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Structural Effects of Cross-Linking in Polymer-Bound Bromotris(triphenylphosphine)rhodium(I) Catalyst by X-Ray Absorption Studies

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Received August 5, 1977*

Abstract: The influence of cross-linking by divinylbenzene (DVB) in styrene polymer-bound bromotris(triphenylphosphine)-rhodium(I) catalyst has been studied by extended x-ray absorption fine structure (EXAFS) spectroscopy. We report here that the 2% DVB cross-linked polymer-bound rhodium catalyst has two phosphorus atoms at 2.16 (1) and 2.32 (1) Å and two bromine atoms at 2.49 (1) Å as nearest neighbors to the rhodium atom thereby consistent with a dimeric structure. On the other hand, the 20% DVB cross-linked polymer-bound catalyst is found to be a four-coordinate polymer-attached monomer with three phosphorus atoms, one at 2.14 (1) Å and two at 2.26 (1) Å, and one bromine atom at 2.50 (1) Å from the rhodium atom. This study suggests that there is probably some degree of cross-linking between 2 and 20% which is optimum in catalytic activity, and that not all the phosphorus atoms are polymer bound.

Introduction

In a recent communication,[1] we demonstrated that extended x-ray absorption fine structure (EXAFS) could be used to determine the interatomic distances and coordination of Wilkinson's catalyst, $RhCl(PPh_3)_3$,[2-4] and polymer-bound Wilkinson's catalyst.[5] It was reported that polymer-bound Wilkinson's catalyst was a chloro-bridged dimer. This polymer-bound catalytic dimer was supported on a polystyrene cross-linked with 2% divinylbenzene (DVB) skeleton.

One of the major catalytic influences in polymer-bound catalyst is the degree of cross-linking of styrene by divinylbenzene.[6] Our previous results suggest that cross-linking of 1-2% produces dimeric structures inside the swellable insoluble polymer gel where the polymer molecule is mobile enough to form chelates resulting in dimers of the rhodium complex attached to the phosphinated resin support. However, it has been proposed that higher cross-linking in the 20% range renders the ligands attached to this polymer resin less mobile and more brittle.

The catalytic activity generally decreases when the homogeneous catalytic analogue is bound to the polymer framework.[6] We suggested[1] that one of the reasons for the slower rate of hydrogenation could be the formation of the catalytically less active halogen-bridged dimer.[7] In contrast, it has been shown that a high degree of cross-linking could help break up any aggregates formed.[6]

We report a study of the structural changes found in 2% DVB–styrene and 20% DVB–styrene polymer-bound $RhBr(PPh_3)_3$ catalyst[25] by the technique of extended x-ray absorption fine structure (EXAFS). The polymer-bound bromotris(triphenylphosphine)rhodium(I) was chosen both because its structure was unknown and because measurements can be done on both Rh and Br as absorbers to give indepen-

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dent measurements for the Rh–Br bond distance. This x-ray absorption technique for the determination of interatomic distances has been used previously to determine bond distances in iron–sulfur proteins,[8] copper salts in aqueous solutions,[9] and in polymer-bound rhodium(I) catalysts.[1]

Experimental Section

The 2% and 20% DVB–styrene polymer-bound $RhBr(PPh_3)_3$ catalyst was purchased from Strem Chemicals. It was prepared by a method similar to that in ref 5 which involved refluxing benzene containing $RhBr(PPh_3)_3$ and the particular cross-linked phosphinated polystyrene resin. The analyses of the polymer-bound resin were the following: 2% cross-linked catalyst, 17.5% P and 2.28% Rh; 20% cross-linked catalyst, 6.5% P an 1.47% Rh.

The photoabsorption K edges of Rh and of Br in 2% and 20% DVB–styrene polymer-bound bromotris(triphenylphosphine)rhodium(I) catalyst were measured using the tunable x-ray synchrotron source at the Stanford Synchrotron Radiation Project, Stanford University. The instrumentation has been previously described.[10,11]

The relationship $\mu x = \ln (I_0/I)$, where μ is the linear absorption coefficient and x is the thickness, is obtained by measuring the intensity of the incident x-ray radiation I_0 passing through an ionization chamber (He + N_2), then transmitted through the sample, and finally monitoring I, the transmitted intensity, by a second ionization chamber (N_2). The absorption is then plotted against the photon energy.

