DOE/ER/05563-3

"APPLICATIONS OF FUNCTIONALIZED POLYMERS IN CATALYSIS"

Progress Report 3

July 15, 1979 - July 1, 1980

David E. Bergbreiter

Principal Investigator

Texas A & M Research Foundation
Faculty Exchange Box H
College Station, Texas 77843

July 1, 1980

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. DE-AS05-77ER05563

APPROVED FOR RELEASE OR
PUBLICATION - O.R. PATENT GROUP
BY. GGG...... DATE. 9/6/80

Progress Report Abstract

Research on applications of polymers in catalysis has encompassed three areas: the use of functionalized polymers to detect soluble intermediates in heterogeneous Group VIII metal catalyzed arene hydrogenations; a study of olefin isomerization and hydrogenations catalyzed by polystyrene supported bis(cyclopentadienyl) titanium dichloride and an alkylmagnesium halide; and the acceleration in rate of an olefin hydrogenation catalyzed by homogeneous rhodium and ruthenium complexes as a result of absorption of triphenylphosphine by silver(I) polystyrenesulfonate. The first two studies are complete and the results summarized. The initial results from the third project are discussed.

In the first project we found that polymer bound trapping agents were unable to detect soluble intermediates such as dienes, free radicals, or reducing agents in platinum catalyzed benzene hydrogenation at 60 p.s.i. H_2 and 30°C. The inability to detect diene intermediates was shown to be the result of the lower reactivity of the polymeric reagent versus an active catalyst. The polymer supported titanium catalysts studied were unusual in that immobilization of a catalyst in this case altered the catalyst's specificity relative to its homogeneous counterpart. Preliminary results from the third project are also presented which demonstrate the potential of simple functionalized polymers to improve existing homogeneously catalyzed reactions. Rate increases for olefin hydrogenations using $ClRh(Ph_3P)_3$, $HRh(CO)(Ph_3)_3$, $HRuOAc)(Ph_3P)$, $H_2Ru(Ph_3P)_4$, $Cl_2Ru(Ph_3P)_3$, and $Cl_2Ru(Ph_3P)_4$ were seen and ranged from 25 - 3000%.

PROGRESS REPORT

Introduction

Our original goal in this research project was to demonstrate some of the unique applications possible for functionalized polymers in catalytic reactions. During the first two years of this project we concentrated our studies on the possible utility of organic polymers containing reactive groups as mechanistic probes of heterogeneous Group VIII catalyzed hydrogenation reactions. We were specifically interested in testing for the possible intermediacy (if any) of dienes, monoenes, free radical species, or soluble reducing agents in arene hydrogenations. For reasons outlined below, we have now discontinued this part of our project to concentrate our efforts on more fruitful avenues of research. We also explored the catalytic chemistry of polystyrene bound titanium complexes. These studies focused on reactions of alkenes (isomerization and hydrogenation) catalyzed by polystyrene bound bis(cyclopentadienyl)titanium dichloride which had been allowed to react with an alkyllithium or alkylmagnesium reagent. The results of this completed research are detailed below. Finally, during the past year, our major effort has been directed toward what we believe is a novel and useful application of polymers to homogeneous catalysis. Specifically, we have successfully prepared polymeric cofactors which can be used to activate conventional homogeneous olefin hydrogenation catalysts. Rate accelerations in olefin hydrogenations have been as high as 10-30 fold in some cases.

