Hydrogenation of *cis*-1,4-Poly(isoprene) Catalyzed by OsHCl(CO)(O$_2$)(PCy$_3$)$_2$

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ABSTRACT: The quantitative hydrogenation of *cis*-1,4-poly(isoprene) (CPIP) provides an easy entry to the alternating copolymer of ethylene–propylene, which is difficult to prepare by conventional polymerization. The homogeneous hydrogenation of CPIP, in the presence of OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ as catalyst, has been studied by monitoring the amount of hydrogen consumed during the reaction. The final degree of olefin conversion measured by computer-controlled gas uptake apparatus was confirmed by infrared spectroscopy and ^{1}H nuclear magnetic resonance analysis. Kinetic experiments for CPIP hydrogenation in toluene solvent indicate that the hydrogenation rate is first order with respect to catalyst and carbon–carbon double bond concentration. A second-order dependence on hydrogen concentration for low values and a zero-order dependence for higher values of the hydrogen concentration was observed. The apparent activation energy for the hydrogenation of CPIP over the temperature range of 115–140°C was 109.3 kJ/mole. Mechanistic aspects of this catalytic process are discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 142–152, 2003

Key words: rubber; poly(isoprene); polymer modification; catalytic hydrogenation

INTRODUCTION

Polydiene-based polymers are widely used as rubbers, binders, and adhesives due to their high strength and good elastic properties. However, a disadvantage of these materials is their poor aging behavior, which is caused by the oxidation of residual double bonds in the polydienes, resulting in deterioration of the structural properties of the polymers. Chemical modification of polydiene-based polymers by hydrogenation is one of the important methods for improving and changing the properties of unsaturated elastomers toward greater stability against thermal, oxidative, and radiation-induced degradation.

There are many reports of hydrogenation of polybutadiene (PBD), acrylonitrile–butadiene copolymer (NBR), and styrene–butadiene copolymer (SBR) using transition metal compound catalysts.[1–3] For example, RuCl$_2$(PPh$_3$)$_3$ and RhCl(PPh$_3$)$_3$ complexes were found to be suitable catalyst systems for the hydrogenation of PBD[4] and NBR,[5] respectively. In addition, a metallocene catalyst system, primarily the bis(η^5-cyclopentadienyl)cobalt (Cp$_2$Co) combined with *n*-butyllithium (n-BuLi), was found to be active for hydrogenation of polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) block copolymer.[6] A Ziegler–Natta-type catalyst prepared with nickel acetylacetonate and n-BuLi has been used to hydrogenate the styrene–butadiene copolymer in cyclohexane.[7]

Of the many metal complexes capable of catalyzing olefin hydrogenation, those based on Rh, Ru, and Pd have been most successful for polydiene hydrogenation. A study of the hydrogenation of NBR catalyzed by an Os complex [OsHCl(CO)(O$_2$)(PCy$_3$)$_2$] catalyst has shown that it is among the most active of catalysts known and the mechanism for the reaction was elucidated.[8] What was most unusual was that under certain conditions, a second-order dependence on hydrogen concentration was observed for the hydrogenation process.

Poly(isoprene) has been used extensively in the automobile and adhesive industries. It is preferably used in blends with other rubbers, such as PBD or SBR, to improve their processability. Thus, hydrogenation of poly(isoprene) improves the heat and oxygen resistance of the rubber, producing essentially an alternating copolymer of ethylene–propylene, which is difficult to prepare by conventional polymerization.[9]

Poly(isoprene) has been hydrogenated by a number of methods including using noncatalytic reagents, such as *p*-toluenesulfonyl hydrazide (TSH).[10,11] Shahab and Basheer[12] studied different catalytic methods for poly(isoprene) hydrogenation in the form of natu-

ral rubber. One method used a homogeneous catalyst, $RhCl(PPh_3)_3$, and another used a heterogeneous catalyst, Pd supported on $CaCO_3$. However, these systems suffer a drawback in that long reaction times with high catalyst loading are required.[13]

The primary purpose of this work was to study the hydrogenation of *cis*-1,4-poly(isoprene) (CPIP) in the presence of $OsHCl(CO)(O_2)(PCy_3)_2$ as catalyst. Kinetic data were collected within a statistical framework, which defined the effect of concentration of catalyst and polymer, hydrogen pressure, and temperature on catalytic activity. The kinetics of the reaction and the proposed mechanism for CPIP hydrogenation by $OsHCl(CO)(O_2)(PCy_3)_2$ are reported.

EXPERIMENTAL

Materials

Reaction gas

The reaction gas used for the hydrogenation experiments was oxygen-free hydrogen with a purity of 99.99% obtained from Praxair, Inc.

Solvent

Reagent grade toluene was obtained from BDH (Toronto, Canada). Monochlorobenzene (MCB), xylene, ethanol, methoxyethanol, hexane, and tetrahydrofuran were purchased from Fisher Scientific Ltd. (Fairlawn, NJ).All solvents were used as received.

Catalyst

$RhCl(PPh_3)_3$[14] and $RuCl(CO)(styryl)(PCy_3)_2$[15] were prepared according to literature methods. $[Ir(COD)py-(PCy_3)]PF_6$ was obtained from Strem Chemicals (Newburyport, MA). $OsHCl(CO)(O_2)(PCy_3)_2$ was prepared by refluxing $OsCl_3 \cdot 3H_2O$ with PCy_3 (both from Strem Chemicals) in methoxyethanol according to the procedures of Esteruelas and Werner.[16] The corresponding dioxygen adduct, $OsHCl(CO)(O_2)(PCy_3)_2$, was prepared by exposing a suspension of $OsHCl(CO)(PCy_3)_2$ in hexane to pure O_2 as detailed by Esteruelas et al.[17]

cis-1,4-poly(isoprene)

High molecular weight CPIP with 97% of *cis* isomer used in this study was Natsyn (Goodyear, Akron, OH) obtained from Bayer, Inc. (Sania, Canada), and Scientific Polymer Products, Inc.

Hydrogenation within a batch reactor

Hydrogenation reactions were carried out in a 300 mL Parr autoclave reactor (Moline, IL). The amount of 2.65 g of CPIP was mixed with 130 mL of solvent. The catalysts were weighed and dissolved under N_2 with 20 mL of solvent, and filled into a catalyst addition device. The mixture in the autoclave was degassed by bubbling hydrogen gas through it for 20 min at 13.8 bar H_2 pressure at room temperature. The autoclave was then heated to the desired reaction temperature with agitation at 600 rpm. When the temperature of the autoclave stabilized, the catalyst addition device was pressurized to the reaction pressure with hydrogen gas in order to charge the catalyst solution into the mixture.

The autoclave was then pressurized to the reaction pressure. Hydrogen gas was pressurized into the autoclave as required in order to maintain a constant reaction pressure throughout the reaction period. After reaction, the hydrogenated product was isolated by precipitation with ethanol, filtered, and dried under vacuum.

