**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

# The Preparation and Selectivity of a Polymer-Attached Rhodium(l) Olefin Hydrogenation Catalyst

Robert H. Grubbs[a]; Leroy C. Kroll[a]; Edward M. Sweet[a]
[a] Department of Chemistry, Michigan State University, East Lansing, Michigan

**To cite this Article** Grubbs, Robert H. , Kroll, Leroy C. and Sweet, Edward M.(1973) 'The Preparation and Selectivity of a Polymer-Attached Rhodium(l) Olefin Hydrogenation Catalyst', Journal of Macromolecular Science, Part A, 7: 5, 1047 — 1063

**To link to this Article: DOI:** 10.1080/10601327308060481

**URL:** http://dx.doi.org/10.1080/10601327308060481

J. MACROMOL. SCI.—CHEM., A7(5), pp. 1047-1063 (1973)

# The Preparation and Selectivity of a Polymer-Attached Rhodium(I) Olefin Hydrogenation Catalyst

ROBERT H. GRUBBS, LeROY C. KROLL, and EDWARD M. SWEET

Department of Chemistry
Michigan State University
East Lansing, Michigan 48823

## ABSTRACT

A homogeneous hydrogenation catalyst [tris(triphenylphosphine)chlororhodium(I)] was attached to a polystyrene support by phosphine links. The attached catalysts were easily removed from the reaction mixture and could be used many times with little loss of activity. A study of the relative rate of reduction vs olefin size indicated that the attached catalysts showed a selectivity for smaller molecules. A model based on the random sizes of the pores in the polymer was developed. The effective pore size was found to be only 5-10% that of the size measured by other techniques. Suspension of the polymer attached catalyst in polar solvents allowed the reduction of nonpolar hydrocarbons in the presence of polar olefins.

## INTRODUCTION

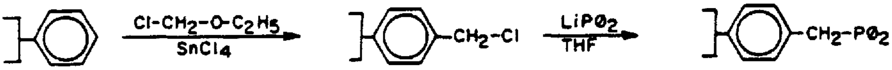
In the past few years rapid advances have been made in the area of transition metal homogeneous catalysis [1]. For example, new soluble transition metal complexes have been found which catalyze the reduction of unsaturated organic [2] and inorganic molecules [3], the hydroformylation of olefins [4], and the polymerization of olefins [5]. These catalysts are generally more selective and function under milder conditions than their heterogeneous counterparts. As a source of principles for the further improvement of these catalyst systems, the salient features of enzyme systems, the most efficient specific catalysts, were examined.

A general feature of many enzymes is the presence of an active site situated in a cleft or solvent channel in an ordered insoluble polymer. This simple feature imparts three important features to the enzyme catalyst: 1) A homogeneous catalyst is converted into a heterogeneous catalyst. This feature allows easy separation of the reagent and substrate without loss of activity. 2) The selectivity of the reagent is increased. Since the solvent channel has a size restriction and polar properties, the diffusion rate of a substrate molecule from the bulk of the solution through the solvent channel to the reaction site is determined by the overall molecular size and polarity of the substrate molecule. Consequently, the relative reaction rates of two substrates is the result of differences in molecular size and polarity. 3) Reagents are present at the active site which have no homogeneous counterparts. The surrounding polymer protects the active site from reagents which destroy the catalytic activity of a similar species in solution.

With these observations in mind, a catalytic system based on a known homogeneous catalyst was designed which should incorporate the simple features outlined above. After the preparation of such systems, they were investigated to determine size and polar selectivities. Experiments concerning advantage 3 above will be reported later.

## PREPARATION OF POLYMER ATTACHED CATALYSTS

Polystyrene cross-linked with 2% divinylbenzene was chosen as the polymer. Earlier workers had developed procedures for functionalizing the polymer with chloromethyl groups [6]. Merrifield [7] demonstrated that these functional groups were distributed throughout the polymer and that the major portion of the reactions with these groups took place inside of the polymer. Consequently, attachment of a catalysts to the polymer through the chloromethyl units should place the catalyst inside of the polymer as required by the model developed above. Since many of the simpler catalysts contain a phosphine ligand, the chloromethyl groups were converted to phosphines by the following procedure:



~10% Substitution

Tris(triphenylphosphine)chlororhodium(I) [2], a homogeneous hydrogenation catalyst, was chosen as the catalyst to use in testing the principles outlined above since its homogeneous reactions have been studied in detail and it catalyzes the reduction of olefins by hydrogen at conveniently measurable rates at atmospheric pressure and room temperature. The catalyst was attached to the polymer by stirring a suspension of the phosphinated copolymer with one equivalents of the catalyst in benzene for 2 to 4 weeks.

At the conclusion of the equilibration period the deep red beads were washed with deoxygenated benzene until the rinses were colorless for 3-5 successive cycles. Fresh oxygen-free benzene was then added and, after equilibration of the catalyst under hydrogen at 1 atm for at least 1 hr, an olefin was added. A steady uptake of hydrogen then commenced and the reduced hydrocarbon could be observed by vapor phase chromatography analysis.