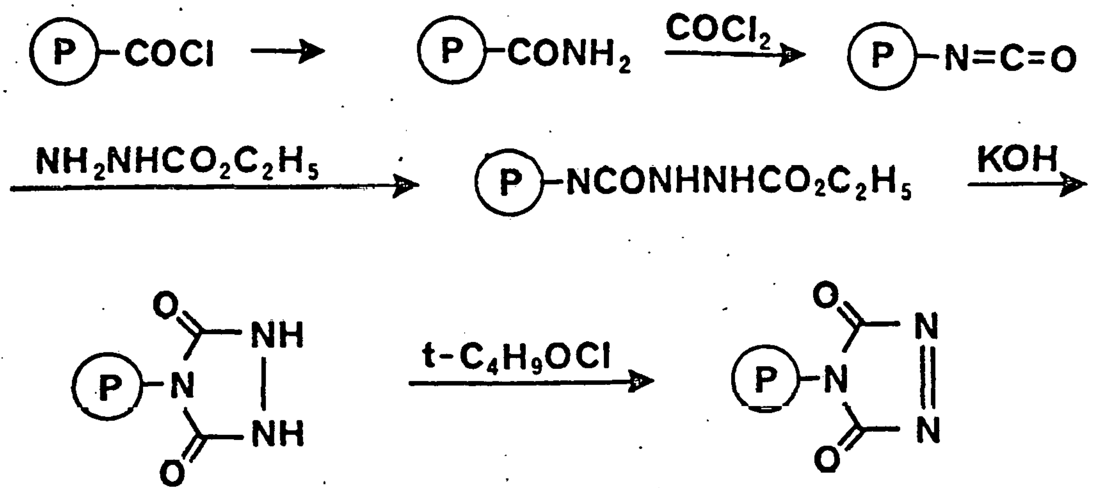
Progress

Polymeric Mechanistic Probes for Heterogeneous Catalytic Reactions

In our original proposal we had suggested that suitably functionalized polymers could be useful for detection of soluble intermediates in heterogeneous catalytic reactions. Indeed, suitably functionalized polymers had been successfully used in "three phase" tests prior to our work to detect reactive intermediates such as cyclobutadiene.[1] In our case, we were interested in trying to prove the presence or absence of soluble intermediates such as free radicals, soluble reducing agents, intermediate dienes, or intermediate monoenes in arene hydrogenations catalyzed by Group VIII metals.[2] We expected to detect such intermediates by adding a polymer containing a reactive trapping agent to an arene hydrogenation. Subsequent isolation of the polymer and cleavage of the trapping agent and any trapped products from the polymer could then be carried out to test for soluble intermediates. Unfortunately, after preparing several different types of polymers and testing for several types of soluble intermediates we only obtained negative evidence. In some cases, the polymeric reagents simply did not have enough reactivity to compete with an active catalyst for such intermediates.

The first polymeric trapping agents we prepared and used were polymer bound nitroxyl radicals. Using literature procedures we prepared polystyrene-bound nitroxyl radicals and polyethylene-bound nitroxyl radicals.[3-5] The polystyrenes used had 2%, 6%, and 20% DVB-crosslinking. The polyethylene was in the form of a low density powder. We were able to successfully show that these polymers could trap free radicals generated from AIBN decomposition. We were also successful at showing that they were susceptible to reduction by at least some reducing agents although the reactivity of the polymeric nitroxyl groups was clearly lower than that of homogeneous analogs.[6] If these polymer bound free radicals successfully trapped radical intermediates or soluble reducing agents in catalytic hydrogenations or arenes, (we studied palladium and mainly platinum catalyzed reactions at less than 100 psi of hydrogen at 30°C) we expected to find alkoxyamines or hydroxyamines as products on the polymers. Although early studies did suggest some reduction of the polymeric nitroxyl groups had occurred (the esr signal diminished ca. 2-3 fold), no reproducible and unambiguous evidence for either free radical or soluble reducing agents as intermediates was obtained. That is, no hydroxylamine or alkoxyamine was ever successfully isolated from the polymer. At these mild reaction conditions of 30°C and under 100 psi of hydrogen we concluded that free radicals and soluble reducing agents were not present or could not be detected by this technique.

We also successfully prepared a polymer bound dienophile, **1**, which we hoped to use as a test for soluble diene intermediates. The homogeneous analog of this polystyrene-bound triazoline-3,5-dione is reputed to be one of the most efficient dienophiles known and had the additional virtue of easy chemical transformation so as to reform the original trapped diene for possible analysis by gas chromatography (equation 1).[7,8] However, when this



1

(1)

polymeric trapping agent was added to a platinum catalyzed arene hydrogenation at 30°C and 60 psi of hydrogen no dienes were trapped. This was shown by isolation of the polymer and lithium aluminum hydride treatment as outlined in equation 1 or by ir spectroscopy of the polymer. Control experiments showed that authentic soluble dienes could be trapped, albeit at relatively slow rates. Isolation of the polymer and LAH treatment did regenerate diene as expected. Separate experiments were then used in this case to show that the lack of trapped diene from an arene hydrogen in the presence of 1 was due to the inactivity of the polymeric trapping agent relative to the activity of the hydrogenation catalyst. In these experiments, diene was added to an ongoing hydrogenation that contained both catalyst and polymeric triazoline-3,5-dione. The failure of the trapping agent to detect simple dienes like cyclohexadiene under these conditions showed the polymer to be ineffective as a mechanistic probe for these intermediates.

Since the above studies employed reactive functional groups on a polymer but still produced ineffectual trapping agents for the applications of interest to this proposal, we concluded that it would be more profitable to apply our limited resources to some of the other research outlined below which was proving to be more productive. Our results in attempting to develop polymer mechanistic probes did, however, underscore some of the limitations of polymers in catalysis. Specifically, the diffusional limitations involved when a crosslinked polymer is used, the modified microenvironment within a polymer matrix which modifies a bound reagent's reactivity, and the difficulties of complex multistep syntheses which must be carried out on insoluble materials each represent significant problems inherent in this application of polymers to heterogeneous catalysis.

Olefin Isomerization and Hydrogenation Catalyzed by Polymer Bound Titanium Catalysts

Polymer immobilization of catalysts has become a fashionable area of research. This is because catalyst immobilization can provide derivatives of mild and selective homogeneous catalysts that have the experimental simplicity of a heterogeneous catalyst. In all but a few cases, immobilization produces catalysts that function similarly to their homogeneous analogs, i.e. the immobilized catalysts catalyze the same reaction as their homogeneous counterparts.[9,10] Thus, it was surprising to find that our studies of the reactions of olefins with reduced titanium species bound to polymers (which are now complete) showed a significant alteration in the specificity of these polymer supported catalysts. Further, these catalysts exhibited rather interesting (but unexplained) effects depending on which reducing agent was used to generate the active catalyst.

