Hydrogenation of Natural Rubber with Ru[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$ as a Catalyst

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ABSTRACT: Ru[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$ (where PCy$_3$ is tricyclohexylphosphine) functions as an efficient catalytic system for the hydrogenation of natural rubber. Furthermore, the addition of an acid plays an important role in promoting the hydrogenation process. The quantitative hydrogenation of natural rubber results in a polymer akin to an alternating ethylene–propylene copolymer. Kinetic studies have been carried out via the monitoring of the amount of hydrogen consumed: first-order behavior has been observed with respect to the carbon–carbon double-bond concentration, catalyst concentration, and hydrogen pressure, and an inverse dependence on the added PCy$_3$ concentration has been found. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2399–2406, 2005

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INTRODUCTION

Natural rubber (NR) is harvested from the latex of the Brazilian rubber tree, *Hevea brasiliensis.* NR consists of polyisoprene, with an almost 100% cis configuration, and possesses small amounts of abnormal groups such as aldehyde and epoxide. The nonaqueous components of the latex are mixtures of 94 wt % rubber hydrocarbon. The nonrubber components include protein, lipids, and carbohydrates.[1] Because NR cannot have its natural polymerization process tailored like polymerization processes employed in the synthetic rubber industry, chemical modification is a useful postprocess for the alteration of the polymer composition that may provide improvements in certain physical and chemical properties of such unsaturated elastomers. Hydrogenation is a simple method for polymer modification that reduces the degree of C=C unsaturation present in the polymer, and this allows for greater stability against thermal, oxidative, and radiation-induced degradation.[2–4] The quantitative hydrogenation of NR produces an alternating copolymer of ethylene and propylene.[5,6] The catalytic hydrogenation of diene-based polymers can be achieved with either heterogeneous or homogeneous catalyst systems.[7] However, a slow reaction and incomplete reduction result in heterogeneous catalytic hydrogenation because of the high tendency of the polymer molecules to become absorbed on the catalyst, and this then renders the catalyst inefficient or ineffective.[8] Singha et al.[5] reported the quantitative hydrogenation of NR with RhCl(PPh$_3$)$_3$ as a catalyst at a high catalyst loading and for a long reaction time (>20 h).

We recently reported an efficient catalyst, Ru[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$ (where PCy$_3$ is tricyclohexylphosphine), for the hydrogenation of synthetic polyisoprene (CPIP).[9] However, the hydrogenation of NR is much more difficult because of the nonrubber components present in NR. Here we report the hydrogenation of NR (STR 5L) in the presence of the homogeneous catalyst Ru[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$. The effects of the catalyst level, polymer concentration, hydrogen pressure, and temperature were investigated. Because the catalytic activity of this catalyst for olefin hydrogenation has been found to be enhanced by the addition of a protic acid,[10] this was also considered in this study.

EXPERIMENTAL

Materials

NR (STR 5L) was provided by Chalong Latex Industry Co., Ltd. (Bangkok, Thailand). Reagent-grade chlorobenzene (MCB) was obtained from Fisher Scientific, Ltd., (Toronto, Canada) All solvents were used as received. The hydrogen gas had a purity of 99.99% and was supplied by Praxair, Inc., (Mississauga, Canada). Ru(CH=CH)(Ph)Cl(CO)(PCy$_3$)$_2$ was prepared

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TABLE 1
Effect of the Addition of Various Acids on NR Hydrogenation

Entry	Acid	Acid added (equiv)	Hydrogenation (%)	Time (h)
1	—	0.0	98.7	21
2	Succinic acid	7.0	80.0	4
3	3-Chloropropionic acid	7.7	97.7	4
4	p-TSOH	4.4	99.2	4

Conditions: temperature T = 160°C; P_{H_2} = 40.3 bar; [C=C] = 260 mM; [Ru] = 200 μM in 150 mL of chlorobenzene.

according to the procedures outlined in the literature.[11] p-Toluenesulfonic acid (p-TsOH), 3-chloropropionic acid, and succinic acid were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

