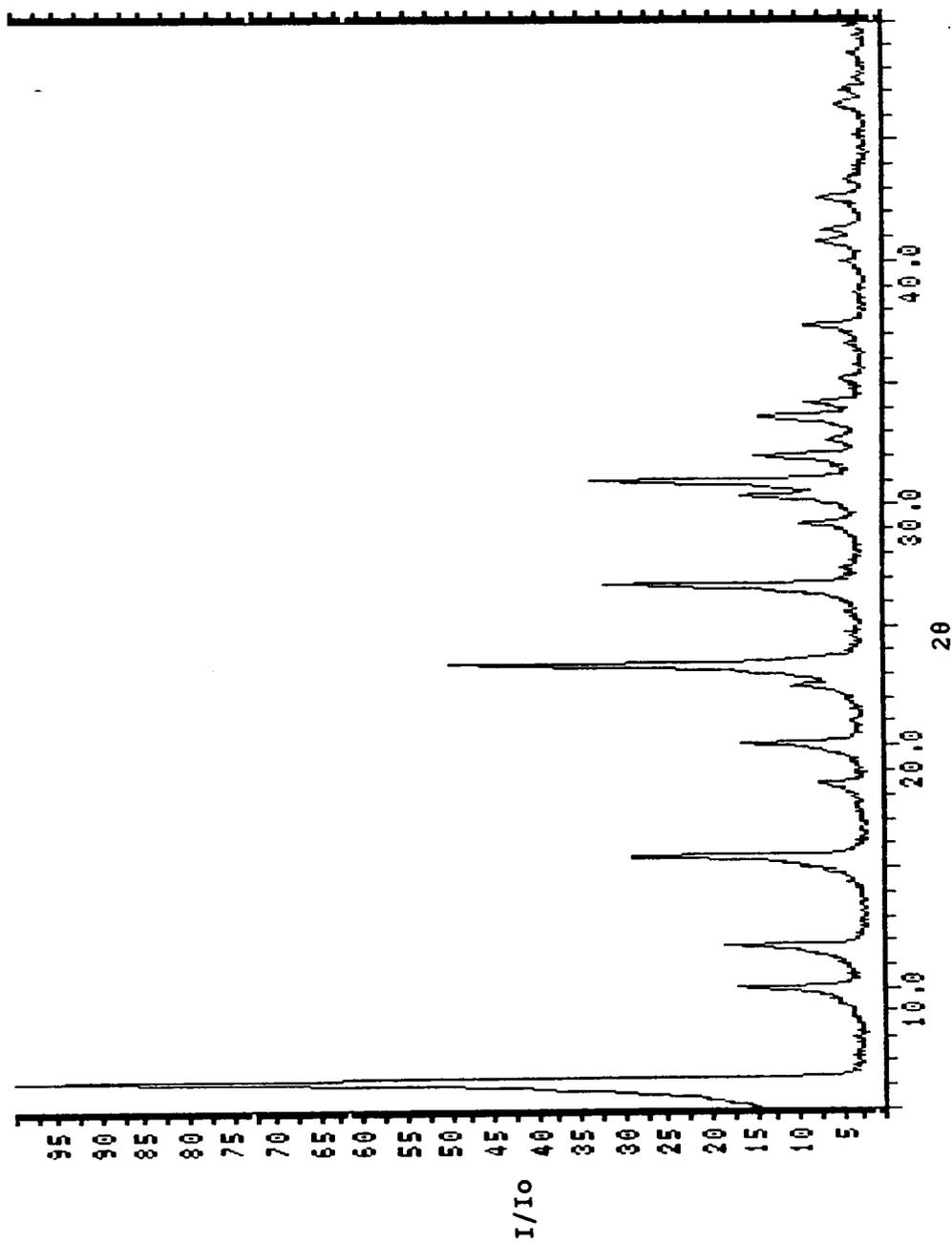


Figure 12. X-ray Spectrum for RhNaX Reacted in the Presence of PMe_2Ph

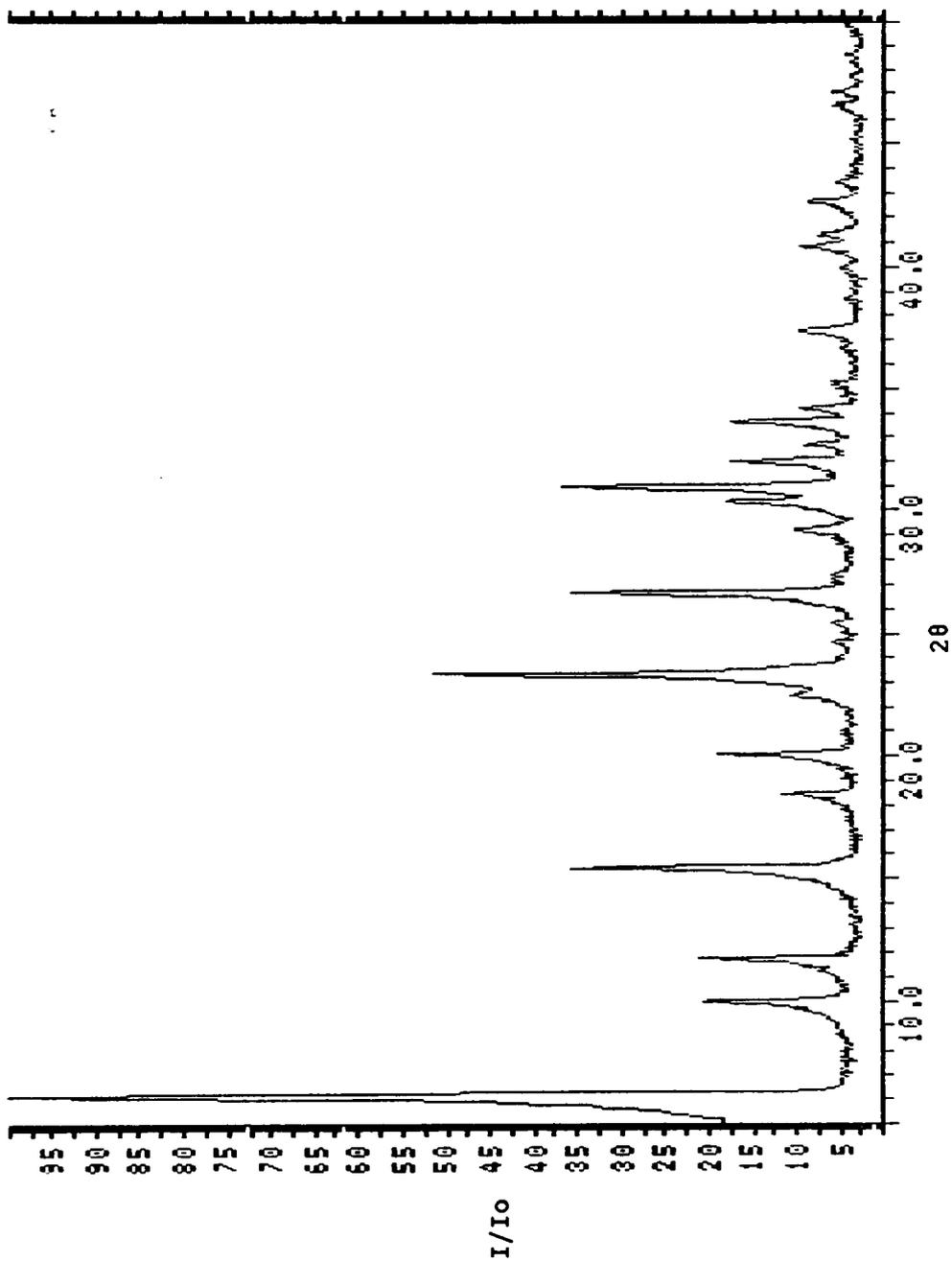


Figure 13. X-ray Spectrum for RhNaX Reacted in the Presence of PMe_2Ph and Ph_3CSH

inside the NaX pore system. From the experimental results, it was seen that when this mercaptan was added, the conversion was essentially zero both for the homogeneous ($\text{HRh}(\text{CO})(\text{PPh}_3)_3$) and heterogeneous RhNaX cases at this temperature (Tables 3 and 4).

Table 3 shows the heterogeneous hydroformylation results for RhNaX (cation exchanged from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) at 50°C with three different rhodium weight loadings of 1%, 3%, and 0.1%. For the 1% series, it can be seen that with no phosphine or mercaptan modification, there was a low conversion, around 9%, and that selectivity to aldehydes was only 0.33 while the n/b was moderately high at 2.86. The addition of PPh_3 had little effect on the conversion and n/b, lowering them only slightly, but the selectivity for this run was 1.00. Note also that rhodium elution decreased from approximately 1% to approximately 0.5% upon addition of PPh_3 . It must be pointed out, however, that these readings are at the low end of the detection limits for rhodium. The addition of PMe_2Ph had the largest effect, yielding an order of magnitude drop in conversion, to 0.85, and keeping rhodium elution to below detection limits. Finally, note that no 2-ethylpentanal was observed for any of the 1% RhNaX runs. For the unmodified run, this was probably due to too short a reaction time, as 2-hexenes were formed by isomerization, which would have been expected to further hydroformylate. For the PMe_2Ph modified

run, only traces of 2-hexenes were observed, while for the PPh_3 modified run, there was no isomerization. In all three runs, no hydrogenation occurred.

