AN ANALYSIS OF THE SELECTIVITY OF THE OLEFIN HYDROGENATION CATALYST TRISTRIPHENYLPHOSPHINECHLORORHODIUM (I) SUPPORTED ON 2% DIVINYLBENZENE CROSSLINKED POLYSTYRENE BEADS

A Dissertation
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Edward Marsh Sweet
1976

This is to certify that the

thesis entitled

AN ANALYSIS OF THE SELECTIVITY OF THE OLEFIN
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TRISTRIPHENYLPHOSPHINECHLORORHODIUM(I)
SUPPORTED ON 2% DIVINYLBENZENE CROSSLINKED
POLYSTYRENE BEADS

presented by

Edward Marsh Sweet

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Robt H. Grubbs
Major professor

Date Aug 10, 1977

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ABSTRACT

AN ANALYSIS OF THE SELECTIVITY OF THE OLEFIN HYDROGENATION CATALYST TRISTRIPHENYLPHOSPHINECHLORORHODIUM(I) SUPPORTED ON 2% DIVINYLBENZENE CROSSLINKED POLYSTYRENE BEADS

By

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An investigation was conducted to determine what factors cause the observed alteration from homogeneous solution selectivity when $RhCl(PPh_3)_3$ is supported on polystyrene-2% divinylbenzene copolymer beads (1,2).

An initial study used beads on which a portion of the pendant phenyl groups were substituted with CH_2PPh_2 groups, giving a pendant group equivalent to benzyldiphenylphosphine. Equilibration with $[RhCl(COE)_2]_2$ (COE=cyclooctene) in deficiency or in excess, followed by 1/3 equivalent of triphenylphosphine per equivalent of rhodium, gave an active hydrogenation catalyst. Significant alteration in selectivity from an otherwise similar catalyst prepared with $RhCl(PPh_3)_3$ was noted for the catalyst prepared from an excess of $[RhCl(COE)_2]_2$. Alteration in selectivity was attributed to different ratios of phosphine to rhodium produced by different methods of preparation. Interpretation of overall selectivity was not possible since several

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species containing mixtures of bead-phosphine and triphenylphosphine were possible.

A bead support was made containing pendant phenyl groups substituted with PPh_2, giving a supported phosphine equivalent to triphenylphosphine. Equilibration with either an excess or a deficiency of $RhCl(PPh_3)_3$ gave an active hydrogenation catalyst. Comparison of the supported catalyst selectivity with homogeneous catalyst selectivity indicates that the active site of the supported catalyst experiences a small significant phosphine concentration. There is evidence for selectivity with changing molecular volume. At least some of the selectivity is caused by restricted diffusion of alkene to the active site.

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By

Edward Marsh Sweet

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1976

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Few successful undertakings are the result of one persons efforts alone. Many have contributed to this work, for which I am grateful.

Foremost among those mentioned must be Dr. R. H. Grubbs, my research preceptor, who envisioned and directed the project, and the members of my committee, both present and past, who provided much insight and many ideas. I wish to thank Dr. P. Rasmussen and Mr. V. Shull for assistance with the electron microprobe work, Mr. Bob DeVries and Mrs. S. C. H. Su for assistance with some of the experimental work, and the members of the Michigan State University Analytical Chemistry Consulting Service for design and construction of the digital time logger, and Mrs. Shirley Goodwin for typing the dissertation.

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I. INTRODUCTION

General

Over the past several years there has been growing interest in attaching homogeneous transition metal catalysts to insoluble polymer supports. This technique gives a catalyst with properties generally similar to the homogeneous analogue. A large number of catalysts has been supported in this manner. As several reviews have appeared recently covering this topic (1,2,3), I will not enumerate them here.

A primary advantage of supported over homogeneous catalysts is the ease with which they may be removed from the reaction mixture by filtration once the reaction is completed. The product is obtained free of catalyst, eliminating a sometimes difficult separation step, while the catalyst is retained in an active form which may be reused.

Activation (4) and alteration in selectivity (1,5,6,7) has sometimes been noted when a homogeneous catalyst is supported. It is toward determining factors affecting the selectivity in the system of tristriphenylphosphinechlororhodium(I), $[RhCl(P\emptyset_3)_3]$, attached to polystyrene copolymerized with 2% divinylbenzene that this work is directed.

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$RhCl(P\emptyset_3)_3$ was one of the first homogeneous catalysts supported on polymers (6,8,9). The 2% divinylbenezene-styrene copolymer substituted with phosphine equivalents is a support that has been widely used for this and other transition metal catalysts. The presence of phosphine allows a large number of transition metal species to be supported. A study of the system $RhCl(P\emptyset_3)_3$ on 2% cross-linked polystyrene may be applicable to other systems using this support.

Supported $RhCl(P\emptyset_3)_3$ is, like the homogeneous species, an efficient olefin hydrogenation catalyst at room temperature and atmospheric pressure (6,10). Therefore, the rate of reaction can be measured with reasonable precision by monitoring the uptake of hydrogen with time. Studies of the kinetics of the homogeneous catalyst have provided much mechanistic information. A comparison of these two systems should offer some insight into the nature of the supported catalyst.

The Nature of the Support

Divinylbenzene crosslinked polystyrene beads have been used in diverse ways; such as, ion exchange resins, supports in the Merrifield solid phase peptide synthesis, and the stationary phase in gel permeation chromatography.

Two broad classifications of beads exist. The macroporous (macroreticular) resins are produced in a manner

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that leaves small channels throughout the bead which remain on removal of solvent from the bead. Microporous beads, which were used throughout this work are essentially homogeneous. Microporous beads can be further subdivided based on degree of crosslinking, expressed as the divinylbenzene content of the polymerization mixture, which generally ranges from 1 to 8%. The degree of crosslinking affects the swelling ratio in a given solvent, and the exclusion limit (the largest molecular weight species that will enter the bead), both decreasing with increasing crosslink density. In general, observations of properties of beads made at one crosslink density should be applicable to others with due consideration made for a change in magnitude of that property.

Polystyrene beads of several kinds have been used as the stationary phase in gel permeation chromatography since its inception (10,11). The primary cause of separation is believed to be an exclusion of large volume molecules by the stationary phase, which leads to the highest molecular volume species being eluted before to the lower. The basic equation for GPC interpretation is

$$V_r = V_o + K_{GPC}V_s,$$

where V_r is retention volume, V_o is the volume of solvent outside of the stationary phase, and V_s is the volume of

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solvent within. K_{GPC} represents the fraction of the stationary phase accessible to the molecule (10,13).

Other factors, such as flow effects and restricted diffusion have some influence, and have at times been advanced as the primary factor in separation (14). However, a static partitioning experiment shows good correlation between the distribution coefficient and K_{GPC} for the packing used (15), indicating that the separation is essentially an equilibrium process.

While gel permeation chromatography is normally applied to polymers, it has been known from its inception that GPC is capable of separating small molecules. Moore, in his original paper, separated xylenes (M.W. 106, diameter 8.9 Å) from perchloroethylene (M.W. 166, diameter 7.7 Å) (11). Indeed, the technique is more selective toward small molecules than large ones. Thus, oligomers may be separated into individual components of $(\text{monomer})_n$ length (16), while the normal GPC of a full polymer gives a molecular weight distribution not resolved into components.

GPC is one basis for the concept of an exclusion limit. Here the exclusion limit is the smallest molecular volume, or weight, species that will pass through the column with V_r equal to V_o. Below this point, V_r is greater than V_o, and some separation occurs indicating that the species is entering the stationary phase.

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The results and concepts of gel permeation chromatography should be directly applicable to the 2% crosslinked microporous beads used in this study. With the exception that the beads used are somewhat larger than usual for GPC, they are identical to those sometimes used as a stationary phase.

Less directly related are the ion exchange resins. One of the few instances of determination of the pore size distribution of a microporous resin in the swollen state was made by Krska and Dusek for a sulfonated polystyrene resin at 15% crosslink density. They found a pore size distribution in the range of 5 to 10 Å (17). Comparison of their system with the one of interest must be made with caution. Ion exchange resins are so highly functionalized with hydrophylic groups that they become hydrophylic. The polymer backbone and major portion of the pendant groups remain hydrophobic. The observed pores could be due to association of hydrophobic portions of the polymer, and not due to any inherent structure.

The results from gel permeation chromatography indicate that size selectivity will be observed on the support. The magnitude for a given size range, particularly for the size range of 6 to 12 Å where selectivity has been observed in the reduction of alkenes (4,18), cannot accurately be assessed based on GPC.

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The presence of a pore size distribution in the range of 6 to 12 Å is shown by an ion exchange resin with a crosslink density of 15%. Reduction of crosslink density to 2% for the support would indicate that such a pore size distribution would occur at somewhat larger sizes than 6 to 12 Å.

The Hydrogenation of Olefins With Tristriphenylphosphinechlororhodium(I)

Mechanism

The primary purpose of this work is not to provide further mechanistic study of olefin hydrogenation by $RhCl(R\O_3)_3$. A consistent method for evaluation of, and comparison among, the rates of reduction of various alkenes is needed. These rate comparisons, denoted as relative rates under given conditions, may be compared to relative rates from the bead supported catalyst. This may provide insight into the environment of the catalytic site on the supported catalyst. The validity of this insight depends directly on the validity of the rate comparisons made in homogeneous solution. Thus a detailed discussion of the homogeneous solution mechanism and its relation to the rate expression seems in order.

The original investigation of the kinetics of this reaction was by Wilkinson and co-workers (10). They believed the catalyst dissociated completely in solution to give Rh

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give $RhCl(P\emptyset_3)_2$, which underwent oxidative addition of hydrogen to this followed by fast addition of alkene to give products. The formation of an olefin complex $RhCl(P\emptyset_3)_2$ (olefin) was postulated to account for observed olefin inhibition of the reaction. Subsequent investigation by various workers showed that the primary species present in the absence of hydrogen was $RhCl(P\emptyset_3)_3$ while in the presence of alkene and hydrogen, $RhClH_2(P\emptyset_3)_2$(olefin) was formed (19-23).

Detailed reinvestigation of the kinetics has been made by Siegel and Ohrt (23), and Halpern and co-workers (22,24). Tolman has investigated certain aspects of the reaction not considered by others (25). These three studies will be the basis for the following consideration of a mechanism. Many of the conclusions of Siegel and Ohrt, drawn from measurement of overall rate as a function of various concentrations of hydrogen, alkene, catalyst, and phosphine, have been largely displaced by instrumental observation, or lack of observation, of intermediates and their formation constants, by the latter two workers. Their work still provides a large body of experimental evidence for interpretation. A mechanism based on these three studies is outlined in Figure 1.

Figure 1. Probable mechanism of alkene hydrogenation catalyzed by $RhClL_3$.

a) Path 1--Halpern's mechanism.
Path 2--Tolman's dimeric mechanism applicable under some circumstances.

b) $\underset{\longleftarrow}{\overset{K_n}{\longrightarrow}}$ Thermodynamic equilibrium in reaction path k_n is the associated rate toward $RhClH_2L_3$, $RhClH_2L_2S$, or $H_2[RhClL_2]_2$.

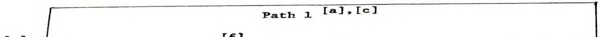
$\underset{\longleftarrow}{\overset{K_9}{\longrightarrow}}$ Formal thermodynamic equilibrium independent of path.

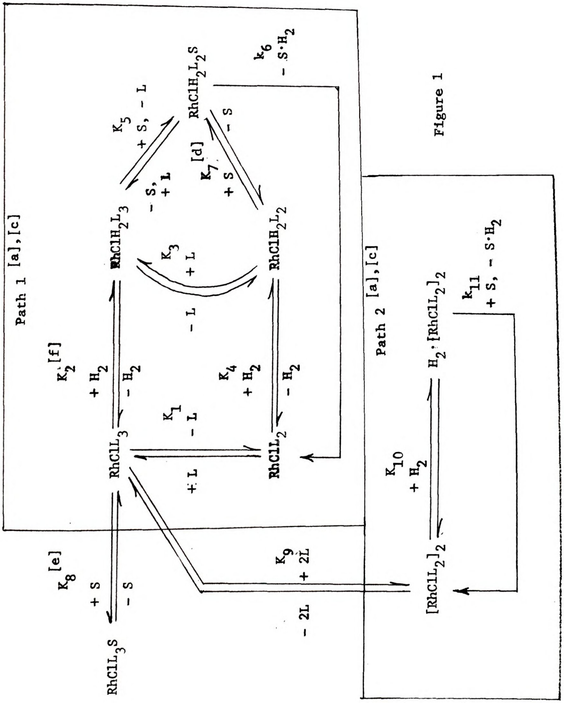
c) Underlined species are present in significant amounts at 1 atm H_2 and 25°C under at least some conditions.

d) This reaction is not included by Halpern.

e) Species formed by this reaction are unlikely.

f) This route accounts for only a small portion of hydrogen addition under most conditions.




Path 1 [a],[c]
Path 2 [a],[c]
$RhClL_3S$
K_8 [e]
+ S
- S
$RhClL_3$
K_1
- L
+ L
$RhClL_2$
K_2 [f]
+ H_2
- H_2
K_4
+ H_2
- H_2
$RhClH_2L_3$
$RhClH_2L_2$
K_3
+ L
- L
K_5
+ S, - L
- S, + L
$RhClH_2L_2S$
K_7 [d]
+ S
- S
k_6
- $S \cdot H_2$
K_9
+ 2L
- 2L
$[RhClL_2]_2$
K_{10}
+ H_2
$H_2 \cdot [RhClL_2]_2$
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+ S, - $S \cdot H_2$

Figure 1

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There is general agreement that, starting with $RhClL_3$, the predominant species in solution during hydrogenation at one atmosphere pressure, are $RhClH_2L_3$ and $RhClH_2L_2S$ ($L = P\emptyset_3$, S = olefin). Marginally significant amounts of $RhClL_3$ (1 to 5%) may also exist at low alkene concentrations due to the equilibrium $H_2 + RhClL_3 \overset{K_2}{\rightleftharpoons} RhClH_2L_3$. Siegle and Ohrt also report evidence for a species identified as $RhClL_3S$ (S = cyclohexene); Tolman, however, sees no change in the P^{31}NMR spectrum of $RhClL_3$ on addition of cyclohexene, which casts extreme doubt on its existence. Halpern and Tolman both find evidence for formation of small concentrations of $RhClL_2$ and $RhClH_2L_2$. These are intermediates in the principle route for addition of hydrogen to $RhClL_3$ except in the limit of very high phosphine concentration. Tolman sees P^{31}NMR spectroscopic evidence for $RhClH_2L_2$ in dichlormethane at 26°C, though the concentration is small and quite uncertain.

Tolman presents evidence that $[RhClL_2]_2$ and $[RhClL_2]_2H_2$ can be present in significant concentrations under some circumstances. In the case of $L = P(p\text{-tolyl})_3$, it is a hydrogenation catalyst, although under some of the conditions used, the results and kinetics were obscured by presence of large quantities of $RhClH_2L_2S$ formed by dissociation of the dimer. He indicates that the rate of dimer hydrogenation is independent of alkene concentration above 0.3 M alkene,

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indicating that most dimer exists as $[RhClL_2]_2$ and the rate by this route then becomes the rate of formation of $H_2[RhClL_2]_2$. While the importance of this dimeric form to the overall kinetics is unclear, some qualitative observations can be made. Given an initial set of conditions, increasing hydrogen pressure or phosphine concentration will increase the relative amount of monomer present, based on the two formal equiliberia,

$$[RhClL_2]_2 + 2L \rightleftharpoons 2RhClL_3$$

$$[RhClL_2]_2 + 2H_2 + 2L \rightleftharpoons 2RhClH_2L_3$$

and mass action. The presence of $H_2 \cdot RhClL_2$ and $RhClH_2L_2S$ alter the relative amounts of monomeric and dimeric species present from the values predicted by the above equiliberia, but do not affect the basic argument. In the presence of hydrogen, an increase of olefin concentration will increase the relative amount of monomer present by formation of $RhClH_2L_2S$.

The primary path for hydrogenation of olefins is as follows:

a) Oxidative addition of hydrogen to minute quantities of $RhClL_2$ gives $RhClH_2L_2$, which is rapidly converted to $RhClH_2L_3$.

b) Equilibrium concentrations of $RhClH_2L_3$ and $RhClH_2L_2S$ are established and maintained.

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c) The alkene complex $RhClH_2L_2S$ decomposes to give products.

Consideration of a Rate Expression

It is clear from the preceding that several mechanistically important species are present in sufficiently low concentrations that they do not affect either rhodium or phosphine concentration. Halpern's work shows that all rate constants prior to the rate limiting decomposition of $RhClH_2L_2S$ to products are sufficiently fast to consider these reactions as thermodynamic equiliberia within the monomer system. Assuming that only $RhClH_2L_2S$ and $RhClH_2L_3$ are present in significant quantity, he gives the rate expression:

$$- \frac{ds}{dt} = \frac{k_6 K_5 [C_o] [S]}{[L] + K_5 [S]} \quad , \qquad (1)$$

where $[C_o]$ is total rhodium concentration. [L] is total phosphine in solution, both catalyst generated and added, which reduces the utility of this form since at low concentrations of added phosphine, or in the absence of added phosphine, the quantity generated by the catalyst in formation of $RhClH_2L_2S$ can be substantial.

A more useful form can be obtained by explicit consideration of catalyst generated phosphine and added phosphine. Solution of the equation for the equilibrium indicated by K_5 with such consideration leads to the expressi

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$$-\frac{ds}{dt} = \frac{k_6([L_o] + K_5[S]}{2} \left(-1 + \sqrt{\frac{1+4K_5[S][C_o]}{([L_o] + K_5[S])^2}}\right). \qquad (2)$$

Taking a two term Taylors series expansion of (2) about 1 gives (1), showing that it is a special case of (2). Another special case of (2) is when no added phosphine is present. This gives--

$$-\frac{ds}{dt} = \frac{k_6K_5[S]}{2} \left(-1 + \sqrt{1 + \frac{4[C_o]}{K_5[S]}}\right). \qquad (3)$$

Terms for dimeric catalyst formation have not been included. Any attempt to derive a rate expression including these terms, even without including catalyst contributions to total phosphine explicitly, produces equations of higher order than quadratic, which, coupled with the inclusion of several more terms, would produce an expression of such complexity that it would be practically useless for the purpose at hand. The course chosen is to assume monomeric behavior as described by Halpern. Where deviations occur, consideration will be given to the possibility that they are caused by dimer formation.

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II. RESULTS AND DISCUSSION

Bead Preparations

Two broad routes to functionalizing the initial styrene-divinylbenzene copolymer were used, chloromethylation and electrophylic bromination (18). This was followed by substitution of diphenylphosphide for halogen and addition of a rhodium(I) chloride species, either as $RhClL_3$ or $[RhCl(cyclooctene)_2]_2$. These two routes are summarized in Scheme I (Figure 2).

Initial chloromethylation produces a catalyst where Rh(I) is attached by one or more phosphine groups roughly equivalent to benzyldiphenylphosphine. Initial bromination produces a catalyst where Rh(I) is attached to one or more phosphines roughly equivalent to triphenylphosphine.

A few comments on the two procedures are in order.