Hydrogenation reactions

The hydrogenation of NR was investigated in the presence of Ru[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$ by the measurement of the amount of hydrogen consumed with time with a gas uptake apparatus developed by Mohammadi and Rempel.[12] The hydrogenation apparatus was maintained at a constant temperature (±1°C) and pressure (±0.02 bar) throughout the reaction. Typically, a 150-mL polymer solution was prepared and transferred into the reactor. The catalyst and acid were weighed into a small glass bucket, which was placed in a port in the reactor head. The solution was deoxygenated by partial evacuation and purging with hydrogen gas. The reactor was pressurized and then stirred at 1200 rpm. Once the liquid–vapor equilibrium of the system was established at the desired reaction temperature, the catalyst was dispersed in the solution with an overpressure of hydrogen. After the gas consumption had leveled off or ceased, the reactor was cooled. After the cooling, the product was removed via precipitation with ethanol and then dried *in vacuo*.

Characterization

The final degree of hydrogenation measured by gas uptake was confirmed by NMR spectroscopy analysis. ^{1}H-NMR spectra were recorded on 3% (w/v) solutions of the rubber in CDCl$_3$ with an Avance 300-MHz spectrometer (Bruker, Mississauga, Canada). Upon hydrogenation, peaks at 1.7, 2.2, and 5.2 ppm, which were assigned to —CH$_3$, —CH$_2$—, and =CH groups, respectively, disappeared, and new peaks appeared at 0.8 and 1.1–1.8 ppm, which were attributed to saturated —CH$_3$— and —CH$_2$— groups.

Gel permeation chromatography (GPC) was performed with a Waters GPC system fitted with a Waters Ultrastyragel 104-Å column (Toronto, Canada).

Samples of 0.2% polymer solutions in tetrahydrofuran (THF) were prepared. The system detectors were a Wyatt Dawn DSP-F multi-angle laser light scattering detector (Santa Barbara, CA) operating at 630 nm and a Waters DR 401 differential refractive-index detector (Milford, MA). Wyatt Astra software was used for data analysis.

Thermal analysis

Differential scanning calorimetry (DSC) analysis was carried out on a Netzsch DSC200 (Burlington, MA). For a typical analysis, an approximately 20-mg sample was first cooled to −100°C with liquid nitrogen and then heated under a nitrogen flow at a heating rate of 10°C/min to 40°C. Al$_2$O$_3$ was used as the reference sample. The middle of the incline was taken to be the glass-transition temperature (T_g). Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409C. The temperature was increased under a nitrogen atmosphere from 50 to 800°C at a constant heating rate of 10°C/min. The initial decomposition temperature (T_{id}) and the maximum decomposition temperature (T_{max}) were determined.

RESULTS AND DISCUSSION

Effect of the addition of various acids on NR hydrogenation

The quantitative hydrogenation of NR with Ru-[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$ in chlorobenzene can be achieved at a catalyst concentration of 200 μM, 160°C, and 40.3 bar of hydrogen pressure within 21 h. The hydrogenation of NR is much slower than the rate of CPIP hydrogenation in chlorobenzene catalyzed by Ru complexes under the same conditions.[9] This may be due to the high molecular weight of the rubber and impurities present in NR. In an effort to increase the catalyst activity for the hydrogenation reaction, the effect of acid addition on the reaction rate has been explored. The effects of the addition of various acids on the hydrogenation of NR with Ru[CH=CH(Ph)]-Cl(CO)(PCy$_3$)$_2$ as the catalyst are summarized in Table I (entries 2–4). The hydrogenation rate of NR with the

TABLE II
Summary of Kinetic Data from the Study of NR Hydrogenation Catalyzed by Ru[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$