As early as 1931, Kronig proposed the first theory of EXAFS in solids.[12] The current theoretical basis for the EXAFS effect has been advanced by several groups.[13-17] Various methods of data analysis have been published.[16,18-20]

It has been shown[14,16,18,21] that the modulation $\Delta\mu$ of the x-ray absorption coefficient of an atom is given by

$$\frac{\Delta\mu}{\mu} = \sum_j \frac{-N_j |f_j(k,\pi)|}{R_j^2 k} e^{-2\sigma_j^2 k^2} \sin(2kR_j + \phi_j(k)) \qquad (1)$$

where N_j is the number of scattering atoms j at a distance R_j from the absorbing atom with a Debye–Waller-like factor $e^{-2\sigma_j^2 k^2}$. The
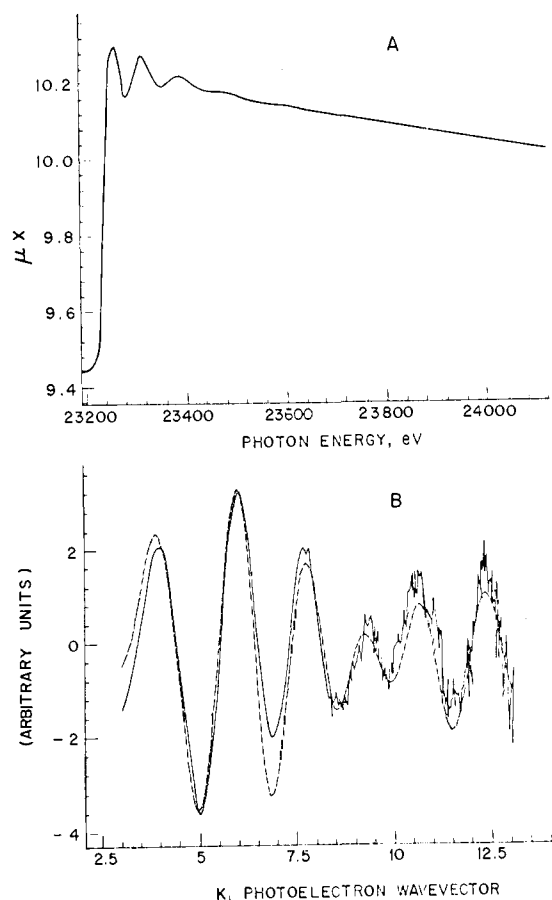
Figure 1. A. The data for 2% DVB–styrene where $\mu x = \log I_0/I$ is plotted against photon energy. B. The raw EXAFS (—) and Fourier filtered EXAFS (- - -) for 2% DVB–styrene polymer-bound catalyst.
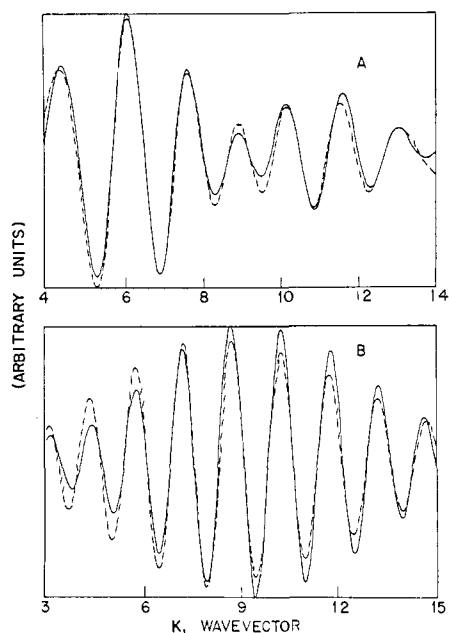

Figure 2. A. The fit (- - -) of the EXAFS data (—) of 2% cross-linked DVB–styrene polymer-bound RhBr(PPh₃)₃ catalyst where Rh is the absorber. B. The fit (- - -) of the EXAFS data (—) of 2% cross-linked DVB–styrene polymer-bound RhBr(PPh₃)₃ catalyst where Br is the absorber.