Hydrogenation using gas uptake apparatus

The hydrogenation of CPIP was carried out in the presence of $OsHCl(CO)(O_2)(PCy_3)_2$ in toluene under various reaction conditions. The amount of 1.3–5.5 g of CPIP was dissolved in 150 mL of solvent in the dark and vigorously degassed in the autoclave before the addition of catalyst. The hydrogenation gas uptake apparatus, a high-pressure variation of that developed by Mohammadi and Rempel[18] was maintained at constant temperature $\pm$ 1°C and pressure $\pm$ 0.02 bar throughout the hydrogenation. Once the experimental equilibrium temperature and pressure were established, the $OsHCl(CO)(O_2)(PCy_3)_2$ was dispersed in the solution using an agitation rate of 1200 rpm. Each experiment proceeded until gas consumption ceased, after which the reactor was quickly cooled, and the product isolated by precipitation with ethanol and drying under vacuum.

Characterization

The final degree of olefin conversion was quantified by infrared (IR) spectroscopy and ^1H nuclear magnetic resonance (^1H-NMR) spectroscopic analysis. ^1H-NMR spectra of polymer samples were recorded on a Bruker 200 MHz spectrometer, using $CDCl_3$ as the solvent. Fourier transform infrared (FTIR) spectra were obtained with a Bio-Rad FTS 3000X spectrometer (Cambridge, MA). The IR samples were prepared by casting polymer films from solution onto sodium chloride disks.

Viscosity measurement

The viscosity of dilute polymer solutions [0.12500 $\pm$ 0.00015 g of hydrogenated *cis*-1,4-poly(isoprene)
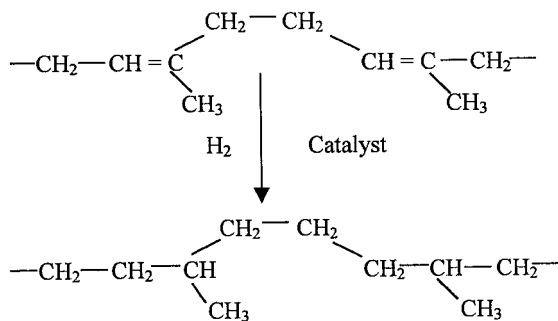
Scheme 1 Hydrogenation of CPIP in the presence of OsHCl(CO)(O$_2$)PCy$_3$)$_2$.

(HCPIP)/25 mL of toluene] were measured at 35°C by using an Ubellohde capillary viscometer. Sample filtration through a coarse, sintered-glass filter provided a means of detecting insoluble gel. The relative viscosity data (η_{rel}) are reported as the polymer solution viscosity relative to that of toluene solvent at 35°C.

Experimental design

Specific combinations of factor levels were selected according to a structured design.[19] The principal factors of interest were the influences of the concentration of catalyst ([Os]) and CPIP ([C=C]), and hydrogen concentration ([H$_2$]) on the rate of hydrogenation. The secondary factors of interest were the effect of varying the reaction temperature and solvent type on hydrogenation. Principal factor combinations conformed to a central composite structure, consisting of a univariate or "one-at-a-time" series to study the influence of each factor while holding all others constant, and a two-level factorial series of experiments to identify joint interactions. The influences of temperature and solvent have been investigated by univariate experiments alone. Selection of the factor level ([Os], [C=C], [H$_2$]) considered catalyst weighing precision, the viscosity of polymer solution, and the hydrogenation rate that the apparatus could effectively control and monitor.

RESULTS AND DISCUSSION

Initial studies in the batch reactor

The hydrogenation of CPIP in the presence of OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ can be represented by Scheme 1. The final degree of hydrogenation of CPIP was confirmed by IR spectroscopy and ^{1}H-NMR spectroscopic analysis. Figure 1 shows the FTIR spectra of CPIP and HCPIP. The most apparent change in the FTIR spectra are the reduction in the bands at 1663 and 836 cm^{-1} due to C=C stretching and olefinic C—H bending, as the extent of hydrogenation of C=C increased.

The ^{1}H-NMR spectra of CPIP and HCPIP are shown in Figure 2. The ^{1}H-NMR spectrum of CPIP shows signals at 1.75, 2.12, and 5.25 ppm, which are attributed to —CH$_3$, —CH$_2$—, and olefinic protons, respectively. In comparison, the signal in the ^{1}H-NMR spectrum of hydrogenated CPIP at 5.25 ppm is very small and new signals appear at 0.8 and 1.2 ppm, attributed to —CH$_3$, —CH$_2$—, and —CH in the hydrogenated polymer. The final conversion levels were determined by comparison of the integrals of signal at 5.25 ppm with the integrals for saturated protons in the range of 0.8–1.2 ppm.

Table I shows the results for hydrogenation of CPIP in a batch reactor using different catalysts, solvents, and reaction temperatures. All the catalysts investigated are active for diene polymer hydrogenation. However, RhCl(PPh$_3$)$_3$ was not effective as a catalyst for hydrogenation of CPIP as little or no hydrogenation was seen under the investigated conditions. However, Singha et al.[13] reported that 80% hydrogenation of natural rubber was obtained using 1.3 mol % of RhCl(PPh$_3$)$_3$ as a catalyst in toluene at a hydrogen pressure of 40 kg/cm^2, and reaction temperature of 100°C for 22 h. We suppose that the difference in their results from the present investigation was due to the very high amount of catalyst and hydrogen pressure used by Singha et al.[13]

RuCl(CO)(styryl)(PCy$_3$)$_2$, OsHCl(CO)(O$_2$)(PCy$_3$)$_2$, and [Ir(COD)py(PCy$_3$)]PF$_6$ were found to be active for hydrogenation of CPIP. At 160°C using RuCl(CO)(styryl)(PCy$_3$)$_2$ as catalyst in toluene solvent, >90% hydrogenation can be achieved after 20 h. Martin[20] reported that RuCl(CO)(styryl)(PCy$_3$)$_2$ could be used successfully as a catalyst for hydrogenation of poly(isoprene) and 80% hydrogenation in chlorobenzene could be achieved using 77.76 μM catalyst at a reaction temperature of 160°C and hydrogen pressure of 40.3 bar. However, the hydrogenation rate was extremely slow, with a pseudo first-order rate constant (k') of 0.00009 s^{-1} and roughly 80% conversion was attained before the gas uptake monitoring program was stopped.

[Ir(COD)py(PCy$_3$)]PF$_6$ was dissolved in polar solvents, which could also dissolve CPIP. Solvents such as chloroform and monochlorobenzene were the best solvents for this study. It was found that the optimal reaction temperature for this catalyst system appeared to be ~100°C; 90% hydrogenation in MCB and chloroform could be obtained after 6 and 7 h, respectively.

OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ was observed to be a very efficient catalyst for hydrogenation of CPIP. The rate of hydrogenation was faster than either the RuCl(CO)(styryl)(PCy$_3$)$_2$ or the [Ir(COD)py(PCy$_3$)]PF$_6$. The extent of hydrogenation increased with increasing reaction temperature. At 130°C, the OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ was capable of hydrogenating ≥90% of the C=C bonds of the CPIP within 30 min. From the results of these preliminary

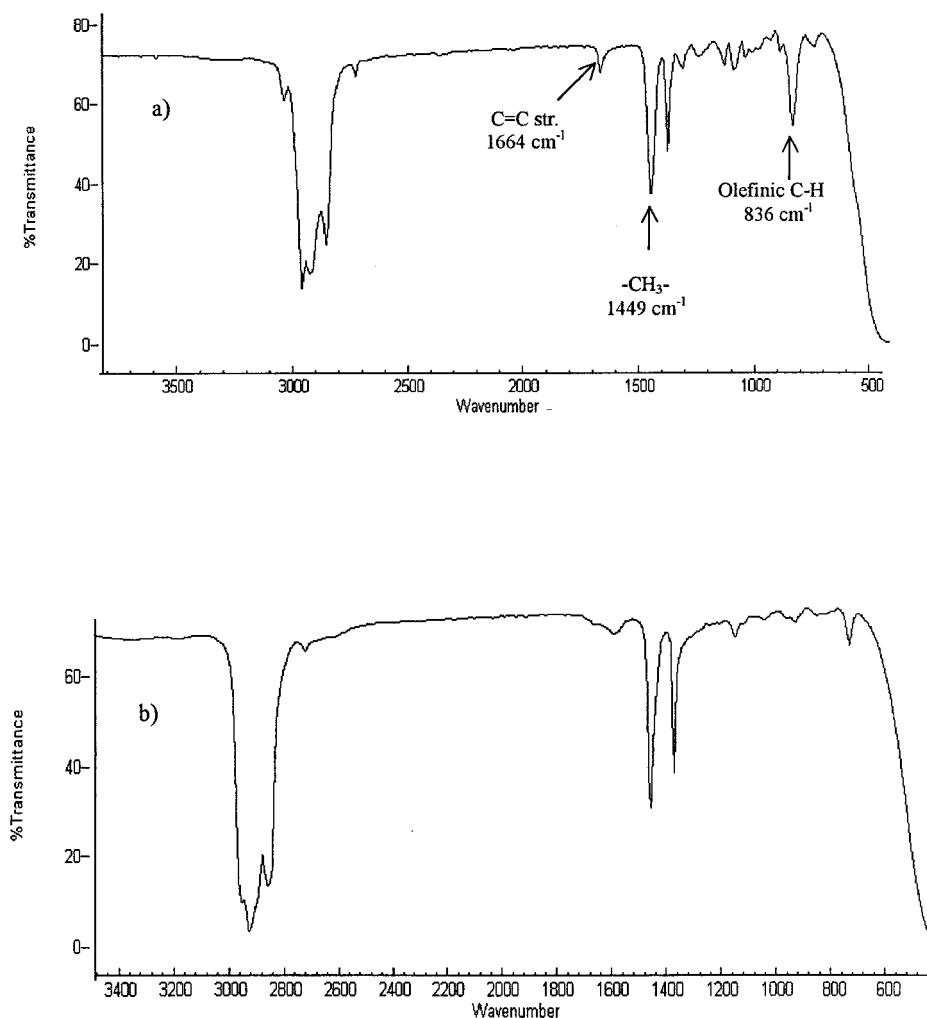**Figure 1** FTIR spectra of (a) CPIP and (b) HCPIP.

experiments, $OsHCl(CO)(O_2)(PCy_3)_2$ was chosen for a detailed mechanistic study of CPIP hydrogenation.

Hydrogenation of CPIP using $OsHCl(CO)(O_2)(PCy_3)_2$

Over the range of process conditions studied, $OsHCl(CO)(O_2)(PCy_3)_2$ functioned as an efficient catalyst system for the quantitative hydrogenation of CPIP in toluene. A representative hydrogen uptake profile corresponding to the consumption of olefin is presented in Figure 3(a). A hydrogen consumption plot shows an apparent first-order rate dependence for hydrogenation of the carbon–carbon double bond concentration. The first-order rate constant was derived from the slope of the linear $\ln(1 - x)$ vs time plot [Fig. 3(b)] in accordance with eq. (1) (where x is conversion and k' is the pseudo first-order rate constant).

$$\frac{-d[C{=}C]}{dt} = k' \, [C{=}C] \qquad (1)$$

Factorial design experiments

A thorough kinetic study improves our knowledge not only of how each factor affects k' alone (as probed by the univariate experiments) but also whether factors act in combination. In this section of work, the three variables, which are expected to have an effect on k' are the concentration of catalyst and carbon–carbon double bond, and hydrogen pressure. When using two level fractional factorial design, the number of experiments can be optimized. For each variable, a lower "− level" and higher "+ level" was chosen for the range of concentration to be studied. The catalyst concentration, carbon–carbon double bond concentration, and hydrogen pressure range from 40 to 80 μM, 260 to 530 mM, and 13.8 to 27.6 bar, respectively. The results of the factorial experiment are summarized in Table II. A Yates calculation[19] for the hydrogenation of CPIP and the results of the factorial analysis are shown in Tables III and IV, respectively. Comparison of the estimation with their standard errors suggests
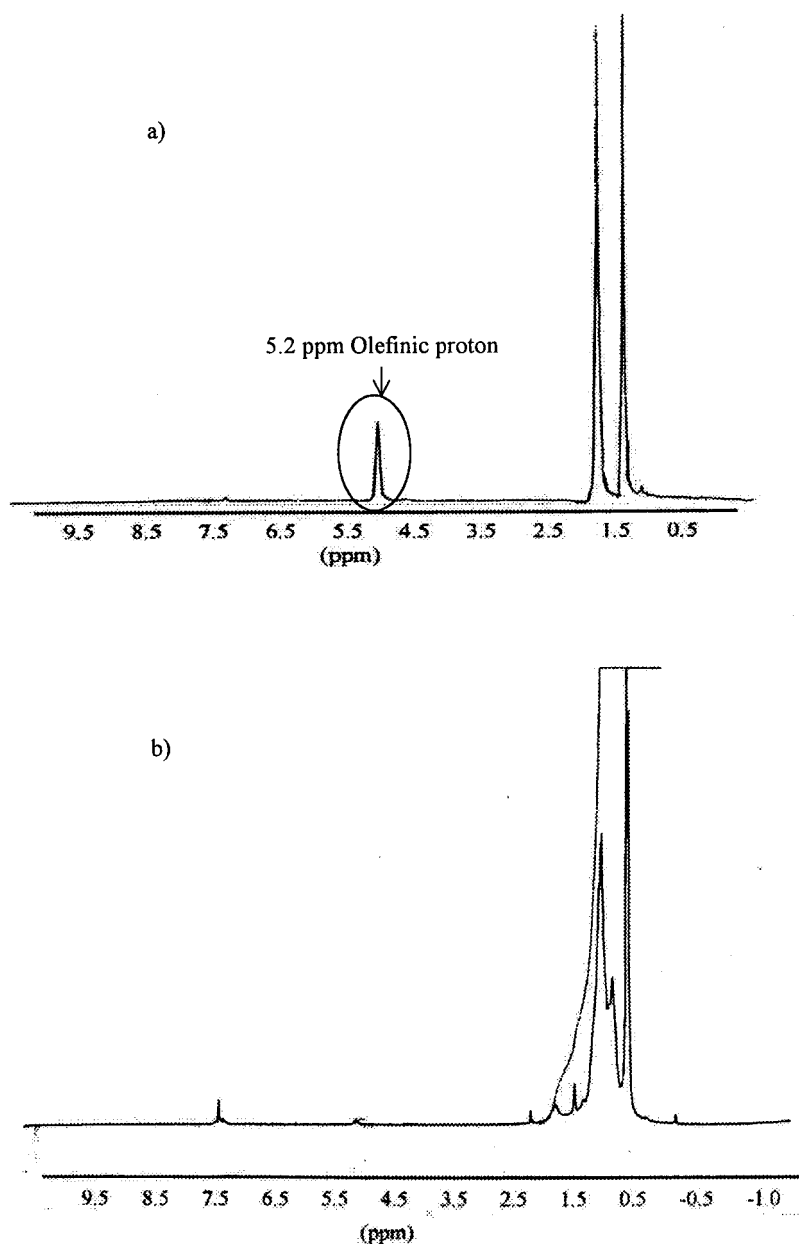
a)