Experiment	[Ru] (μM)	[C=C]$_0$ (mM)	P_{H_2} (bar)	Temperature (°C)	$k' \times 10^3$ (s^{-1})	Hydrogenation (%)	Time (h)
1	50	260	40.3	160	0.07	21.9	1.05
2	80	260	40.3	160	0.28	72.1	1.66
3	150	260	40.3	160	0.63	96.8	1.61
4	200	260	40.3	160	1.18	97.5	0.94
5	30	130	40.3	160	0.18	47.1	0.91
6	50	130	40.3	160	0.46	49.8	0.49
7	100	130	40.3	160	0.91	83.8	0.58
8	150	130	40.3	160	1.39	90.3	0.32
9	200	130	40.3	160	1.71	97.0	0.32
10	200	260	19.7	160	0.50	89.0	1.52
11	200	260	54.1	160	1.51	98.0	0.74
12	200	260	67.9	160	1.95	97.6	0.52
13	200	420	40.3	160	0.69	93.4	1.33
14	200	260	40.3	90	0.33	75.4	0.79
15	200	260	40.3	110	0.59	85.1	0.63
16	200	260	40.3	140	0.91	99.4	1.45
17	200	260	40.3	170	1.04	94.0	0.73
18	200	260	40.3	180	0.75	74.6	0.74
19	200	130	40.3	100	1.08	78.4	0.38
20	200	130	40.3	120	1.78	98.0	0.48
21	200	130	40.3	140	2.74	97.1	0.35

Solvent = chlorobenzene; volume = 150 mL; [p-TsOH] = 8.8 equiv.

ruthenium complex in the presence of a small amount of added acid is greatly enhanced in comparison with that for NR with the Ru complex without added acid. p-TsOH is the most efficient acid promoter for the hydrogenation of NR because the sulfonic acid is more acidic than the other selected carboxylic acids. This suggests that the strong acid can accelerate the activity of the Ru complex more than the weaker acids in the following order: p-TsOH > 3-chloropropionic acid > succinic acid.

Kinetics of NR hydrogenation with Ru[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$

A detailed kinetic study of the hydrogenation of NR in the presence of Ru[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$ and p-TsOH in chlorobenzene has been conducted in an attempt to gain a better understanding of the reaction mechanism. A summary of the results for a series of experiments showing the effect of the reaction variables on the pseudo-first-order rate constant k' is provided in Table II. In all cases, the reaction gives rise to typical first-order plots up to high levels of conversion, as shown in Figure 1. Thus, the hydrogenation rate is proportional to the double-bond concentration as follows:

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

First-order rate constants for a variety of reaction conditions have been obtained from straight-line

first-order plots (Fig. 1) and are summarized in Table II.

Effect of the ruthenium concentration

Two sets of experiments in which the ruthenium concentration was varied over the range of 30–200 μM at 160°C with 8.8 equiv of p-TsOH were performed to determine the influence of the catalyst concentration on the rate of hydrogenation. In the first set of experiments, the initial concentration of the polymer was kept at 260 mM under 40.3 bar of hydrogen pressure, and in the second set of experiments, the polymer concentration was 130 mM. The pseudo-first-order rate constant, as a function of the Ru concentration, at both levels of olefin concentration is linearly proportional to the total concentration of ruthenium, as illustrated in Figure 2. This agrees well with the investigation of CPIP[9] and nitrile–butadiene copolymer (NBR)[11] hydrogenation with the same ruthenium system.