The unmodified 3% RhNaX run showed an order of magnitude higher conversion over that of the 1% RhNaX, while yielding the same selectivity of 0.33 and a similar but slightly lower n/b of 2.68. The rhodium elution was higher for this run, at approximately 6% compared to a 1% loss for the 1% RhNaX. This indicates that the higher conversion is probably a result of solution activity, with a higher solution concentration of eluted rhodium for the higher loading of rhodium on NaX. At this weight percent loading, the addition of PPh_3 had the effect of raising the selectivity to 1.00, while reducing rhodium elution only slightly from 4.5(-6) to 4(-6) moles eluted. Conversely, the addition of PPh_3 at this higher weight loading lowered conversion significantly, from 84.89% to 18.11%, and increased n/b slightly, from 2.68 to 2.88 from the unmodified 3% run. The addition of PMe_2Ph again sharply curtailed reactivity, yielding only a 1.36% conversion, which, however, was all aldehydes. Similar to the 1% results, rhodium elution was lowered for the PMe_2Ph modified run, from approximately 6% to approximately 5%. N/b also fell to 1.12 for this run, but this is not significant since the conversion was so low. Finally, a run with Ph_3CSH and no phosphines yielded an even lower conversion of 0.95%,

but a 1.00 selectivity to aldehydes. An unrealistically low n/b was also observed for this run, but again this is not significant due to the very low conversion. Most importantly, note that rhodium elution dropped to approximately 2% for this run, a possible indication of pore blockage by the mercaptan.

The 0.1% RhNaX results show simply that with the high amount of Ph_3CSH required to poison homogeneous rhodium activity, no conversion was observed with or without PMe_2Ph .

Table 4 shows the results of heterogeneous hydroformylation with $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{NaX}$ and $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{NaX}$. These results are similar to those in Table 3 except that in this case there was a high conversion with a 1% rhodium loading and no phosphine or mercaptan modification. The selectivity was also higher for the unmodified run, at 0.68, while n/b was lower, at 1.03. Rhodium elution was an order of magnitude higher here, at approximately 10%. Also, similar to the results in Table 3 was the fact that the addition of PPh_3 only lowered conversion slightly, while raising selectivity, but only to 0.79, not 1.00 in this case. Conversely, n/b was raised significantly upon addition of PPh_3 , from 1.03 to 2.44, and rhodium elution also increased, from 10% to 15%. The addition of PMe_2Ph with this catalyst had the effect of stopping all conversion, while still yielding a rhodium elution of approximately 2%.

The effect of a pretreatment of heating the catalyst in a 315°C oven for 19 hours prior to reaction in order to remove the NH₃ ligands was tested with little effect on the conversion and selectivity of the unmodified catalyst, but resulted in an increase in n/b from 1.03 to 1.21, and an increase in rhodium elution from 10% to 20%. A catalyst which was previously dried in an oven at 315°C and was reacted in the presence of Ph₃CSH gave the curious result of approximately 6% conversion all to hexane, a fact which cannot be explained at this time.

In addition, the effect of NaX cation exchange with [Rh(NH₃)₅Cl]Cl₂ was compared to the results with [Rh(NH₃)₅H₂O]Cl₃. For [Rh(NH₃)₅H₂O]NaX, conversion was slightly lower for the unmodified run as compared to [Rh(NH₃)₅Cl]NaX, and selectivity decreased from 0.68 to 0.47. N/b increased from 1.03 to 1.96, however, and rhodium elution increased from 10% to 25%. The addition of PMe₂Ph to this catalyst curtailed conversion to only 2.71%, but the selectivity and n/b were raised, to 0.98 and 2.44, respectively. Similar to previously described results, the addition of PMe₂Ph reduced the rhodium elution (from 25% to 5%) for [Rh(NH₃)₅Cl]NaX and [Rh(NH₃)₅H₂O]Cl₃ (from 10% to 2%). Also note that the PMe₂Ph modified [Rh(NH₃)₅H₂O]NaX catalyst eluted less rhodium than the [Rh(NH₃)₅Cl]NaX catalyst.

For all of the heterogeneous studies at 50°C, the addition of PMe_2Ph strongly hindered or stopped catalyst activity. It also curtailed rhodium elution, possibly by forming a rhodium-phosphine complex which either preferentially remained inside the zeolite or was simply too large to diffuse out. This complex may also have been a factor in the lack of reactivity since the 1-hexene may not have had enough room to fit inside the zeolite supercage in the presence of the complex, or the aldehyde products may not have had enough room to diffuse back out.

In addition to the above comments, there are several other possible reasons why little or no intrazeolitic activity was observed at 50°C. There may not have been optimum combination of: reaction temperature, pressure, contact time, CO/H_2 , weight percent rhodium loading on the catalyst, phosphine or mercaptan loadings, or reactant concentration.

Thus, it appears that at 50°C, all activity observed with the heterogeneous catalysts came from surface and/or solution catalysis. For all heterogeneous reactions in which PMe_2Ph or Ph_3CSH was present, there was virtually no reactivity and the slight percentage of products observed were most likely just background in the GC.

In comparing the results at 50°C with those of Davis et al.,²² it is likely that the claim of different reaction behavior as proof of Type II and Type III behavior (surface

activity and intrazeolitic activity, respectively), was not correct. The results here show that for those runs where a high conversion is observed, the rhodium elution is also high. This indicates that in the work by Davis et al.²² and in this study, that there may be surface activity, but that the majority of the observed reactivity at 50°C probably resulted from rhodium eluted into solution, although the possibility of surface catalysis still remains unresolved. However, it is unlikely that any intrazeolitic activity is occurring at 50°C.