Originally we hoped to prepare a polymeric version of the titanium hydrometallation catalyst first described by Finkbeiner and Cooper (equation 2).[11,12] Indeed, while our studies were in progress, catalytic hydroalumination of olefins using the same polymer bound catalyst we discuss below was reported.[13]

$$\mathrm{RCH = CH_2} \quad \xrightarrow[\mathrm{(CH_3)_2CHMgBr}]{\mathrm{cat.\ C_{P_2}TiCl_2}} \quad \mathrm{RCH_2CH_2MgBr} \qquad (2)$$

When we attempted reaction 2 with polystyrene bound bis(cyclopentadienyl) titanium dichloride (2) we saw mainly olefin isomerization and little or no hydrometallation. This olefin isomerization catalyst could be prepared either on a 2% divinylbenzene-crosslinked polystyrene support or on a 20% divinylbenzene-crosslinked polystyrene support.[14] Addition of excess alkylmagnesium bromide or chloride to either polymeric titanium complex suspended in ether resulted in a change in the color of either polymeric titanium complex from an initial red to black. The rate of the color change varied for different alkylmagnesium halides and corresponded roughly to the efficacy of the resulting catalyst (vide infra). Similar color changes were observed on addition of hydrocarbon solutions of n-butyllithium, sec-butyllithium, and tert-butyllithium. The observed color changes were all reversible in that work-up using dilute HCl regenerated the polymers 2.

Addition of a terminal olefin to the catalyst prepared from 2 and an organomagnesium reagent resulted in isomerization of the starting alkene (equation 3). This isomerization was successful with 1-butene, 1-pentene,

$$RCH_2CH{=}CH_2 \xrightarrow[R'MgBr]{Ps\text{-}CpTi(Cp)Cl_2 \quad (2)} \begin{array}{l} RCH{=}CHCH_3 \\ \text{(mainly } E\text{)} \end{array} \qquad (3)$$

and 1-octene. Internal olefins apparently do not react further. In long term experiments in which fresh charges of Grignard reagent and starting alkene were periodically added, turnover numbers (total mmol alkene isomerized/mmol Ti) as high as 1000 were achieved. Less than 15% of the starting alkene formed alkane in contrast to the homogeneous reaction which produced 70% alkane (by protonation on aqueous HCl work-up of an intermediate alkylmagnesium halide).

The relative efficacy of various Grignard reagents for promoting the isomerization was tert-butyl > isopropyl > n-butyl. Methylmagnesium bromide was ineffective at generating an olefin isomerization catalyst. Typical product mixtures from these isomerizations were: 1-octene, E-2-octene (84%), Z-2-octene(12%), n-octane(4%): 1-butene; E-2-butene(72%), Z-2-butene(28%): 1-pentene; E-2-pentene(85%), Z-2-pentene(15%). The starting 1-alkenes were typically completely consumed. Alkyllithium reagents were ineffective at producing this isomerization catalyst although they are known to form olefin hydrogenation catalysts.[15]

Although we typically used gas chromatography to follow these reactions we also found ^{13}C NMR of sealed tubes containing substrate alkene, a Grignard reagent, and polymeric catalyst could conveniently be used to follow these reactions. In these experiments, the polymer and catalyst were not detectable because of line broadening. We believe this procedure could be generally useful in studying reactions involving polymer bound catalysts so long as all substrates and reagents can be contained in an NMR tube.

The reasons for altered catalyst specificity and the cation effect are not known. Nevertheless, our studies show that immobilization of homogeneous catalysts can achieve not only activation and experimental simplicity but also modified catalyst selectivity.

The organomagnesium reduced catalysts described above differ in their activity as olefin isomerization catalysts compared to organolithium reduced catalysts. Earlier, Grubbs and Brubaker had described the increased hydrogenation activity of polymer supported bis(cyclopentadienyl)titanium dichloride which had been reduced with n-butyllithium.[15] Compared to soluble systems, the polymer bound catalysts Grubbs and Brubaker prepared were 10-20x more active. This increased activity was originally ascribed to site isolation of "titanocene" on the highly crosslinked (20% DVB) polystyrene used as a support. Since our catalysts seemed to differ from these organolithium reduced catalysts, we decided to also briefly investigate the activity of an organomagnesium reduced polymeric Cp_2TiCl_2 as a hydrogenation catalyst for olefins.

When terminal alkenes were added to the catalysts we had previously used for olefin isomerization under hydrogen, hydrogenation occurred. Typically the initial rates of styrene hydrogenation were 2-4 times faster than those of an organolithium reduced catalyst. However, the reaction rates all decreased fairly rapidly over a 30 min period. The earlier relationships between the nature of the reducing agent (prim-, sec-, or tert-alkylmagnesium reagents) were not as pronounced in hydrogenation catalysts. In this case, the most active catalyst was that prepared using cyclohexylmagnesium bromide as a reducing agent although the tert-butylmagnesium reduced catalyst was nearly as reactive (initial rates of ca. 20 mmol H_2/mmol Ti-min, and 18 mmol H_2/mmol Ti-min, respectively. No effect was seen on changing from a polymer support that was 20% versus 2% DVB-crosslinked polystyrene. As was seen in the case of the olefin isomerization reaction, internal alkenes were unreactive. Cyclohexene was not reduced over a 12 h time period under conditions where a comparable amount of styrene was completely reduced in 10 min. Unexpectedly, the polymeric hydrogenation catalyst prepared from the polymeric titanium(IV) precursor and a Grignard reagent was substantially less active as an olefin hydrogenation catalyst than its soluble analog. Although the homogeneous catalyst solution in this case hydrogenated styrene at a rate ca. 10x faster than the polymer supported catalyst, the homogeneous catalyst also deactivated rather rapidly.