The plots of NR hydrogenation show a positive intercept with respect to the Ru concentration, whereas this behavior has not been observed for CPIP hydrogenation.[9] This can be explained, in that some portion of the Ru catalyst was sacrificed as a result of impurities in NR. It appears that about 45 μM of the active catalyst was destroyed when the concentration of rubber was 260 mM, but at a lower concentration of the polymer (130 mM), a much smaller amount of the catalyst was sacrificed. Therefore, increasing impuri-
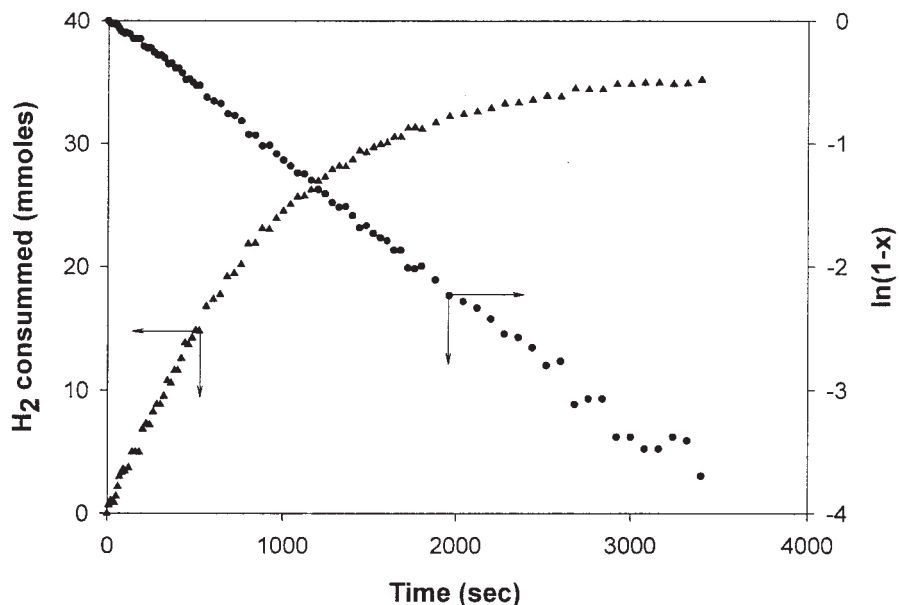
Figure 1 Hydrogen consumption plot for NR hydrogenation ($[Ru] = 200 \ \mu M$; $[C{=}C] = 260$ mM; $[p\text{-TsOH}] = 8.8$ equiv; P_{H_2} = 40.3 bar; temperature = 160°C in 150 mL of chlorobenzene).

ties as the concentration of NR increases results in a decreasing amount of the active catalyst for the hydrogenation reaction.

Effect of the hydrogen pressure

A first-order rate dependence on the hydrogen concentration tends to suggest that a single reaction mechanism is probably involved for the hydrogenation of the polymer (Fig. 3). A similar observation was made from the H_2 univariate experiments of CPIP[9] and NBR.[11] This investigation illustrated a first-order behavior with respect to the experimental rate constant on the hydrogen pressure that seems to be characteristic of this ruthenium catalyst. In contrast, the extent of hydrogenation of NR in the presence of $RhCl(PPh_3)_3$ increased with an increase in the hydrogen pressure at a low hydrogen concentration and leveled off at a higher hydrogen concentration.[5] Gan et al.[6] hydrogenated NR in hexane with nickel 2-ethyl-
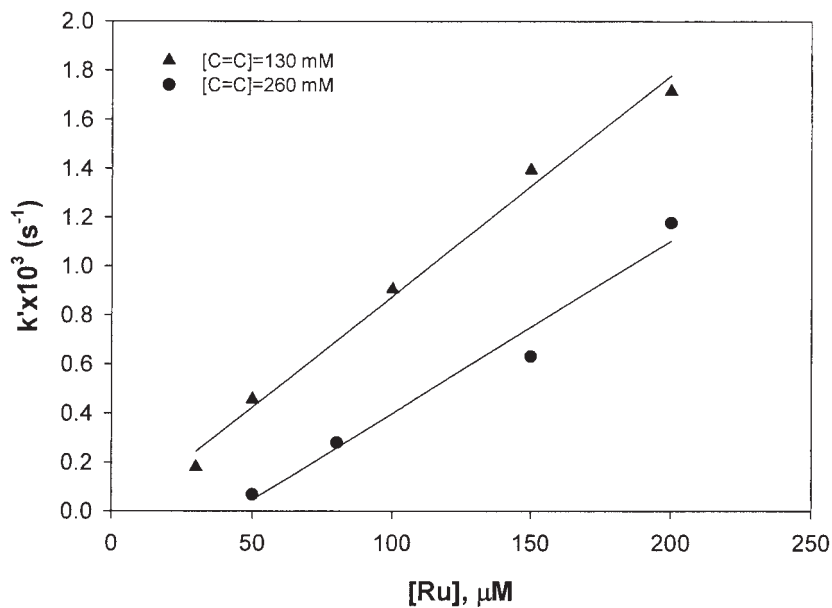