$\phi_j(k)$ and $f_j(k,\pi)$ are an energy-dependent phase shift and an electron backscattering form factor, respectively. The conversion from photon energy to photoelectron wave vector k is given by $k = (2m(E -$
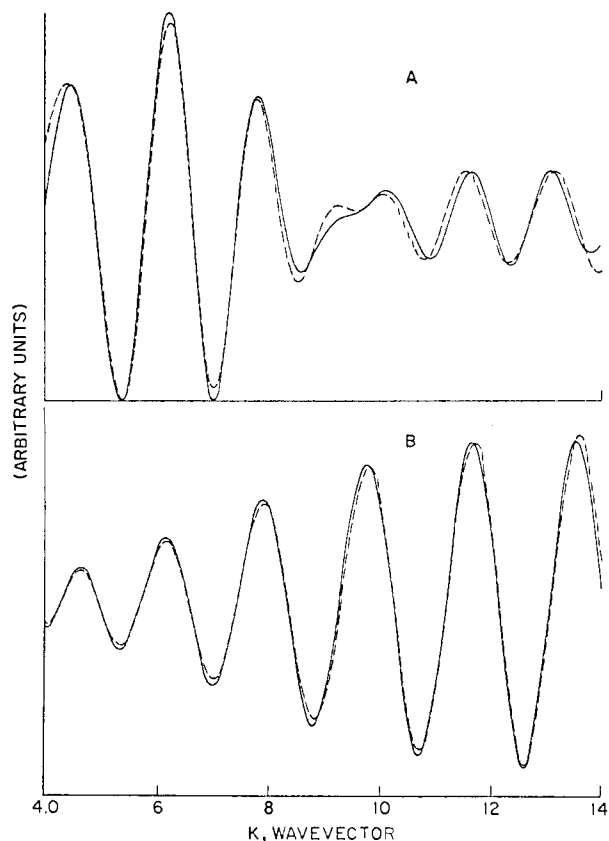

Figure 3. A. The fit (- - -) of the EXAFS data (—) of 20% cross-linked DVB–styrene polymer-bound RhBr(PPh₃)₃ catalyst where Rh is the absorber. B. The fit (- - -) of the EXAFS data (—) of 20% cross-linked DVB–styrene polymer-bound RhBr(PPh₃)₃ catalyst. where Br is the absorber.

$E_0))^{1/2}/\hbar$, where E is the photoelectron energy, which is varied in the present study.

Figure 1A depicts the data, $\log I_0/I$ vs. energy near the Rh absorption edge, and Figure 1B shows the raw EXAFS data for 2% DVB–styrene polymer-bound RhBr(PPh₃)₃ with the Fourier filtered data superimposed over the raw EXAFS data. Figures 2 and 3 show the EXAFS data for 2 and 20% polymer-bound rhodium(I) catalysts, respectively. In Figures 2A and 3A, rhodium is the absorber in 2 and 20% cross-linked species, respectively, whereas in Figures 2B and 3B, bromine is the absorber in the 2 and 20% cross-linked species where the absorption (arbitrary units) is plotted against k, the photoelectron wave vector after the background absorption has been removed. The threshold energy E_0 was initially chosen in a systematic way for both Rh and Br edges at the first maximum of the absorption curve.

In the next step in the data analysis,[21] EXAFS of Rh (Figure 4) and Br (Figure 5) in 2 and 20% cross-linked polymer-bound rhodium(I) catalyst were inverted by Fourier transforms giving the results shown in Figures 4 and 5. The curve fitting of the Fourier filtered data (Figures 2 and 3) is based on transferability[18-21] of theoretical phase shifts[19] and of theoretical amplitudes.[20] It was shown previously that theoretical phase shifts ϕ_j and amplitudes f_j can be used to accurately predict interatomic distances ± 0.01 Å in known single-distance systems.[13,19]

In the data analysis, N_j and R_j for 2 and 20% cross-linked polymer catalyst were determined by fitting each of the Fourier filtered data (Figures 2 and 3) which included only nearest-neighbor contributions as predominant peaks in the Fourier transforms (Figures 4 and 5) with the function

$$\frac{\Delta\mu}{\mu} = N_{P_1} \sin\left(2kR_{P_1} + \phi_P(k)\right)f_P(k)e^{-2\sigma P^2_1 k^2}$$

$$+ N_{P_2} \sin\left(2kR_{P_2} + \phi_P(k)\right)f_P(k)e^{-2\sigma P^2_2 k^2}$$

$$+ N_{Br} \sin\left(2kR_{Br} + \phi_{Br}(k)\right)f_{Br}(k)e^{-2\sigma Br^2 k^2} \quad (2)$$

Table I

	Distances,[a] Å Rh EXAFS			Distances,[c] Å Br EXAFS	
	Rh–P$_1$	Rh–P$_2$	Rh–Br	Br–Rh[a]	Br–Rh[b]
2% cross-linked polymer-bound catalyst	[1][d] 2.16 (1)	[1][d] 2.32 (1)	[2][d] 2.49 (1)	2.50 (1)	2.506 (4)
20% cross-linked polymer-bound catalyst	[1][d] 2.14 (1)	[2][d] 2.26 (1)	[1][d] 2.49 (1)	2.50 (1)	2.485 (8)