Chloromethylation followed by phosphination in the manner of Grubbs and Kroll (6) is the simpler of the two methods, requiring fewer steps and less operation under inert atmospheres. A disadvantage, for my purpose, became apparent during the work. Equilibration of the Rh(I) species and triphenylphosphine with the beads will potentially produce several species equivalent to $RhClL_{3-n}L'_n$

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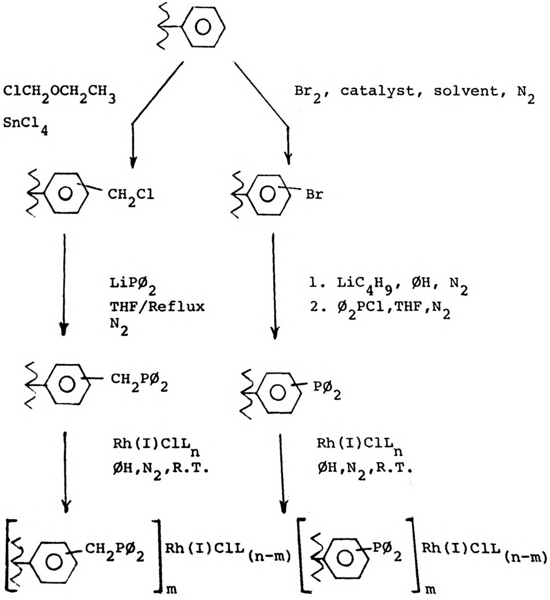

Figure 2. Scheme I--bead functionalization.

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($L = P\emptyset_3$, $L' = \emptyset CH_2P\emptyset_2$, $n = 1,2,3$). At least some of the attached Rh(I)Cl units have two or more bead phosphines attached (8,18). The inherent differences in reactivity between these species could affect the observed reactivity and selectivity. Only two species, $RhClL_3$ and $RhClL'_3$, can be produced in solution with certainty.

Several routes to brominated polymer were tried. Use of bromine and anhydrous ferric chloride gave moderate bromination (3.8% substitution versus 9.5% possible based on bromine). The polymer was appreciably darkened, probably due to decomposition; however, the presence of residual iron compounds was not ruled out. Bromine and borontrifluoride in nitromethane gave little substitution (0.43% versus 9.8% possible) although this procedure has given reasonable results on a 20% crosslinked macroreticular polymer using identical material and conditions (18). The use of bromine and borontrifluoride in nitrobenzene produced a polymer relatively colorless (very light brown) and containing an acceptable amount of bromine. Twice the theoretical amount of bromine and borontrifluoride was used to obtain the desired degree of substitution (5.2% versus 10.5% theoretical for batch 4, 11.5% versus 17.4% theoretical for batch 5). It is possible the reaction becomes quite slow as concentration of bromine and borontrifluoride decrease, leading to the requirement for an excess to achieve reasonable reaction rate.

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The cause for low reactivity of the beads in nitromethane is uncertain. Nitromethane does not appreciably swell 2% crosslinked microporous beads; it may be that little of the reactants enter the beads.

Phosphination of the aryl brominated beads was accomplished in two steps. Initial lithium exchange using excess n-butyl lithium in benzene produced reddish brown beads. Addition of a two molar excess, based on bromine available for exchange, of chlorodiphenylphosphine followed by reflux did not completely remove the color; addition of water did. Evidently insufficient phosphine was present to completely react with the lithiated phenyl groups. Subsequent microprobe analysis showed that phosphorous was absent from the very center of the bead but present to a significant depth. This indicates that the wash procedure did not remove all of the excess butyl lithium. Since substantial phosphine was present, these beads were used for further preparations.

A potentially useful observation from this is that phenyl-lithiated beads provide an internal colorimetric indication for completion of reaction with an electrophile. When reaction is complete the beads become significantly lighter in color.

Rhodium(I) was attached to the phosphinated beads by ligand exchange from $RhCl(P\emptyset_3)_3$ and $[RhCl(cyclooctene)_2]_2$ in benzene. $RhCl(P\emptyset_3)_3$ requires several weeks to assure

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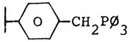
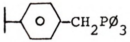
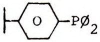
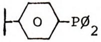
completion, while $[RhCl(cyclooctene)_2]_2$ is complete in several days. The use of a deficiency of either markedly shortened the time required to reach equilibrium. A deficiency of $RhCl(PØ_3)_3$ was almost completely absorbed from solution in about two days, while a deficiency of $[RhCl(cyclooctene)_2]$ was completely absorbed in several hours.

A summary of preparation for each batch of beads used in this study is given in Table 1.

Table 1. Synopsis of Bead Preparations

Batch	Bead Phosphene Type	Equilibrated Species and Conditions	Analysis
1A	 $-CH_2PØ_3$	Deficient $[RhCl(COE)_2]_2$	2.08% Rh 1.77% P
1B	 $-CH_2PØ_3$	Excess $[RhCl(COE)_2]_2$	2.62% Rh 1.76% P
5A	 $-PØ_2$	Deficient $RhCl(PØ_3)_3$	0.32,0.42,0.29% Rh 0.86,0.87% P
5B	 $-PØ_2$	Excess $RhCl(PØ_3)_3$	0.47,0.76% Rh 0.93% P

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Characterization of Beads

Swelling of Ratios

Swelling ratios for 32 to 35 mesh, unfunctionalized beads are presented in Table 2. As used here, swelling ratio is defined as the apparent relative increase in volume of beads on adding solvent (Swelling ratio = V(wet)/V(dry)). Measurement of volumes was done in a graduated cylinder, wet volume was measured four hours after adding solvent except for cyclohexane which required two days to reach equilibrium.

This is intended as a rapid, simple method for quantification of the observation that some solvents are better for swelling beads than others, and not as a general substitute for methods employing gain in weight on swelling.

Table 2. Swelling Ratios

Solvent	Swelling Ratio [V(wet)/V(dry)]
Benzene	3.90±0.20
Toluene	3.45±0.18
Tetrahydrofuran	3.65±0.12
Ethylether	2.05±0.11
Nitrobenzene	2.35±0.13*
Nitromethane	1.10±0.07*
Cyclohexane	1.95±0.10

*Beads float in this solvent.

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Density

The density of 32 to 35 mesh, unfunctionalized beads was measured in ethanol and benzene. Values found were 1.021±0.051 g/ml for benzene and 1.005±0.007 for ethanol.

These values are based on the difference in volume of solvent required to fill a volumetric flask containing a weighed quantity of beads and the volume of the flask.

There is no significant difference between the apparent density in the solvent of high swelling ratio and the solvent for low swelling ratio, indicating that swelling ratio is a reasonably good indication of internal volumes accessible to solvent.

Microprobe Analysis

The electron microprobe provides a rapid, nondestructive technique for elemental analysis of materials within a small volume area (26,27).

In this technique a narrow (0.5 micron diameter) beam of high energy (10 to 25 kV) electrons is focused on the sample. X-rays characteristic of each element present are emited from a 1 to 10 micron diameter volume. These are resolved, detected and counted.

This technique was used to obtain the location of elements within beads from each batch used.

Count rate is plotted on a recorder while the stage, on which the bead section is held, is moved at a constant rate. The recorder trace then corresponds to elemental

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density as a function of location. Representative spectra are presented in Figures 3 through 7. The spectra of batches 5A and 5B are identical. Only batch 5A is shown.

Comparison of the scan of batch 5 brominated beads with the batch 5A phosphorous spectrum shows that while bromine was distributed throughout the bead, phosphorous was located primarily in the outer sections. This confirms the indication that insufficient chlorodiphenylphosphine was added during the synthesis of this batch.

Two methods of sample preparation were used. The first consists of cutting a bead in half with a razor blade. Preswelling of the bead in benzene is helpful, and the operation is best conducted under a low power microscope. The cut bead may readily be examined under the microscope to determine how near a centering cut was made. The method presents some difficulty in actually obtaining a spectrum. Preferably the surface to be scanned should be parallel to the stage. It is very difficult to align the cut surface to the stage with the needed degree of precision when this method of bead cutting is used. Constant refocusing of the electron beam is required as the scan is taken. This requirement does not present insuperable difficulty for a skilled operator, and adequate spectra are obtained.

The second method of sample preparation starts with casting the beads in an epoxy matrix. When set, the matrix

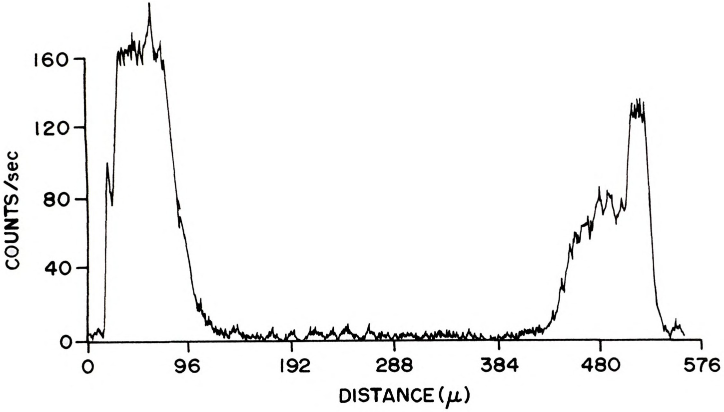

Figure 3. Microprobe spectrum of Batch 1A; Rh L_α, 15 kV, 0.050 μA, half bead section.

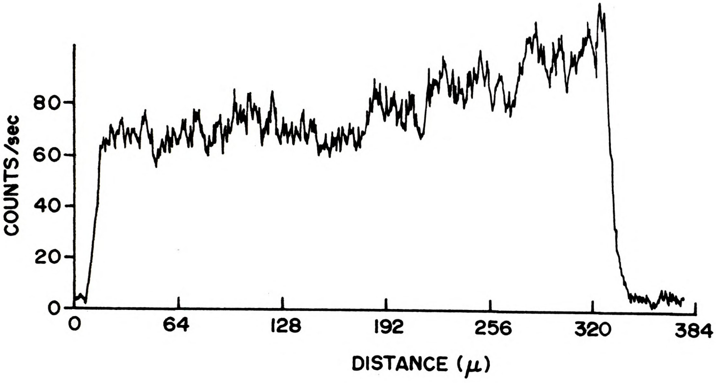

Figure 4. Microprobe spectrum of Batch 1B Rh L_α, 25 kV, 0.050 μA, section.

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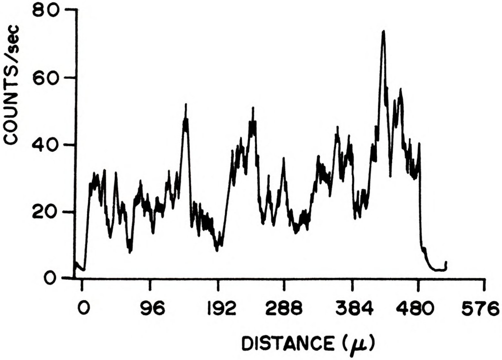

Figure 5. Microprobe spectrum of Batch 5
Br L_{α}, 16 kV, 0.023 μA, half bead
(bromine distribution prior to phosphination).

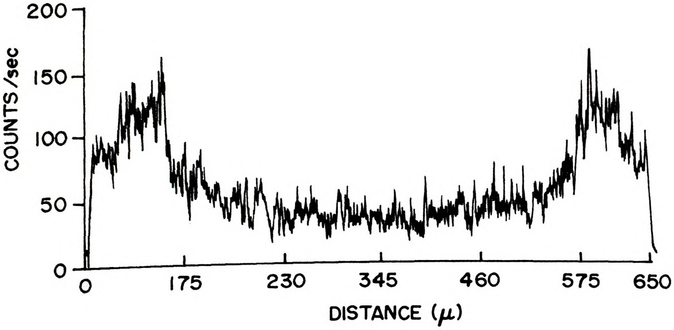

Figure 6. Microprobe spectrum of Batch 5A, P P L_α, 15 kV, 0.032 μA, section.

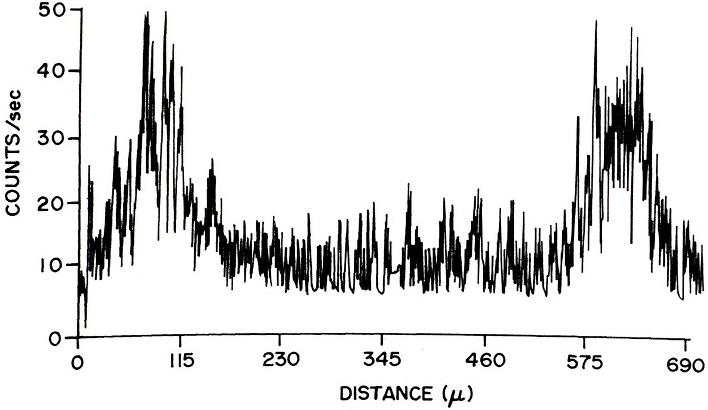

Figure 7. Microprobe spectrum of Batch 5A, Rh Rh L_α, 15 kV, 0.032 μA, section.

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is cut at 5 to 10 micron thickness on a microtome. This gives thin sections of beads which can be mounted and scanned with ease. There are several disadvantages to this method. It is difficult to guarantee that the section obtained is from a point near the center of the bead. To overcome this, a great many bead sections were cut and only the largest were used. The process of examining sections and comparing their size under a microscope is quite tedious. With this method it is not possible to preswell the beads with benzene. When swelling was attempted, the epoxy matrix became too soft to cut at the desired thickness. Without swelling, the beads are quite brittle and often shatter, break, or come out of the matrix. The probable cause of these problems is a difference in hardness between beads and the epoxy matrix. It seemed that linear polystyrene would be an ideal polymer matrix for polystyrene beads.

Polystyrene beads were successfully polymerized into styrene by using benzoylperoxide. Attempts to polymerize beads containing attached rhodium, while producing a good polymer, always showed evidence of rhodium diffusion into the matrix. Polymerization was attempted in a sealed tube under vacuum after freeze thaw degassing using either benzoylperoxide or azobisisobutrylnitrile as initiator. Both showed some indication of rhodium within the matrix. Heating beads with styrene under the same conditions also

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produced a light red styrene solution. Evidently styrene forms a sufficiently stable complex with some of the rhodium present to remove it from the beads.

The use of a polystyrene matrix could prove quite satisfactory for other species which are more firmly attached than this one. Preliminary evaluation indicates that the matrix can be cut at one to five micron thickness quite well. The embedded beads must be colored; otherwise, it is impossible to distinguish between bead and matrix.

For qualitative work, the most satisfactory of the above techniques is cutting the bead in half, because of the ease of preparation and the greater certainty of seeing the true center cross-section.

An attempt was made to obtain elemental ratios of rhodium to phosphorous on several beads. This would be of interest particularly for batch 1A where phosphorous was distributed uniformly throughout the bead while rhodium was localized. The gross analysis cannot reflect the local ratios. A series of such local analyses would also be a useful supplement to the gross analysis on both batch 5A and 5B where the rhodium gross analysis showed some variance. Such ratios can be obtained with relative ease by comparison of unknown relative count rates for each element with the relative count rates from a standard of known composition.

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In the attempt to obtain this information the standard, $RhCl(P\emptyset_3)_3$, decomposed producing small quantities of an unidentified yellow material where the electron beam made contact. The results from batch 5A were obtained using this standard. $RhCl(P\emptyset_3)$ was included in a styrene polymerization mixture, which was cut at 2 micron thickness and used as the standard for batches 1A, 1B, and 5B. It was hoped the thin section would dissipate heat better than the bulk solid. While no physical evidence of decomposition was noted, the results are in gross disagreement with the analytical data, even on beads of batch 1B which are completely saturated with rhodium. The results are reported for interest in Table 3. Comparison between different batches, which was the purpose, should not be made since each is compared to the standard separately. Within each batch some comparisons can be made.

Those batches made by initial chloromethylation (1A and 1B) are rather more uniform, both within each bead and between different beads, than those made by initial bromination (5A and 5B).

If the analysis of perrhodiated batch 1B is considered indicative of its true phosphorous to rhodium ratio, the ratio is 2.23 = P/Rh. Compared to that based on the standard as P/Rh = 3 of 7.2, the standard had actually decomposed to $Rh\ P_{0.93}$.

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Table 3. Phosphorous to Rhodium Ratios by Microprobe Analysis

Bead 1	Bead 2	Bead 3
Batch 1A Average 9.6		
10.14±0.83	10.17±0.81	10.26±0.81
9.66±0.79	9.76±0.78	9.74±0.80
8.10±0.63	9.26±0.74	9.76±0.77
Batch 1B Average = 7.2	Analysis = 2.23	
7.08±0.56	7.43±0.60	7.42±0.67
7.50±0.61	7.47±0.60	6.90±0.54
7.26±0.56	6.82±0.55	6.61±0.52
Batch 5A		
13.35±1.35	2.20±0.17	9.25±0.80
10.81±0.87	3.41±0.18	12.20±1.09
12.15±0.94	8.18±0.44	10.34±0.69
Batch 5B		
12.68±1.09	17.35±1.27	15.23±1.27
15.75±1.25	18.23±1.53	13.42±1.05
15.34±1.24	18.00±1.50	16.25±1.36

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No extensive effort was made to find a more satisfactory standard.

Studies on Benzyldiphenylphosphine Equivalent Beads

Bead Hydrogenations

From the results of Kroll on catalysts of this type equilibrated with $RhCl(P\phi_3)_3$, the maximum difference in rates of reduction were seen to occur using 1-hexene, cyclohexene, and cyclooctene (18). Therefore, these alkenes were used in this study.

Two batches of beads were employed, both made by equilibration of $[RhCl(COE)_2]$ with phosphinated polymer followed by addition of triphenylphosphine. In contrast to $RhCl(P\phi_3)_3$ equilibration, this procedure gives beads that are extremely oxygen-sensitive in the dry state.

Batch 1A was shown by microprobe analysis to contain rhodium primarily in the outer half of the bead, as observed along a diameter (corresponding to roughly 2/3 of the volume on the bead). Batch 1B contained rhodium of equal density throughout.

The results of hydrogenations using batches 1A and 1B are presented in Table 4; data from Kroll Batch E (18) are included for comparison with $RhCl(P\phi_3)_3$ equilibrated beads of otherwise similar preparation. Correction factors are those of reference 18.

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Table 4. Relative Rates of Hydrogenation Using Benzyldiphenylphosphine Equivalent Beads of Various Preparations

Batch / Substrate	1A		1B		LK-E (18)*		
	Relative Rate Beads	Corrected Relative Rate	Relative Rate Beads	Corrected Relative Rate	Relative Rate Beads	Corrected Relative Rate	Correction Factor = 1/RR Homogeneous CHX = 1
Cyclohexene	1.00±0.03	1.00±0.03	1.00±0.10	1.00±0.10	1.00	1.00	1.00
1-Hexene	1.21±0.03	1.08±0.03	0.73±0.07	0.65±0.06	1.27	1.13	0.89
Cyclooctene	0.27±0.06	0.32±0.07	0.35±0.03	0.41±0.04	0.23	0.27	1.18

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*Correction factors (reference 18): cyclohexene 1.00; 1-hexene 0.89; cyclooctene 1.18; converted to cyclohexene = 1.00 from 1-hexene = 1.00.

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The results were rather unexpected. Batch 1A and LK-E showed similar activity despite a difference in location of rhodium within the polymer. Batch 1B showed a much decreased relative rate for 1-hexene and a somewhat increased relative rate for cyclooctene when compared to batches 1A and LK-E. The change in order of relative rates from 1-hexene greater than cyclohexene in the cases of 1A and LK-E to cyclohexene greater than 1-hexene for 1B seemed most significant.