Two different batches of polymer-attached catalyst were prepared by this procedure. The first batch of catalyst was prepared from 100-200 mesh 2% cross-linked polystyrene beads. This catalyst reduced 1 M cyclohexene at a rate of 0.28 ml $H_2$ (1 atm)/min per gram of beads. The second sample of catalyst was prepared from 30-80 mesh 2% cross-linked polystyrene beads. This catalyst reduced 1 M cyclohexene at a rate of 0.216 ± 0.02 ml $H_2$ (1 atm)/min per gram of beads. The catalyst could be easily separated by simple filtration and be reused many times.

A linear relationship was found between bead quantity and observed rate of reduction of cyclohexene for small quantities of beads. In our apparatus significant deviations from linearity were observed for quantities of beads which gave reduction rates greater than 3.0 ml $H_2$/min (1 atm). Bead quantities were chosen to yield reduction rates below this value (Fig. 1).

A plot of hydrogen uptake vs time for the reduction of cyclohexene by the polymer-attached catalyst fit (Fig. 2) the same rate expression as the homogeneous catalyst [2]. This demonstrates that attachment of the catalyst to the polymer does not change the mechanism of reaction.

The absolute activity of the catalyst was decreased on attachment to the polymer. A suspension of the attached catalyst that was 40 mM in rhodium gave a rate reduction similar to a 2.5-mM solution of the rhodium catalyst.

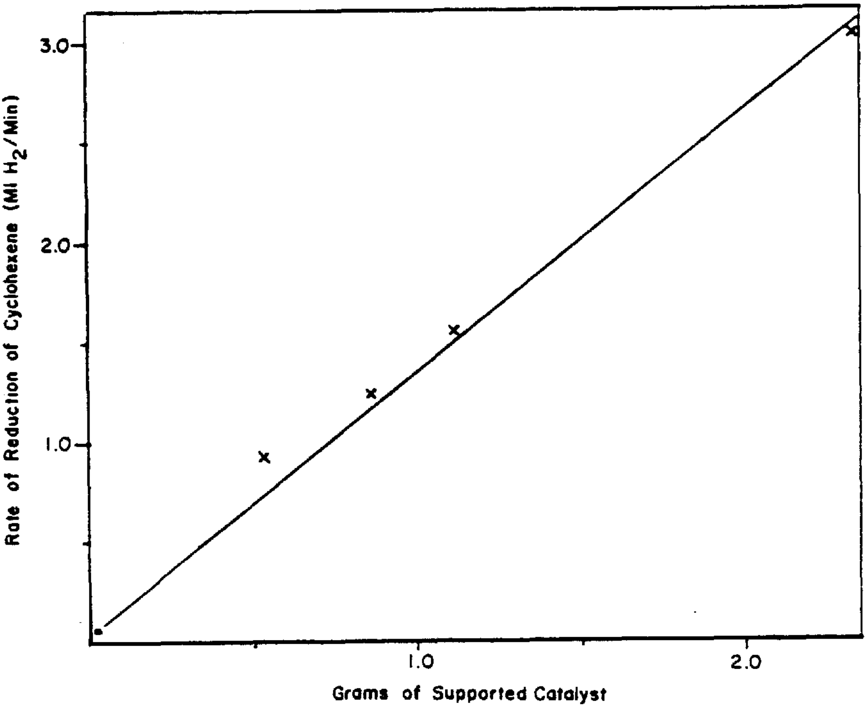


FIG. 1. Plot of reduction rate of cyclohexene by Batch B catalyst vs quantity of catalyst used.

## SELECTIVITY ON THE BASIS OF OLEFIN SIZE

The relative rates of reduction of a variety of reasonably rigid olefi of different molecular sizes were determined. The relative rates were determined by setting the rate of reduction of cyclohexene before and after the run on each olefin equal to 1.0. Different batches of the catalyst vary in activity.

Both sets of catalysts showed a decrease in rate as the size of the olefin increased. In order to probe the relationship of size to rate of reduction, a plot of molecular diameter vs relative rate was prepared. The relative molecular diameters were measured from (Prentice-Hall) molecular models. Homogeneous rate corrections were made by dividing out the relative rate differences for each of the olefins as determined with tris(triphenylphosphine)chlororhodium(I) in benzene. As can be seen in Fig. 3, a plot of the relative rate of reduction on the