[a] The distances were obtained by fitting the data with the function in eq 1. [b] The distances were obtained by an empirical data analysis technique. [c] The data give a single frequency for Br EXAFS. [d] Number of bonds of this type.
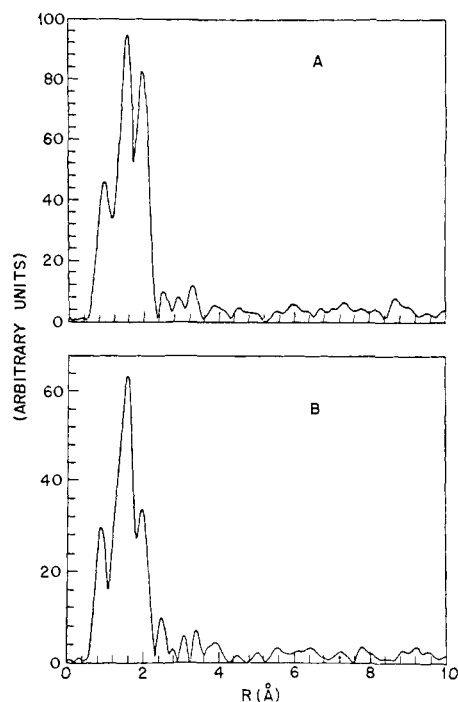

Figure 4. A. Fourier transform of the EXAFS data of 2% cross-linked DVB–styrene polymer-bound RhBr(PPh$_3$)$_3$ catalyst where Rh is the absorber. B. Fourier transform of the EXAFS data of 20% cross-linked DVB–styrene polymer-bound RhBr(PPh$_3$)$_3$ catalyst where Rh is the absorber.
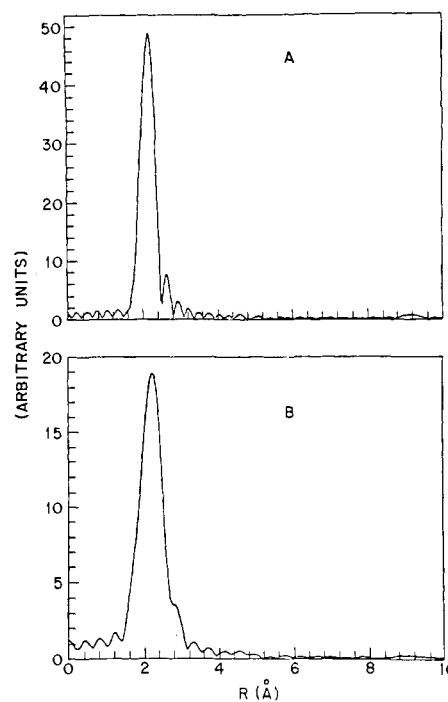

Figure 5. A. Fourier transform of filtered EXAFS data of 2% cross-linked DVB–styrene polymer-bound RhBr(PPh$_3$)$_3$ catalyst where Br is the absorber. B. Fourier transform of filtered EXAFS data of 20% cross-linked DVB–styrene polymer-bound RhBr(PPh$_3$)$_3$ catalyst where Br is the absorber.

Results

The results of the fitting procedure are summarized in Table I and Figure 6. Our data include the Rh EXAFS and the Br EXAFS of 2 and 20% cross-linked polymer-bound catalyst. We therefore have four independent sets of data, one for each edge of the 2 and 20% cross-linked catalyst. In addition, the results give three distinct determinations of the Rh–Br interatomic distance: the first from the Rh–EXAFS and the second from the Br–EXAFS fitted with theoretical functions whereas the third is from the Br–EXAFS fitted with empirically derived amplitude and phase functions.[18]

The significant phase shift difference ($\sim$1.84 rad) between $\phi_P(k)$ and $\phi_{Br}(k)$ enables one to distinguish between phosphorus and bromine contributions.[13] This fitting technique also gave information about the number of phosphorus vs. bromine (scatterers) atoms attached to the rhodium (absorber) atom. In Figure 6 the sum of the squares of the fit residuals (χ^2) is plotted for several values of $N_P = N_{P_1} + N_{P_2}$ and N_{Br}. In this fit of the data only integral N_{P_1}, N_{P_2}, and N_{Br} values were considered.

The 2% cross-linked polymer-bound catalyst has the best fit (cf. curve A in Figure 6) at P:Br ratio of 2:2 (viz., N_{P_1}: N_{P_2}:N_{Br} = 1:1:2). For Rh(I) species, this can only be achieved through dimerization. Similar results were found for the 2%

cross-linked chloro analogue.[1] The interatomic distances (cf. Table I) such as Rh–P$_1$ of 2.16 (1) Å and Rh–P$_2$ of 2.32 (1) Å were found in the 2% cross-linked polymer catalyst. The short Rh–P distance of 2.16 (1) Å can reasonably be assigned to the bond between the rhodium atom and the phosphine attached to the polymer because of the sterically less hindered diphenylphosphine ligand. The Rh–Br bond distance in 2% cross-linked polymer catalyst was found by three independent methods to be 2.50 (1) Å (Table I).