5.2 ppm Olefinic proton

9.5   8.5   7.5   6.5   5.5   4.5   3.5   2.5   1.5   0.5
(ppm)

b)

9.5   8.5   7.5   6.5   5.5   4.5   3.5   2.5   1.5   0.5   -0.5   -1.0
(ppm)

Figure 2 ^{1}H-NMR spectra of (a) CPIP and (b) HCPIP.

that the main effect of catalyst concentration, [Os], and hydrogen pressure, [H$_2$], require interpretation, while the existence of other two- and three-factor interactions are not highly significant.

The main effect of a variable should be individually interpreted only if there is no evidence that the variable interacts with other variables. When there is evidence of one or more such interpretation effects, the variables of interest should be considered jointly. Table IV shows that the catalyst concentration and hydrogen pressure have a positive effect and the carbon–carbon double bond concentration has a very small negative effect on the rate constant. The strongest effect was the catalyst concentration (0.00174 ± 8.03E-05).

Univariate kinetic experiments

The result of the factorial analysis established the significance of joint factor interactions without determining their functional form. The univariate components of the central composite design augment the factorial study by exploring how each factor influences the hydrogenation rate in isolation.

Effect of catalyst concentration

In order to investigate the effect of catalyst concentration on the initial rate of polymer hydrogenation, a series of hydrogenation experiments in which the cat-

TABLE I
**Results of CPIP Hydrogenation Using Different Catalysts**

Catalyst	[Catalyst] (mM)	Temperature (°C)	P_{H_2} (bar)	[C=C][c] (mM)	Solvent	Results
$RhCl(PPh_3)_3$	0.3943	100	27.6	260.10	Toluene	Little hydrogenation, after 20 h
	0.0721	130	27.6	260.10	Toluene	No hydrogenation
	0.0721	120	55.2	260.15	MCB	Little hydrogenation, after 20 h
$RuCl(CO)(styryl)(PCy_3)_2$	0.0804	100	27.6	260.20	Toluene	Very little hydrogenation, after 20 h
	0.0804	160	27.6	260.10	Toluene	>90% hydrogenation, after 20 h
$[Ir(COD)py(PCy_3)]PF_6$	0.0828	100	27.6	260.20	Toluene	Little hydrogenation, after 20 h[a]
	0.0828	100	27.6	260.20	$CHCl_3$	>90% hydrogenation, after 7 h
	0.0828	100	27.6	260.10	MCB	>90% hydrogenation, after 6 h
$OsHCl(CO)(O_2)(PCy_3)_2$	0.0787	100	27.6	260.20	Toluene	>90% hydrogenation, after 16 h
	0.0787	130	27.6	260.20	Toluene	>90% hydrogenation, after 30 min
	0.0787	130	27.6	260.10[b]	Toluene	>90% hydrogenation, after 30 min
	0.0787	130	27.6	260.10[b]	MCB	>90% hydrogenation, after 30 min
	0.0787	130	27.6	260.10[b]	Benzene	>90% hydrogenation, after 30 min

[a] The catalyst was poorly soluble in the solvent.
[b] CPIP was obtained from Bayer, Inc. The others experiments was obtained from Scientific Polymer Products, Inc.
[c] [C=C] is defined as the weight of CPIP divided by molecular weight of repeating unit.

alyst concentration was varied over the range of 20–150 μM was carried out. The concentration of carbon–carbon double bond was 260 mM, at 130°C in toluene. The hydrogen pressure was varied from 13.8 to 34.5
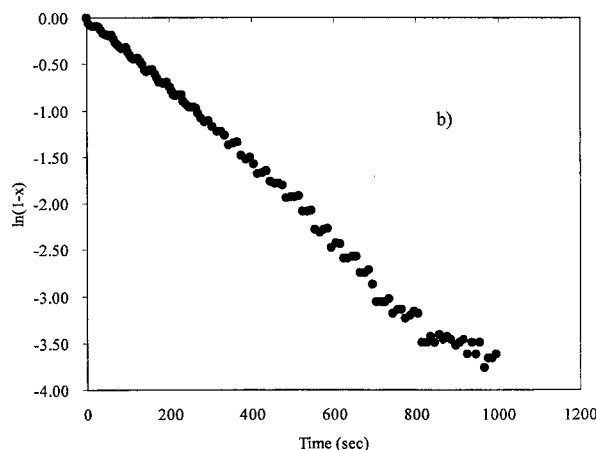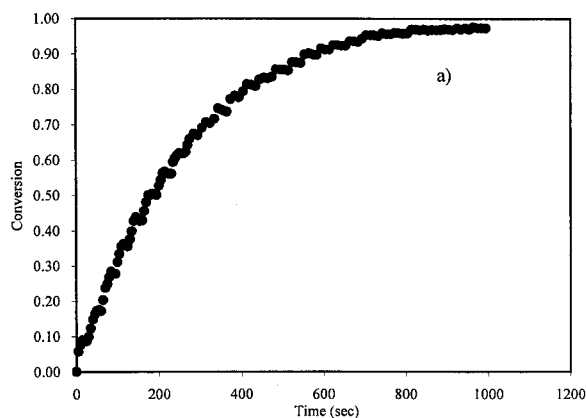
Figure 3 Hydrogenation of CPIP: (a) olefin conversion profile and (b) first-order log plot. [Os] = 70 μM; P_{H_2} = 20.7 bar; [C=C] = 260 mM; T = 130°C.

bar. The results of these experiments are given in Table V. Plots of hydrogenation rate constant vs concentration of catalyst are fairly linear for each pressure as shown in Figure 4. It can be concluded from this plot that the reaction is first order with respect to the concentration of catalyst. This agrees very well with the observations by Parent et al.[8] for NBR hydrogenation using $OsHCl(CO)(O_2)(PCy_3)_2$ as a catalyst. A first-order response of k' to concentration of $OsHCl(CO)(O_2)(PCy_3)_2$ suggests that the active complex is a mononuclear species.