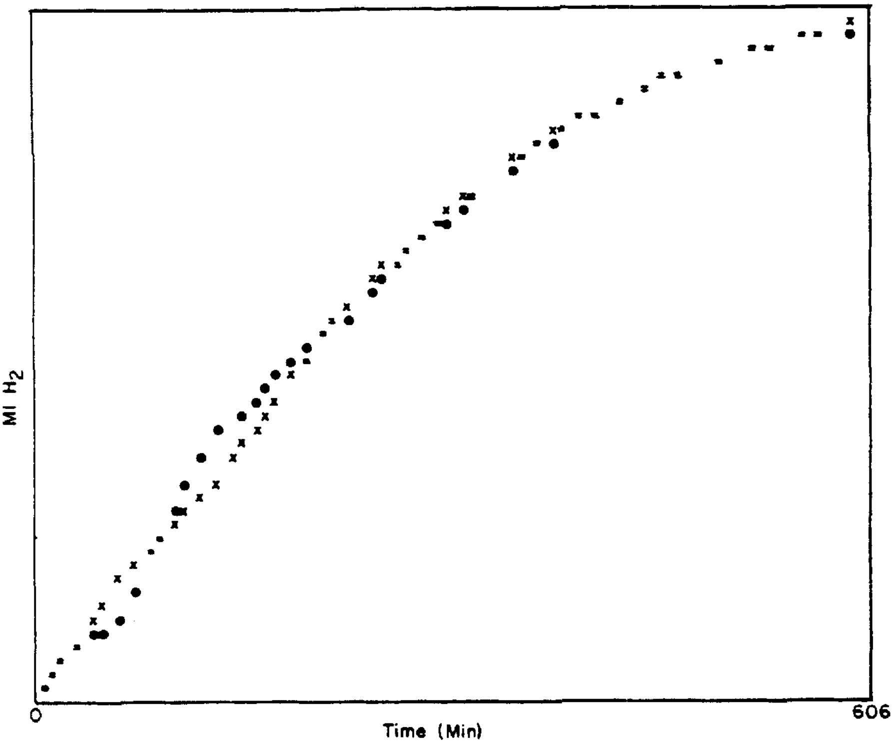


FIG. 2. Comparison of hydrogen uptake in the reduction of cyclohexene with the supported catalyst to the curve calculated from Rate = $K_1[S]/(1+K_2/[S])$. (●) calculated point; (×) experimental point, (=) identical calculated and experimental points.

100-200 mesh beads vs molecular size of the olefin gives a smooth curve which levels off at larger molecular sizes. The greatest selectivities per unit size are between 1-hexene, cyclohexene, and cyclooctene. A similar plot for the reduction rate of these three olefins on the 30-80 mesh beads is shown in Fig. 4.

In benzene the two sizes of beads gave similar size-rate relationships. However, the smaller beads (Fig. 3) gave a rate difference of 2.6 units/Å between hexene and cyclooctene whereas the larger diameter beads gave a rate difference of 1.3 units/Å for the same olefins.

This difference in behavior suggested that the pore sizes of the two sets of beads were different with the larger mesh having the largest pores. It is well known that an increase in solvent polarity decreases

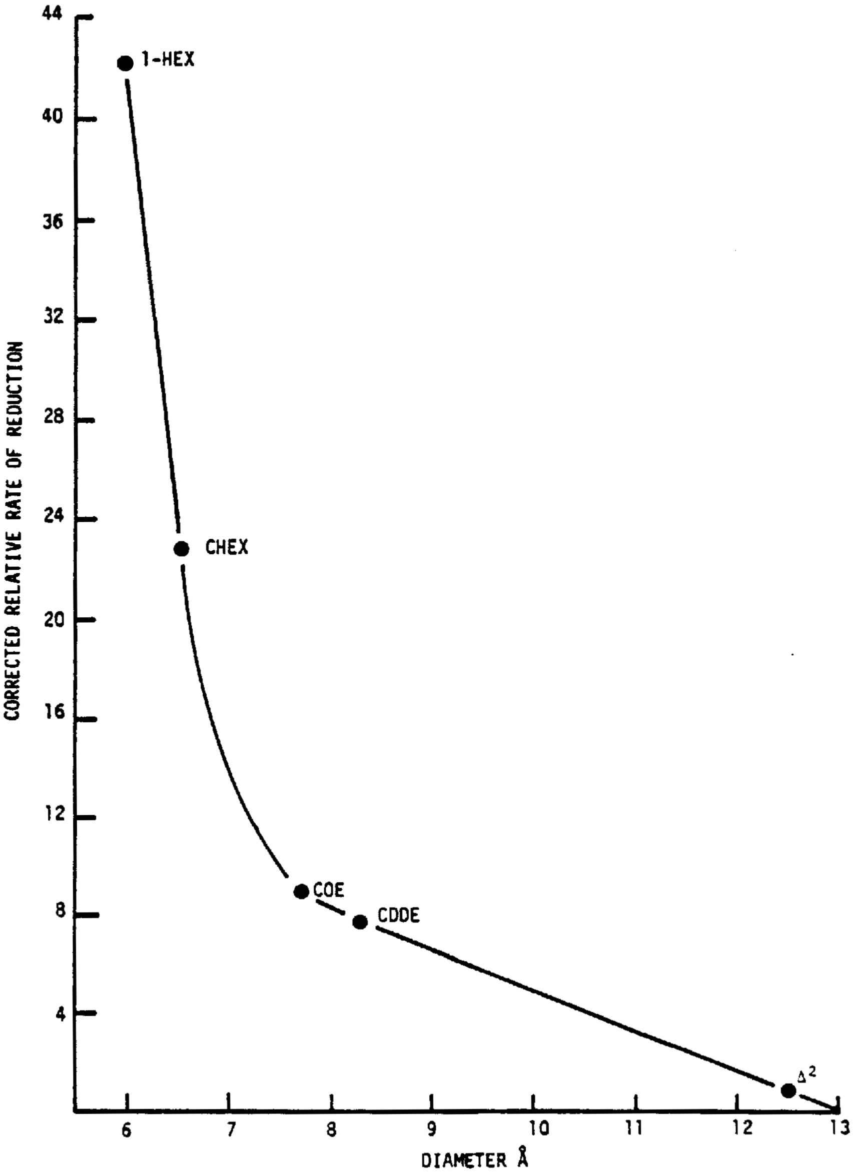


FIG. 3. Plot of corrected relative rate of reduction at 1 atm of $H_2$ of various olefins in benzene vs olefin size using 100-200 mesh, 2% cross-linked polystyrene, rhodium(I) catalyst. 1-HEX = 1-hexene, CHEX = cyclohexene, COE = cyclooctene, CDDE = cyclododecene, $\Delta^2$ = $\Delta^2$-cholestene and rate $\Delta^2$ = 1.0.

the swelling of polystyrene beads. Consequently, the changes in relative rates with the polarity of the solvent used with the polymer catalysts were investigated. The size-rate relationship for the larger mesh catalysts should approach that of the smaller mesh polymer if the difference in activity is only due to differences in pore size. Figure 2 shows the size-rate plots obtained in this study.