The phosphorous/rhodium mole ratio ($R_{P/Rh}$) on these beads was somewhat lower than that on beads using $RhCl(P\phi_3)_3$ for rhodium equilibration. For comparison, ratios based on elemental analysis were:

LK-E, $R_{P/Rh} = 3.2$; 1A, $R_{P/Rh} = 2.8$; 1B, $R_{P/Rh} = 2.2$.

It has been shown that changing the ratio of phosphorous to rhodium ratio at a given rhodium concentration will change the rate. The absolute rate and magnitude of change is phosphene dependent (28). The relative rate differences between the several batches might be caused by their different ratios of phosphine to rhodium.

In a partial test of this hypothesis, one equivalent of triphenylphosphine was added to beads of batch 1B which had been used for hydrogenations. This should increase the phosphine to rhodium ratio on the beads. Some rhodium was removed from the beads in the process. After thoroughly

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washing the beads free of soluble rhodium, relative rates of hydrogenation for 1-hexene to cyclohexene were measured. Absolute and relative rates for reductions after adding phosphine are presented in Table 5, and depicted as a function of run sequence in Figure 8. Relative rates are taken with the average cyclohexene rate equal to 1.0.

The rate of reduction of 1-hexene falls dramatically as the run sequence progresses, while the rate for cyclohexene remains constant within the reproducibility of the rates. 1-Hexene is initially faster than cyclohexene and falls toward a relative rate in the vicinity of that seen before adding phosphine.

Homogeneous Catalyst Hydrogenations

An investigation of the effect of phosphine ratio on rate, similar to that of Wilkinson and co-workers (28), was undertaken for benzyldiphenylphosphine. Triphenylphosphine was included for comparison.

The rate for 20 ml of a solution, 1.01×10^{-3} M in rhodium, as a function of substrate, phosphine, and phosphine to rhodium ratio, is presented in Table 6. This data is plotted in Figures 9 and 10.

For benzyldiphenylphosphine, cyclohexene and 1-hexene rates are nearly identical above a ratio of 2.25 P/Rh. 1-Hexene shows a lower rate below a P/Rh ratio of 1.75.

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Table 5. Rate versus Run Sequence--Batch 1B After Adding Triphenylphosphine

Run	Substrate	Rate (ml/min)	Relative Rate $\overline{R}_{CHX} = 1.00$
1	cyclohexene	0.517	1.25
2	cyclohexene	0.399	0.97
3	cyclohexene	0.364	0.88
4	cyclohexene	0.389	0.94
5	cyclohexene	0.447	1.08
6	cyclohexene	0.302	0.73
7	1-hexene	0.576	1.40
8	1-hexene	0.506	1.22
9	————	Temperature of reaction out of bounds	
10	cyclohexene	0.421	1.02
11	cyclohexene	0.391	0.95
12	1-hexene	0.392	0.95
13	1-hexene	0.339	0.82
14	cyclohexene	0.443	1.07
15	1-hexene	0.300	0.73
16	cyclohexene	0.424	1.03

$\overline{R}_{CHX} = 0.4127 \pm 0.056$

$\sigma_m = 0.018$

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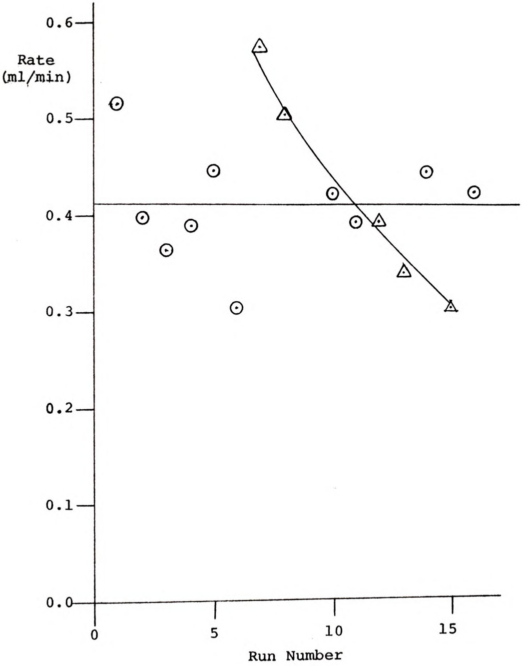

Figure 8. Rate versus run for Batch 1B after adding triphenylphosphene. △ 1-Hexene, ⊙ Cyclohexene.

Table 6. Rates of Hydrogenation for Variation in Phosphine to Rhodium Ratio

Table 6. Rates of Hydrogenation for Variation in Phosphine to Rhodium Ratio

20.0 ml at 1.0×10^{-3} M Rh, 1.0 M alkene, 25.0°C

Phosphine Substrate Ratio P/Rh±0.05	Rate (ml/min)±5.0% Benzyldiphenyl 1-Hexene	Rate (ml/min)±5.0% Benzyldiphenyl Cyclohexene	Rate (ml/min)±5.0% Triphenyl 1-Hexene	Rate (ml/min)±5.0% Triphenyl Cyclohexene	Relative Rate 1-Hexene/cyclohexene $Ø_2RCH_2Ø$	Relative Rate 1-Hexene/cyclohexene $Ø_3P$
1.01				1.02		
1.04	0.85	1.33			0.64	
1.12			1.51			
1.39	1.36	1.95			0.70	
1.73	2.05	2.42			0.85	
1.90	2.60					
2.00			7.94	4.55		1.75
2.08	2.11	2.84			0.74*	
2.25						
2.29	2.22					
2.43	2.10	1.92			1.09	
2.77	1.42					
2.99		1.26				
3.00			6.28	4.22		1.49

*From Figure 9; this ratio seems unrepresentative.

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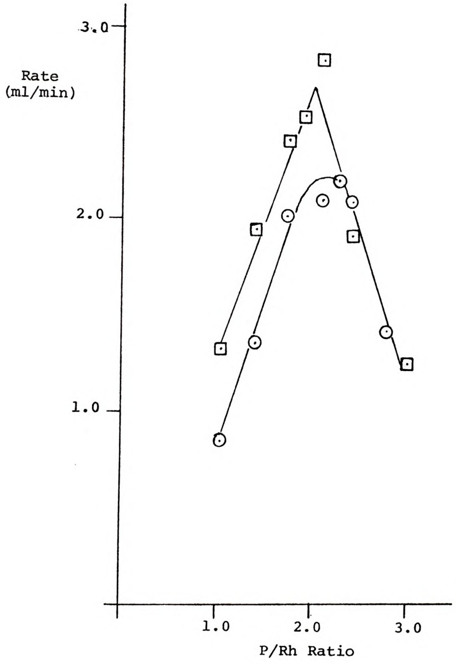

Figure 9. Rate versus phosphine to rhodium ratio for benzyldiphenylphosphine. ⊙ 1-Hexene, ⊡ Cyclohexene.

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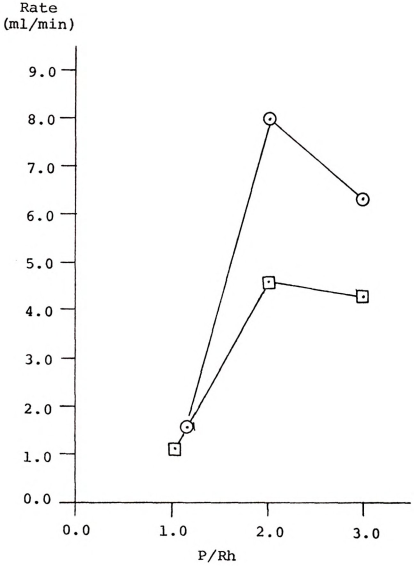

Figure 10. Rate versus phosphine to rhodium ratio for triphenylphosphine. ⊙ 1-Hexene, ⊡ Cyclohexene.

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The qualitative results obtained using triphenylphosphine indicate that 1-hexene is reduced at a rate greater than cyclohexene over a wide range of phosphine to rhodium ratios. Both alkenes show substantially greater rates with triphenylphosphine than with benzyldiphenylphosphine.

There is variation of the relative rates with changing P/Rh ratio. The nature of this variation is dependent upon the phosphine.

Analysis of Results on Benzyldiphenylphosphine Equivalent Beads

Use of deficient rhodium, as $[RhCl(COE)_2]_2$, allows the preparation of beads containing rhodium preferentially located in the outer portions of the bead. Use of an excess of this complex gives a uniform distribution of rhodium similar to use of excess $RhCl(P\emptyset_3)_3$.

The selectivity of bead catalysts prepared from $RhCl(P\emptyset_3)_3$ and a deficiency of $[RhCl(cyclooctene)_2]_2$ is similar, while the selectivity of the bead catalyst prepared from excess $[RhCl(cyclooctene)_2]$ is quite different particularly with respect to the comparison between 1-hexene and cyclohexene. The gross and local P/Rh ratios are different for each of the three methods of preparation.

Any analysis of this system requires some assumptions be made on the nature and number of phosphines associated with each rhodium atom. The P/Rh local ratio, while more indicative than gross analysis of this characteristic, is not

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not necessarily the true number of phosphines associated with each rhodium atom. It does set an upper limit. Steric effects could reduce the availability of some pendant phosphine groups. Chemical reaction of pendant phosphines with chloromethyl groups during preparation of phosphinated polymer has been suggested as another source for loss of available phosphine (2).

Both benzyldiphenylphosphine (beads) and triphenylphosphine are employed in each method of syntheses. The order of addition and quantities of the latter differ substantially between the methods of preparation. While studies have shown that bidentate and tridentate "chelation" of rhodium by bead phosphine occurs (4,7,18), the conditions employed in synthesis from $RhCl(PØ_3)$ produces large quantities of free triphenylphosphine (one $PØ_3$ per bead phosphine used). It does not seem unreasonable that a mixture of bead benzyldiphenylphosphine and unattached triphenylphosphine complexes could exist under these conditions.

In the case of beads prepared from $[RhCl(COE)_2]_2$ the above arguments do not apply. Chelation would seem to be certain if bead phosphines are available. The coordination of rhodium with bead phosphine would seem to be a purely kinetic process. Once a rhodium attaches a phosphine it is limited in mobility to a rather small area of the bead, enough to coordinate with one or possibly two additional phosp

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phosphines. Sufficient equilibrium between two coordinate and three coordinate species may be present in the deficient rhodium beads to allow the majority of species to achieve a three-coordinate state.

For beads made with excess $[RhCl(COE)_2]_2$ the ability to achieve high coordination is not present as all phosphines in the vicinity will be occupied by rhodium. Thus, some rhodium of low phosphine coordination will be present.

In light of the analytical and microprobe results, the relative rates may be rationalized. The reduction of 1-hexene is faster than cyclohexene by beads on which rhodium is primarily three coordinate. When the coordination of rhodium is decreased, to the vicinity of two, the inherent reactivity of the species changes, in particular decreases, toward 1-hexene relative to cyclohexene.

The addition of triphenylphosphine to the beads supports this view, if one assumes some species such as $(\text{bead-benzyldiphenylphosphine})_2RhClP\emptyset_3$ is formed from the two coordinate species. This restores the selectivity to at least that of $RhCl(\text{benzyldiphenylphosphine})_3$. Since the triphenylphosphine is not attached to the beads, as it is labelized by the reaction, it diffuses off of the beads, restoring the catalyst to its inherent reactivity before addition.

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Change in the phosphine to rhodium ratio upon changing the method of synthesis of catalyst provides some explanation for alterations in selectivity. The study of rate as a function of the phosphine to rhodium ratio does not explain the observed relative rate of 1-hexene reduction for beads of batch 1A or batch LK-E. If all phosphine present is polymer bound, and thus equivalent to benzyldiphenylphosphine, the 1-hexene relative rate should be about 1.0, while the observed relative rate is significantly greater.

The observed relative rate for 1-hexene could be the result of steric exclusion by the support being greater for cyclohexene than for 1-hexene. It is also possible that the inherent relative rate of a species containing triphenylphosphine is higher for 1-hexene. The difference in rates and relative rates between benzyldiphenylphosphine species and triphenylphosphine species is so great that even a small number of species containing triphenylphosphine as a ligand could account for this effect. Note also that any triphenylphosphine containing species must be of the low coordination form,

$$(\text{bead-Ch}_2\text{P}\emptyset_2)\text{RhCl}(\text{P}\emptyset_3),$$

since a third phosphine, if $\text{P}\emptyset_3$, will be removed during hydrogenation and difuse away. Where the species is $(\text{bead-CH}_2\text{-P}\emptyset_2)_3\text{RhCl}$ or $(\text{bead-Ch}_2\text{-P}\emptyset_2)_2$, the phosphine will not leave.

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Studies on Triphenylphosphine Equivalent Beads

Bead Hydrogenations

Much of the uncertainty in interpretation of results for the benzyldiphenylphosphine equivalent beads stems from the possibility that more than one type of phosphine is present. It is, of course, impossible to exactly duplicate a bead attached phosphine in solution. It is possible to generate a polymer phosphine-solution phosphine pair that is far more similar than the polymer bound equivalent of benzyldiphenylphosphine-triphenylphosphine pair used.

Two possibilities present themselves--either make the solution phosphine benzyldiphenylphosphine, or make the polymer bound phosphine equivalent to triphenylphosphine.

The latter pair was chosen, partly because of its greater activity and partly because of the lower air sensitivity of triphenylphosphine. The ready availability of the well-characterized triphenylphosphine based homogeneous catalyst was also a consideration.

Beads containing a diphenylphosphide group directly attached to the pendant phenyl group were successfully synthesized as batch 5, giving a close equivalent of triphenylphosphine.

Two batches of beads containing rhodium were made by equilibration with $RhCl(P\emptyset_3)_3$ in benzene.

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Batch 5A contains less than the maximum possible rhodium content. In synthesis of this batch, the solution was almost completely decolorized, changing from dark maroon to a faint yellow. Batch 5B was made in a similar manner except that sufficient $RhCl(P\emptyset_3)_3$ was added to maintain the solution as a dark maroon.

The analytical data for both batches are quite variable. The color, which is of some use in determining the rhodium content, was quite different. In solution, batch 5A was orange, which changed to dark yellow on drying; batch 5B was maroon in solution and became dark orange on drying.

Relative rates of reduction for a number of alkenes were measured in toluene for both batches. These results are presented in Table 7.

The effect of swelling ratio on relative rate was examined for batch 5A using three solvents of different swelling ratio. These results are presented in Table 8.

Alkenes were all 1.0 molar in solvent. They were chosen since they represent the size (molecular volume) range over which the maximum change in relative rate occurred using benzyldiphenylphosphine equivalent beads. A second requirement was that the molecule be relatively rigid, and roughly spherical.

β-pinene showed a constant pattern of increasing rate in time, in contrast to other alkenes, which showed a

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Table 7. Effect of Loading on Relative Rates

Alkene	Relative Rate in Toluene	
	Batch 5A	Batch 5B
Cyclopentene	1.80 (0.15)	1.75 (0.03)
Cyclohexene	1.00 (0.04)	1.00 (0.05)
Cycloheptene	0.97 (0.06)	0.81 (0.05)
1-Hexene	1.26 (0.11)	0.92 (0.04)
Cyclooctene	0.64 (0.05)	0.43 (0.08)
Beta-pinene	0.35 (0.02)	0.08 (0.003)

Table 8. Relative Rates of Reduction in Several Solvents of Different Swelling Ratio for Batch 5A

Alkene	Solvent		
	Benzene SR 3.90	Toluene SR 3.45	Cyclohexene SR 1.95
Cyclopentene	2.10 (0.20	1.80 (0.15)	1.73 (0.38)
Cyclohexene	1.00 (0.07)	1.00 (0.04)	1.00 (0.15)
Norbornene	----	1.31 (0.09)	----
Cycloheptene	0.95 (0.07)	0.97 (0.06)	0.54 (0.08)
1-Hexene	----	1.26 (0.11)	----
Cyclooctene	0.68 (0.04)	0.64 (0.05)	0.105 (0.080)
Camphene	----	0.29 (0.01)	0.038 (0.001)
Beta-pinene	0.14 (0.01)	0.35 (0.02)	0.059 (0.007)

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decrease of rate in time. All rates were extrapolated to the time of introduction of alkene, so this abnormality should have no major effect on the relative rate.

There is some increase in selectivity with increased catalyst loading. The selectivity remains essentially unchanged on going from toluene to benzene. It does change significantly toward higher relative rates for smaller alkenes on going from toluene to cyclohexane.

Determination of Constants Within the Rate Expression for the Homogeneous Catalyst

Halpern's rate expression for hydrogenation of alkenes by $RhCl(P\emptyset_3)_3$ and its various modified forms were used for evaluation of constants, k_6 and K_5, throughout this section.

Consideration of the most general form,

$$(2) \quad -\frac{ds}{dt} = \frac{k_6([L_o] + K_5[S])}{2}\left(-1 + \sqrt{1 + \frac{4K_5[C_o][S]}{([L_o] + K_5[S])^2}}\right)$$

shows that the same constants describe the phosphine, alkene, and catalyst dependence. Thus, determination of constants by observing rate as a function of any one or a combination of these variables should be possible.

The initial attempt to determine both constants was by variation of catalyst concentration at 1.0 M alkene concentration. The rates obtained vary with catalyst concentration in a manner described by equation 3.

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$$(3) \qquad -\frac{ds}{dt} = \frac{k_6K_5[S]}{2} \left(-1 + \sqrt{1 + \frac{4[C_o]}{K_5[S]}}\right) .$$

The results from variation of catalyst concentration for cyclohexene are presented in Table 9, and plotted in Figure 11. The data were fit by KINFIT (29) to equation 3. While the fit was satisfactory, the parameters were so highly coupled that the estimated deviation was almost as large as the parameters.

Observation of rate as a function of alkene concentration was next undertaken. Hydrogen uptake was monitored over the entire course of a run until all of the initial alkene had been used. One option of program SAMV (30) is output of rate versus volume of hydrogen used. Volume of hydrogen may be converted into alkene concentration within program KINFIT and the data from a single run used to obtain estimates of the required constants.

Four runs were made in this manner using catalyst concentrations of 1.0×10^{-3}M and initial alkene concentrations of 0.5 M. Phosphine concentration was varied for each run and ranged from 0.1×10^{-3} M to 0.5×10^{-3} M.

Values of k_6, K_5, and their product k_6K_5 are presented in Table 10. These values are plotted versus phosphine concentration in Figures 12, 13, and 14 respectively. There is a clear variation of parameters concomitant with phosphine concentration, which indicates that the rate

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Table 9. Rate versus Catalyst Concentration for 1.0 M Cyclohexene

$C\times10^4$ (moles/l)		$R\times10^5$ (moles-ℓ^{-1}-sec^{-1})	
Value	σ	Value	σ
10.03	0.091	14.76	0.126
6.32	0.076	11.28	0.036
3.99	0.026	7.61	0.032
3.98	0.023	8.00	0.097
2.51	0.016	5.56	0.026
1.58	0.021	4.23	0.018
1.002	0.013	3.10	0.015
0.500	0.013	1.66	0.008
0.443	0.005	1.22	0.007

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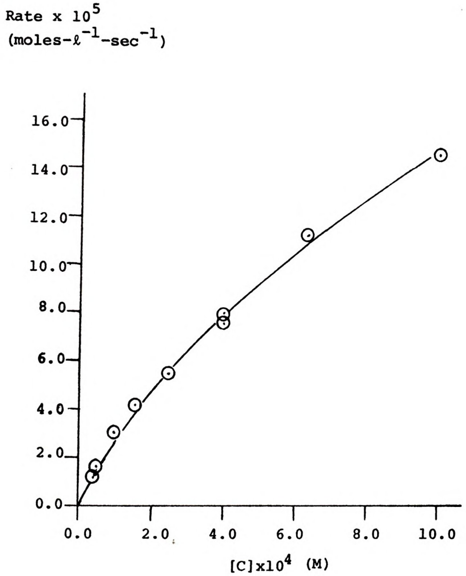

Figure 11. Rate versus $\mathrm{RhCl(PØ_3)_3}$ concentration for 1.0 M cyclohexene.
⊙ experimental, — calculated, $k_6 = 0.303$, $K_5 = 4.72 \times 10^{-4}$.