6.4 125°C Hydroformylation

The catalytic activity was higher at 125°C than at 50°C as may be expected. At the lower temperature, PMe_2Ph strongly curtailed conversion, whereas at the higher temperature there was complete or nearly complete conversion for the RhNaX with 20 moles $\text{PMe}_2\text{Ph}/\text{mole Rh}$ (Table 5) the homogeneous $\text{Rh}_4(\text{CO})_{12}$ with 32 moles $\text{PPh}_3/\text{mole Rh}$ and for $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ with 20 moles $\text{PPh}_3/\text{mole Rh}$ (Table 7). Initially, it was thought that the RhNaX showed intrazeolitic activity at 125°C because at this 'low' phosphine loading, the addition of 20 moles $\text{Ph}_3\text{CSH}/\text{mole Rh}$ did not poison all activity. The results in the first four rows of Table 5 show that when both PMe_2Ph and Ph_3CSH were present at 20

moles/mole Rh the selectivity was lowered somewhat, but the n/b was raised significantly. A preferential formation of the normal aldehyde could be interpreted as an indication of intrazeolitic activity. Note, however, that approximately 20% of the rhodium was eluted into solution at these conditions. It should be pointed out that the second and fourth rows show results for repeat runs at the conditions of the first and third rows, respectively. The catalysts used were cation exchanged in different batches and, therefore, variations in conversion, selectivity and n/b may be due to slight variations in the rhodium loading on the zeolite.

In accordance with the 50°C results, Table 5 shows that a RhNaX catalyst with a 3% loading of rhodium gives a much higher conversion than an 0.5% RhNaX at the same conditions (ratios of PMe_2Ph and Ph_3CSH). Note, however, that the rhodium elution from the 3% RhNaX was an order of magnitude higher than that of the 0.5% RhNaX.

Since the phosphine appeared to have a beneficial effect at this temperature, the effects of higher loadings were tested. With 100 moles PMe_2Ph /mole Rh and 20 moles mercaptan/mole Rh, using the catalyst RhNaX (Table 5), the conversion was nearly complete, and the selectivity was also significantly improved to near 1.0 (all aldehyde products). N/b for these runs was lower than the values observed with a 20/20 $\text{PMe}_2\text{Ph}/\text{Ph}_3\text{CSH}$ ratio, but higher than for the runs in

the absence of mercaptan. The last two rows of Table 5 will be discussed later in this section.

Table 6 shows the results of 125°C hydroformylation by another heterogeneous catalyst: $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{NaX}$. Like the 50°C results, only a 1% rhodium loading was necessary to give 100% conversion with this catalyst, and in the presence of PMe_2Ph , only a 1% loading was necessary for high conversion as compared to the 3% loading with the RhNaX cation exchanged from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. This result may indicate differences in the rhodium zeolite interactions which lead to rhodium elution. Note that for both of these heterogeneous catalysts in the presence of Ph_3CSH , the conversion was less than 1%. Thus it is likely that without phosphine modification, no intrazeolitic activity is possible for these catalysts. It was also observed that for heterogeneous catalysts reacted at 125°C with no phosphine modification that the catalyst turned color from the initial white or yellow to a dark brown or black. This may be due to the reduction of the rhodium to rhodium metal, which is inactive for hydroformylation.

Companion studies with the homogeneous catalysts (Tables 7 and 8) at high loadings of PMe_2Ph or PPh_3 with no mercaptan showed the same high conversions at the both the 'low' and 'high' phosphine loadings as seen with RhNaX at 'high' phosphine loadings. However, for comparisons within the homogeneous results, greatly improved selectivities were ob-

served at the higher loadings: 0.75 to 1.0 for $\text{Rh}_4(\text{CO})_{12}$ as the ratio of PPh_3 went from 32 to 100 moles phosphine/mole rhodium and 0.78 to 0.96 for $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ with an increase in the PPh_3 /rhodium ratio of 20 to 100. For $\text{Rh}_4(\text{CO})_{12}$, n/b increased to approximately the same value seen for RhNaX indicating that reactivity observed in the heterogeneous case may have been from solution (or surface) rhodium which was not poisoned by the mercaptan (rather than from intrazeolitic activity). Homogeneous studies with mercaptan were performed in order to determine the effect of the mercaptan on solution phase hydroformylation. Table 8 shows that for $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ with 20 moles/mole Rh of PPh_3 and Ph_3CSH there was a conversion of 5.36%. Also for $\text{Rh}_4(\text{CO})_{12}$ (Table 7) with 32 moles PMe_2Ph /mole Rh and 20 moles Ph_3CSH /mole Rh, a conversion of 9.34% was observed in only 1.5 hours. Clearly, under these conditions, the mercaptan was not acting as a complete poison for rhodium in solution.