The active species on the polymer resin in either the isomerization or hydrogenation reactions has not been characterized. In part, this is because immobilized catalysts are as difficult and intractable to examine and study as are ordinary heterogeneous catalysts. Since the results seem to suggest involvement of both the magnesium and the alkyl group with the active catalyst center, some sort of ate complex like those described a decade ago[16] by Brintzinger may be the actual active catalyst in these reactions.

We have shown several things in our studies of olefin reactions catalyzed by polymer bound titanium catalysts. First, it is possible to ① alter catalyst activity through polymer immobilization. If the reasons for altered activity were understood and if alteration in catalyst activity could be systematically controlled, such effects could become an additional and substantial advantage for immobilized catalysts. Second, our results further illustrate the ② complexities of using catalysts that are present in a polymer matrix in that processes established in solution may occur with very different relative rates using polymeric catalysts.

Polymeric Cofactors for Homogeneous Catalysts

The major thrust of our research during the past year has been directed toward this application of polymers in catalysis. We believe this is a unique and novel application of polymeric reagents to catalysis which could be of general utility and applicability. The basic idea underlying this work is that polymeric reagents can be used to modify homogeneous catalysts in unique ways so as to produce more active species. An example of such an interaction would be the removal of a nonvolatile triphenylphosphine ligand from a transition metal complex to produce a more coordinatively unsaturated and, hence, more active catalyst in situ. We had hoped to design a polymer that could absorb such a nonvolatile phosphine ligand selectively without deleterious interaction with a catalyst. This has been accomplished. We further expected that in some cases rate accelerations would be seen for conventional homogeneously catalyzed reactions like olefin hydrogenations. We now have approximately 10 examples of such rate accelerations ranging from 25 - 3000%. Specific details about the polymeric phosphine absorbers used and catalytic systems studied are described below.

We initially set out to prepare a polymeric phosphine absorber because of the known tendency for transition metal phosphine complexes to dissociate triphenylphosphine in equilibria like equation 4.[17] Such equilibria typically favor the more coordinatively saturated species.

$$X_mML_n \rightleftarrows X_mML_{n-1} + L \qquad (4)$$

However, the less coordinatively saturated complex is often more active as a catalyst. Thus, if we selectively removed triphenylphosphine from a solution of a catalytically active transition metal phosphine complex, we would shift equilibrium 4 and in this manner increase the catalytic activity of a conventional homogeneous catalyst. To do this we sought to prepare an appropriate polymeric phosphine absorber. Such a polymeric phosphine absorber should meet several criteria. First, it should not be catalytically active itself. Second, it should not affect the homogeneous catalyst either by poisoning it or absorbing it from solution. Third, it must be efficient at removing triphenylphosphine from solution to operate effectively on the time scale of a catalytic reaction. Fourth, such a polymer should be reasonably stable, simple to prepare and experimentally easy to use. The polymers we found to be most useful in this regard were simple metal salts of polystyrenesulfonic acid. We used a commercially available ion exchange resin (Amberlyst 15) to prepare this phosphine absorbing polymer. This type of ion exchange resin is a macroreticular polymer with large (400 Å) pores to facilitate its application to nonaqueous solution chemistry. Unexceptional procedures were used to exchange metal cations onto this polymer.[18] These metal ion containing polymers were checked for triphenylphosphine absorption by observing the change in triphenylphosphine concentration in THF or acetone solution by ^{1}H nmr. Results of these experiments are summarized in Table I. ~~Silver(I) polystyrenesulfonate was clearly the most efficient phosphine absorber, and~~ this polymer was used in subsequent studies.

TABLE 1. Absorption of PPh_3 by Metal-Ion Substituted Polystyrenesulfonate

Metal Ion	%PPh_3 Absorbed from 0.04 M THF Solution (12 h)
Co^{+3}	0
Co^{+2}	10
Ni^{+2}	10
Cu^{+2}	50
Ag_+	100 (1 h)