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Table 10. Observed Values of k_6 and K_5 Obtained from Alkene Dependence of Rate with Small Quantities of Added Triphenylphosphine

$[RhCl(P\phi_3)_3] = 1.00x10^{-3}$ M

$[P\phi_3]x10^{-3}$(M)	k_6(sec^{-1})	K_5x10^5(unitless)	$k_6K_5x10^5$(sec^{-1})
0.1119 (0.0055)	0.879 (0.311)	4.109 (0.737)	3.61 (0.64)
0.2000 (0.010)	0.636 (0.045)	7.497 (0.956)	4.77 (0.27)
0.2927 (0.015)	0.623 (0.057)	8.093 (0.727)	5.04 (0.01)
0.5014 (0.025)	0.367 (0.039)	15.25 (2.03)	5.60 (0.15)

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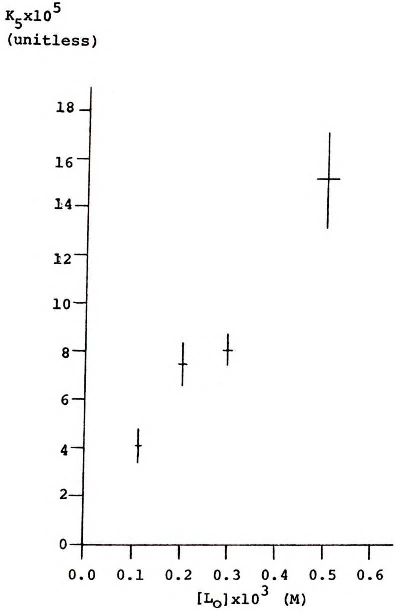

Figure 12. K_5 (observed) vs [L_o] from alkene dependence of rate for cyclohexene.

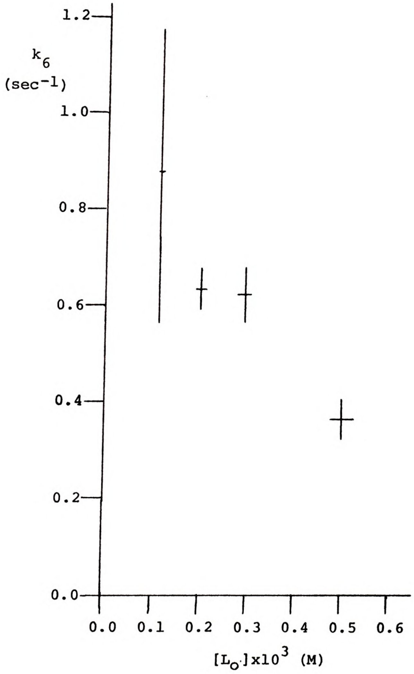

Figure 13. k_6 (observed) vs $[L_o]$ from alkene dependence of rate for cyclohexene.

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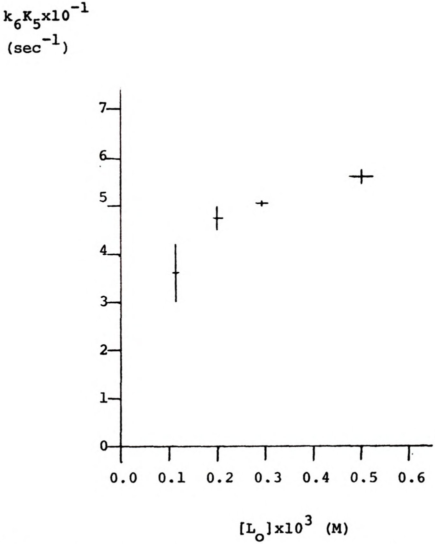

Figure 14. k_6K_5 (observed) versus $[L_o]$ from alkene dependence of rate for cyclohexene.

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expression does not properly describe the alkene dependence for the phosphine concentrations used. The decrease in the value of k_6K_5 with decreasing phosphine concentration indicates dimer formation is removing catalyst from the more active monomer system. This removal of catalyst should be greater at low phosphine concentrations than at high phosphine concentrations since added phosphine reduces dimer formation.

The final method of obtaining the constants of the rate expression was addition of large quantities of triphenylphosphine. Concentrations of triphenylphosphine ranged from 5.0×10^{-3} M to 100.0×10^{-3} M. The nominal catalyst concentration was 1.0×10^{-3} M and alkene concentration was 1.0 M.

The rates were normalized to 1.0 ℓ of solution and inverted by program EVLT (30). These were then entered into KINFIT versus phosphine concentration. The data were fit to the inverse of equation 1.

$$\frac{1}{R} = \left(\frac{1}{A\,[C]\,[S]}\right)[L] + \frac{1}{k_6\,[C]} \qquad (4)$$

$$(A = k_6K_5)$$

Inclusion of catalyst and alkene concentrations, as calculated by EVLT, gave a slightly smaller error. While nominally 1.0×10^{-3} M and 1.0 M respectively, there were slight variations.

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The inverse rate versus phosphine concentration data for cyclohexene are presented in Table 11 and plotted in Figure 15.

Values of A and k_6 for other alkenes obtained in this manner are given in Table 12. Having the values of A, the original rate versus catalyst concentration experiments become useful. With the product $k_6K_5 = A$, either k_6 or K_5 can be obtained independently. k_6 was obtained using equation 3 in KINFIT as

$$R = \frac{A}{2}\left(-1 + \sqrt{1 + \frac{4k_6[C_o]}{A}}\right) .$$

K_5 was then calculated from A and k_6. Values obtained in this manner are given in Table 13.

Analysis of Results for Triphenylphosphine Beads

An analysis of relative rates obtained on the supported catalyst is undertaken to answer two questions. First, how does the inherent reactivity of the active site within the supported catalyst compare with the reactivity of the homogeneous catalyst? Second, are factors other than inherent reactivity of the active site required to explain the observed relative rates?

Two assumptions are made throughout the analysis; triphenylphosphine and the supported phosphine are sufficiently similar to produce catalysts which would have similar

Tab

Table 11. Inverse Rate Versus Phosphine Concentration Data for Cyclohexene

1.00×10^{-3} M $\mathrm{RhCl(P}\phi_3\mathrm{)_3}$

1.00 M Cyclohexene

$[L] \times 10^3$ (M)		$1/R \times 10^{-4}$ (sec-ℓ-mole^{-1})	
4.016	(0.055)	9.780	(0.484)
5.056	(0.126)	8.276	(0.221)
10.00	(0.14)	21.11	(0.79)
21.08	(0.17)	34.72	(1.67)
49.91	(0.17)	76.33	(5.41)
59.01	(0.12)	95.67	(3.16)
69.12	(0.15)	120.4	(4.4)
78.61	(0.16)	133.7	(1.7)
87.75	(0.16)	149.5	(6.8)
97.62	(0.18)	173.2	(7.4)

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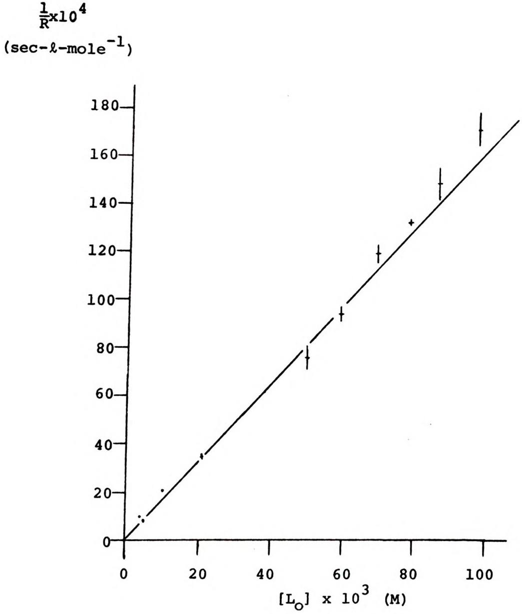

Figure 15. Inverse rate versus [L_o] for 1.0 x 10^{-3} M $RhCl(P\emptyset_3)_3$ and 1.0 M cyclohexene.

Tab

Table 12. $k_6 x K_5$ Values. From the Dependence of Rate on Triphenylphosphine

$$\frac{1}{R} = \frac{[L_o]}{k_6 K_5 [C_o][S]} + \frac{1}{k_6 [C_o]}$$

Alkene	$k_6 K_5 x 10^6$ (sec^{-1})	k_6 (sec^{-1})
Cyclopentene	93.25 (1.47)	1.57 (3.63)
Cyclohexene	61.40 (2.24)	0.110 (0.043)
Cycloheptene	63.37 (4.42	-0.42 (1.98)
Cyclooctene	30.44 (2.96)	0.130 (0.189)
Norbornene	80.77 (7.96)	-0.0055 (0.0012)
Camphene	8.82 (0.48)	0.056 (0.172)
1-Hexene	94.47 (7.22)	0.118 (0.420)

Tab

Table 13. k_6 and K_5 Values

Alkene	k_6(sec^{-1})	K_5x10^4(unitless)
Cyclopentene	0.555 (0.101)	1.68 (0.30)
Cyclohexene	0.209 (0.017)	2.94 (0.26)
Cycloheptene	0.365 (0.012)	1.74 (0.13)
Cyclooctene	0.463 (0.021)	0.657 (0.070)
Norbornene	0.361 (0.017)	2.24 (0.24)
Camphene	0.108 (0.0090)	0.817 (0.081)
1-Hexene	0.839 (0.054)	1.13 (0.11)

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activity under similar conditions, and the concentration of hydrogen within the supported catalyst is sufficiently close to the concentration in solution to have no effect on catalyst activity. The former assumption seems justified since the supported phosphine is aryl-diphenyl substituted while the latter is reasonable since the hydrogen molecule, being much smaller than the alkenes employed, is less subject to steric constraint and has a greater rate of diffusion than any alkenes used. In addition, the catalyst is almost zero order in hydrogen concentration at one atmosphere pressure.

These assumptions lead to the relative rates of alkene reduction being a function of alkene and phosphine concentration at each active site integrated over the fraction of active sites available to each alkene. The inherent reactivity of the active site is dependent on both phosphine and alkene concentration. It is useful to define a reactivity based upon phosphine concentration alone at an alkene concentration of one molar, since the concentration of alkene at the active site is, through the diffusion constant, related to the size of the alkene, as is the fraction of active sites available to the alkene. The phosphine concentration at the active site is assumed to be independent of alkene size.

Absolute rates for homogeneous solution hydrogenations with 1.0 M alkene concentration can be calculated from equ

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equation 1 for a given phosphine and catalyst concentration. Dividing the rate of the compared alkene by the rate of the standard (cyclohexene) gives a relative rate dependent only on phosphine concentration. The expression for calculating homogeneous solution relative rates is:

$$RR = \frac{k_6' \; K_5'}{[L] + K_5'} \; / \; \frac{k_6 K_5}{[L] + K_5}$$

where RR is the relative rate, [L] is phosphine concentration, primed constants are for the compared alkene and unprimed are for the standard.

The comparison between the supported catalyst and the homogeneous solution catalyst is made through a corrected relative rate (CRR):

$$CRR = RRB/RR,$$

where RRB is the relative rate obtained with the supported catalyst.

If the homogeneous solution relative rates are obtained for conditions adequately describing the supported catalyst active site conditions and if all alkenes have equal accessibility to all active sites, then all corrected relative rates should be 1.0 within the associated error.

Obviously there are an infinite number of possible phosphine concentrations with corresponding homogeneous solution relative rates and corrected relative rates.

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In the face of this number of possibilities the two limiting cases of very high and very low phosphine concentration present themselves. These limits are approximated when [L] is either much greater or much less than K_5[S] in equation 1 for all alkenes considered. In either limit, the relative rate becomes independent of phosphine concentration. In that they are limits, the true phosphine concentration must lie at or between these limits and likewise the homogeneous solution relative rates. The corrected relative rates for these limits must then bracket 1.0 if phosphine concentration is the only factor affecting the selectivity of the supported catalyst. If both limiting corrected relative rates are less than (or greater than) 1.0 for a given alkene the relative rate on the supported catalyst cannot be accounted for based on phosphine concentration alone.

Equilibration studies have suggested that the polymer supported phosphine has substantial mobility (8,18). Assuming a polymer density of 1.0 and 0.86% phosphorous (the lowest analysis), a uniform distribution of pendant phosphine groups would give a phosphine concentration of 0.28 M within the polymer. Even an order of magnitude less effective phosphine would give relative rates closely approximating the limit of high phosphine concentration. Equilibration studies show phosphine mobility on a rather long time scale (hours to weeks) which may not be significent to the hydrogenation reaction. Since the reactions

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were conducted well below the glass transition temperature of polystyrene (about 100°C) (40), substantial short term immobility of the pendant phosphine groups is possible, leading to a low effective phosphine concentration.

Relative rates of reduction for homogeneous catalyst solutions at 1.0 M alkene concentration and the limiting phosphine concentrations are presented in Table 14. The low phosphine concentration limiting relative rates are designated RRI and the high phosphine concentration limiting relative rates are designated RRII. The corresponding corrected relative rates are CRRI and CRRII respectively, and are presented in Table 15 for batch 5A and Table 16 for batch 5B.

The observed relative rates for batch 5A are consistent with the inherent reactivity of the active site being the primary factor determining relative rates. All corrected relative rates (plus or minus two standard deviations) bracket 1.0 for this batch. Effects due to molecular size are obscured due to uncertainty in the absolute reactivity of the active site. Neither the high or low phosphine concentration limits describe the activity of the active site leading to the requirement for a small, significant phosphine concentration to be present at the active site. It should be emphasized that this is a kinetically required phosphine concentration at an average active site and does

Table 14. Relative Rates of Reduction for Homogeneous Solutions of $RhCl(P\emptyset_3)_3$ in Toluene

Alkene	Relative Rate (Cyclohexene - 1.0)	
	Infinite dilution RRI	High Phosphene RRII
Cyclopentene	2.65 (0.53)	1.52 (0.06)
Cyclohexene	1.000 (0.081)	1.000 (0.036)
Cycloheptene	1.75 (0.15)	1.03 (0.08)
Cyclooctene	2.21 (0.21)	0.496 (0.051)
Norbornene	1.72 (0.16)	1.32 (0.13)
Camphene	0.517 (0.060)	0.143 (0.009)
1-Hexene	4.01 (0.42)	1.54 (0.13)

See Batch 5A (Deficient Rh)

Table 15. Corrected Relative Rates for Batch 5A (Deficient Rh)

Alkene	Molar Volume of Pure Alkene (ml/mole)	Observed Relative Rate[a]	Low Phosphine[a] Correction Factor[b]	Low Phosphine[a] Corrected Relative Rate	High Phosphine[a] Correction Factor[b]	High Phosphine[a] Corrected Relative Rate
Cyclopentene	88.25	1.80 (0.15)	2.65 (0.53)	0.68 (0.15)	1.52 (0.06)	1.18 (0.11)
Cyclohexene	94.76	1.00 (0.05)	1.00 (0.08)	1.00 (0.09)	1.00 (0.04)	1.00 (0.05)
Norbornene	109.6	1.31 (0.09)	1.72 (0.16)	0.762 (0.088)	1.32 (0.13)	0.99 (0.12)
Cycloheptene	116.9	0.97 (0.06)	1.75 (0.15)	0.55 (0.06)	1.03 (0.08)	0.94 (0.08)
1-Hexene	125.0	1.26 (0.11)	4.01 (0.42)	0.31 (0.04)	1.54 (0.13)	0.82 (0.10)
Cyclooctene	130.1	0.64 (0.05)	2.21 (0.21)	0.29 (0.04)	0.496 (0.051)	1.39 (0.17)
Camphene	161.2	0.29 (0.01)	0.517 (0.060)	0.56 (0.07)	0.143 (0.009)	2.02 (0.14)

[a] All relative rates are based on cyclohexene = 1.00.

[b] The correction factor is the relative rate for homogeneous $RhClL_3$ in Table 14, thus CRR = ORR/CF; CRR = corrected relative rate, ORR = observed relative rate, CF = correction factor.

Rhodium)

Table 16. Corrected Relative Rates for Batch 5B (Saturated Rhodium)

Alkene	Molar Volume of Pure Alkene (ml/mole)	Observed Relative Rate[a]	Low Phosphine		High Phosphine[a]	
			Correction Factor[b]	Corrected Relative Rate	Correction Factor[b]	Corrected Relative Rate
Cyclopentene	88.25	1.75 (0.03)	2.65 (0.53)	0.66 (0.13)	1.52 (0.06)	1.15 (0.05)
Cyclohexene	94.76	1.00 (0.05)	1.00 (0.09)	1.00 (0.09)	1.00 (0.04)	1.00 (0.06)
Cycloheptene	116.9	0.81 (0.05)	1.75 (0.15)	0.46 (0.05)	1.03 (0.08)	0.79 (0.08)
1-Hexene	125.0	0.93 (0.04)	4.01 (0.42)	0.23 (0.03)	1.54 (0.13)	0.60 (0.06)
Cyclooctene	130.1	0.43 (0.08)	2.21 (0.21)	0.19 (0.04)	0.496 (0.051)	0.87 (0.18)

[a] All relative rates are based on cyclohexene = 1.00.

[b] The correction factor is the relative rate for homogeneous $RhClL_3$ in Table 14, thus CRR = ORR/CF; CRR = corrected relative rate, ORR = observed relative rate, CF = correction factor.

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not represent the phosphine concentration available to an active site over a long period of time, nor does it represent the phosphine concentration at any particular active site. Limits may be set on this effective phosphine concentration. Assuming deviations from limiting relative rates would be detected only if the effective phosphine concentration is greater than ten times the largest K_5 or less than one-tenth of the smallest K_5, the effective phosphine concentration lies within the range of 6.6×10^{-6} M and 2.9×10^{-3} M. The upper limit of this range is clearly much less than the calculated minimum concentration on the polymer which indicates substantial immobility of pendant phosphine groups on the time scale of the reaction.

In contrast to batch 5A, the relative rates of the more heavily leaded batch 5B cannot be due to phosphine concentration at the active site. The corrected relative rates are less than 1.0 when taken at either limit for all alkenes larger than cyclohexene. There is some decrease in relative rate associated with increasing molecular size. A more dramatic indication of the alkene size dependence of the relative rate is obtained from comparison of relative rates between the two batches of catalyst. The ratio of relative rates obtained with batch 5B to those of batch 5A is given in Table 17. A plot of the ratio versus molecular volume of the alkene is presented in Figure 16.