Effect of hydrogen pressure

In this series of experiments, the hydrogen pressure was varied over the range of 3.45–69 bar at 130°C in toluene. The concentration of catalyst and polymer

TABLE II
Result from 2^3 Factorial Design for CPIP Hydrogenation

Experiment	[Os] (mM)	[C=C] (mM)	P_{H_2} (bar)	Temperature (°C)	$k' \times 10^3$ (s^{-1})
1	0.0404	259.80	13.8	130	2.59
2	0.0403	260.20	13.8	130	2.55
3	0.0801	260.20	13.8	130	4.20
4	0.0798	259.90	13.8	130	4.05
5	0.0401	259.80	27.6	130	3.27
6	0.0403	259.80	27.6	130	3.40
7	0.0798	260.10	27.6	130	5.25
8	0.0802	260.00	27.6	130	4.90
9	0.0402	520.49	13.8	130	2.44
10	0.0398	520.49	13.8	130	2.10
11	0.0798	520.49	13.8	130	4.20
12	0.0802	520.29	13.8	130	4.16
13	0.0402	519.90	27.6	130	3.03
14	0.0398	520.49	27.6	130	3.25
15	0.0798	520.00	27.6	130	4.46
16	0.0798	520.29	27.6	130	4.75

TABLE III
Yate's Algorithm Calculation of the 2^3 Factorial Experiments

Test	Design matrix variables[a] [Os]	[H₂]	[C=C]	K' Average	1	Algorithm 2	3	Divisor	Estimate	Identification
1	−	−	−	0.00257	0.00670	0.01511	0.02888	8	0.00361	Average
2	+	−	−	0.00413	0.00841	0.01377	0.00695	4	0.00174	[Os]
3	−	+	−	0.00334	0.00645	0.00330	0.00259	4	0.00065	[H₂]
4	+	+	−	0.00508	0.00730	0.00365	0.00106	4	0.00026	[Os] [H₂]
5	−	−	+	0.00227	0.00156	0.00172	−0.00134	4	−0.00033	[C=C]
6	+	−	+	0.00418	0.00174	0.00087	0.00036	4	0.00009	[Os][C=C]
7	−	+	+	0.00314	0.00191	0.00019	−0.00084	4	−0.00021	[H₂][C=C]
8	+	+	+	0.00461	0.00147	−0.00045	−0.00063	4	−0.00016	[Os][H₂][C=C]

[a] [Os] is concentration of catalyst (μM): (−) 40 and (+) 80. [H₂] is hydrogen pressure (bar): (−)13.8 and (+) 27.6. [C=C] is concentration of double bond (mM): (−) 260 and (+) 530.

were kept constant at 70 μM and 260 mM, respectively. The results of these experiments are presented in Table V and Figure 5. The results shown in Figure 5 suggest that, as observed for the hydrogenation of NBR in the present of $OsHCl(CO)(O_2)(PCy_3)_2$, a second-order dependence on hydrogen pressure is most likely below 13.8 bar. Above this, the influence of hydrogen pressure continued to decline with increasing pressure until essentially no difference was observed between 34.5 and 69 bar. The hydrogenation rate tends toward a zero-order dependence as hydrogen pressure increased. This shift in [H₂] order is accompanied by changes in the influence of [C=C]. With increase in pressure, the conversion vs time plots became increasingly linear for approximately the first 70% of conversion as shown in Figure 6. The shift from second order to zero order with respect to hydrogen pressure was also observed on hydrogenation of NBR using $OsHCl(CO)(O_2)(PCy_3)_2$. Conversely, the hydrogenation of SBR using $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ was found to be zero order with respect to hydrogen pressure.[8]

TABLE IV
The Calculated Effects and Standard Errors for 2^3 Factorial Experiment

Effect	Estimate ± standard error
Average	0.00361 ± 1.61E-09
Main effects	
Concentration of catalyst, [Os]	0.00174 ± 8.03E-05
Pressure, [H₂]	0.00065 ± 8.03E-05
Concentration of double bond, [C=C]	−0.00033 ± 8.03E-05
Two-factor interactions	
[Os] × [H₂]	0.00026 ± 8.03E-05
[Os] × [C=C]	0.00009 ± 8.03E-05
[H₂] × [C=C]	−0.00021 ± 8.03E-05
Three-factor interaction	
[Os] × [H₂] × [C=C]	−0.00016 ± 8.03E-05