Initial results for hydrogenations of styrene, cyclohexene, and 1-octene using $ClRh(Ph_3P)_3$ as a homogeneous catalyst in the presence of silver(I) polystyrenesulfonate beads ("beads") were somewhat disappointing. Wilkinson's catalyst is one of the best studied homogeneous olefin hydrogenation catalysts[19] and we initially felt that it would be a good system to test our proposal because of the known importance of coordinatively unsaturated complexes (formed by phosphine dissociation) in the catalytic cycle.[20] Apparently the silver(I) centers on the polymer do not compete effectively with soluble $ClRh(Ph_3P)_2$ (or the corresponding dihydride) for free triphenylphosphine ligand. Nevertheless, we were able to demonstrate that the silver(I) polymer did absorb triphenylphosphine selectively from solutions of $ClRh(Ph_3P)_3$ in toluene. It is known that Wilkinson's catalyst in solution will slowly form dimer at low concentrations of triphenylphosphine.[21] We found dimer formation was accelerated in the presence of "beads." This dimer formation was observed both by ^{31}P NMR and by the formation of small pale red crystals in the previously homogeneous solution.[22] Under conditions of catalysis (H_2 atmosphere), dimer formation does not occur even in the presence of beads presumably because of the formation of $H_2RhCl(Ph_3P)_3$ which dissociates to a smaller extent and has a concomitantly smaller tendency to dimerize. Other evidence for absorption of triphenylphosphine from solutions of Wilkinson's catalyst comes from experiments in which hydrogenation of styrene was carried out in the presence of excess triphenylphosphine, a known poison of this homogeneous catalyst. Figure I shows the rate of a styrene hydrogenation without and with added triphenylphosphine. When "beads" were added to the poisoned reaction at the point indicated by the arrow, the rate of hydrogenation increased to that observed in the absence of excess ligand. Taken together, these experiments show that the phosphine absorbing polymer does absorb triphenylphosphine without interacting deleteriously with Wilkinson's catalyst.

To insure that the effects we were seeing did indeed reflect the unique properties of a polymeric phosphine absorbing agent, we also added silver(I) p-toluenesulfonate to a solution of styrene, $ClRh(Ph_3P)_3$, and hydrogen. The catalysis quickly stopped and a black insoluble precipitate formed. Apparently the polymeric structure of our additive avoids this unwanted side reaction in accord with our expectations.