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Table 17. The Ratio of Relative Rates of Alkene Reduction for Batch 5B Compared to Batch 5A

Alkene	Molar Volume (ml/mole)	Relative Rate Ratio Batch 5B/Batch 5A
Cyclopentene	88.25	0.972 (0.083)
Cyclopentene	94.76	1.00 (0.071)
Cycloheptene	116.9	0.835 (0.073)
1-Hexene	125.0	0.738 (0.072)
Cyclooctene	130.1	0.672 (0.135)

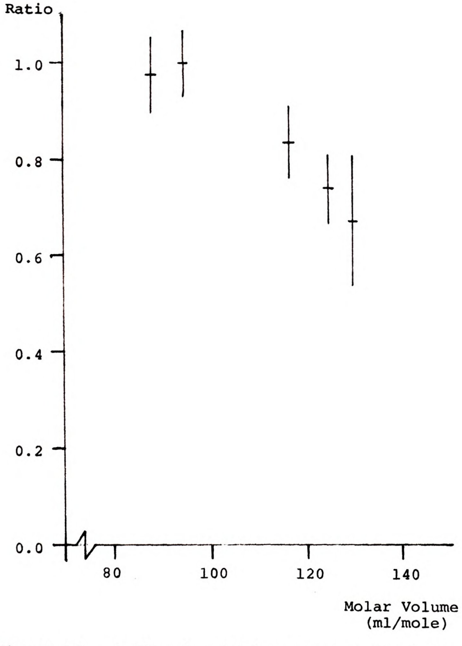

Figure 16. Ratio of relative rates of Batch 5B to Batch 5A versus molar volume of the alkene.

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Two factors could produce the observed alkene size dependence; diffusion of the alkene to the active site and steric exclusion of alkenes above a certain critical size from a given active site. Diffusion serves to reduce the concentration of alkene within the polymer below that of the external solution (31). The concentration of alkene at a point within the polymer is inversely proportional to the molar volume and rate of use. Precise calculation of rate and derivatively, relative rates, in a variable order system is quite complex (31). An alteration of selectivity upon an increase in loading is indicative of diffusion influence upon the rate. The possibility of steric exclusion of the alkene from the active site is also present. A recent study has demonstrated a substantial increase in steroselectivity of a similarly supported catalyst compared to the homogeneous catalyst in a system where diffusional effects were not possible (41).

Qualitatively, diffusion reduces the concentration of the alkene while steric exclusion reduces the concentration of catalyst available to an alkene. These two alternatives cannot be unambiguously distinguished within the limits of the present study since both serve to lower the relative rate of reduction with increasing molecular volume. The change in selectivity with change in loading indicates that at least some of the selectivity of batch 5B is due to diffusio

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diffusion of the alkenes to the active site at rates which are an inverse function of the molecular volume.

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III. CONCLUSIONS

1. The supported catalyst shows selectivity substantially different from the homogeneous analogue. Some portion of the observed selectivity is due to the inherent reactivity of the tested alkenes in the presence of catalyst with added triphenylphosphine. Superimposed upon this is a selectivity based on molecular volume. The increase in selectivity with increased loading suggests that at least some portion of the size selectivity is caused by restricted diffusion of alkenes to the catalytic site.

2. Given solvents of equal polarity, there is an increase in selectivity in going to a solvent of lower swelling ratio.

3. The bead supported catalyst prepared from an excess of $[RhCl(COE)_2]_2$ shows a different selectivity than that prepared from an excess of $RhCl(P\emptyset_3)_3$. This change in selectivity is due primarily to the inherent reactivity of the catalytic site at different phosphene concentrations.

4. The electron microprobe is a useful instrument for determining the location of elements within the polymer bead. The heat generated by electron beam contact with the

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material being analyzed may alter its composition under some circumstances.

5. When lithiated polymer (i.e., polymer on which some of the pendant phenyl groups have lithium substituted for hydrogen and are equivalent to phenyl lithium) reacts with an electrophile, addition of the electrophile should continue until the polymer ceases to be red or brown. The color change indicates completion of reaction.

Suggestions for Further Work

1. $RhCl(P\emptyset_3)$ should be supported on 20% macrorecticular polymer. This should produce a very active catalyst not subject to major diffusion effects and phosphine inhibition.

2. Further studies of selectivity should include molecules much larger than the ones used here. Preferably, all molecules should have very similar reactivity at all phosphine concentrations.

Two types of compounds might fit the latter requirement. Straight chain 1-alkenes are reasonably available to long lengths; allyl ethers of straight chain alcohols, or other alcohols, are fairly easily prepared from the readily available alcohols.

3. A catalyst is needed which is not dependent on its ligand environment. Its kinetics should be well-defined in homogeneous solution. The catalyst should preferably be

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first order in alkene concentration, or zero order over a large concentration range.

With such a system it might be possible to separate diffusional effects, which lower the effective alkene concentration, and steric effects, which lower effective catalyst concentration.

4. The microprobe work should be continued. The results indicate that x-ray fluorescence might also be a satisfactory method of gross analysis under somewhat milder conditions than the microprobe.

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IV. EXPERIMENTAL

General

Analytical

All NMR spectra were run on a Varian T-60 spectrometer. All gas chromatographs were taken on a Varian Aerograph Model 90-P using 1/4 inch columns. Melting points were taken using a Thomas-Hoover capillary melting point apparatus and are not corrected.

Microanalyses were performed by Galbraith Laboratories, Inc. Microprobe spectra were obtained on an American Research Laboratories EMX-SM Microprobe.

Materials

All solvents were reagent grade. These were obtained from various major manufacturers through the Michigan State University chemistry department. They were used as received without any attempt to remove organic impurities.

All aprotic solvents used for inert atmosphere work or hydrogenations were distilled from sodium or potassium benzophenone ketyl under a nitrogen atmosphere. Kontes solvent stills were employed. Solvents were stored for up to two days in type 2 flasks on some occasions, with no noticeable effect on reactions. Use immediately after distillation was preferred, but not always possible.

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Protic solvents used for inert atmosphere work were purged with nitrogen, introduced through a gas dispersion tube placed near the bottom of the container, for at least 15 minutes.

All alkenes were of at least 95% purity. Except for cyclohexene, these were purchased from Chemical Samples Company or Aldrich Chemical Company. Cyclohexene was obtained from Matheson, Coleman & Bell or J. T. Baker Chemical Company.

Except for beta-pinene, all alkenes were distilled from sodium or potassium under nitrogen. Potassium was invariably used for alkenes boiling below 80°C. Beta-pinene was found to be unstable to this procedure. It was stirred over activated aluminia for at least one hour, filtered through a fritted funnel, and distilled under nitrogen.

All liquid alkenes were distilled immediately prior to use. Solutions of solid alkenes, made from distilled material, were freeze thaw degassed prior to use.

All gases were obtained from Air Reduction Corporation through Michigan State University Stores. Argon and pre-purified nitrogen were used as received. Hydrogen (analysis stated as 99.95%) was passed through two 40 mm by 0.9 m columns of BASF-BTS catalyst heated to 140°C. Between the two catalyst tubes and after the final tube, it was passed

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through a similar tube of 4A molecular sieves at room temperature. Final purification was by either of two methods. Altech "oxytrap" tubes were placed in the line. These proved quite efficient and convenient, but their low flow rate at low pressure presented some problems. Gas washes containing sodiumbenzophenone-ketyl in toluene proved quite satisfactory.

Rhodiumtrichloridetrihydrate ($RhCl_3 \cdot 3H_2O$) was obtained from Engelhard Industries Incorporated and used as received. n-Butyl lithium was purchased from Alpha Inorganics. Triphenylphosphine was obtained from Pressure Chemical Company and was recrystallized twice from 95% ethanol prior to use. The twice recrystallized phosphine was stored under an inert atmosphere or recrystallized a third time immediately prior to use. Chlorodiphenylphosphine (technical) was obtained from Aldrich Chemical Company. It was distilled under vacuum (0.5 torr) and stored under nitrogen in a type 2 flask.

Polystyrene beads were obtained gratis from Dow Chemical Company.

Any other chemicals were reagent grade obtained from major manufacturers by the Michigan State University chemistry department.

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Special Equipment

Several special flasks were used for various purposes. For brevity these are described here and referred to by name where they are used. They are modified round bottom flasks.

Type 1 Flask. The type 1 flask is a $ 24/40 single neck round bottom flask. A standard taper 2 mm stopcock is attached at an angle of about 45° to the neck.

Type 2 Flask. This flask is identical to a type 1 flask except that an additional stopcock is attached opposite the first.

A type 2 flask, when sealed with a glass stopper, is as reliable for inert atmosphere work as a Schlenk tube. Large volumes of liquid may be stirred with greater efficiency.

Type 3 Flask (Bead Hydrogenation Reaction Vessel). This is a type 1 flask fitted with a 40 mm extra coarse frit attached to the side opposite the 2 mm stopcock. The frit is covered on the outside by a bubble to which a 2 mm stopcock is attached.

Reaction Flask Connector. This device consists of a 24/40 male and 24/40 female ground-glass joint connected to either end of a 4 mm stopcock. It is used to attach a type 1 or type 3 flask to the hydrogenation apparatus. On completion of the reaction, the stopcock is closed and the reaction

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reaction flask with adaptor removed, leaving the beads under a nondestructive atmosphere.

Preparations

Tristriphenylphosphinechlororhodium(I)

$RhCl(P\emptyset_3)_3$ was prepared by the method of Wilkinson and co-workers (10,32). The work-up differed slightly in that it was accomplished under nitrogen.

A 1 liter 3-neck round bottom flask was fitted with a condenser topped by a nitrogen inlet system with bubbler, two glass stoppers, a magnetic stirring system and heating mantle. Two and eight-tenths g $RhCl_3 \cdot 3H_2O$ (0.0106 mole) was placed into the flask which was then thoroughly purged with nitrogen.

Seventy ml of oxygen free ethanol was placed into the round bottom flask. This was stirred until the $RhCl_3 \cdot 3H_2O$ dissolved.

One hundred and twenty g of triphenylphosphine was dissolved in 350 ml of warmed (about 50^oC) oxygen free ethanol. This was poured into the round bottom flask containing $RhCl \cdot 3H_2O$ in ethanol.

The round bottom flask was closed except for the nitrogen inlet system atop the condenser, and the mixture was stirred at reflux for at least three hours.

Upon cooling to room temperature, the mixture was filtered through a frit under nitrogen. The solid was washed wi

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washed with three 100 ml portions of oxygen-free ethanol and two 100 ml portions of ethyl ether.

The solid was dried under vacuum (0.1 torr or less) for 6 hours. Caution: vacuum must be applied slowly or rapid evaporation of ether will cause some of the product to be drawn into the vacuum system.

Yield: 6.84 g (70% based on $RhCl_3 \cdot 3H_2O$) of maroon microcrystalline solid.

This preparation was repeated several times on various scales up to 5.0 g of initial $RhCl_3 \cdot 3H_2O$.

Benzyldiphenylphosphine

Benzyldiphenylphosphine was prepared by a method similar to the direct method of Tamborski and co-workers (33). All operations were performed under a nitrogen atmosphere using oxygen-free solvents.

Three and one-half g of clipped lithium ribbon (0.507 mole) was placed into a 500 ml type 2 flask equipped with a magnetic stirrer and under a nitrogen atmosphere. An addition funnel was attached to the flask and purged with nitrogen. One hundred ml of tetrahydrofuran was placed in the flask, and 80 ml of THF was added to the funnel with 34.0 ml (0.188 mole) of chlorodiphenylphosphine.

The phosphine solution was added to the stirred lithium/THF mixture dropwise over a two hour period. An ice bath was periodically used to keep the reaction temperature below about 50°C.

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The reaction mixture was stirred for four hours after completion of the addition. Stirring then ceased and the solids allowed to settle.

The liquid was transferred to a second 500 ml type 2 flask by syringe.

The solid remaining in the first flask was washed with two 50 ml portions of THF which were then added to the second flask. The second flask was fitted with an addition funnel, into which 80 ml THF and 270 ml (0.235 mole) benzylchloride was placed. This solution was added to the stirred contents of the flask over a two hour period. Near the end of the addition, the contents of the flask were observed closely. Addition ceased when only a faint red color remained. The mixture was stirred for 30 minutes. One hundred ml of saturated aqueous ammonium chloride was added; the resulting mixture was stirred for 12 hours.

Most of the organic layer was transferred, by syringe, to a 500 ml type 2 flask containing about 50 g of anhydrous calcium chloride. The aqueous layer was washed with two 75 ml portions of benzene and this was added to the THF solution. The organic portion was stirred two hours with the calcium chloride.

The dried solution was transferred in portions to a 500 ml type 1 flask set up as the pot of a vacuum distillation apparatus. The solvent was removed by distillation

under nitrogen. As solvent was removed, more of the solution was added and distillation continued. Much foaming was noted during distillation. The calcium chloride was washed twice with 50 ml portions of benzene, which were added to the pot. When 100 to 150 ml remained, vacuum was applied and continued until bubbling ceased in the pot (pot temperature about 50°C). The system was filled with nitrogen and the pot removed. The residue in the pot was recrystallized from warm absolute isopropanol in four portions.

Yield: 28.3 g (first crop of crystals) of a white solid. M.P. 72-73.5°C (sealed evacuated tube).

H'NMR: (resonances from internal TMS in CCl_4) δ3.37 (2H), δ7.07 (5H), δ7.25 (10H). The signals at δ7.07 and δ7.25 are broad and not well separated.

IR: A thin film was prepared by melting the compound between two NaCl plates on a hotplate inside of a glovebox. This showed no evidence of P = O stretch by comparison with a sample similarly prepared which had been exposed to air in THF.

Biscyclooctenerhodium(I) Chloride Dimer $[RhCl(cyclooctene)_2]_2$ or $[RhCl(COE)_2]_2$

This preparation is similar to that of Porri and coworkers (34). All operations were performed under a nitrogen atmosphere using oxygen-free solvents.

Two and one-tenth grams of $RhCl_3 \cdot 3H_2O$ and 50 ml of absolute ethanol were placed into a Schlenk tube. Six ml of cyclooctene, freshly distilled from sodium under nitrogen, was added. The solution was stirred for four days. The resulting precipitate was filtered from the solution on a frit, washed twice with ethanol, and dried under vacuum for six hours.

Yield: 1.12 g of a yellow solid (42.4% yield).

Preparation of Beads

Batch 1 (Benzyldiphenylphosphine equivalent beads)

Chloromethylation

The method used was that of Pepper, Paisley and Young (35). Two hundred seventy ml of chloromethylethylether was placed in an Erlenmeyer flask which was placed in an ice bath. The contents were stirred until cool (about 5°C) and 2.7 ml (4.0 g, 0.024 mole) of stanic chloride was added. Stirring continued for 5 minutes.

This solution was added to 30.7 g of polystyrene beads (2% corsslinked with divinylbenzene, 30-80 mesh, 0.284 mole as styrene) in a 500 ml round bottom flask. A drying tube containing calcium chloride was placed onto the flask and the mixture stirred at room temperature for five hours.

The beads were removed from the solution by vacuum filtration on a sintered glass fritted funnel and washed twice, while in the funnel, with 1:1 dioxane:water.

They were transferred to an Erlenmeyer flask and stirred for five minutes with a 1:1 mixture of 10% hydrochloric acid and dioxane. Upon filtration, they were washed twice with dioxane, transferred to a flask and stirred with dioxane for five minutes, filtered, and washed twice more with dioxane. The beads were dried under vacuum for one day.

Phosphination

This procedure is similar to the method of Grubbs and Kroll (4,18), based on the method of Tamboriski et al. (33).

All operations were performed under nitrogen with solvents prepared as previously described.

Four and two-tenths g (0.61 mole) of clipped lithium ribbon was placed into a 400 ml Schlenk tube and 200 ml of tetrahydrofuran added by syringe. An addition funnel was attached and 100 ml of THF was mixed with 24 ml (0.133 mole) chlorodiphenylphosphine therein. This solution was added to the stirred lithium-THF mixture over a period of 20 minutes. The reaction mixture rapidly turned dark red during the addition. On completion of addition, the Schlenk tube was sealed and the mixture stirred for 24 hours.

Twelve g of chloromethylated beads were placed into a 500 ml type 1 flask, a magnetic stirring bar was added and a condenser attached. Three hundred ml of the red solution in the Schlenk tube was transferred to the flask using a 50 ml syringe, and a 18 gauge needle. The stirred mixture

of beads and lithiodiphenylphosphine in THF was refluxed for 24 hours. Upon cooling, 100 ml of an oxygen-free aqueous ammonium chloride solution, made from 150 ml saturated ammonium chloride solution and 20 ml water, was added. The mixture was stirred three hours. Liquid was removed by forcing it out under nitrogen pressure through a gas dispersion tube inserted through a rubber stopper. A rubber tube leading to a flask was attached to the dispersion tube. The beads were then washed with 150 ml portions of the following solvents or solvent mixtures: 1:1, water:THF, twice; 1:1 10% aqueous Hcl:THF; 3:7 water:THF; THF; 7:3 THF:benzene; 1:1, THF:benzene; 3:7 THF:benzene; benzene, twice. Solvent removal was by the method described above. The beads were dried under vacuum (0.1 torr or less) for 24 hours at room temperature. They were stored under nitrogen until used.

Batch 1A

All operations were under nitrogen. All solvent transfers were by syringe. Seven and ninety-four hundredth g of phosphinated beads (Batch 1) were weighed into a Schlenk tube, 0.531 g of $[RhCl(COE)_2]_2 (1.483x10^{-3}$ eq Rh) was added, a stirring bar inserted, and the vessel was evacuated and filled with nitrogen; 150 ml of benzene added, the vessel sealed, and the mixture stirred for 24 hours. The liquid was removed and the beads were washed with two 50 ml

portions of benzene, then stirred with a 100 ml portion for 24 hours.

As this solvent was quite clear at the end of 24 hours, 0.5296 g of triphenylphosphine ($2.0x10^{-3}$ mole) was added; the solution slowly became a light maroon. The beads were stirred in this solution for 24 hours, then repeatedly washed with 100 ml portions of benzene until the last wash remained clear for 24 hours. They were then dried under vacuum (0.1 torr or less) for 24 hours at room temperature.

Batch 1B

All operations were under argon and all solvent transfers by syringe. Two and one-tenth g of beads (Batch 1) were weighed into a Schlenk tube and 0.532 g ($1.48x10^{-3}$ eq Rh) was added. The vessel was evacuated and filled with argon, 50 ml of benzene added, the vessel sealed and the mixture stirred for 5 days. This solution was removed and the beads washed once with 100 ml of benzene; 0.320 g of $[RhCl(COE)_2]_2$($0.892x10^{-3}$ eq Rh) was dissolved in benzene in a separate Schlenk tube. This solution was transferred to the vessel containing the beads; the vessel sealed and the beads stirred with this for two days. The beads were washed repeatedly until no color remained in the solution. They were then dried under vacuum for 24 hours. Argon was introduced and 0.5075 g of triphenylphosphine ($1.94x10^{-3}$ mole) in 60 ml of benzene was added, the vessel was sealed,

and the contents were stirred for 24 hours. The beads were repeatedly washed with benzene until a wash remained clear for 24 hours; then dried under vacuum for 24 hours and stored under argon.