These data do not show a simple relationship between solvent composition and relative rate. Two opposing factors are apparently operative in this case. As the polarity increases, the size of the solvent channels decrease while concurrently a polar gradient is established across the bead surface. Since the polymer is nonpolar, the polar gradient will operate to increase the concentration of nonpolar substrates inside of the polymer bead. The decreased size of the solvent channels should increase the magnitude of the relative rate ratios while the polar gradient should tend to level the effect of the size differences of the hydrocarbons. The data in Figure 2 suggests that the polarity "hydrophobic" effects are the predominate factors at 1:1 ethanol-benzene with the size effects returning in pure ethanol.

A scheme for reduction by the attached catalyst is

$$\text{olefin} + \text{polymer-catalyst} \xrightarrow[k_{-d}]{kd} [\text{olefin-polymers}] \xrightarrow{k_r} \text{hydrocarbon} + \text{polymer-catalyst}$$

The olefin in solution equilibrates with the polymer before reduction by the catalyst. The kinetic equation then becomes

$\text{Rate} = k_r[\text{O-P.C.}]$ $[\text{O}]$ = olefin concentration

$= k_r K[\text{O}][\text{P.C.}]$ $[\text{P.C.}]$ = catalyst concentration

$$\text{Relative rate} = k_r{}'K'[\text{S}][\text{P.C.}]$$

$$\frac{\text{Relative rate}}{k_r{}'} = \text{connected relative rate} = \text{CRR}$$

$\text{CRR} = K''[\text{P.C.}]$ for constant olefin concentrations; assuming $K''$ is constant for certain relative sized substrates and pores then,

$$\text{CRR}/K = [\text{P.C.}]$$

A model will now be developed for calculating the change in effective catalyst concentration on changing olefin size.

A composite rate-size relationship can be constructed from Figs. 3 and 4 for different sized olefins and for reactions under different solvent conditions. Such a curve, Fig. 5, shows a flat portion for both small and large molecules, with a steep slope in between. This is a characteristic curve for the integrated area under a random distribution curve [8]. This provides a reasonable model for the

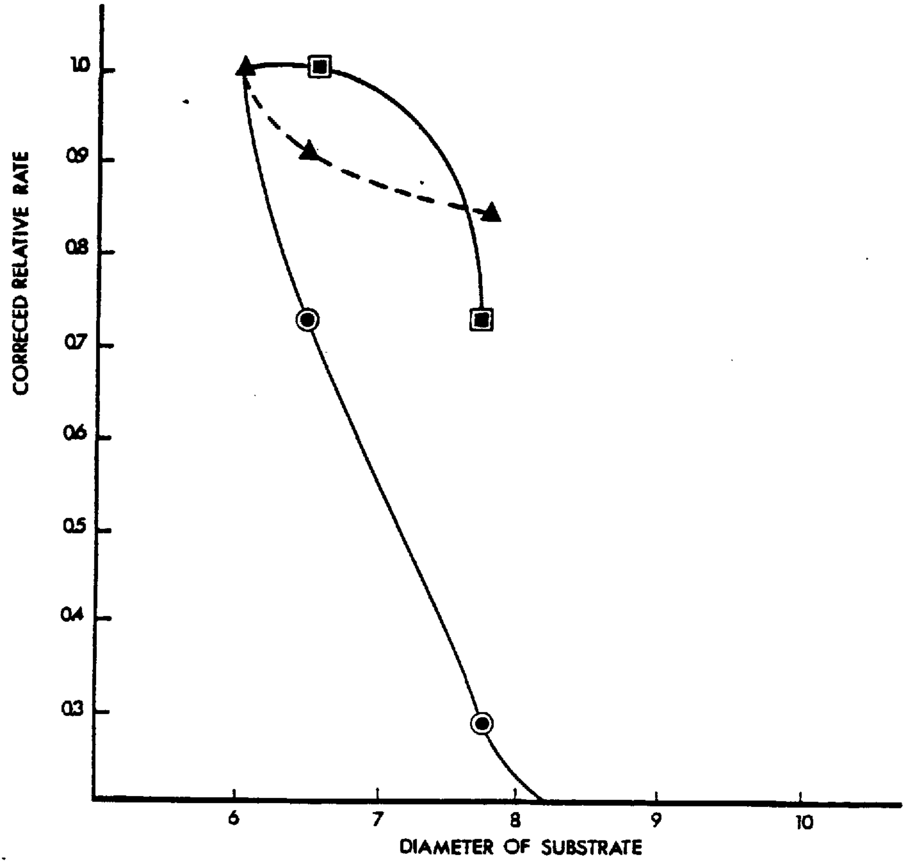


FIG. 4. Plot of corrected relative rate of reduction at 1 atm $H_2$ of 1-hexene, cyclohexene, and cyclooctene vs olefin size using 30-80 mesh, 2% cross-linked polystyrene rhodium(I) catalyst. (◉) Benzene; ▣ = 1:1 benzene:ethanol; (▲) = ethanol. In each solvent the relative rate of 1-hexene is 1.