TABLE V
Kinetic Results of Univariate Experiments

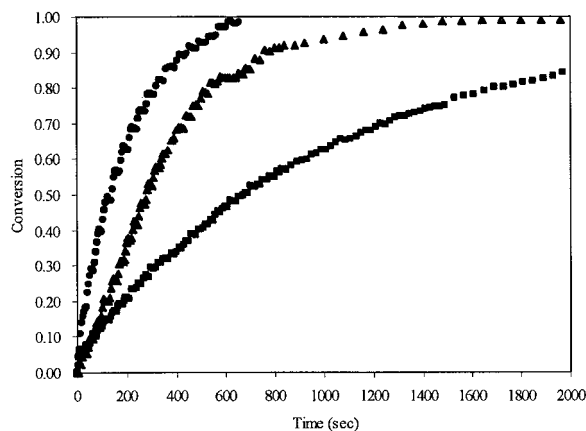| Experiment	[Os] (mM)	[C=C] (mM)	P_{H_2} (bar)	Temperature (°C)	$k' \times 10^3$ (s⁻¹)
1	0.0215	260.39	13.8	130	0.86
2	0.0499	260.29	13.8	130	2.91
3	0.0699	260.19	13.8	130	3.98
4	0.0997	259.51	13.8	130	5.37
5	0.1200	260.29	13.8	130	6.74
6	0.0218	260.19	20.7	130	1.67
7	0.0302	260.49	20.7	130	2.44
8	0.0497	259.70	20.7	130	3.02
9	0.0697	260.09	20.7	130	4.14
10	0.0700	260.19	20.7	130	4.20
11	0.1000	260.39	20.7	130	5.89
12	0.1199	259.80	20.7	130	7.25
13	0.0297	260.29	34.5	130	2.35
14	0.0300	260.09	34.5	130	2.28
15	0.0497	260.19	34.5	130	3.51
16	0.0496	260.29	34.5	130	3.28
17	0.0703	260.00	34.5	130	4.95
18	0.0703	259.90	34.5	130	4.36
19	0.0999	260.29	34.5	130	6.15
20	0.1199	260.29	34.5	130	7.13
21	0.1499	260.09	34.5	130	8.88
22	0.0708	260.09	3.45	130	0.91
23	0.0699	259.51	3.59	130	1.16
24	0.0700	259.51	5.38	130	2.09
25	0.0700	259.70	6.9	130	3.68
26	0.0699	260.19	6.90	130	3.55
27	0.0699	260.29	48.3	130	5.07
28	0.0703	259.90	69.0	130	5.16
29	0.0700	64.19	20.7	130	4.09
30	0.0703	95.99	20.7	130	4.06
31	0.0703	129.02	20.7	130	4.01
32	0.0700	194.02	20.7	130	4.02
33	0.0698	393.92	20.7	130	4.06
34	0.0703	530.78	20.7	130	3.93
35	0.0699	260.29	20.7	115	1.15
36	0.0697	260.00	20.7	120	1.73
37	0.0698	260.19	20.7	125	2.73
38	0.0700	260.19	20.7	135	5.90
39	0.0702	259.51	20.7	140	8.95
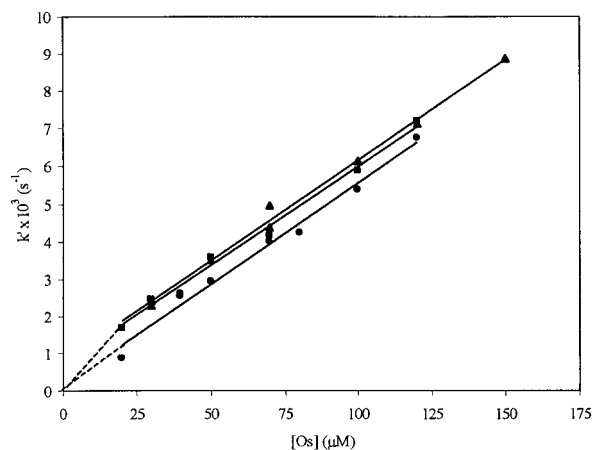
Figure 4 Effect of catalyst concentration on the hydrogenation rate at various pressures. [C=C] = 260 mM; T = 130°C; (●) 13.8 bar, (■) 20.7 bar, and (▲) 34.5 bar.


Figure 6 CPIP conversion profile at various pressures. [Os] = 70 μM; [C=C] = 260 mM; T = 130°C; (■) 3.45 bar, (▲) 6.9 bar, and (●) 69 bar.

Effect of polymer concentration

A series of hydrogenation experiments in toluene with catalyst concentration of 70 μM, hydrogen pressure of 20.7 bar, reaction temperature of 130°C and concentration of carbon–carbon double bond over the range of 260–530 mM, was carried out to investigate the effect of carbon–carbon double-bond concentration on the hydrogenation rate constant. The results of these experiments are summarized in Table V. As mentioned above, the hydrogenation of CPIP followed pseudo first-order kinetics to greater than 90% conversion of the double bonds [Figs. 3(a) and 3(b)]. This behavior was observed for all sets of substrate concentrations and reaction conditions. A plot of hydrogenation rate constant vs concentration of polymer displayed in Figure 7 shows that the hydrogenation rate constant remain relatively constant over the range of the concentration of carbon–carbon double bond investigated. For hydrogenation of NBR, the nitrile groups within this material are known to reversibly

coordinate to OsHCl(CO)(O$_2$)(PCy$_3$)$_2$; therefore, the hydrogenation activity decreased dramatically as the polymer loading was increased.[8] Similar observation was found for hydrogenation of NBR using RuCl(CO)(styryl)(PCy$_3$)$_2$.[21]

Effect of reaction temperature

Experiments were carried out from 115 to 140°C with concentration of catalyst of 70 μM, concentration of carbon–carbon double bond of 260 mM, and at hydrogen pressure of 20.7 bar. The results of the hydrogenation are presented in Table V. An Arrhenius plot of the data is illustrated in Figure 8. The activation energy calculated from least squares regression analysis (R^2 = 0.999) of ln (k') vs 1/T was 109.32 kJ/mol. This estimation indicates that the experiments were carried out without mass transfer limitation. For hydrogenation of NBR using OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ as catalyst, an activation energy value of 96 kJ/mol was reported by Parent et al.[8]

Figure 5 Effect of hydrogen pressure on the hydrogenation rate. [Os] = 70 μM; [C=C] = 260 mM; T = 130°C.
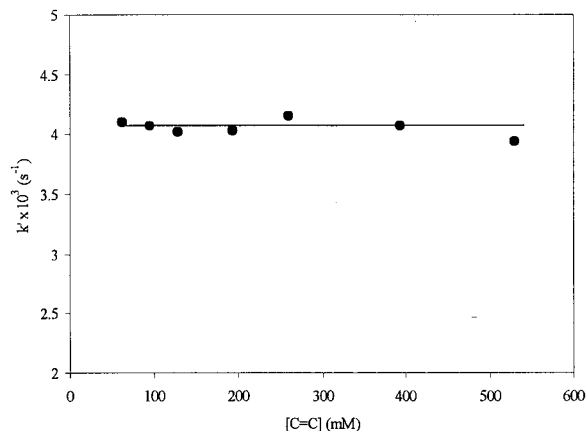
Figure 7 Effect of polymer concentration on the hydrogenation rate. [Os] = 70 μM; P_{H_2} = 20.7 bar; T = 130°C.
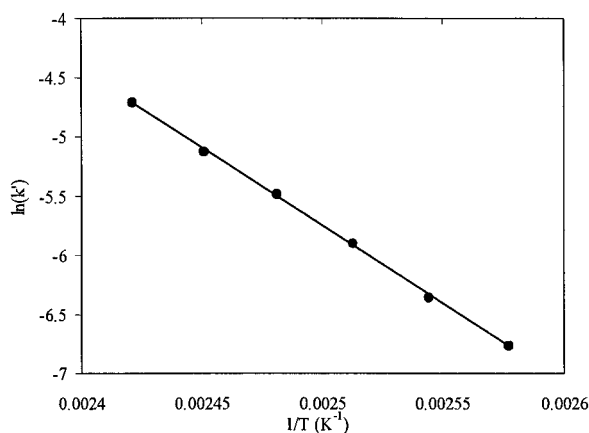
Effect of solvent

A series of experiments were undertaken using different solvents for CPIP hydrogenation at the base condition ([Os] = 70 μM, P_{H_2} = 20.7 bar, [C≡C] = 260 mM, and T = 130°C). Acetone and MEK were not used as solvent since the OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ catalyst is inactive in ketone solvents.[8] The effects of solvent type on hydrogenation rate are summarized in Table VI. It was found that the rate constant varied with the nature of solvent in this order: tetrahydrofuran > chlorobenzene > toluene > xylene.