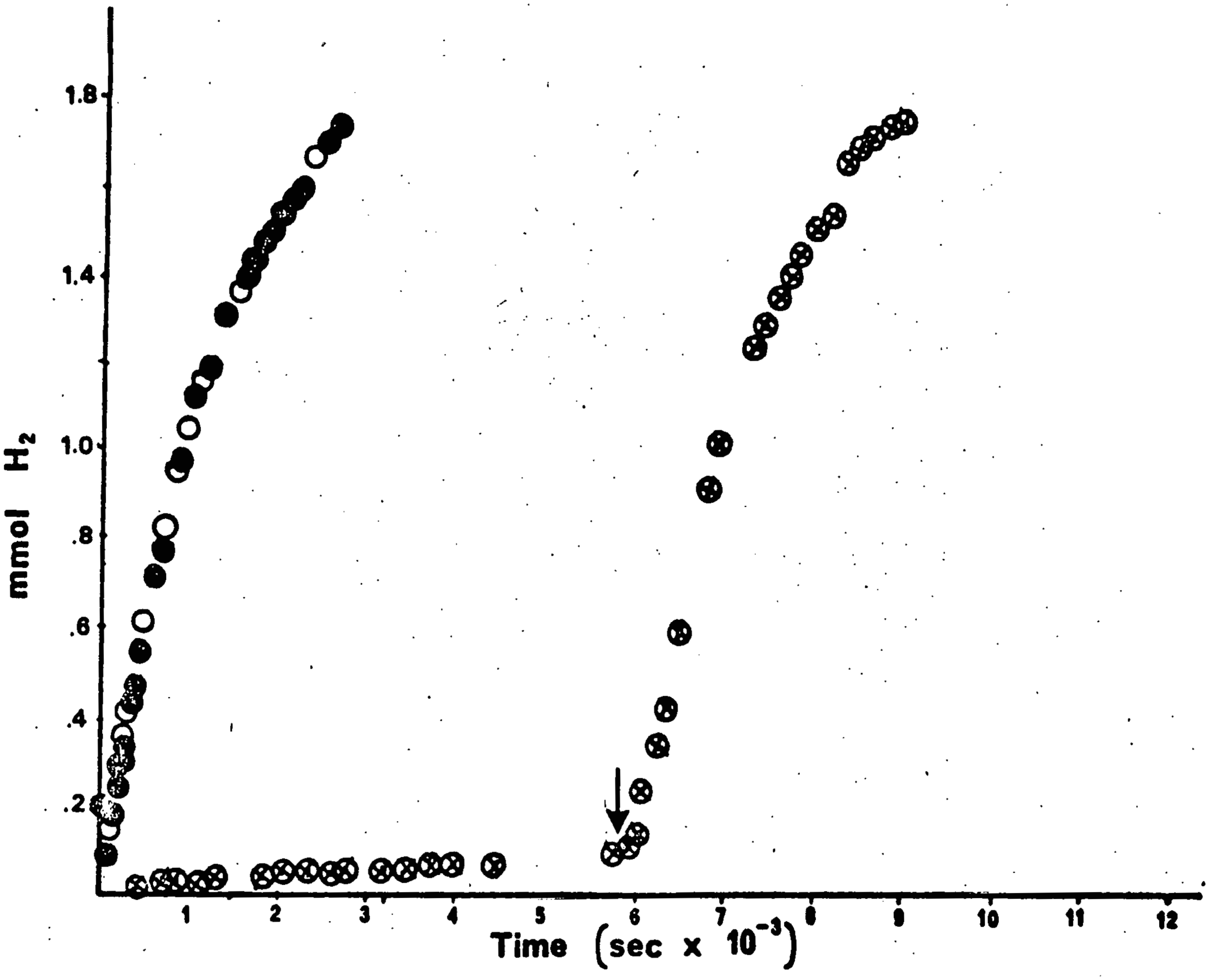


Figure 1. Hydrogenations of styrene (0.11 $\underline{M}$) catalyzed by 2.3 x 10^{-3} $\underline{M}$ $ClRh(Ph_3P)_3$ in toluene at 25.0°C in the absence of both beads of silver(I) polystyrene sulfonate and any excess triphenylphosphine (●), in the presence of beads of silver(I) polystyrene sulfonate (O), and in the presence of excess triphenylphosphine (1.6 x 10^{-2} $\underline{M}$) (⊗). The effect of rate acceleration in the latter experiments reflects addition of beads of silver(I) polystyrene sulfonate at 5900 sec (arrow in figure).

The inability of silver(I) polystyrenesulfonate to effectively compete for the dissociated triphenylphosphine ligand appeared to be the reason for lack of any enhanced hydrogenation rate in presence of silver(I) polystyrenesulfonate. Therefore, displacement of a triphenylphosphine ligand prior to catalysis in the presence of "beads" might lead to enhanced hydrogenation activity. Fortunately,[23] $ClRh(Ph_3P)_3$, which is only a poor hydrogenation catalyst for ethylene, reversibly forms a π-complex with ethylene; this is stable in solution only under an ethylene atmosphere.[24] In the event, $ClRh(Ph_3P)_3$ was dissolved under ethylene

$$3\ ClRh(Ph_3P)_3 + C_2H_4 \rightleftarrows (C_2H_4)Rh(Ph_3P)_2 + Ph_3P \quad K_{eq} \cong 0.4 \tag{5}$$

atmosphere in presence of "beads;" after 900 s another alkene was added and after 1000 s the ethylene was removed under vacuo. The resulting suspension hydrogenated various alkenes from 1.3 to 12 times faster than a solution which underwent ethylene pretreatment in absence of "beads" or a $RhClL_3$ solution which contained no polymeric reagent and did not undergo ethylene pretreatment, i.e., an unmodified hydrogenation (Table II). Apparently, ethylene displaces triphenylphosphine from $RhClL_3$, allowing triphenylphosphine to be absorbed by the "beads" while preventing dimerization of $ClRh(Ph_3P)_2$. Addition of alkene and removal of ethylene allows formation of a $ClRh(Ph_3P)_2$(alkene) complex. Hydrogenation then occurs at a faster rate. The rate enhancement observed is greatest for those alkenes which form strong complexes with rhodium and are slowly hydrogenated consistent with formation of a higher concentration of $ClRh(Ph_3P)_2$(alkene) in solution than would be found in presence of "beads" but in absence of ethylene pretreatment.

Application of ligand absorbing polymers to other conventional homogeneous catalysts have also led to rate increases in hydrogenation of olefins. For example, when styrene hydrogenation catalyzed by $HRh(CO)(Ph_3P)_3$ was carried out in the presence of silver(I) polystyrenesulfonate, a 1.3-1.4 fold rate increase was seen. This rate increase was seen in over twenty separate experiments at various concentrations of catalyst (below 3×10^{-3} M hydrogenation rates were not appreciably affected by the presence of "beads") and was determined after the catalysis had proceeded for 10 min.

Table II. Hydrogenation of alkenes by $ClRh(PPh_3)_3$ after ethylene pretreatment.[a]

alkene	[alkene], $\underline{M}$	rate in presence of polymer[b]	rate in absence of polymer[b]	rate enhancement
1-hexene	0.35	23.9	12.2	1.96
cyclohexene	0.29	18.1	13.4	1.35
norbornene	1.03	36.6	21.3	1.72
norbornadiene	1.09	4.23	0.35	12.1
ethylene	--	4.4	0.74	5.8
styrene	0.21	60.	60.	1.0

[a] $ClRh(PPh_3)_3$ (3 $m\underline{M}$) was dissolved in toluene under ethylene (one atmosphere), the alkene to be hydrogenated was introduced, and the solution was degassed three times. Hydrogen was then added and maintained at one atmosphere. All reactions were carried out at a constant temperature of 25.0°C. [b] "Polymer" refers to silver(I) polystyrenesulfonate; the rate is expressed as mmol hydrogen consumed/$[ClRh)PPh_3)_3]\cdot$ min.

Earlier studies with this catalyst had suggested that phosphine dissociation was an important step in hydrogenation reactions catalyzed by $HRh(CO)(Ph_3P)_3$.[25] Our results could therefore be explained by assuming phosphine absorption in this case.

A brief survey of other catalysts for possible activation has been carried out. The preliminary results show that modest accelerations of olefin hydrogenations can be achieved in many systems. Catalysts examined in this survey included $Cl_2Ru(Ph_3P)_3$, $Cl_2Ru(Ph_2P)_4$, $H_2Ru(Ph_3P)_4$, $HRh(Ph_3P)_4$, $HRu(OAc)(Ph_3)_3$, $ClIr(CO)(Ph_3P)_2$ and $ClRh(EtPh_2P)_3$.[26] Rate accelerations varied up to about 200% and are the result of only a few experiments in each case. It is quite possible that more extensive studies as were carried out with the rhodium systems would produce more dramatic results.