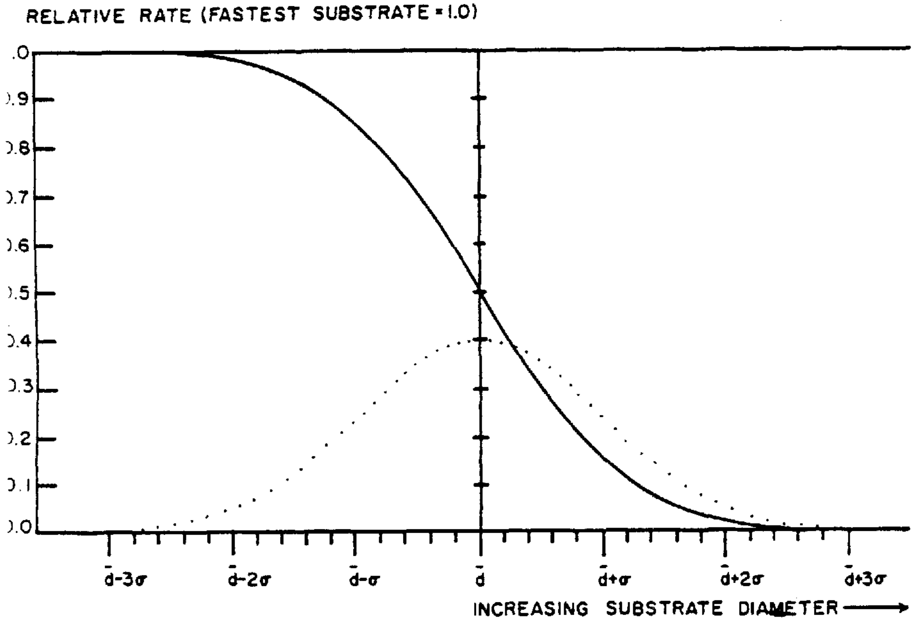


FIG. 5. Composite plot of size-rate relationship.

selectivity of the catalysts. Since the polymer was formed with random cross-links, there is a random distribution of sizes of solvent channels. As the substrate approaches the surface of the polymer, only those channels that are of a minimum size and larger in relation to the substrate will result in an effective reaction. The rate of reaction will therefore be related to the total number of effective solvent channels and consequently the effective concentration of catalyst.

Figure 6 shows the fit of the data in Fig. 3 to the following equation [8]:

$$\text{Adjusted relative rate} = K_1 - \frac{1}{\sigma(2\pi)^{1/2}} \int_0^D \exp\left[-\frac{1}{2}\left(\frac{D-\mu}{\sigma}\right)^2\right] dD$$

Although the fit is reasonable, this does not prove the model above since there are few data points compared to the number of variable