The coordinating power of the solvent is of importance and it should have sufficient coordinating power to displace the phosphine ligand. Table VI shows that the hydrogenation rate was increased in solvents, which may coordinate with the Os complex catalyst. It has been proposed that the strong coordinating solvent can promote the dissociation of phosphine ligand and the formation of a very active 14-electron osmium trihydride species.[22]

Relative viscosity of hydrogenated CPIP

In order to investigate the presence of side reactions, such as degradation and crosslinking during the chemical modification processes, the modified polymer product was examined. Dilute solution viscometry has been employed to follow the change of the physical properties of polymer by monitoring the shifts in molecular weight that are created by crosslinking. The method has the drawback of an ambiguous relationship of viscosity (η) to molecular weight, especially for copolymers with composition or structure diversity. Nevertheless, the space occupied by a macromolecule in solution is related to its molecular weight and evident in the solution viscosity. Therefore, the viscosity of a dilute CPIP solution relative to pure solvent (η_{rel}) provides a simple and

TABLE VI
Effect of Solvent on the Hydrogenation of CPIP[a]

Solvent	$k' \times 10^3$ (s^{-1})	% Hydrogenation	Reaction time (min)
Toluene	4.14	97.68	≈15
Xylene	1.14	95.89	≈60
Tetrahydrofuran	7.92	98.32	≈5
Chlorobenzene	4.66	97.94	≈15

[a] [Os] = 70 μM, P_{H_2} = 20.7 bar, [C≡C] = 260 mM, at 130°C.

effective means of measuring the consequences of crosslinking. The kinetics of the hydrogenation of CPIP have been studied extensively. Over the range of conditions explored in this work, ([Os] = 30–150 μM, [C≡C] = 260–530 mM, P_{H_2} = 6.9–69 bar at 130°C), it was found that the relative viscosity of hydrogenated
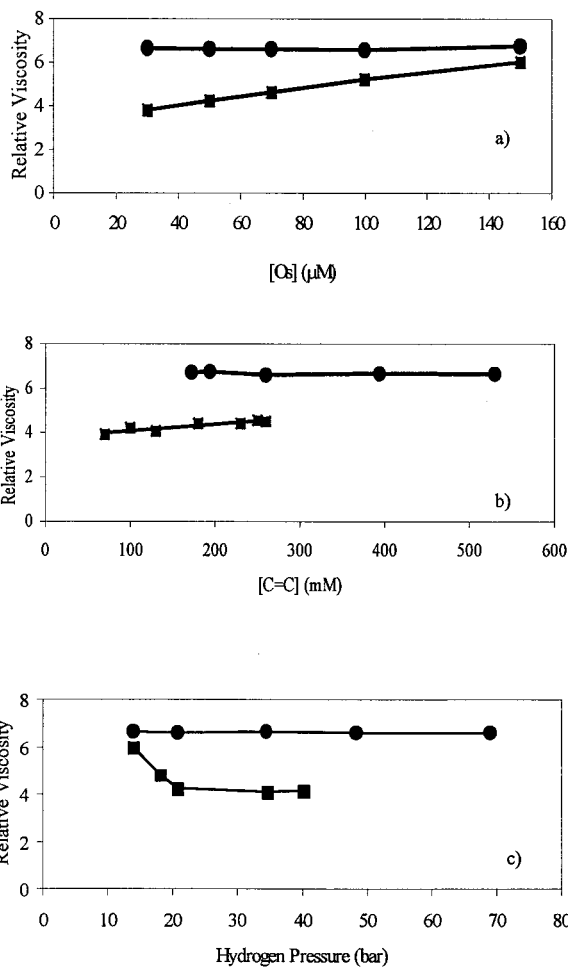
Figure 9 (a) Relative viscosity as a function of total metal loading: P_{H_2} = 20.7 bar; [C≡C] = 260 mM; T = 130°C; [CN] = 172 nM; (●) HCPIP; (■) HNBR. (b) Relative viscosity as a function of polymer loading P_{H_2} = 20.7 bar; T = 130°C; (●) HCPIP, [Os] = 70 μM; (■) HNBR, [Os] 80 μM. (c) Influence of pressure on relative viscosity: [C≡C] 260 mM; T = 130°C, [CN] = 172 mM; (●) HCPIP, [Os] = 70 μM; (■) HNBR, [Os} = 80 μM.

Figure 8 Arrhenius plot for the hydrogenation of CPIP. [Os] = 70 μM; P_{H_2} = 20.7 bar; [C≡C] = 260 mM; T = 115–140°C.

$OsHCl(CO)(O_2)(PCy_3)_2 \longrightarrow OsHCl(CO)(PCy_3)_2$

K_{H_2}, $[H_2]$

$OsHCl(CO)(H_2)(PCy_3)_2$

K_p $-[P]$

$OsHCl(CO)(H_2)(PCy_3)$

Alkane

k_{rds} K_1, $[H_2]$

$OsH_2Cl(CO)(H_2)(PCy_3)$ $OsH_3Cl(CO)(H_2)(PCy_3)$

K_2, $[C=C]$
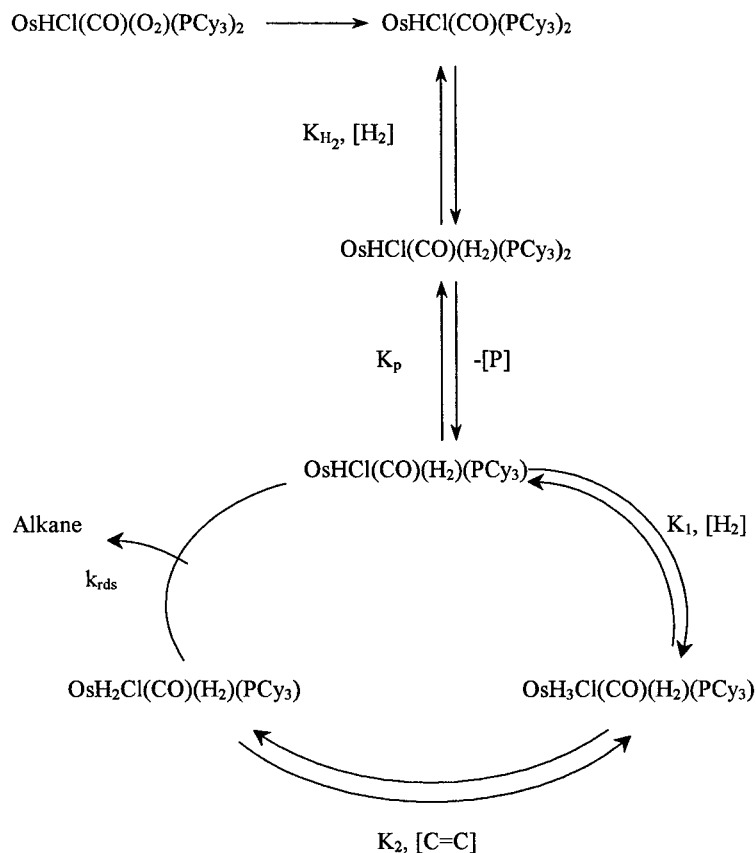
Scheme 2 Proposed mechanism for hydrogenation of CPIP.