The most interesting of the other catalysts surveyed for rate accelerations were $Cl_2Ru(Ph_3P)_3$ and $Cl_2Ru(Ph_3P)_4$. Significant rate accelerations were seen for both catalysts. The largest rate increase was seen for the tetrakis-(triphenylphosphine) complex. In this case, addition of silver(I) polystyrenesulfonate to 1-hexene (0.3 M, 1.6 M) hydrogenation catalyzed by 3×10^{-3} M solutions of $Cl_2Ru((Ph)_3P)_4$ in toluene led to thirty-fold rate increases. However, in this case we could not rule out the possibility that silver(I) polystyrenesulfonate merely promotes formation of the very active hydrogenation catalyst $HClRu(Ph_3P)_3$ by removal of both a triphenylphosphine ligand and chloride (from hydrogen chloride) anion.[27] We have briefly explored this possibility by using an anion exchange resin in its hydroxide form (Dowex 21x) and neutral alumina, both of which could be expected to be efficacious at removing HCl. A rate acceleration was seen in each of these cases but was less than that seen with the triarylphosphine absorbing polymer beads, suggesting that ligand absorption of triphenylphosphine is also a factor in activation of $Cl_2Ru(Ph_3P)_4$ catalyzed hydrogenations using silver(I) polystyrenesulfonate. Hydrogenations of 1-hexene using $Cl_2Ru(Ph_3P)_3$ were also studied. In these latter cases 20-fold rate accelerations for 1-hexene hydrogenation were seen. However, the absolute rate (based on Ru concentration) was typically less for this tris(triphenylphosphine) complex. Further study is continuing to understand the origin of these rate differences.

In summary, our research has encompassed three different projects. The first project studied the efficacy of polymers containing groups designed to intercept possible soluble intermediates in a heterogeneous hydrogenation reaction. Although several types of functionalized polymers were prepared and shown to be reactive toward the intermediates in question, the functionalized polymers could not be shown to be competitive with an active catalyst for trapping reactive intermediates. The second project which has been completed produced unexpected results showing that polymer immobilization of catalysts may alter both the reactivity and selectivity of a homogeneous catalyst. The chemistry of the olefin isomerization and hydrogenation catalysts studied and the effects of the reducing agent on catalyst activity are very interesting and warrant further investigation, especially in view of the renewed interest in the chemistry of olefins and early transition metals. Finally, our more recent work has produced a novel and generally useful polymeric additive for homogeneous catalysts that removes nonvolatile triphenylphosphine ligands *in situ* without interacting with the catalytically active complex. Application of polymers to catalysis in this manner is a new idea which we think has significant promise. Our demonstrations of 12-fold increases in hydrogenation rates using $ClRh(Ph_3P)_3$, 30-fold increases in hydrogenation rates for $Cl_2Ru(Ph_3P)_4$ and modest rates with many other catalysts are preliminary results which clearly show the potential of this concept.

References

1. J. Rebek, Jr., *Tetrahedron*, 35, 723 (1979).

2. G. C. Bond and B. P. Wells, *Adv. Catal.*, 15, 91 (1964); S. Siegel, *Adv. Catal.*, 16, 123 (1966); A. W. Weitkamp, *Adv. Catal.*, 18, 2 (1968); and F. Hartog, J. H. Tebben, and C. A. M. Weterings, *Proc. Int. Congr. Catal.*, *3rd.*, 2, 1210 (1965).

3. Nitroxyl spin labels have been previously attached to polystyrene, cf. S. L. Regen, *J. Am. Chem. Soc.*, 99, 3838 (1977) and references therein. In our case, we used ester and amide bonds to attach the nitroxyl spin labels to this polymer.

4. J. R. Rasmussen, E. R. Stedronsky, and G. M. Whitesides, *J. Am. Chem. Soc.*, 99, 4736 (1977); and J. R. Rasmussen, D. E. Bergbreiter, and G. M. Whitesides, *J. Am. Chem. Soc.*, 99, 4746 (1977).

5. The attachment of nitroxyl spin labels to polystyrene and polyethylene by ester and amide bonds was verified by ESR and IR spectroscopy after extraction of the functionalized polymers (ethanol, 24 h).

6. The results of these experiments were summarized in Progress Report 2 for this proposal.

7. B. T. Gillis and J. D. Hagarty, *J. Org. Chem.*, 32, 330 (1967).

8. D. H. R. Barton, T. Shiori, and D. A. Widdowson, *J. Chem. Soc. (C)*, 1968 (1971).

9. Y. Chauvin, D. Commereuc and F. Dawans, *Prog. Polym. Sci.*, 5, 95 (1977); and G. Manecke and P. Reuter, *Pure Appl. Chem.*, 51, 2313 (1979).

10. P. Perkins and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 101, 3985 (1979). There is a possibility that metal(0) may be the catalytic species in this catalyst.

11. G. D. Cooper and H. L. Finkbeiner, *J. Org. Chem.*, 27, 1493 (1962); and G. D. Cooper and H. L. Finkbeiner, *J. Org. Chem.*, 27, 3395 (1962).