Using the catalyst $\text{Rh}_4(\text{CO})_{12}$ (Table 7), the amount of mercaptan which poisoned all rhodium activity in solution in the presence of PMe_2Ph was found. The amount was 60 moles Ph_3CSH /mole Rh for 10 moles PMe_2Ph /mole Rh. When this amount was used for heterogeneous hydroformylation with RhNaX (Table 5), only a few percent conversion was observed (which may have been only background from the GC).

The phosphines may be expected to act as bases, and the mercaptan as an acid. Because of the large excesses (compared to rhodium) of both phosphine and mercaptan in many experiments, an acid-base reaction between these two components probably occurred, yielding products which were inert as catalyst modifiers. As a result, the rhodium would only be affected by any mercaptan or phosphine left over from the neutralization.

It also must be pointed out that the RhNaX results with the phosphines and mercaptan should be directly compared to homogeneous results with the same phosphine and mercaptan loadings with care. Since the mercaptan is too large to penetrate the zeolite pore system, it can only modify or act upon rhodium in solution, which was generally only about 20% of the total rhodium in the reactor as well as the rhodium used in the homogeneous results. In other words, there was five times as much mercaptan available per rhodium molecule in the heterogeneous experiments as compared to the analogous homogeneous experiments. Therefore, there may have been some intrazeolitic activity from RhNaX (solution or surface rhodium being poisoned by the mercaptan under conditions where the mercaptan did not poison all the rhodium in a homogeneous experiment.

6.5 Hydrogenation

Due to the large quantities of mercaptan required to poison solution rhodium, there was a possibility that it was clogging the zeolite pores. This clogging could be a result of either reaction between the mercaptan and the zeolite itself, or due to physical adsorption.

As an alternative procedure for attempting to observe intrazeolitic activity, the hydrogenation reaction was studied. Here, excess phosphine was expected to act as a poison for rhodium hydrogenation in solution.^{18, 28} Very low rhodium concentrations were used for the heterogeneous studies, making it impossible to accurately scale down the phosphine and mercaptan loadings. Thus, the concentrations of these modifiers were in great excess.

At 125°C, it can be seen from Table 9 that for RhNaX (from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) in the presence of PPh_3 , approximately 25% of the 1-hexene hydrogenated to hexane and approximately 30% isomerized to 2-hexenes in 15 hours. In the presence of both PPh_3 and Ph_3CSH , there was no hydrogenation, and less than 3% isomerization in 22 hours. This result may indicate pore blockage by the mercaptan, or may be a result of the acid-base reaction between the phosphine and mercaptan previously discussed. Two runs were performed with this catalyst in the presence of Ph_3CSH at 125°C. Neither showed any

hydrogenation activity in 22 hours, and less than 2% isomerization was observed for one of the runs (possibly GC background). Like the observation for 125°C that the catalyst turned black after reaction if not in the presence of phosphine, the catalyst used for hydroformylation was observed to darken after reaction if no phosphine was present. It did not turn black, but since there was only an 0.1% weight loading of rhodium on the zeolite, this darkening was probably also an indication of rhodium being reduced to rhodium metal.

At 60°C with RhNaX (from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$), Table 9 shows that in the presence of PPh_3 , approximately 19% of the 1-hexene hydrogenated to hexane, and no isomerization was observed in 24 hours. Note the difference between this run and the 125°C result for RhNaX in the presence of PPh_3 where approximately 30% isomerization was observed. At 125°C in the presence of both PPh_3 and Ph_3CSH , less than 3% isomerization occurred in 22 hours, whereas at 60°C, more than 13% isomerization occurred in 24 hours. Since the 60°C run with both PPh_3 and Ph_3CSH was a continuation of the previous run with the mercaptan added after 24 hours, the 18.27% hydrogenation to hexane observed was only that hexane left in the reactor from the earlier run. Again, the 60°C result of no hydrogenation in the presence of Ph_3CSH may be a result of pore blockage or neutralization of the phosphine.

The results for $\text{Rh}_4(\text{CO})_{12}$ shown in Table 10 do not support the expectation that excess PPh_3 poisons solution hydrogenation at either 125°C or 60°C . At both temperatures, approximately 56% of the 1-hexene hydrogenated to hexane. In addition, more than 40% isomerization to 2-hexenes was observed. The effect of using a different phosphine, $\text{P}(t\text{-Bu})_3$ was also studied. At 60°C , in the presence of this phosphine, only 1.51% hydrogenation was observed, but more than 98% isomerization occurred. Therefore, heterogeneous catalyst modification with this phosphine was not tried.