Figure 2 Effect of the Ru concentration on the rate constant k' (P_{H_2} = 40.3 bar; temperature = 160°C; $[p\text{-TsOH}] = 8.8$ equiv).
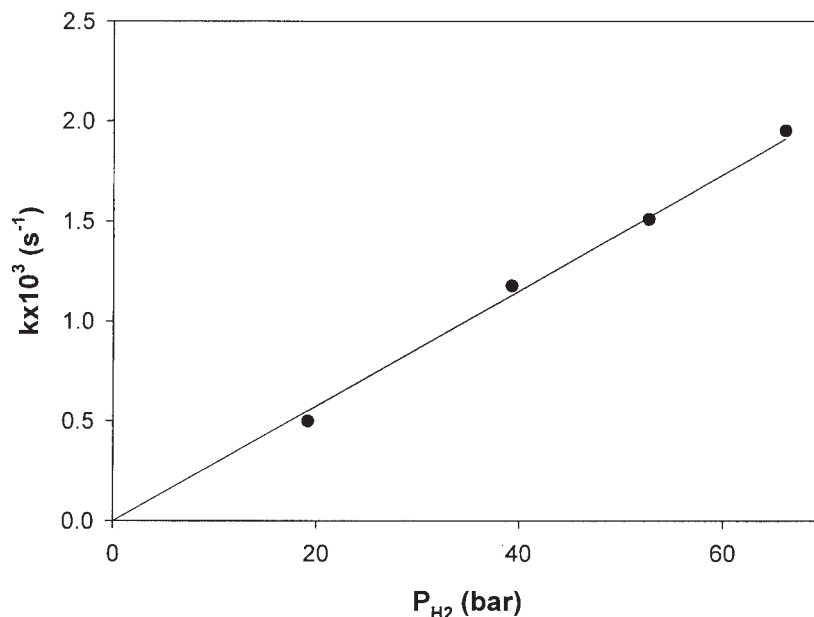
Figure 3 Effect of P_{H_2} on the rate constant k ([C=C] = 260 mM; [Ru] = 200 μM; temperature = 160°C; [p-TsOH] = 8.8 equiv).

hexanoate in combination with triisobutylaluminum. The rate of reaction also increased with a higher initial hydrogen pressure.

Effect of the double-bond concentration

As mentioned previously, the hydrogenation profiles that followed pseudo-first-order behavior with respect to the C=C concentration should, by definition, be independent of the amount of olefin charged to the reactor. The hydrogenation rate constant of NR, however, decreased with increasing polymer concentration (Table II, experiments 4, 9, and 13). Therefore, the inverse behavior of the C=C concentration on increasing C=C concentration can be attributed to the effect of impurities within NR upon decreasing catalyst activity.

Effect of added PCy$_3$

The dependence of the initial hydrogenation rate on the addition of PCy$_3$ was investigated to understand the function of the PCy$_3$ ligand in the role of the active Ru species in the catalytic mechanism. When amounts ranging from 0.2 to 1.5 equiv (1.5 times the number of moles of the catalyst in the reactor) of PCy$_3$ were used, the rate constant decreased with increasing PCy$_3$ concentration (Fig. 4). It is evident that adding PCy$_3$ retards the potential activity of the ruthenium complexes for hydrogenation. This may be explained by the inhibition of phosphine dissociation from ruthenium hydride species:

$$RuHCl(CO)(PCy_3)_2 \underset{}{\overset{k_D}{\rightleftharpoons}} RuHCl(CO)(PCy_3) + PCy_3$$

$$(2),$$
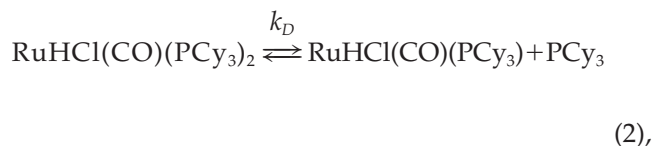
where k_D is the dissociation equilibrium constant.