In the 20% cross-linked polymer-bound catalyst, the analysis of the coordination number shows that the best fit (cf. curve B, Figure 6) occurs at a P:Br ratio of 3:1 (viz., N_{P_1}:N_{P_2}:N_{Br} = 1:2:1). In Table I, the distances found in the 20% cross-linked polymer-bound catalyst were Rh–P$_1$ of 2.14 (1) Å, two Rh–P$_2$ bonds of 2.26 (1) Å, and one Rh–Br of 2.49 (1) Å. For steric reasons the short Rh–P distance of 2.14 (1) Å can again be assigned to rhodium bonded to the phosphine of the phosphinated polymer.

It should be pointed out that in both 2 and 20% cross-linked polymer-bound catalyst (Figure 6), the χ^2 of the best fit is at least a factor of 2 better than the others despite the deceptively shallow minima portrayed in the figure. In particular, the χ^2 of the 3:1 (P:Br ratio) model is about twice that of the 2:2 model in the 2% case whereas the χ^2 of the 2:2 (P:Br ratio)
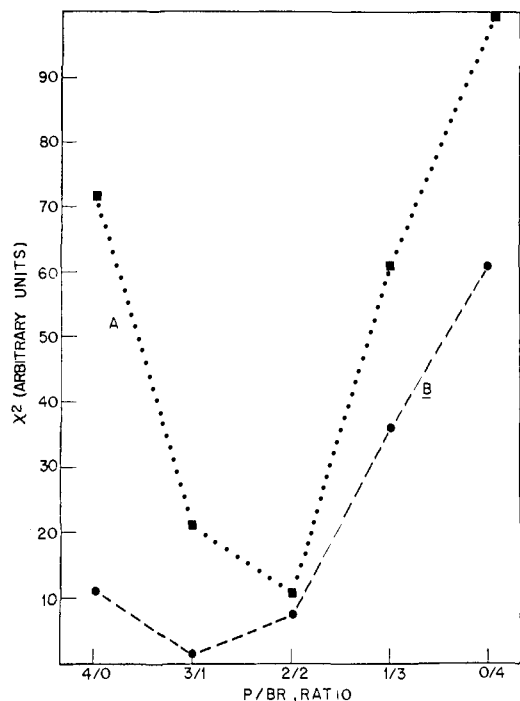
Figure 6. Plot of χ^2 (sum of squares of residuals) vs. P:Br ratio. χ^2 minimum occurs at P:Br of 2:2 for 2% cross-linked DVB–styrene polymer-bound RhBr(PPh$_3$)$_3$ catalyst (curve A) and 3:1 for 20% cross-linked DVB–styrene polymer-bound RhBr(PPh$_3$)$_3$ catalyst.

model is about eight times that of the 3:1 model in the 20% case. While these variations of χ^2 are statistically significant and thus indicative of major structural change at the active site of the catalyst in going from 2 to 20% cross-linking of the polymer, it should be cautioned that we cannot rule out a small percentage of local structures other than the ones suggested by the best fits.

Discussion

It has been suggested[22,23] that 2% cross-linked DVB–styrene copolymers are mobile enough to allow ligands attached to the polymer beads to act as chelates. Consequently, the 2% cross-linked copolymer is not rigid enough to prevent dimerization of attached unstable species. But if a 20% cross-linked polystyrene were used to prepare a polymer-bound catalyst, one would expect that there is less mobility of the polymer chains than in the 2% cross-linked polymer. In addition, one of the physical consequences of cross-linking a linear polymer

is a reduction in its volume capacity. A major part of the contraction, however, is due to changes in local molecular packing, leading to decreases in occupied and free volume.[24]

Our structural results supports the chemical observations of various workers.[22,23] We find that dimerization occurs in 2% cross-linked DVB–styrene polymer bound bromotris(triphenylphosphine)rhodium(I). However, dimer formation is substantially reduced in 20% cross-linked DVB–styrene polymer-bound bromotris(triphenylphosphine)rhodium(I).

These findings would suggest that if there is a catalytic activity trade-off due to the reduction in dimer formation vs. a decrease in the occupied and free volume in the polymer-bound catalyst, then there is probably some degree of cross-linking between 2 and 20% which is optimum. In addition, this study demonstrates the utility of EXAFS in the study of structural problems for which x-ray crystallography could not or has not been applied.

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