Most of the hydrogenation experiments in this study were performed at 60°C in order to compare the results with those of Corbin et al.¹⁸ Corbin et al. claim that selective poisoning of surface and intrazeolitic rhodium activity is possible through the use of either large or small phosphines, respectively. They measured the selectivity for hydrogenation of two different sized cyclic olefins. They found that tri-n-butylphosphine, which is too bulky to enter the zeolites used, raised the selectivity to approximately 4 in favor of hydrogenation of the smaller olefin, presumably by poisoning surface and solution rhodium activity. No mention was made by Corbin et al.¹⁸ of isomerization, one of the dominant reactions observed in this study. Also, the $\text{Rh}_4(\text{CO})_{12}$ results in this study of hydrogenation in the presence of the bulky phosphine PPh_3 do not support the claim

of Corbin et al. that a bulky phosphine poisons solution or surface rhodium activity.

Thus, the hydrogenation results were inconclusive. Excess PPh_3 did not poison rhodium activity in the homogeneous studies. Therefore, it is not likely that PPh_3 poisoned solution or surface rhodium activity in the heterogeneous studies. Also, the RhNaX runs with PPh_3 and Ph_3CSH may have shown little conversion either due to pore blockage or neutralization of the phosphine. Finally, the low or zero conversion observed in the RhNaX runs with Ph_3CSH may have been due either to pore blockage or the previously observed inability of zeolite-supported rhodium to act as a catalyst when not in the presence of phosphine. Phosphines may be needed in order to suppress the reduction of the rhodium to rhodium metal at 125°C .

6.6 Reaction Profiles

A series of runs were performed in which reaction profiles were measured by connecting the batch reactor to the automatic sampling system described in the Materials and Methods section. Samples were drawn from the reactor at predetermined intervals and analyzed on-line by a GC and integrator. Thus, reactant and product concentrations were determined as a function of time for a given reaction as it proceeded.

These profiles can be useful in determining the optimum time required to maximize the concentration of the desired product(s). They are also helpful in determining the behavior and the effect of modification on reaction intermediates (such as 2-hexenes for these hydroformylation studies). Finally, reaction profiles are useful for showing induction periods required for a given catalyst and reaction.

Figures 4 and 5 show the reaction profiles for $\text{Rh}_4(\text{CO})_{12}$ at 125°C with and without PMe_2Ph . All of these profiles show good continuity for the results at the different sampling times, attesting to the accuracy of samples taken by this method. From Figure 6 it can be seen that conversion was complete in less than one hour for the unmodified $\text{Rh}_4(\text{CO})_{12}$, and in about four hours for the $\text{Rh}_4(\text{CO})_{12}$ modified with PMe_2Ph . Thus, after this time, changes in concentrations, selectivity, and n/b are due to secondary reactions such as hydroformylation of 2-hexenes to 2-ethylpentanal and 2-methylhexanal. Comparing Figures 4 and 5, it can be seen that the addition of 112 moles $\text{PMe}_2\text{Ph}/\text{mole Rh}$ had several effects. As expected^{2,9} the excess phosphine sharply curtailed isomerization, resulting in a much higher n/b throughout the profile. It can be seen in Fig. 6, however, that n/b was still decreasing after 20 hours for the phosphine-modified run, rather than leveling off, as did the n/b for the unmodified run. Selectivity was much higher for

the phosphine-modified case, due to the decreased isomerization.

The effect of phosphine modification was also studied for the heterogeneous RhNaX (from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$). When no PMe_2Ph was added, no conversion was observed in 24 hours at 125°C . Figure 7 show the concentrations of 1-hexene, heptanal and 2-methylhexanal as a function of time for samples taken approximately every three hours. Figure 8 shows the analysis of these results in terms of selectivity, conversion and n/b. In the presence of 100 moles PMe_2Ph /mole Rh and 20 moles Ph_3CSH /mole Rh (Figs. 7 and 8), no isomerization or hydrogenation was observed. Therefore, the selectivity was 100% to aldehydes immediately and remained so for over 20 hours. The reaction rate was slower, as expected, compared to the homogeneous catalyst. N/b remained around 2.7 for the entire time; quite different behavior from the previously discussed homogeneous run where n/b started at that ratio for the phosphine-modified case, but then declined. The invariant n/b for the RhNaX is because no isomerization was observed. The RhNaX result at 20 hours compares well with the batch results at these concentrations of PMe_2Ph and Ph_3CSH previously discussed (Table 5). In all batch cases (with or without pretreatment), at 21 hours, the conversion and the selectivity were essentially 100%, and n/b varied only from 2.7 to 3.0.

The reaction profile for $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ at 125°C with 100 moles PPh_3 /mole rhodium (Fig. 9) shows intermediate behavior between the limits of the $\text{Rh}_4(\text{CO})_{12}$ results with and without dimethylphenylphosphine. Unlike the previous studies with PMe_2Ph , isomerization was not inhibited by PPh_3 . Isomerization resulted in a lower selectivity at all points in the profile as compared to both $\text{Rh}_4(\text{CO})_{12}$ and RhNaX with PMe_2Ph . Also, n/b was initially high, but rapidly declined (similar to the $\text{Rh}_4(\text{CO})_{12}$ run without phosphine).