12. For a recent synthetic application of this procedure see J. J. Eisch and J. H. Merkley, *J. Am. Chem. Soc.*, 101, 1148 (1979).

13. E. C. Ashby and S. A. Noding, *J. Org. Chem.*, 44, 4364 (1979).

14. The catalyst is commercially available on 20% DVB-crosslinked polystyrene and was purchased from Strem Chemicals, Newburyport, Massachusetts.

15. R. H. Grubbs, C. Gibbons, L. C. Kroll, W. D. Bonds, Jr. and C. H. Brubaker, Jr., *J. Am. Chem. Soc.*, 95, 2373 (1973); and W. D. Bonds, Jr., C. H. Brubaker, Jr., E. S. Chandrasekaran, C. Gibbons, R. H. Grubbs, and L. C. Kroll, *J. Am. Chem. Soc.*, 97, 2128 (1975); and R. Grubbs, C. P. Lau, and C. Brubaker, Jr., *J. Am. Chem. Soc.*, 99, 4519 (1977).

16. J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Am. Chem. Soc.*, 94, 1219 (1972) and references to earlier work cited therein.

17. B. R. James, "Homogeneous Hrdrogenation"; John Wiley & Sons: New York, 1973; and G. W. Parshall, "Homogeneous Catalysis"; John Wiley & Sons: New York, 1980.

18. K. Dorfner, "Ion Exchangers: Properties and Applications"; Ann Arbor Science Publishers, Inc.: Ann Arbor, Michigan, 1973.

19. G. Dolcetti, N. W. Hoffman, *Inorg. Chem. Acta.*, 9, 269 (1974); R. E. Harmon, S. K. Gupta, and D. J. Brown, *Chem. Rev.*, 73, 21 (1973).

20. D. D. Lehman, D. F. Shriver, and I. Wharf, *J. Chem. Soc., Chem. Commun.*, 1486 (1979); H. Arai and J. Halpern, *J. Chem. Soc., Chem. Commun.*, 1571 (1971); D. R. Eaton and S. R. Stuart, *J. Am. Chem. Soc.*, 90, 4170 (1968); P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc.*, 97, 4221, (1975); and J. Halpern, T. Okamoto, and A Zakhariev, *J. Molecular Catal.*, 2, 65 (1976) and references in each.

21. S. H. Strauss and D. F. Shriver, *Inorg. Chem.*, 17, 3069 (1978); R. A. Porter and D. F. Shriver, *J. Organometal. Chem.*, 90, 41 (1975); and M. Hidai, T. Kuse, T. Hidita, Y. Uchida, and A. Misono, *Tetrahedron Lett.*, 1715 (1970).

22. ^{31}P NMR spectra were similar to those reported for the more soluble dimer containing a tri-*p*-tolylphosphine ligand (reference 24).

23. Y. Ohtain, A. Yamagishi, and M. Fujumoto, *Bull Chem. Soc. Jpn.*, 52, 2149 (1979).

24. C. A. Tolman, P. S. Meakin, D. L. Lindmer, and J. P. Jesson, *J. Am. Chem. Soc.*, 96, 2762 (1974); and Y. Ohtain, A Yamagishi, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, 52, 69 (1979); 52, 1537 (1979); 52, 3437 (1979); and 50, 1453 (1977).

25. C. O'Connor and G. Wilkinson, *J. Chem. Soc. (A)*, 2660, (1968); 2665 (1968).

26. No rate acceleration was seen in preliminary experiments using either $ClIr(CO)(Ph_3P)_2$ or $ClRh(EtPh_2P)_3$.

27. P. S. Hallmann, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. (A)*, 3143 (1968).

PRESENTATIONS AND PUBLICATIONS

Presentations

David E. Bergbreiter, M. S. Bursten, and Gregory L. Parsons, an invited paper at a symposium entitled "Heterophase Attached Homogeneous Catalysis," Houston American Chemical Society Meeting, March 25, 1980.

This DOE sponsored research was also discussed during two industrial seminars at Bell Laboratories, Murray Hill, N.J., December 1979, and Gulf Oil, Houston, Texas, February 1980.

"Polymeric Cofactors for Homogeneous Catalysis," D. E. Bergbreiter, M. S. Bursten, and G. L. Parsons, plenary lecture presented June 13 at the First China-Japan-United-States Seminar on Organometallic Chemistry, June 13, 1980, in Beijing, China.

Publications

"Polymeric Cofactors for Homogeneous Catalysis", D. E. Bergbreiter and M. S. Bursten, submitted for publication to J. Am. Chem. Soc.

"Polymer-Bound Titanium Olefin Isomerization Catalysts", D. E. Bergbreiter and G. L. Parsons, submitted for publication to J. Organometal. Chem.

"Rate Accelerating Polymeric Cofactors in Homogeneous Hydrogenation of Alkenes", D. E. Bergbreiter and M. S. Bursten, submitted to Macromolecular Science - Chemistry.

"The Crystal Structure of Dichlorobis(triphenylphosphine)norbornadiene)ruthenium," D. E. Bergbreiter, B. Bursten, M. S. Bursten, and F. A. Cotton, submitted to J. Organometal. Chem.