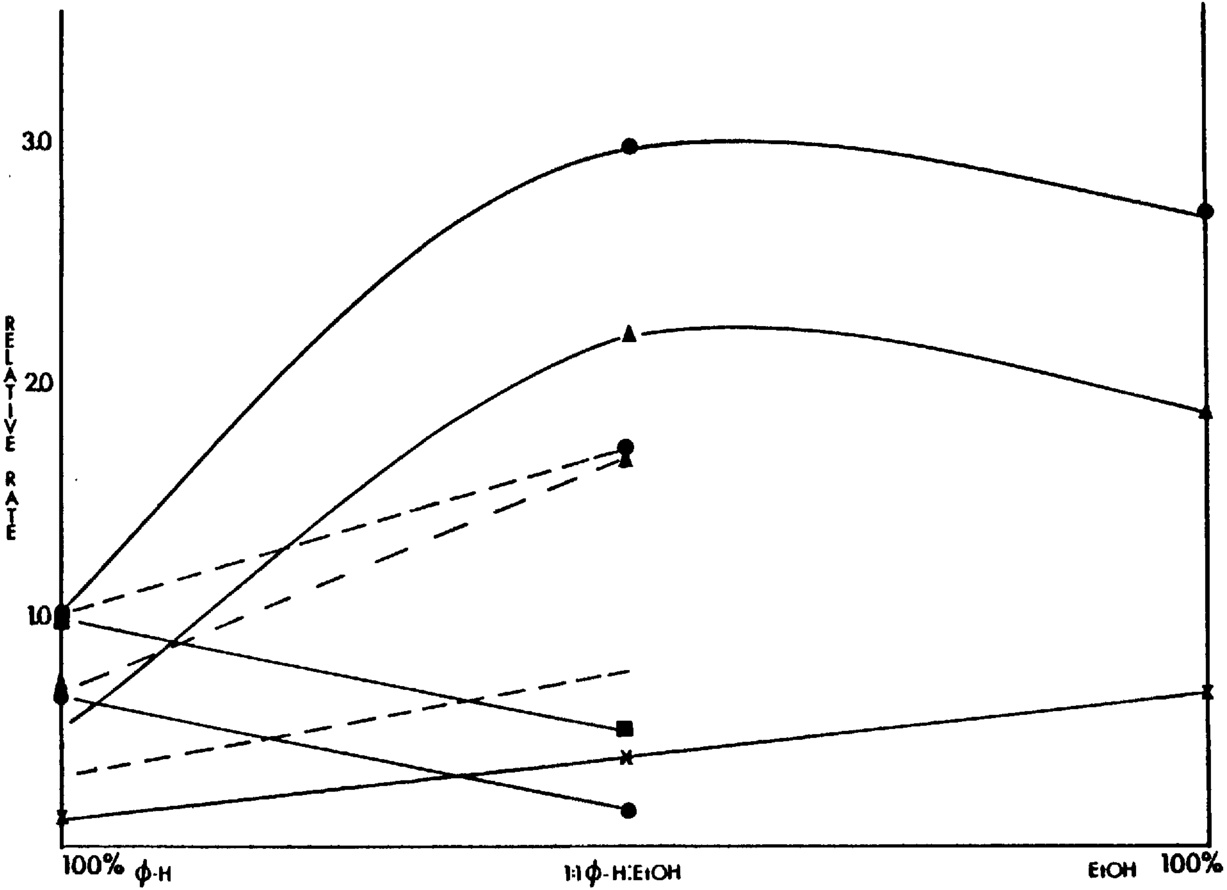


FIG. 6. Plot of reduction rates vs solvent composition. (--) Corrected relative rates; (—) relative rates of reduction: (●) 1-hexene; (▲) cyclohexene; (×) cyclooctene; (■) 4-pentene-1-ol.

parameters. However, if the model is accepted, the calculated parameters are interesting. The calculated average pore size for effective reaction rates is 6.7 Å. Although the measured pore size of 2% cross-linked material is 150-200 Å, it is reasonable that the solvated olefins will appear much larger than measured and our model probably underestimates the pore diameter [9]. However, this calculation provides a guide for the selection of pore sizes for specific catalysts supports.

## POLAR SELECTIVITY

The samples of attached catalysts prepared contain the catalytic sites surrounded by nonpolar-aromatic groups. Consequently, if the bulk solvent around the surface of the polymer is more polar than benzene, two major changes should occur in the catalyst: 1) the pores decrease in size (see above) and 2) a polar gradient will be built up between the bulk solvent and the localized environment of the catalytic center. Factor 1 should decrease the rate of diffusion of the olefin to the catalytic center, whereas Factor 2 should increase the diffusion rate of nonpolar olefins to the catalytic site and impede the diffusion of polar olefins to the reactive center. Figure 6 shows that the selectivity of the catalyst was changed when the polarity of the solvent was increased. The nonpolar olefins all show a rate enhancement as the percentage of ethanol is increased until high concentrations of ethanol apparently begin to shrink the pore sizes and the size effects again become important. After correction of the rates for homogeneous reactivity differences, the rate of reduction of cyclohexene increased by a factor of 2.4 when the solvent was changed from benzene to 1:1 benzene ethanol. Corrected rates are not available for pure ethanol since tris(triphenylphosphine)chlororhodium(I) is not soluble in this solvent. The change in rate with solvent composition of olefinic alcohols shows the opposite trend. Allyl alcohol was reduced 4.3 times slower in 1:1 ethanol:benzene than in pure benzene, and 4-penten-1-ol was reduced 1.9 times slower under similar conditions. This change represents a minimum value since allyl alcohol normally is reduced 2.6 [2] times faster than 1-hexene under homogeneous conditions. The overall polar effect on changing from homogeneous conditions to polar heterogeneous conditions is a factor of 14.2 times slower.

These data demonstrate that the polar and size effects suggested by the simple model are real and of sufficient magnitude to be of potential practical use.

## EXPERIMENTAL

### Materials

All solvents used were A.C.S. reagent grade; all benzene and tetrahydrofuran used were further purified by distillation from sodium metal under nitrogen. Ethanol used for solvent was distilled from sodium ethoxide and diethyl phthalate under nitrogen. All alkenes used for reductions were at least 95% pure, further purified by distillation from sodium under nitrogen; except for allyl alcohol, which was distilled from its sodium salt and diallyl phthalate, and $\Delta^2$-cholestene, which was used as prepared by the method of Douglas et al. [10] after repeated recrystallization from ethanol.

The chloromethylethyl ether was technical grade, used as supplied by Aldrich Chemical Co. The stannic chloride was A.C.S. reagent grade. $RhCl_3.3H_2O$ was used as purchased from Engelhard Industries. Triphenylphosphine and diphenylphosphine chloride were purchased from Pressure Chemical Co.; the former was recrystallized from absolute ethanol and benzene; the latter was distilled and stored under nitrogen. Lithium ribbon used was 99.9% purity.

The sytrene-divinylbenzene copolymer beads were a gift from The Dow Chemical Co. They were 2% divinylbenzene (1.8% cross-linked). Beads of two sizes were used: 100-200 mesh and 30-80 mesh. The latter were preferable because of their greater ease of filtration.

Curve fitting was done using a CDC-6500 computer belonging to Michigan State University with program KINFIT. KINFIT is a general purpose curve fitting program providing a least square's fit to a function which may be expressed in either normal equation or differential equation form [11].

### Bead Preparation Reactions

### Chloromethylations

The method of Pepper, Paisley, and Young [6] was used. For every 12 g of copolymer beads, 100 ml of chloromethylethyl ether and 4 g of stannic chloride were used to effect chloromethylation. After mixing of the ether with the catalyst in a cooled flask, the beads were added and stirred at room temperature for the desired time under a tube of Drierite. The reaction was terminated by the addition of 50% aqueous dioxane. Rinsing with aqueous dioxane containing 10% HCl and then several dry dioxane rinses was followed by vacuum drying.