7.0 CONCLUSIONS

1. Zeolite crystallinity was not lost under reaction conditions
2. No activity was observed at 125°C without the presence of phosphines.
3. The $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]\text{NaX}$ catalyst elutes more rhodium than the RhNaX cation exchanged from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ when reacted at 50°C.
4. It was not conclusively determined whether or not intrazeolitic activity is occurring at either 50°C or 125°C.
5. Homogeneous rhodium-phosphine complexes are able to hydrogenate 1-hexene at either 60°C or 125°C.

8.0 RECOMMENDATIONS

1. Find or synthesize a heterogeneous mercaptan to use in place of the triphenylmethylmercaptan which may have clogged the zeolite pores.
2. Statistically optimize the process variables such as temperature, pressure, H_2/CO , and reagent concentrations.
3. Compare homogeneous and heterogeneous activity with the mercaptan and phosphines at the same concentrations of solution rhodium (as measured by rhodium elution).
4. For a heterogeneous run with mercaptan and phosphine in which there was some conversion (but no homogeneous conversion at similar conditions) filter solution under nitrogen and run just solution and/or just catalyst again to see whether reactivity is coming from rhodium eluted into solution or intrazeolitic activity.

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APPENDIX A

A.1 MMD-1 Program

```
-----  
AAA > Nested loop: time before  
BBB > valves open  
CCC Time valve 2 stays open  
DDD Additional time valve 1 stays open  
EEE Time before sample  
FFF Time before valve returns to "load"  
GGG > Nested Loop; time between  
HHH > samples  
-----
```

```
000 076 001  
002 323 000  
004 315 162 003  
007 076 000  
011 323 000  
013 076 AAA  
015 036 BBB  
017 315 162 003  
022 035  
023 302 017 003  
026 075  
027 302 015 003  
032 076 006  
034 323 000  
036 036 CCC  
040 315 162 003  
043 035  
044 302 040 003  
047 076 002  
051 323 000  
053 036 DDD  
056 315 162 003  
060 035  
061 302 056 003  
064 076 000  
066 323 000  
070 036 EEE  
072 315 162 003  
075 035  
076 302 072 003  
101 076 050  
103 323 000  
105 315 162 003  
110 076 000
```

112 323 000
114 036 FFF
116 315 162 003
121 035
122 302 116 003
125 076 020
127 323 000
131 315 162 003
134 076 000
136 323 000
140 076 GGG
142 036 HHH
144 315 162 003
147 035
150 302 144 003
153 075
154 302 142 003
157 303 000 003
162 006 020
164 315 174 003
167 005
170 302 164
173 311
174 016 035
176 026 177
200 025
201 302 200 003
204 015
205 302 176 003
210 311
211 000
212 000