CPIP (6.5–6.8) was higher than that of CPIP (4.48). The increase of relative viscosity suggests that no degradation occurred during the catalytic hydrogenation reaction.

Figures 9(a), 9(b), and 9(c) illustrate the effect of catalyst concentration, carbon–carbon double-bond concentration, and hydrogen pressure on the relative viscosity of HCPIP, respectively. This figure also shows results for $OsHCl(CO)(O_2)(PCy_3)_2$ on CPIP hydrogenation, as compared with the results of hydrogenation of NBR.[23] The relative viscosity of HCPIP is constant with increasing the concentration of catalyst, carbon–carbon double bond, and hydrogen pressure.

The relative viscosity quantifies the amount of crosslinking produced over the time taken to complete the hydrogenation process. For the HNBR system, the hydrogenation reaction was affected by crosslinking, which probably involves residual C=C reactivity and possibly is influenced by the presence of CN group. The constant relative viscosity of HCPIP for a range of reaction condition suggests that no crosslinking occurred during the hydrogenation process.

Reaction mechanism and rate law

The catalytic chemistry of the $OsHCl(CO)(O_2)(PCy_3)_2$ has been extensively investigated, resulting in greater understanding of trace intermediates that bring about the observed kinetic behavior. Scheme 2 illustrates a catalytic mechanism that is consistent with the kinetic data of Table V reported herein and the previous work of hydrogenation of NBR using $OsHCl(CO)(O_2)(PCy_3)_2$.[8]

Parent et al.[8] proposed that the dihydrogen ligand of $OsHCl(CO)(H_2)(PCy_3)_2$ does not add oxidatively to the metal in such a manner to permit either the insertion of olefin or the elimination of an alkyl ligand. While the η^2-H_2 ligand may indeed participate in olefin hydrogenation, it is proposed that it cannot do so in the absence of the second molecule of hydrogen. This unconventional assumption is required to account for the second-order behavior observed for NBR hydrogenation. Without it, a mechanism containing a single rate-determining step cannot be derived.

An observed kinetic isotope effect implicates cleavage of a bond to hydrogen in the rate-limiting reaction.[8] This could result from the insertion of olefin into an Os—H bond or by a reductive elimination of an osmium-alkyl to yield the saturated product. The proposed mechanism does not discriminate between these possibilities. Rather, it assumes one of these processes is rapid relative to its rate-determining counterpart. Accordingly, olefin hydrogenation could be governed by the rate expression:

$$\frac{-d[\mathrm{C}{=}\mathrm{C}]}{dt} = k_{\mathrm{rds}}\,[\mathrm{OsH_3Cl(CO)(H_2)(PCy_3)(C{=}C)}] \quad (2)$$

A material balance on the osmium charged to the system is given by

$$[\mathrm{Os}]_T = [\mathrm{OsH_3Cl(CO)(H_2)(PCy_3)(C{=}C)}]$$
$$+ [\mathrm{OsH_3Cl(CO)(H_2)(PCy_3)}] + [\mathrm{OsHCl(CO)(H_2)(PCy_3)}]$$
$$+ [\mathrm{OsHCl(CO)(H_2)(PCy_3)_2}] + [\mathrm{OsHCl(CO)(PCy_3)_2}]$$
$$(3)$$

Applying the equilibrium relations defined in Scheme 2, the concentration of $\mathrm{OsH_3Cl(CO)(H_2)(C{=}C)(PCy_3)}$ may be substituted into eq. (2) to provide the resulting rate law, as shown by

$$\frac{-d\,[\mathrm{C}{=}\mathrm{C}]}{dt} = \frac{[\mathrm{Os}]_T K_{H_2} K_p K_1 K_2\,[\mathrm{C}{=}\mathrm{C}]\,[\mathrm{H_2}]^2}{[\mathrm{P}] + K_{H_2}\,[\mathrm{P}][\mathrm{H_2}] + K_{H_2} K_p[\mathrm{H_2}] + K_{H_2} K_p K_1[\mathrm{H_2}]^2\,(1 + K_2\,[\mathrm{C}{=}\mathrm{C}])} \quad (4)$$

The rate expression derived from the mechanism is consistent with the observed kinetic data. Given this expression, it would be expected that there would be a first-order dependence on [Os] and a first-order dependence on [C=C] providing that the term $K_{H2} K_p K_1[\mathrm{H_2}]^2(1+K_2[\mathrm{C}{=}\mathrm{C}])$ is small relative to the others in the dominator of eq. (4). We observe second-order behavior with respect to hydrogen pressure at relatively low pressures (=13.8 bar). Further increase in pressure yielded a diminished influence on the activity until the process was virtually indifferent to hydrogen pressure. A shift to a zero order is expected at extreme pressure. Most importantly, eq. (4) predicts that an increase in $\mathrm{H_2}$ pressure when the term $K_{H2} K_p K_1[\mathrm{H_2}]^2(1+K_2[\mathrm{C}{=}\mathrm{C}])$ is the predominant term of eq. (4), will eventually lead to a zero-order dependence on [C=C] as was observed experimentally.

CONCLUSIONS

CPIP can be hydrogenated using as number of catalyst but the most efficient one is $\mathrm{OsHCl(CO)(O_2)(PCy_3)_2}$. $\mathrm{RhCl(PPh_3)_3}$ is an efficient catalyst for hydrogenation of most olefin polymers, but the activity is rather low for hydrogenation of CPIP. $\mathrm{OsHCl(CO)(O_2)(PCy_3)_2}$ has been shown to be the most active catalyst for the hydrogenation of CPIP in toluene. Kinetics studies showed that the process was first order with respect to [Os] and [C=C]. A second-order to zero-order dependence on hydrogen pressure was found. The apparent activation energy was found to be 109.32 kJ/mol. The proposed mechanism and the rate expression for hydrogenation of CPIP using $\mathrm{OsHCl(CO)(O_2)(PCy_3)_2}$ were consistent with the kinetic data. Uniform viscosity of HCPIP produced under a variety of reaction condition suggested that there was possibly no degradation and crosslinking effect over the range of conditions used for the hydrogenation process.

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