### Phosphinations

All steps were carried out under dry nitrogen with deoxygenated solvents. Lithiodiphenylphosphine was prepared from lithium metal and diphenylphosphine chloride by the "Direct Method" of Tamborski et al. [12]. After the phosphine chloride in tetrahydrofuran was added to lithium metal clippings in an equal volume of tetrahydrofuran, the reaction was stirred for 10-20 hr. For every gram of lithium, 5.8 g of diphenylphosphine chloride and 60 ml of tetrahydrofuran were used. After the lithium reagent was formed, the solution was filtered through glass wool and added to the chloromethylated beads to be phosphinated. This mixture was refluxed for 1-2 days, then cooled, and the supernatant liquid was decanted. Saturated $NH_4Cl$ was then added to the beads and stirred for several hours; rinses of distilled water, distilled water with a trace of HCl, distilled water and tetrahydrofuran, and finally dry tetrahydrofuran followed. The beads were then dried in a vacuum.

## Rhodium Treatment

$RhCl(P\phi_3)_3$ was prepared by the method of Wilkinson et al. [2] from $RhCl_3.3H_2O$ and recrystallized triphenylphosphine. The complex was then dissolved in benzene and phosphine-treated beads were added, so that approximately equal amounts of Rh and poly-$P\phi_2$ groups were present. This was equilibrated for 1-4 weeks, then drained, and the beads were rinsed repeatedly with benzene until no coloration of the rinses was noted. Vacuum drying followed.

## Specific Bead Preparations

Batch A. Twelve grams of 100-200 mesh 2% divinylbenzene copolymer beads were treated with 100 ml of chloromethylethyl ether and 4 g of stannic chloride. After reacting for 5 hr at room temperature, the beads were rinsed and vacuum dried. Analysis of a sample of the dried beads using the method in Pepper, Paisley, and Young's [6] paper indicated 9.3% of the styryl residues have $-CH_2Cl$ groups.

The beads were treated with lithiodiphenylphosphine made from 1.4 g of lithium metal and 8 g of diphenylphosphine chloride in 100 ml of tetrahydrofuran (filtered before bead addition). After refluxing for 48 hr, the beads were hydrolyzed and rinsed, then vacuum dried. Another chloride analysis indicated about 0.5% of the styryl residues still had $-CH_2Cl$ groups. An elemental analysis indicated about 0.63 mM of $-P\phi_3$ sites per gram of beads.

A 3.2-g sample of the phosphinated beads was equilibrated with 3.22 g of $RhCl(P\phi_3)_3$ in 40 ml of benzene under argon for 1 month. After rinsing with benzene aliquots for 4 days, the beads were vacuum dried and then used for alkene reductions.

Batch B. Twenty grams of 2% divinylbenzene copolymer beads (30-80 mesh) were treated with 160 ml chloromethylethyl ether and 6 g stannic chloride at room temperature for 5 hr. After rinsing and vacuum drying, a solution of lithiodiphenylphosphine made from 3.0 g of lithium and 17.6 g of diphenylphosphine chloride in 325 ml of tetrahydrofuran was reacted with them for 24 hr at reflux. After neutralization of the residual lithiodiphenylphosphine by 100 ml of saturated

$NH_4Cl$ solution, rinsing and drying of the beads in a vacuum was carried out. After equilibration with 13.2 g $RhCl(P\phi_3)_3$ in 350 ml benzene for 10 days, the beads were rinsed for 9 days with benzene aliquots and then dried and used for reductions.

A. Comparison of rate laws ($Rh(P\phi_3)_3Cl$ to bead-supported catalyst). Extended time runs (to near completion) were made with both $Rh(P\phi_3)_3$ and bead catalysts using cyclohexene as substrate, Volume of $H_2$ used (V) was recorded as a function of time(t). Initial concentration of substrate was about 1 M.

These data were fit to

$$(V = V_\infty(1 - e^{-At + FBV})$$

where $V_\infty$ (volume $H_2$ used at $t = \infty$), A, and B are made adjusted parameters in the program. F is a factor employed to convert volume $H_2$ used to a substrate concentration term. The above equation was derived by integration of a rearrangement of Wilkinson rate law for $Rh(P\phi_3)_3Cl$ [2], which is

$$\frac{dS}{dt} = \frac{kK_1[C][P][S]}{1 + K_1[P] + K_2[S]} = \frac{A[S]}{1 + B[S]} \quad A = \frac{kK_1[C][P]}{1 + K_1[P]}, \; B = \frac{K_2}{1 + K_1[P]}$$

[C], [S], and [P] are concentrations of catalyst, substrate, and pressure of hydrogen, respectively. B, which represents the complexation of substrate to catalyst at constant P, and goodness of fit were compared.