<u>Batch 2</u>

All operations were conducted under nitrogen to exclude atmospheric moisture. Forty and two-tenth g of beads (30-80 mesh, 2% crosslinked with divinylbenzene, 0.372 mole as styrene) were weighed into a type 1 flask. The flask was then purged with nitrogen; 200 ml reagent nitromethane from a freshly opened bottle was added followed by 5.4 g of anhydrous ferric chloride. Nineteen ml (0.074 mole) of a 10% V/V solution of bromine in nitromethane was added over a half hour period. The flask was then closed, covered with aluminum foil, and the contents were stirred for 24 hours under nitrogen.

The solution was removed from the beads and they were washed consecutively with nitromethane, saturated sodium bisulfite in nitromethane, and nitromethane. They were transferred to a Soxhlet extractor and washed with nitromethane for 48 hours. Upon removal, they were dried under vacuum for 24 hours.

Yield: 38.8 g of yellow-brown beads.

Analysis: C, 89.13%; H, 7.48%, Br, 2.72%

3.8% substitution.

Batch 3

Fifty-eight and one-half g of beads (28-32 mesh, 0.563 mole) were placed in a 1000 ml, 3-neck, round bottom lask. The system was evacuated and filled with nitrogen, an atmosphere of which was thereafter maintained during the course of the reaction; 300 ml of nitromethane from a freshly opened bottle was added; 3.8 g of borontrifluoride gas (0.056 mole) was bubbled into the liquid and 2.8 ml of bromine (8.79 g, 0.055 mole) in 100 ml of nitromethane was added over a one-half hour period. The flask was sealed, covered with aluminum foil, and the mixture stirred for 36 hours at room temperature. The liquid was removed. Use of a nitrogen atmosphere ceased at this point.

The beads were washed consecutively with dichloromethane:methanol mixtures in proportions 1:0, 9:1, 3:2, 2:3, 1:9, 0.1. Then methanol:water washes in proportions 3:1, 3:2, 2:3, 0:1, were performed followed by water:tetrahydrofuran, 2:1, 1:2, 0:1. They were then washed with dichloromethane:THF in proportions 1:2, 2:1, 1:0. All washes were done in the reaction flask, the liquid being removed from the beads after each wash using an aspirator attached to a gas dispersion tube frit as a filter.

Batch 4

This batch was intended as a test for the use of nitrobenzene as a solvent. During work with the two preceding

batches, nitromethane was found to be a poor swelling solvent for the beads. Nitrobenzene, while not excellent, is about the same as ethyl ether, and much better than nitromethane. Five g of beads (32-35 mesh, 425-500 μ, 0.0459 moles as styrene) were placed in a 250 ml single type 1 flask. The flask was evacuated and filled with nitrogen, an atmosphere of which was maintained throughout the course of the reaction.

Solutions of borontrifluoride and bromine were prepared; 3.3 g of BF_3(0.0487 mole) was bubbled into 100 ml of nitrobenzene giving a solution 0.487 m, BF_3; 1.00 ml Br_2 (3.12 g, 0.0195 mole) was added to and mixed with 100 ml nitrobenzene, giving a solution 0.193 M in Br_2. Ten ml of the BF_3 solution (0.00487 mole BF_3) and 25 ml of the Br_2 solution (0.00483 mole Br_2) were added to the flask containing the beads. The flask was closed, covered with aluminum foil and stirred, 1.00 ml aliquots of solution were taken periodically and analyzed for total bromine content. The aliquot was placed in an Erlenmeyer flask, excess Br_2 converted to Br^- with aqueous Na_2SO_3, and Br^- determined by the Volhard procedure. After four days no further significant change in bromide concentration was noted. The beads were then subjected to the following work-up in air.

The reaction solution was removed and the beads washed twice with nitrobenzene, thence consecutively with nitrobenzene:THF mixtures in proportions 4:1, 2:1, 1:1, 1:2, 1:4,

1:0, and 1:0. They were washed with THF:water mixtures in proportions 10:1, 1:1, 1:0, and 1:0, and thereafter dried under vacuum at 70°C for 24 hours.

Analysis: Br 3.83%, 3.87%

5.18% substitution.

Batch 5

Bromination

Forty and six-tenths g of beads (32-35 dry mesh, 425-500 μ, 0.390 mole as styrene) were placed into a 2-liter 3-neck round bottom flask. The flask was evacuated and filled with nitrogen. Nine hundred ml of nitrobenzene (dried for 2 days over 4A molecular sieves) was added to the flask and 5.2 g (0.077 mole) BF_3 was bubbled in. With the contents stirring vigorously, 3.9 ml (0.068 mole) Br_2 was added. The flask was placed in an ice bath and the mixture stirred fifteen minutes, then it was removed and stirring proceeded at room temperature. The flask was covered with aluminum foil. Stirring continued for 60 hours. The solution was removed and the beads washed three times with nitrobenzene, then with THF:nitrobenzene mixtures in proportions 1:10, 1:3, 1:1, 3:1, 10:1, 1:0, and 1:0. The beads were stirred with 1:10, water:THF for one hour. The THF:water wash was repeated five times. On the last wash no Br^- was detected by addition of a silver nitrate solution to the filtrate. The beads were then washed twice

with THF and dried at 120°C for 24 hours.

Analysis: 8.10% Br

11.5% substitution.

Phosphination

This entire procedure was conducted under nitrogen using solvents prepared for inert atmosphere work as described previously. Thirty-eight and one-tenth g of brominated beads were placed in a 500 ml type 2 flask. The flask was stoppered, evacuated, and filled with nitrogen. Two hundred ml of benzene was added followed by 60 ml of 2.4 M butyl lithium in hexene. The flask was closed and the mixture stirred for three days under nitrogen. The solution was removed from the beads (gas dispersion tube method), and 50 ml of 2.4 M n-butyl lithium in hexane with 50 ml of benzene was added--this was stirred for two days. The solution was removed and the beads washed two times with 150 ml portions of benzene, stirring each time for one hour. The beads were then dried under vacuum until they were free-flowing. Thirteen ml chlorodiphenylphosphine (0.0721 mole) in 100 ml THF was added. The reaction mixture became quite warm and turned red. Two hundred ml additional THF was added and the mixture was stirred one hour at room temperature. It was then refluxed for 24 hours. The solution was cooled and removed from the beads. They were washed five times with THF. The beads retained some reddish

brown color after the THF washes--although they were much lighter than after removing the initial reaction solution. They were washed with a 2:1:1 mixture of THF, water, and saturated aqueous NH_4Cl which quickly removed the color.

The beads were washed twice with 1:1 THF:water, stirring each wash for 15 minutes, followed by a 1:1 THF:water wash which was stirred for three hours. They were then washed with 3:7 water:THF (15 min stirring) and pure THF (1 hour stirring). The beads were washed twice with ethyl ether for three hours; after removing this the beads were vacuum dried at room temperature for 18 hours.

Batch 5A

Twelve and one-hundredths g of phosphenated beads (batch 5) were weighed into a 500 ml type 2 flask; 0.4709 of $RhCl(P\emptyset_3)_3$ was placed therein. The vessel was evacuated and filled with argon, three hundred ml of benzene was added and the mixture stirred for 24 hours. At that point, most of the color was gone from the solution and the beads were light red. The beads were washed repeatedly until the wash remained colorless for 24 hours. They were then dried under vacuum (0.01 torr or less) for 24 hours and stored under argon.

Batch 5B

Eleven and thirty-five hundredths g of phosphenated beads were placed in a 500 ml type 2 flask; 0.80 g

(3.0×10^{-3} mole) of triphenylphosphine was added. The flask was evacuated and filled with argon. Three hundred ml of benzene was added.

One and ninety-five hundredths g of $RhCl(P\phi_3)_3$ (2.11×10^{-3} moles) was added in approximately 0.2 g increments at two day intervals. After completion of addition, the beads were stirred for two weeks. The beads were then washed repeatedly with benzene until the last wash remained colorless for 24 hours. They were dried under vacuum (0.05 torr) for 24 hours at room temperature, then stored under argon.

Densities

One to three g of beads were weighed into a 10.0 ml volumetric flask. Solvent was added from a burette until about 1 ml remained to full. The flask was stoppered and the burette volume noted. The beads sat with solvent 1 hour. Then solvent was again added until it came to the mark. The sum of the two additions is the volume of solvent required (Vr). The difference of this from 10.0 ml is the volume occupied by the beads. Density (D) then becomes

$$D = w/(10.0-Vr),$$

where w is the weight of the beads. All measurements were at ambient temperature (25°C±1°C).

For benzene it was necessary to use weights near 1.0 g since more would completely fill the flask after swelling

in the solvent. The lower swelling ratio in ethanol allowed more beads to be used.

Swelling Ratios

About 2 ml of beads were placed in a 10 ml graduated cylinder and the volume recorded. The cylinder was filled with solvent and the volume of beads was noted periodically (about every hour). The final volume was recorded when no further increase in bead volume was noted over a six hour period. The swelling ratio as used here is:

$$SR = V(\text{final})/V(\text{initial}).$$

Microprobe Analysis

Preparation of Beads Sectioning in a Matrix

Polymerization of Beads into Epoxy

Microscope slides were washed consecutively in ethanolic potassium hydroxide, nitric acid, and distilled water, then dried. Two slides were taped into a V mold using cellophane tape. The ends of the V mold were closed with cellophane tape. A few beads were placed in the bottom of the V and epoxy resin (Buehler, AB EPO-mix) was placed on top of them. The beads were mixed into the epoxy using a nichrome wire. This hardened for 24 hours at room temperature. The polymer was removed from the glass by briefly placing the mold in liquid nitrogen.

Polymerization of Beads into Styrene

Three hundred ml of styrene was washed four times with 100 ml of 10% sodium hydroxide and twice with distilled water. It was then dried first over calcium chloride and then over 4A molecular sieves.

The dry styrene was distilled under vacuum from a pot held at room temperature into a receiver cooled in dry ice-acetone. That portion of the styrene not used immediately was stored under nitrogen in a refrigerator at -10°C. Drying and distillation were repeated prior to each subsequent use.

A 12 inch long 6 mm diameter glass tube was sealed on one end and cleaned with ethanolic potassium hydroxide followed by nitric acid and distilled water. It was then dried.

A 1% W/V solution of either benzoylperoxide or azobisisobutyrlnitrile in the distilled styrene was made.

A small quantity of rhodium containing beads were placed into the tube with about 1 ml of the styrene-initiator mixture. The contents were then subjected to three cycles of freeze-thaw degassing and the tube was sealed under vacuum. The tube was placed in an oven at 60°C for three days. Use of an oil bath at 60°C was tried. Under the condition of a vacuum in the sealed tube, the styrene will reflux since the top part is cooler than the bottom.

In all cases, some evidence of removal of rhodium from the beads was noted as a light red area around the maroon bead. This was more obvious when using benzoylperoxide.

$RhCl(P\varnothing_3)_3$ was polymerized into styrene at about 0.002 g/ml using AlBN as initiator. This was carried out exactly like bead polymerizations.

Sectioning

An epoxy triangle, containing beads, was placed in a microtome. Sections were cut at 10 microns thickness. Only a few sections of many cut were sufficiently intact to be of any use.

These sections were examined under a binocular microscope. The largest diameter bead sections were identified and the sections containing these were mounted. Only by taking the largest diameter bead sections can the possibility of obtaining sections cut from near the edge be eliminated.

Sections were usually mounted on graphite disks. In a few instances quartz plates were used. The purpose of mounting is to keep the sections from moving during further preparation and evacuation of the sample chamber. It amounts to gluing the section to the plate. Three substances were used as glue:

1. Alphacyanoacrylate cement.
2. Graphite electron tube coating.

3. Adhesive from "Scotch" rubberized adhesive masking tape.

The rubber adhesive was found to be the best of the three. There were no problems of having glue get on top of the section, which occurred with the other two. After mounting, the disks (or plates) were coated with graphite from an arc, and placed in the microprobe.

The Half-bead Method

Beads were placed on the stage of a low power binocular microscope. They were held in place with small tweezers and cut in half with a razor blade, then attached to a graphite disk using alphacyanoacrylate cement. The bead and disk were coated with carbon from an arc and inserted into the microprobe.

While this method seems relatively crude, it has the advantage of being fast, and the beads are subject to no chemical influence, save atmospheric oxygen, during sample preparation.

Determination of Elemental Radial Distribution

A selected bead was identified in the microprobe microscope. Using the secondary electron emission scan at fast scan rate, the bead was aligned so that the X axis of the microprobe corresponded to a bead diameter. The X-ray detector was set to obtain a maximum reading on the required wavelength for the desired element.

Beads were scanned by moving the stage at constant speed in the X direction. The electron beam location remains fixed. This was deemed preferable to electron beam scan since the beads are usually of larger diameter than the maximum scan width at lowest magnification. Scans were started and ended about 50 microns from the bead edge. X-ray intensity (counts/sec) was plotted on an X-Y recorder or stripchart recorder driven at constant speed.

Attempted Determination of the Phosphorous to Rhodium Ratio

This technique consists of comparing the relative count rate per element (P/Rh) on beads and a known ratio compound.

Tristriphenylphosphinechlororhodium(I) [$RhCl(P\emptyset_3)_3$], P:Rh = 3:1, was chosen as the standard since it should be quite similar to the species on the bead. This was not successful since $RhCl(P\emptyset_3)_3$ decomposed to a yellow compound of unknown composition under the electron beam. A small quantity of $RhCl(P\emptyset_3)_3$ was polymerized into styrene in the hope that a thin section might provide better heat transfer than the bulk material. No physical evidence of decomposition was seen; however, the results obtained are in gross conflict with the analytical data. Batch 5A used bulk $RhCl(P\emptyset_3)_3$ while 1A, 1B and 5B were analyzed using the polymer trapped $RhCl(P\emptyset_3)_3$ as the standard.

The plate containing the sample and the one containing the standard were simultaneously placed in the instrument. Total counts were recorded from three twenty second periods at each point. Rhodium and phosphorous were each observed simultaneously, using two different X-ray detectors. All samples were run at 15 KEV.

Three points were observed on the standard. Three widely separated points were observed on each of three beads. Background counts were taken on both the standard plate and bead plate. Each point (background, standard, bead) was reduced to a count rate (counts/sec) with associated standard deviation of the mean (cm). Background was subtracted from each point. The phosphorous count rate was divided by the rhodium count rate giving a P/Rh count rate ratio and associated σm for each point. The standard P/Rh count rate was divided by 3 (3 P per Rh in the standard) giving a count rate per atom ratio (R).

R was divided into the count rate ratio for each point on each bead giving the local P/Rh ratio at each point.

The data obtained must be regarded as invalid since there is evidence that the standard decomposed. It does demonstrate that this is a viable technique if a suitable standard can be obtained.

Hydrogenation Procedure

General

All hydrogenations used hydrogen purified in one of the manners described in Materials--Gases.

Hydrogenation rates were monitored using either gas burette measurement of hydrogen volume versus time as measured by a timer reading to 0.01 minute, or by use of the automatic hydrogenation apparatus, SAM (fully described in Appendix I).

Batch 1A and 1B rates were measured by the gas burette method. Rate versus rhodium to phosphine ratio and Batch 5A in toluene data was obtained using SAM in the stripchart output mode using a Sargent-Welsh recorder operating at 1 inch/minute. All other reactions were monitored by SAM using the digital time output mode, with 1 sec being the time unit. In all cases the reaction was set up using the atmospheric hydrogenation apparatus. SAM was used only for the data collection phase of the reaction.

Temperature was maintained by placing the reaction vessel in a water bath maintained in equilibrium with water circulating from a thermostated water bath. All reactions were run at 25°C±0.2°C.

With one exception, all hydrogenations were conducted at a nominal 1.0 M alkene concentration, as calculated assuming the volumes of alkene and solvent are additive.

Given a certain desired total volume of solution, the quantity of alkene required is calculated from its molar volume. Molecular weights and densities used in this calculation were taken from the Handbook of Chemistry and Physics (36), with the exception of norbornene which was taken from Reagents for Organic Synthesis (37). The quantity of solvent was taken as the difference of total volume required and volume of alkene required. Solid alkenes differed slightly. A 2.00 M solution in solvent was made after distillation into a tared flask. This solution was used in a manner identical to liquid alkenes. Prior to each use the alkene solution was subjected to three cycles of freeze thaw degassing followed by introduction of argon into the flask.

Bead Hydrogenations

From 0.5 to 3.0 g of beads were weighed into a type 3 flask or a type 1 flask. A stirring bar was inserted and a reaction vessel adaptor attached using two Kontes "Kem Klamps". This total apparatus is referred to as the reaction vessel.

The reaction vessel was attached to the hydrogenation apparatus. The apparatus was evacuated to about 0.1 torr and filled with hydrogen three times. The stopcock on the reaction vessel adaptor was opened and the reaction vessel evacuated and filled with hydrogen three times.

Sufficient solvent was then introduced so that upon adding the required amounts of alkene, a 1.0 M solution in alkene would produce a total volume of 30.0 ml. All transfers of solvent and alkene were by syringe. The solvent and beads were stirred under hydrogen for 1 hour at 25°C±0.2°C. The required amount of alkene was introduced, and data collection started.

At the end of the reaction the stopcock on the reaction vessel adaptor was closed and the reaction vessel transferred to a vacuum-argon line. The connection to the vacuum-argon line was evacuated and filled with argon three times. Then the stopcock on the reacton vessel adaptor was opened allowing argon to enter the reaction vessel and work-up proceeded. Work-up consisted of removing the reaction solvent and washing the beads three times for 15 minutes each with fresh solvent.

When a type 3 reaction vessel was used, solvent was removed through the frit. For a type 1 reaction vessel solvent was removed using a syringe with a flat tiped 18 gauge needle. This needle was held against the edge of the flask in order to prevent beads from being drawn into the syringe as solvent was removed. For a type 3 flask, it was necessary to apply fresh stopcock grease to the drain stopcock after each work-up. Both input and drain stopcocks were regreased after every three runs. Any removal of the

stopcock was accompanied by a high rate of argon flow to maintain an inert atmosphere over the beads.

After removal of excess solvent and such maintenance as was necessary, the reaction vessel was attached to the hydrogenation apparatus, and set up for another run.

A notable problem in this procedure is that beads are never fully dried between runs. The reasons are twofold. First, complete drying requires 24 hours under a vacuum of 0.1 torr at room temperature, although a close approximation is obtained after six hours. Second, and most important, the apparatus is not completely air tight under vacuum for extended periods. Any attempt to repeatedly dry beads after runs caused substantial loss of activity of the standard alkene over a relatively few runs. The presence of solvent may account for the relatively large deviations of rates observed, since the solvent remaining causes some error in the concentration of alkene. Volumes of total solution much larger than the bead volume were used to minimize the error. The practical problems of solvent transfer and alkene cost somewhat limit how large a total volume of solution one can use. Another possible solution is to use very small quantities of beads, on the order of 0.1 to 0.5 g. The latter procedure presents problems also since this will reduce the rate and make the system relatively more oxygen sensitive.

Alkenes were run alternately with cyclohexene--the standard. Each relative rate is from a comparison of at least two runs of the alkene with the standard.

Each time a new charge of beads was used, at least 10 runs with standard were made with no comparisons, which allowed absolute rates of the standard to stabilize about an average. There was initially a change in rate of the standard with each run.

Hydrogenations Using Homogeneous Tristriphenylphosphinechlororhodium(I)

The purpose of these experiments was to obtain constants within Halpern's rate expression. The experimental procedure used in all is quite similar. Three types of experiments were used: variation of rate versus catalyst concentration, variation of rate with phosphine concentration, and variation of rate with alkene concentration.