Effect of the temperature

The dependence of the hydrogenation rate on the temperature was examined for two sets of experiments, over the range of 100–160°C for a 130 mM initial polymer concentration and over the range of 90–180°C for a 260 mM initial polymer concentration as the base condition. Figure 5 depicts the influence of the temperature on the hydrogenation rate constant. The results show that a temperature increase results in an increasing hydrogenation rate. However, the influence of the temperature results in a decrease in the rate constant at temperatures above 160°C. These results seem to suggest that at a higher temperature, the impurities in NR destroy more of the active catalyst. In other words, there may be two types of NR impurities: the primary one interacts with the active catalyst quite easily, as shown by the results in Figure 2, whereas the secondary impurities are activated at a high temperature that is, higher than 160°C. Thus, an increased amount of dead catalyst at a high temperature results in a slow hydrogenation rate. Our previous studies of CPIP hydrogenation showed that the rate constant increased as the temperature was increased over the range of 130–180°C.[9] It can be concluded, therefore, that the ruthenium catalyst is not decomposed at 160–180°C.
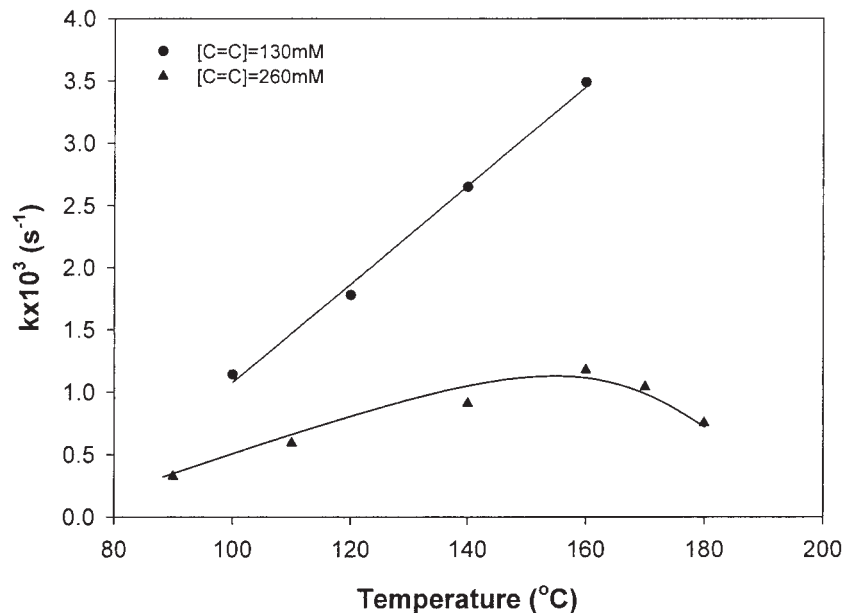
Figure 4 Effect of the temperature on the rate constant k (P_{H_2} = 40.3 bar; [Ru] = 200 μM; [p-TsOH] = 8.8 equiv).