## Reductions.

Batch A. The entire sample of Batch A beads was used for reductions. A magnet stirring bar was put in a Schlenk tube with the beads the tube was then connected to an atmospheric pressure hydrogenation apparatus. Alternate vacuum-hydrogen cycles were used to flush air out of the system, and then benzene was added with a syringe through a septum in the Schlenk tube's sidearm. After two to four more vacuum-hydrogen cycles, the system was stirred at about atmospheric pressure in hydrogen for an hour. The purified alkene to be reduced was then injected so that a total solution volume of 10 ml was reached with the alkene initially at as close to 1 M concentration as practicable. Readings of the system volume with time at atmospheric pressure were then made over a period of 2 to 10 hr at 15 to 30 min intervals. For the $\Delta^2$-cholestene reduction, the steroid was dissolved in 2 ml of deoxygenated benzene and injected as the other alkenes had been; volume readings were made every 30 to 60 min during four 5-hr periods of a 65-hr reduction; 1 ml of cyclohexene was then injected and volume readings were made every half hour (over a 6-hr period). The beads were rinsed with benzene three times and dried between uses. The activity of the catalyst was monitored between olefin runs by measuring the rate of reduction of cyclohexene.

The rates of reduction with various substrates are given in Table 1.

TABLE 1. Rates of Reduction with Various Substrates

| Substrate (1 $\underline{M}$) | Rate (relative to cyclohexene) | $RhCl(P\phi_3)_3$[a] |
|---|---|---|
| Cyclohexene | 1 | 1.0 |
| 1-Hexene | 2.55 | 1.4 |
| $\Delta^2$-Cholestene | 1/32 | 1/1.4 (1/2.3) |
| Octadecene | 1/2.06 | 1/1.4 |
| Cyclooctene | 1/2.54 | 1.0 |
| Cyclododecene (70% cis and 30% trans) | 1/4.45 | 1/1.5 |

[a] Using $RhCl(P\phi_3)_3$ at 2.5 $\underline{mM}$ for a catalyst but with the same procedure and amounts as used for the bead catalyst runs.

Batch B. A. A 10-g sample of these beads was used for an extensive series of reductions (over 75 all together) of a range of unsaturated substrates in varied solvent systems. The same flushing and hour equilibration before alkene injection as used before were used again; the only difference was that the total solution volume used was 40 ml. The beads were again rinsed with benzene and dried between each use.

The reduction rates observed with each substrate are listed in Table 2 (all reductions run in a 25°C constant temperature bath).

B. A 0.5-g portion of Batch B beads was used for reductions of a series of three alkenes in benzene, benzene-ethanol (1:1 vol), and ethanol (Table 3). A solution volume of 20 ml was used, and all other procedures were as noted under A. All reductions were run in a constant temperature bath kept at 25 ± 0.3°C.

## ACKNOWLEDGMENTS

The authors wish to express their appreciation to Drs. J. B. Kinsinger and James L. Dye for their many helpful discussions and to the Research Corporation for partial support of this work.

TABLE 2

| Substrate (1 M) | Relative rate (CHEX) = 1) | Relative rate, $RhCl(P\phi_3)_3$[a] |
|---|---|---|
| 1-Hexene | 0.81 | 1.33 |
| Cyclohexene | 1.00 | 1.00 |
| 4-Pentene-1-ol | 0.82 | 0.7 |
| 4-Pentene-1-ol | 0.43 | (in 1:1 $\phi$H-EtOH) |
| Norbornene | 1.02 | 0.5 |
| 3,5,5-Trimethyl-1-hexene | 0.41 | 0.71 |
| Allyl alcohol | 0.58 | 1.2 |
| 1-Dodecene | 0.57 | 1.17 |

[a] All $RhCl(P\phi_3)_3$ reductions were run as in those run with the Batch A beads, but with 1.0 mM catalyst concentrations. Those values of three significant figures are based on data from at least three reductions.

TABLE 3

| Substrate | Solvent | Relative rate ($\phi$H = CHEX = 1) |
|---|---|---|
| CHEX | $\phi$H | 1.00 |
| CHEX | $\phi$H-EtOH | 4.13 |
| CHEX | EtOH | 3.51 |
| HEX | $\phi$H | 1.25 |
| HEX | $\phi$H-EtOH | 5.48 |
| HEX | EtOH | 4.94 |
| COE | $\phi$H | 0.23 |
| COE | $\phi$H-EtOH | 0.68 |
| COE | EtOH | 0.60 |

## REFERENCES

[1] J. P. Collman, Accounts Chem. Res., 1, 136 (1968).
[2] C. O'Connor and G. Wilkinson, J. Chem. Soc., A, 1968, 2665.
[3] J. E. Bercaw et al., J. Amer. Chem. Soc., 94, 1219 (1972), and references therein.
[4] M. Capka et al., Tetrahedron Lett., 1971, 4787, and references therein.
[5] G. Natta, G. Dall'Asta, G. Mazzanti, and G. Mortoni, Angew. Chem., 76, 765 (1964).
[6] K. W. Pepper, H. M. Paisley, and M. A. Young, J. Chem. Soc., 1953, 4097.
[7] R. B. Merrifield, Science, 150, 178 (1965).
[8] J. E. Freund, Mathematical Statistics, Prentice-Hall, Englewood Cliffs, New Jersey, 1965.
[9] P. Meares, Eur. Polym. J., 1966, 241.
[10] G. H. Douglas et al., J. Chem. Soc., 1959, 1720.
[11] V. A. Nicely and J. L. Dye, J. Chem. Educ., 48, 443 (1971).
[12] C. Tamborski et al., J. Org. Chem., 27, 619 (1962).

Received for publication January 29, 1973