For all reactions, a quantity of $RhCl(P\phi_3)_3$ was weighed into a type 1 flask. Solid triphenylphosphine was also added if required and a stirring bar inserted. A reaction flask adaptor was attached and the flask placed on the hydrogenation apparatus. The system, flask and apparatus, was evacuated and filled with hydrogen three times. Toluene, and triphenylphosphine solution if needed, were added in required amounts and the system closed. The solution was stirred for at least 30 minutes in the water bath at

25.0°C±0.2°C. The required quantity of alkene was then injected and data collection begun. On completion of the reaction the contents of the flask were disposed of.

For rate versus catalyst concentration, catalyst was weighed into the flask. The quantity of solvent and alkene were calculated to give the desired concentration of catalyst and a 1.0 M concentration of alkene.

For rate versus phosphine concentration, catalyst was weighed into the flask. The volumes of toluene and alkene were calculated to give a catalyst concentration of 1.0×10^{-3} M and alkene concentration of 1.0 M. The quantity of triphenylphosphine needed to give the desired concentration was made and a quantity near this was weighed into the flask. Since actual concentration is later calculated, this need not be exactly the desired weight.

For both of these methods, data was collected to 20 points or 30 minutes run time, whichever was greater.

Four runs were made where variation of rate with alkene concentration was observed. For these a quantity of catalyst was weighed into a type 1 flask and this was set up on the hydrogenation apparatus. Since very low concentrations of triphenylphosphine were used, a solution at 10.0×10^{-3} M in toluene was made in a manner analogous to that used for solid alkenes. The required amounts of toluene, triphenylphosphine, and alkene were calculated to

give 1.0×10^{-3} M catalyst, 0.5 M alkene, and the desired concentration or triphenylphosphine.

Two ml and 10 ml burettes equipped with luer joints and needles, and operating under nitrogen were used for all liquid transfers and measurements.

Comparison of Rates for Phosphorous to Rhodium Ratios Less than Three

A 4.02×10^{-3} equivalent/l solution of $[RhCl(COE)_2]_2$ in toluene was made under argon, as was a solution of 6.97×10^{-3} M benzyldiphenylphosphine and 8.07×10^{-3} M triphenylphosphine.

A 250 ml type 1 flask, equipped with a magnetic stirring bar and reaction flask connector was attached to the hydrogenation apparatus.

The system was evacuated and filled with hydrogen three times. The required amount of toluene and phosphine solution was injected, followed by 5.0 ml of rhodium solution. The system was evacuated until the solution just boiled and then refilled with hydrogen. The solution was stirred at 25°C$\pm$0.2°C for 30 minutes. The required amount of alkene was injected and data collection started. At least 20 points were acquired for each run.

Evaluation of Data

Initially all data was obtained as volume of hydrogen used versus time. In the case of runs which were monitored by the gas burette, this is the form in which the data was

recorded. For runs made using time at which the apparatus added an additional known volume of hydrogen to the system, time of the event was recorded. In the former case, volume of hydrogen used versus time was entered directly into program KINFIT (29). Initial rates were obtained by fitting the equation:

$$V = Rt + At^2 + B.$$

The initial rate is R. The additional parameters allow deviation of rate in time and deviation of the initial volume from zero.

For runs using SAM, the output times were converted to volume versus time data using program SAMV (30) or one of several earlier versions which accomplished the same transformation. The calculated volume versus time data were then entered into KINFIT in the same manner as gas burette data. The one exception to this was four runs of rate versus alkene concentration which were evaluated under a different option of SAMV and will be treated separately.

Calculation of Relative Rates

The absolute rate for a given alkene run was divided by the absolute rate for the two standard runs immediately preceding **and** following the run. This gives a total of four comparisons for each hydrogenation, which reduces the effect of the variance in standard absolute rates. Where only one standard was run after the given alkene, only

three comparisons were made. The average of these comparisons and the standard deviation of their mean are reported.

The standard deviation of the mean for the first 8 runs after the breakin is reported for the standard. If more than one set of beads were used, the average standard deviation is reported.

Homogeneous Catalysis Data

The absolute rates are reported for runs where the phosphine to rhodium ratio was varied below 3:1.

For those runs where data was used to evaluate constants within the rate expression, an average rate was obtained from KINFIT for the first 20 points of volume versus time data for each run using the equation

$$V = Rt + A.$$

The initial and average rates were then entered into program EVLT (30), along with the weight of catalyst, volume of solvent, volume of alkene, a concentration of alkene used, weight of phosphine, molecular density of phosphine, and associated estimated errors.

EVLT then averaged the initial and average rate, took a standard deviation, normalized these to 1.0 l of solution, and calculated concentrations of catalyst, alkene, and phosphine. Associated errors were carried through in these calculations.

The required data was entered into KINFIT and the constants obtained.

For runs where phosphine concentration was varied the data were fit to the equation:

$$R = \frac{[L]}{A\ [C]\ [S]} + \frac{1}{k_6 [C]} ,$$

where [L] is phosphine concentration, [C] is catalyst concentration, and [S] is alkene concentration. R is the rate in moles/sec. A is the product k_6K_5. A and k_6 were the parameters adjusted.

Using A as a constant, the rate versus catalyst concentration data were fit to,

$$R = 0.5\ A(-1 + \sqrt{1 + 4\ k_6 [C]/A[S]}\ ) .$$

k_6 is the only adjusted parameter. Errors reported are standard deviations obtained from KINFIT. K_5 was calculated from A and k_6 since $K_5 = A/k_6$.

The special case of four runs where alkene concentration was treated as a variable is now considered.

Output from SAM is in time. Each time represents the time required to use a certain volume of hydrogen. The volume used between any two times is known and constant. Thus the time interval is a measure of rate by

$$R = V/(t_2 - t_1).$$

The volume of hydrogen used since the beginning of the run is also known. Thus the rate as a function of volume of hydrogen used is available. In practice, the mole equivalent of volume was used (n).

This form of output from SAMV was entered into KINFIT. The concentration of catalyst, concentration of phosphine, and total volume of solution (VT) were entered as constants. A set of equations were used which converted moles used to concentration and then entered this into the rate expression for fitting, as follows:

$$[S] = [S_I] - n/VT$$

$$R = \frac{VT \cdot k_6 \cdot ([L] + K_5[S])}{2} \left(-1 + \sqrt{1 + \frac{4K_5[S][C]}{([L] + K_5[S])^2}}\right).$$

It is necessary to multiply the entire expression by total volume, in liters, in order to normalize rates to 1 ℓ. k_6 and K_5 are adjusted parameters.

All computer programs were executed using the CDC 6500 computer at Michigan State University. Much of the intermediate resulting data was stored as card images on permanent file. This was particularly true for output from SAMV, where almost all output was stored in this manner. This data was then entered directly into KINFIT.

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APPENDICES

APPENDIX I

SAM--An Automated Hydrogenation Apparatus

APPENDIX I

SAM--An Automated Hydrogenation Apparatus

The automated hydrogenation apparatus, SAM, had its ultimate origin in an automated oxygen absorbtion instrument described by Krueger (38). This design was modified to give an apparatus which measures volume independent of the reaction system volume, and can be safely operated in a potentially explosive atmosphere. Other changes allow the volume unit to be easily altered and provide simple maintenance.

The basic apparatus consists of the gas control and measurement section and the electronic control section. A diagram of the gas control and measurement section is given in Figure 17, while a schematic diagram of the electronic control section is given in Figure 18. This latter section was designed by the electronic shop personnel of the Michigan State University chemistry department.

The gas control and measurement section is basically a U-tube manometer. The operating electrodes (I) detect when the mercury within the manometer reaches certain limits. When the mercury breaks contact with the longer operating electrode, solenoid C closes, isolating SAM from

Figure 17. SAM--Gas control and measurement section.

Gas Control Section

A - Hydrogen exit to reaction
B - Metal balljoint, $ 18/9, female.
C - Solenoid valve, normally open, Skinner B2DA1200.
D - Solder T.
E - Solenoid valve, normally closed, Skinner B2DA1062.
F - Metering valve, Hoke 1315G4B
G - Hydrogen inlet.

All tubing is 1/4" soft copper. "Swage-lok" connections are used except for metal balljoints (B,V) and the T (D) which are soldered.

Volume Measurement Section

H - Lead wires to operating electrodes terminated by alligator clips.
I - Operating electrodes, 1 mm tungsten rod sealed into glass tubing which is sealed into a $ 14/20 "clearseal" male joint.
J - $ 14/20 "clearseal" female joint.
K - $ 4 mm stopcock.
L - Outlet to gas ballast.
M - Gas burette, 15 mm I.D. tubing.
N - Base electrode and lead.
O - Constriction, about 1 mm opening.
P - Mercury drain.
Q - Stopcock $ 4 mm.
R - 6 mm I.D. tubing.
S - Mercury.
T - 250 ml pressure bulb.
U - Stopcock $ 4 mm.
V - Balljoint, glass § 18/9 female and balljoint, metal § 18/9 male.
W - Mounting panel.

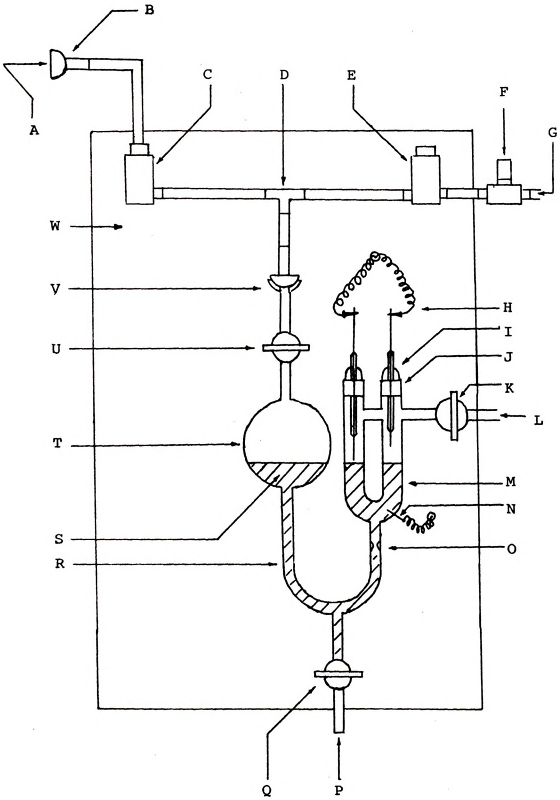

Figure 17

Figure 18. SAM--electronic control section.

Terminals	
A1	Top (full) electrode
A2	Bottom electrode
A3	Middle (empty) electrode
B1	Recorder
B2	Recorder
L1	Time logger
L2	Time logger
SOL	Solenoid valves

Voltages	
V1	5.0V, filtered
V2	10.0V, unfiltered
V3	110V AC

Transistors	
Q1	2N5459
Q2	2N3638
Q3	2N3393
Q4	2N5459
Q5	2N3638
Q6	2N3393
Q7	2N2222
Q8	2N2222

Resistors	
R1	100K
R2	464K
R3	162K
R4	5.1K
R5	10
R6	825
R7	100K
R8	464
R9	162K
R10	5.6K
R11	121
R12	42
R13	5K, 10W
R14	1K
R15	8.2K
R16	1K

Others	
T1	Triac, RCA 40526
S1	SCR
I1	1:1 pulse transformer

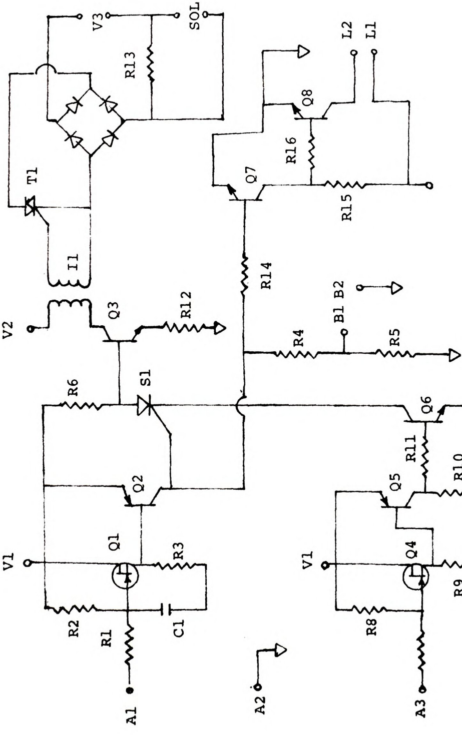
V3
SOL
R13
L2
L1
T1
I1
Q8
R16
Q7
R15
R14
V2
Q3
R12
B1 B2
R4
R5
R6
S1
Q6
Q2
R11
Q5
R10
V1
Q1
R3
R2
R1
C1
V1
Q4
R9
R8
A1
A2
A3

Figure 18

the reaction system, and solenoid E opens. Hydrogen enters forcing the mercury up the gas burette until it contacts the shorter electrode, which causes solenoid E to close and solenoid C to open. This returns the volume of hydrogen within SAM to the reaction system where it is used until contact is again broken with the longer electrode. The electronic control gives different output voltage during the fill cycle and operating cycle. The voltage change at the start of the fill cycle is used to record time. This gives a record of times required for the use of each quantity of hydrogen.

The usual manner of time measurement is from the start of the reaction. Taking the first fill cycle as the start of volume measurement gives

$$V_t = n\overline{V} + V_o$$

where V_t is total volume used at time t, n is the number of fill cycles after the first, $\overline{V}$ is the volume introduced at each fill cycle, and V_o is the volume used prior to the first fill cycle.

The quantity actually measured is a pressure-volume (PV) product, which, like volume at constant pressure, is a measure of the quantity of hydrogen introduced. The fact that pressure change is the quantity detected has some impact on operation. When SAM is isolated during the fill cycle, the initial and final volumes and pressures are

constant and independent of the rest of the system. On completion of the fill cycle, the volume within SAM becomes part of the total volume of the reaction system and the pressure is lower than for SAM alone. The larger the reaction system, the closer its full pressure will approach its refill pressure. This does not affect the accuracy and precision of the volume introduced, but it does affect the precision with which the refill point is measured. Thus the total volume of the reaction system is kept as small as possible.

SAM is designed to be attached to an atmospheric hydrogenation apparatus. This was accomplished through a glass T with a stopcock on each arm of the T. One arm leads to the reaction, one to the atmospheric apparatus and one to SAM. The reaction is set-up with SAM isolated. Then the atmospheric apparatus is isolated and data collected using SAM.

The gas control and measurement section is mounted on a plywood panel with the apparatus supported on wood blocks extending from the panel. Glass portions are held on the blocks by small lengths of 1/4" vacuum tubing, split lengthwise, and securely clamped to the smaller glass tubing. The mounting system is not shown in Figure 16.

For normal operation, a length of vacuum tubing leading to a closed flask is attached at L. This serves as a gas ballast, maintaining a constant pressure with fluctuations in atmospheric pressure. It also keeps mercury vapor

isolated and prevents dirt from entering the apparatus. Stopcock K is closed when electrodes are removed, which maintains pressure within the gas ballast.

The operating electrodes may be removed and cleaned, then reinserted without changing the volume. The volume may be changed easily by using electrodes of different length.

Stopcock Q allows mercury to be easily removed when cleaning the apparatus. Stopcock U is open for operation. When closed, the upper portion of the apparatus may be evacuated. The pressure bulb must be purged by cycling the apparatus for two hours while allowing hydrogen to escape through a bubbler.

Metering valve F is set to provide a low flow rate which will allow equilibrium pressure to be maintained between the pressure bulb and gas burette. Constriction O prevents oscillation of the mercury from side to side.

Standardization is the process of determining the operating volume of the instrument. Two methods have been used. Standardization by rate comparison involves alternately measuring rates by SAM and the atmospheric apparatus for a single hydrogenation run. Rates for Sam are taken as volume units ($\bar{V}$) per second while rates for the atmospheric apparatus are taken as ml/sec. A total of four to eight rates are taken using the atmospheric apparatus and compared

to those obtained on SAM immediately prior to and following the atmospheric rate. Volume is calculated by

$$\bar{V} = R\ (\text{atmospheric})/R(\text{SAM}).$$

$\bar{V}$ is then obtained as ml/volume unit. The average and standard deviation of these measured volume units is then taken.

In the second method, a quantity of alkene is measured into the reaction flask by burette. The total number of volume units, including those extrapolated from V_o back to t_o, is obtained for the entire reaction. Since the total quantity (moles) of alkene is known and the total number of volume units is known, a value for the volume unit is obtained. Several volume unit values obtained in this manner are averaged and the standard deviation is taken.

Time was originally recorded using a stripchart recorder driven at 1 inch/min. When the electronic control output voltage changes, the recorder pen moves, giving a record of the time at which the fill cycle starts.

A digital time logger was later constructed by the Michigan State University Analytical Consulting Service. This instrument utilizes a digital clock with a time base derived from 60 cycle line current. On receiving the output voltage change at the start of the fill cycle, current time is latched. This is converted to serial ASCII and output on

an ASR teletype in a manner analogous to that described by Larsen (39). Output is in a format of 6 digits, the least significant being 1 sec, followed by a space. After ten points a carriage return, line feed and space are output. The output is simultaneously punched on paper tape which can be converted to punched cards for computer input.