Apparent activation energies of 25.3 kJ/mol for a 130 mM polymer C=C concentration over the temperature range of 100–160°C and of 23.3 kJ/mol for a 260 mM polymer C=C concentration over the temperature range of 90–160°C were obtained. These approximations show that increasing the amount of the polymer results in a slight decrease in the apparent hydrogenation of NR with RhCl(PPh$_3$)$_3$;[5] 26.0 kJ/mol was reported for the hydrogenation of NR in the presence of nickel 2-ethylhexanoate and triisobutylaluminum.[6] Although the reason for such a low value of the apparent activation energy is not totally understood, it is believed that there may be a diffusion effect of the active catalyst into the polymer particle due to the high viscosity of the polymer. It is particularly interesting that the apparent activation energy for the hydrogenation of synthetic CPIP, which has a lower weight-average molecular weight (800,000) than that
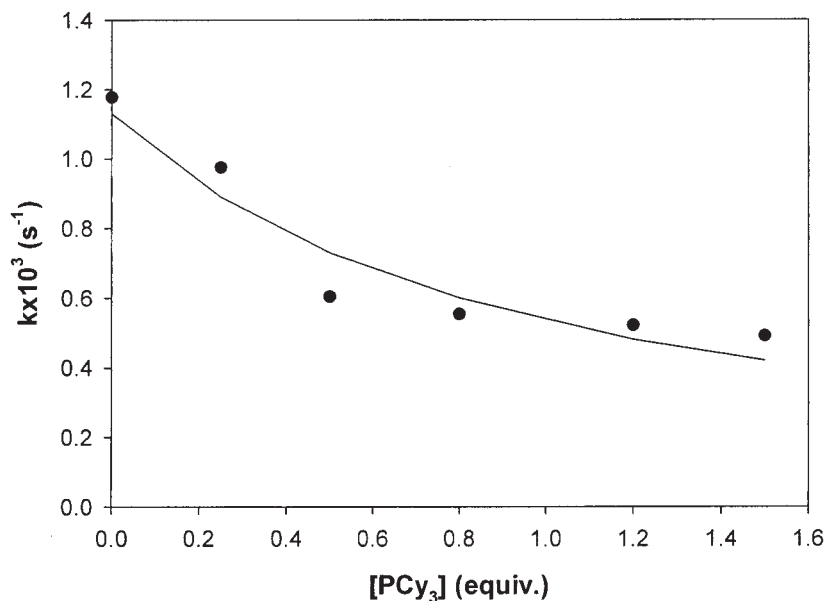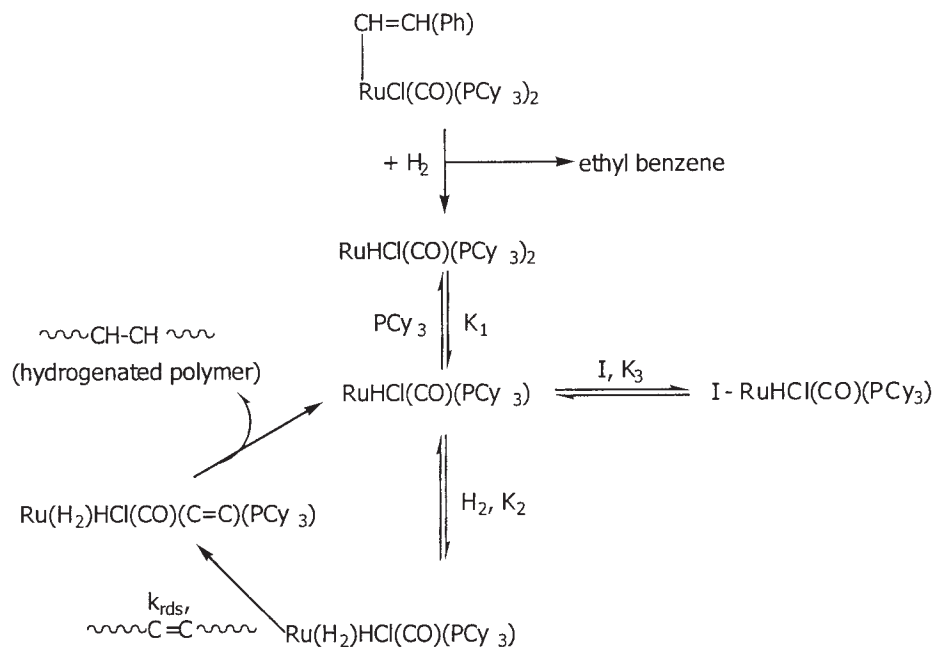

Figure 5 Effect of added PCy$_3$ on the rate constant k ([C=C] = 260 mM; [Ru] = 200 μM; P_{H_2} = 40.3 bar; temperature = 160°C, [p-TsOH] = 8.8 equiv).