A.2 Wiring Diagrams

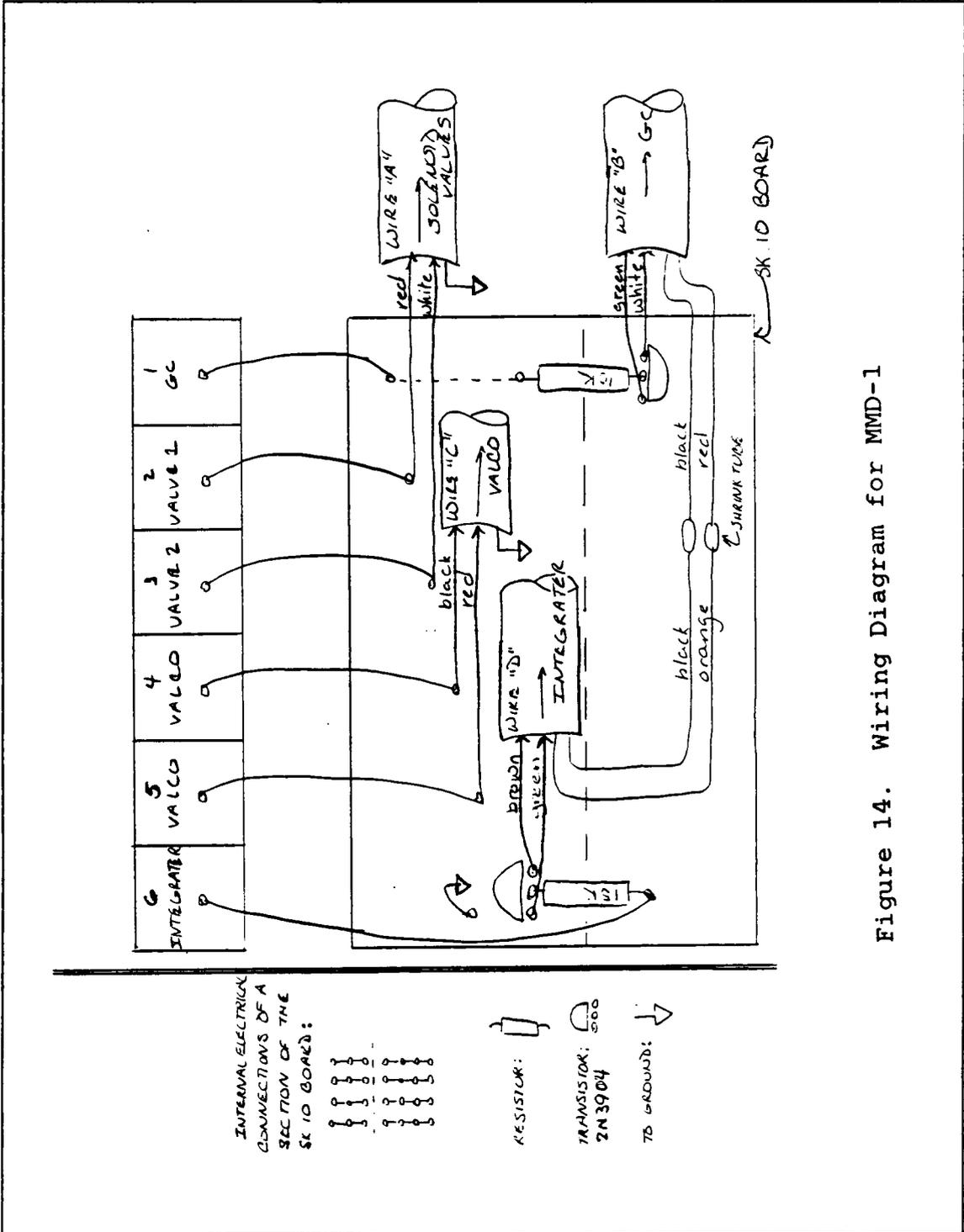


Figure 14. Wiring Diagram for MMD-1

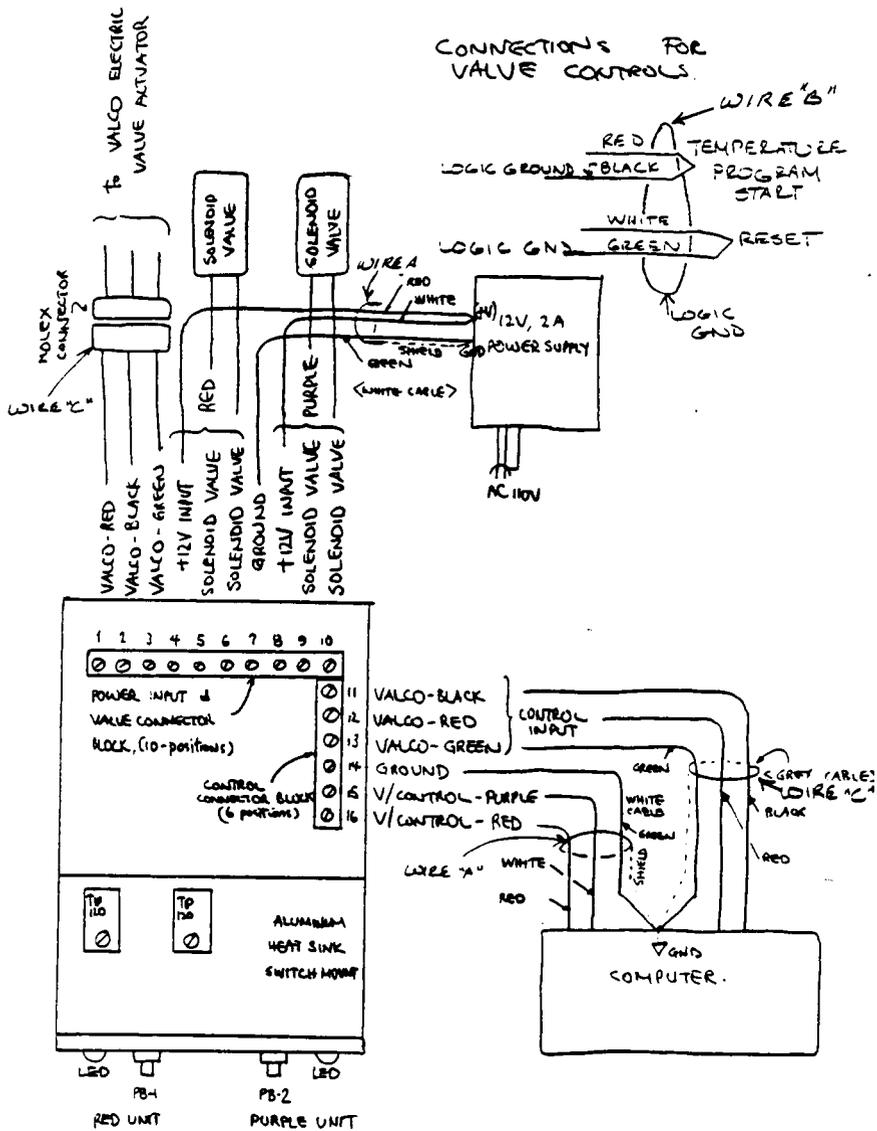


Figure 15. Wiring Diagram for Automatic Sampling System

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the scanned document**