APPENDIX II

Unpublished Computer Programs Used

SAMV

```
      PROGRAM SAMV(INPUT,OUTPUT,TAPE62,TAPE60=INPUT,TAPE61=OUTPUT)
      DIMENSION T(800),VT(800),V(800),VV(800),R(800),VR(800),TB(800),
     1  VTB(800),VB(800),VVB(800),IN(7)
C    ******************************************************************
C       THIS PROGRAM TAKES OUTPUT TIMES FROM SAM AND CONVERTS THESE INTO VOLUME
C       VERSUS TIME DATA SUITABLE FOR INPUT INTO KINFIT. DERIVATIVE FORMS OF RATE
C       VERSUS TIME OR VOLUME MAY ALSO BE OBTAINED.
C       T= TIME, V = VOLUME, R = RATE, TB = AVERAGE TIME, VB = AVERAGE VOLUME
C       PRIMARY VARIABLE NAMES PREFIXED WITH A V ARE VARIANCES OF THAT VARIABLE
C    ******************************************************************
C       THIS PROGRAM IS WRITTEN FOR THE CDC 6500, FORTRAN EXTENDED VERSION 3.0.
C       CERTAIN STATEMENT FORMS ARE NOT UNIVERSALLY COMPATABLE.
C       * IS A FORMAT HOLLERITH FEILD DELIMITER. $ IS A STATEMENT DELIMITER.
C    ******************************************************************
      WRITE(61,200)
  200 FORMAT(1H1)
C    ******************************************************************
C       THIS CARD IS READ ONCE PER RUN.
C       IDO = ,0 - V VS T OUTPUT, 1 - R VS T OUTPUT, 2 R VS V OUTPUT
C       IPON= ,0 - DO NOT WRITE TAPE 62,  1 - WRITE TAPE 62
C    ******************************************************************
      READ(60,100)IDO,IPON
      IPON=IPON+1
  100 FORMAT(2I5)
C    ******************************************************************
C       THIS IS A TITLE CARD FOR THE DATA SET. THIS IS ALSO ENTRY FOR THE
C       PROGRAM LOOP.
C    ******************************************************************
    1 READ(60,101)(IN(J),J=1,7)
  101 FORMAT(7A10)
C    ******************************************************************
C       CHECK FOR END OF FILE
C    ******************************************************************
      IF(EOF(60))999,2
    2 CONTINUE
```

```
C     //////////      SAMV CONTINUED      ////////////////////////////////////////
C    ***********************************************************************
C     THIS IS  THE CONTROL CARD FOR EACH DATA SET.
C     DIFINC, AMMOUNT TO SUBTRACT FROM EACH TIME
C     VOLINC,  VALUE OF THE APPARATUS VOLUME UNIT DURING THE RUN
C     VARVOL,  VRAIANCE OF THE VOLUME UNIT
C     NOPT,  NUMBER OF DATA POINTS ( TIMES ) IN THIS DATA SET
C     IRED,  REDUCTION METHOD, 0 AND  1 = NO REDUCTION, 2 AND GREATER SELECTS
C     EVERY N TH POINT AFTER 1 FOR OUTPUT AS DATA, IRED = N
C     IRED = -1  SELECTS SUBROUTINE TRUNC TO REDUCE DATA, THEN CALLS REDUCE
C     WITH IRED LARGE ENOUGH TO GIVE LESS THAN 99 POINTS IF NEEDED
C     IRED = - 2 ,  CALLS TRUNC FOR AS MANY PASSES AS NEEDED TO REDUCE DATA TO
C     LESS THAN 99 POINTS
C     AS CURRENTLY DIMENSIONED, KINFIT WILL TAKE NO MORE THAN 99 POINTS
C    ***********************************************************************
      READ(60,102)DIFINC,VOLINC,VARVOL,NOPT,IRED
  102 FORMAT(3F10.0,2I5)
      WRITE(61,201)(IN(J),J=1,7)
  201 FORMAT( 5X,7A10)
C    ***********************************************************************
C     READ INPUT TIMES
C    ***********************************************************************
      READ(60,103)(T(J),J=1,NOPT)
      WRITE(61,202)(T(J),J=1,NOPT)
  103 FORMAT(10(1X,F6.0))
  202 FORMAT(10(2X,F10.2))
C    ***********************************************************************
C     CALCULATE VOLUME VERSUS TIME FOR EACH POINT
C    ***********************************************************************
      VAZZ=VOLINC**2
      DO 20 I=1,NOPT
      T(I)=T(I)-DIFINC
      VT(I)=0.25
      V(I)=(I-1)*VOLINC
      VV(I)=EXP(-.0123*T(I))*VAZZ+I*VARVOL
   20 CONTINUE
C    ***********************************************************************
C     THERE FOLLOW A SERIES OF SUBROUTINE CALLS DIRECTED BY THE VALUES
C     SCRIBE WHERE OUTPUT DATA IS WRITTEN AS DIRECTED BY IPON.
C    ***********************************************************************
```

```
C     ////////////      SAMV CONTINUED      ////////////////////////////////////////////
      IF(IRED.LE.-1)CALL TRUNC(T.VT.V.VV.NOPT.IRED)
      IF(IDO.EQ.0)21.30
   21 IF(IRED.GE.2)22.23
   22 CALL REDUCE(T.VT.V.VV.NOPT.IRED)
   23 CALL SCRIBE(T.VT.V.VV.NOPT.IDO.IPON.IN)
      GO TO 1
   30 CALL RATE(T.VT.V,VARVOL.R.VR.NOPT)
      IF(IDO.EQ.1)31,40
   31 CALL TVBAR(T.VT,TB.VTB.NOPT)
      IF(IRED.GE.2)32.33
   32 CALL REDUCE(TB.VTB.R.VR,NOPT.IRED)
   33 CALL SCRIBE(TB.VTB.R.VR.NOPT.IDO,IPON.IN)
      GO TO 1
   40 IF(IDO.EQ.2)41.50
   41 CALL TVBAR(V.VV.VB.VVB.NOPT)
      IF(IRED.GE.2)42,43
   42 CALL REDUCE(VB.VVB.R.VR.NOPT,IRED)
   43 CALL SCRIBE(VB.VVB.R.VR.NOPT,IDO,IPON.IN)
      GOTO 1
   50 WRITE(61,203)IDO
  203 FORMAT(5X,* AN INCORRECT VALUE OF IDO WAS ENTERED. *./.5X,* IDO =
     1 *.I5.*  AND MUST BE 0. 1. OR 2.*)
  999 CONTINUE
      END
```

```
      SUBROUTINE TRUNC(A.B.C.D.N,IRED)
      DIMENSION A(N).B(N).C(N),D(N).IH(800)
C  ***************************************************************
C     THIS SUBROUTINE PERFORMS A RADICAL REDUCTION OF THE-NUMBER OF DATA POINTS.
C     IT ELIMINATES MUCH OF THE DATA NEAR THE START OF THE RUN WHILE RETAINING
C     THAT NEAR THE END.  THIS IS INTENDED FOR USE WITH RUNS TO COMPLETION WHERE
C     THE FRACTIONAL CHANGE IN CONCENTRATION IS SMALL AT THE START AND INCREASES
C  AS THE RUN PROGRESSES.
C  ***************************************************************
    1 INC=0
      I=0
      DO10I=1.N
C  ***************************************************************
C     IZ MAY BE DEFINED AS ANY FUNCTION OF FLOAT(I). THIS VARIABLE AND
C     ASSOCIATED FUNCTION CONTROLS THE RATE OF TRUNCATION.
C     IZ SETS THE RATE OF INCREASE OF INCREMENT TO THE NEXT POINT.
C  ***************************************************************
      IZ=IFIX(SQRT(FLOAT(I)))
      INC=INC+IZ
C  ***************************************************************
C     INC IS THE NUMBER OF POINTS FROM N FOR THE SELECTED POINT TO BE TAKEN
C     IN IS THE INDEX (CONDITIONAL) OF THE NEW POINT.
C     IF IN IS NOT LT 1. IT WILL BE STORED AS IH(I).
C     IF IN IS LT 1. EXIT FROM DO LOOP IS TAKEN AS NO FURTHER REDUCTION IS
C     POSSIBLE.
C  ***************************************************************
   15 IN=N+1-INC
      IF(IN)11.11.12
   12 J=I
      IH(I)=IN
   10 CONTINUE
   11 CONTINUE
```

```
C        ///////////      TRUNC CONTINUED      ////////////////////////////////////////
C     ***********************************************************************************
C        AT THIS POINT, J IS THE LAST NEW POINT INDEX AND N IS THE LAST OLD.
C     ***********************************************************************************
         DO 20L=1,J
C     ***********************************************************************************
C        SINCE THE LARGEST INDEX IH(I) CONTAINS THE LOWEST INDEX OF A POINT TO BE
C        RETAINED, IH(I) MUST BE USED FROM ITS HIGHEST TO LOWEST VALUE INDEX.
C     START, L=1, K=J.   END, L=J, K=1. IH(1)=N
C     ***********************************************************************************
         K=J-L+1
         A(L)=A(IH(K))
         B(L)=B(IH(K))
         C(L)=C(IH(K))
         D(L)=D(IH(K))
   20    CONTINUE
         N=J
         IF(N-99)30,30,31
   31    IF(IRED.EQ.-2)GOTO1
         IRED=N/100+1
   30    CONTINUE
         END

         SUBROUTINE RATE(T,VT,V,VARVOL,R,VR,NOPT)
         DIMENSION T(800),VT(800),V(800),R(800),VR(800)
C     ***********************************************************************************
C        THIS SUBROUTINE CALCULATES THE RATE BETWEEN EACH ADJACENT PAIR OF POINTS
C     ***********************************************************************************
         NOPT=NOPT-1
         DO 10I=1,NOPT
         K=I+1
         DV=V(K)-V(I)
         DT=T(K)-T(I)
         RDT=0.5/DT**2
         RDV=VARVOL/DV**2
         R(I)=DV/DT
         VR(I)=R(I)*SQRT(RDV+RDT)
   10    CONTINUE
         RETURN
         END
```

```
      SUBROUTINE REDUCE(X.VX.Y.VY.NOPT.IRED)
      DIMENSION X(800).VX(800).Y(800).VY(800)
C ************************************************************************
C     THIS SUBROUTINE  SELECTS THE FIRST AND EVERY SUCCEDING N-TH POINT
C     FOR USE WHERE N = IRED .
C ************************************************************************
      IF(IRED.GE.NOPT)1.2
    1 WRITE(61.100)IRED
  100 FORMAT(5X.*IRED=*.I5.* AND IS GT/EQ TO NOPT. NO REDUCTION PERFORMED
     1D.*)
      RETURN
    2 WRITE(61.101)IRED
  101 FORMAT(5X.*REDUCTION PERFORMED. IRED =*.I5)
      NOPT=NOPT/IRED
      DO 10 I=1.NOPT
      K=IRED*(I-1)+1
      X(I)=X(K)
      VX(I)=VX(K)
      Y(I)=Y(K)
      VY(I)=VY(K)
   10 CONTINUE
      RETURN
      END

      SUBROUTINE TVBAR(X.VX.XB.VXB.NOPT)
      DIMENSION X(800).VX(800).XB(800).VXB(800)
C ************************************************************************
C     THIS SUBROUTINE AVERAGES EITHER TIME OR VOLUME BETWEEN EACH ADJACENT
C     PAIR OF POINTS.
C     FOR USE WITH RATES IN TWO OPTIONS 1 OR 2.
C     BEFORE CALLING THIS SUBROUTINE, NOPT HAS BEEN REDUCED TO ONE LESS
C     THAN ITS  ORIGIONAL VALUE BY SUBROUTINE RATE.
C ************************************************************************
      DO 10 I=1.NOPT
      K=I+1
      XB(I)=(X(K)+X(I))/2.
      VXB(I)=(VX(K)+VX(I))/2.
   10 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE SCRIBE(X,VX,Y,VY,NOPT,IDO,IPON,IN)
      DIMENSION X(800),VX(800),Y(800),VY(800),IN(7)
C    ***************************************************************************
C     THIS SUBROUTINE WRITES OUTPUT DATA. IF IPON IS INITIALLY SET TO 1,
C     THE DATA IS SET INTO KINFIT FORMAT. TO INCLUDE CONTROL CARDS AND PARAMETER
C     ESTIMATES AND WRITTEN ON THE FILE DESIGNATED BY TAPE62.
C     THIS FILE MAY BE CATALOGUED AS A PERMANET FILE OR OUTPUT AS PUNCH CARDS.
C     NOTE THAT IPON WAS INCREASED BY 1 IN THE FIRST ARETHIMETIC STATEMENT
C     OF THE MAIN PROGRAM.
C    ***************************************************************************
      GO TO(10,20)IPON
   10 CONTINUE
      WRITE(61,101)(IN(J),J=1,7),IDO,IPON,NOPT
  101 FORMAT(5X,7A10,3I5)
      WRITE(61,102)(X(J),VX(J),Y(J),VY(J),J=1,NOPT)
  102 FORMAT(8(1X,1PE15.7))
      RETURN
   20 CONTINUE
      IF(IDO.EQ.0)U=(Y(3)-Y(2))/(X(3)-X(2))
      IF(IDO.EQ.1)U=(Y(2)+Y(3))/2.
      IF(IDO.EQ.2)U=Y(1)/X(NOPT)
      ITMAX=20
      TEST=0.00001
      C=0.00
      WRITE(62,210)NOPT,ITMAX,TEST
  210 FORMAT(I5,5X,I5,25X,F10.7)
      WRITE(61,101)(IN(J),J=1,7),IDO,IPON,NOPT
      WRITE(62,201)(IN(J),J=1,7),IDO,IPON,NOPT
      WRITE(62,211)U,C,C
  201 FORMAT(7A10,2I3,I4)
  211 FORMAT(3(1PE10.3))
      WRITE(61,102)(X(J),VX(J),Y(J),VY(J),J=1,NOPT)
      WRITE(62,202)(X(J),VX(J),Y(J),VY(J),J=1,NOPT)
  202 FORMAT(8(2PE10.3))
      RETURN
      END
```

EVLT

```
      PROGRAM EVLT(INPUT,OUTPUT,TAPE60=INPUT,TAPE61=OUTPUT,TAPE63)
      DIMENSION IRUN(7)
      REAL  MC,MS ,MDS ,MI   ,ML
      WRITE(61,200)
C   ***********************************************************************
C     START PROGRAM LOOP
C   ***********************************************************************
    3 CONTINUE
C   ***********************************************************************
C     READ TITLE CARD FOR EACH RUN
C   ***********************************************************************
      READ(60,101)(IRUN(I), I=1,7 )
      IF(EOF(60))1,2
    2 CONTINUE
  101 FORMAT(7A10)
C   ***********************************************************************
C     INPUT DATA
C     WC     WEIGHT OF CATALYST    ENTER GRAMS
C     VSOL    VOLUME OF SOLVENT    ENTER ML
C     VSUB    VOLUME OF ALKENE    ENTER ML
C     MDS    CONCENTRATION OF ALKENE    ENTER MOLES/L
C     VL    VOLUME OR WEIGHT OF PHOSPHENE    ENTER ML OR GRAMS
C     CL    CONCENTRATION OF PHOSPHENE    ENTER MOLES/L OR MOLES/1000 G
C     VL    VOLUME OR WEIGHT OF PHOSPHENE    ENTER MOLES/L OR MOLES/1000G
C     WHEN USING WEIGHT A DENSITY OF 1.G/ML IS ASSUMED IMPLICITLY. SINCE
C     THE VOLUME ADDED BY THE SOLID IS QUITE SMALL,THE ERROR INTRODUCED
C     BY THIS APPROXIMATION IS SMALL.
C     AK1    INITIAL RATE FOR THE FIRST 20 POINTS
C     AK2    AVERAGE RATE FOR THE FIRST 20 POINTS
C     AN E PREFIXED TO A VARIABLE NAME IS THE ESTIMATED SIGMA ERROR FOR
C     THAT VARIABLE.  AN R PREFIXED TO THE VARIABLE NAME IS THE RELATIVE
C     ERROR SQUARED.  SOME VARIABLES DROP ONE LETTER FROM THE PRIMARY NAME
C     ON ADDING THE PREFIX.
C   ***********************************************************************
      READ(60,102)WC,EWC,VSOL,ESOL,VSUB,ESUB,MDS,EMD
      READ(60,102)VL,EVL,CL,ECL
      READ(60,102)AK1,AK2,RER
C   ***********************************************************************
C     CALCULATIONS
C   ***********************************************************************
      AK=(AK1+AK2)/2.
      EAK=ABS(AK-AK1)
      CL=CL+1.E-50
      VSOL=VSOL/1000.
```

```
C     //////////      EVLT CONTINUED      ////////////////////////////////////////
      VL=VL/1000.
      A=VL+1.0E-50
      EVL=EVL/1000.
      ESOL=ESOL/1000.
      VSUB=VSUB/1000.
      ESUB=ESUB/1000.
      RVL=(EVL/A )**2
      RCL=(ECL/CL)**2
      RWC=(EWC/WC)**2
      RSUB=(ESUB/VSUB)**2+(EMD/MDS)**2
      RAK=(EAK/AK)**2
      VT=VSUB+VSOL+VL
      EVT=SQRT(EVL**2+ESOL**2+ESUB**2)
      RVT=(EVT/VT)**2
      MC=WC/(925.24*VT)
      RMC=RWC+RVT
      VMC=RMC*MC**2
      EMC=SQRT(VMC)
      RA=AK/VT
      RRA=RAK+RVT
      VRA=RRA*RA**2
      ERA=SQRT(VRA)
      MS=VSUB*MDS/VT
      RMS=RSUB+RVT
      VMS=RMS*MS**2
      EMS=SQRT(VMS)
      ML=CL*VL/VT
      RML=RVL  +RCL+RVT
      VML=RML*ML**2
      IF(ML.EQ.0.0)VML=1.0E-10*VMC
      EML=SQRT(VML)
      RI=1./RA
      VRI=(RRA+RMC)*RI**2
      ERI=SQRT(VRI)
      MI=1./MC
      VMI=RMC*MI**2
      EMI=SQRT(VMI)
C   ***********************************************************************
C     OUTPUT DATA
C     VT IS TOTAL VOLUME OF THE SOLUTION.
C     MC IS CONCENTRATION OF THE CATALYST.
C     MI IS THE INVERSE CONCENTRATION.
C     RA IS THE RATE FOR 1. LITER.
C     RI IS INVERSE RATE.
C     ML IS THE CONCENTRATION OF PHOSPHENE.
C     MS IS THE CONCENTRATION OF ALKENE.
C   ***********************************************************************
```

```
C      ///////////.       EVLT CONTINUED      ////////////////////////////////////////
       WRITE(61,201)   (IRUN(I), I=1,7 )
       WRITE(51,301)
       WRITE(61,202)WC,EWC,VSOL,ESOL,VSUB,ESUR,MDS,EMD,VL,FVL,CL,ECL,
     1 AK1,AK2
       WRITE(61,302)
       WRITE(61,203)VT,EVT
       WRITE(61,207)MS,EMS
       WRITE(61,204)MC,VMC,RA,VRA
       WRITE(61,205)EMC,ERA
       WRITE(61,206)MI,VMI,RI,VRI
       WRITE(61,208)EMI,ERI
       WRITE(61,209) ML,VML,RI,VRI
       WRITE(61,303)
       WRITE(61,210)MC,VMC,RA,VRA,ML,VML,MS,VMS  ,(IRUN(I),I=1,7)
  200  FORMAT(1H1)
  201  FORMAT(/////,* //////////*,5X,7A10,*////////////////////////////*)
  209  FORMAT(/,*   ML,R1   *,5X,4(1PE15.5),/)
  102  FORMAT(8F10.0)
  202  FORMAT(5X,     *         WT. CAT. (G) *,2(5X,1PE15.7),
     1  /,      5X,   *   VOL. SOLVENT  (L) *,2(5X,1PE15.7),
     1  /,      5X,   *VOL. SUBSTRATE  (L) *,2(5X,1PE15.7),
     1  /,      5X,   *     MOL. SUB.  (MO/L)*,2(5X,1PE15.7),
     1  /,      5X,   *    VOL. LIGAND  (L) *,2(5X,1PE15.7),
     1  /,      5X,   *MOL. LIGAND  (MO/L) *,2(5X,1PE15.7),
     1  /,      5X,   *RATES, IN,AV         *,2(5X,1PE15.7),       )
  203  FORMAT(2X,*   VT   *,2(5X,1PE15.7))
  204  FORMAT(/,2X,*MC,RA*,5X,4(1PE15.7) )
  205  FORMAT(12X,1PE15.7,15X,1PE15.7)
  206  FORMAT(//,2X,*MI,RI*,5X,4(1PE15.7))
  207  FORMAT(2X,*   MS   *,2(5X,1PE15.7))
  208  FORMAT(12X,1PE15.7,15X,1PE15.7)
  210  FORMAT(    //,2X,8(1PE15.7),/,1X,*END *7A10,/////)
  301  FORMAT( * XXXXXXXXXX    INPUT DATA    XXXXXXXXXX *)
  303  FORMAT(/* XXXXXXXXXX    MC,VMC,R,VR,ML,VML,S,VS    XXXXXXXXXY * )
  302  FORMAT(/* XXXXXXXXXX    OUTPUT DATA    XXXXXXXXXX * )
       GO TO 3
    1  CONTINUE
       END
000000000000000
000000000000000
```