CH=CH(Ph)
|
RuCl(CO)(PCy$_3$)$_2$

+ H$_2$ ⟶ ethyl benzene

RuHCl(CO)(PCy$_3$)$_2$

PCy$_3$ ‖ K$_1$

~~~CH-CH~~~
(hydrogenated polymer)

RuHCl(CO)(PCy$_3$) ⇌ I, K$_3$ ⟶ I - RuHCl(CO)(PCy$_3$)

H$_2$, K$_2$

Ru(H$_2$)HCl(CO)(C=C)(PCy$_3$)

k$_{rds}$
~~~C=C~~~ Ru(H$_2$)HCl(CO)(PCy$_3$)

Scheme 1 Proposed mechanism for the hydrogenation of NR catalyzed by Ru[C=CH(Ph)]Cl(CO)(PCy$_3$)$_2$.

of NR ($>$1,000,000), has been estimated to be 51.1 kJ/mol.[9]

Reaction mechanism consideration

A plausible reaction mechanism, as illustrated in Scheme 1, is postulated for the hydrogenation of NR with Ru[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$ as the catalyst. A difficult element with the NR hydrogenation data is the effect of impurities in NR. The reaction of Ru[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$ with hydrogen to give the first hydride complex RuHCl(CO)(PCy$_3$)$_2$ and ethyl benzene is rapid. Then, a phosphine ligand dissociates from the hydride complex to form RuH-Cl(CO)(PCy$_3$). The catalytic cycle of NR is similar to that of hydrogenations of substrates lacking impurities,[9] except that the impurities exhibit inhibitory behavior. Therefore, the complex RuHCl(CO)(PCy$_3$) can react with impurities within NR and/or coordinate with H$_2$, and this is followed by the coordination of carbon–carbon double bonds. The lack of a kinetic isotope effect, when deuterium is used in place of hydrogen, implies that the rate-determining step involves the coordination of the catalyst with carbon–carbon double bonds within the polymer chain.

The rate law derived from the proposed mechanism has the following form:

$$-\frac{d[\text{C}=\text{C}]}{dt} = \frac{k_{\text{rds}}K_1K_2K_HP_{\text{H}_2}[\text{Ru}]_T[\text{C}=\text{C}]}{K_1+K_1K_2K_HP_{\text{H}_2} + [\text{PCy}_3] + K_1K_3[\text{I}]} \quad (3)$$

where k_{rds} is the limiting reaction rate constant, K_1 and K_2 are equilibrium constants, K_H is Henry's law con-

stant for the solubility of hydrogen in chlorobenzene, P_{H_2} is the partial pressure of H$_2$, and [Ru]$_T$ is the total Ru concentration. This rate law is in good agreement with the observed reaction kinetics when

$$k' = \frac{k_{\text{rds}}K_1K_2K_HP_{\text{H}_2}[\text{Ru}]_T}{K_1 + K_1K_2K_HP_{\text{H}_2} + [\text{PCy}_3] + K_1K_3[\text{I}]} \quad (4)$$

where K_3 is an equilibrium constant. Because a rigorous first-order dependence on the hydrogen pressure, over the range of study, has been observed, it appears that the term $K_1K_2K_HP_{\text{H}_2}$ in the denominator of eq. (4) is negligible. Thus, the model reduces to the following form:

$$k' = \frac{k_{\text{rds}}K_1K_2K_HP_{\text{H}_2}[\text{Ru}]_T}{K_1 + [\text{PCy}_3] + K_1K_3[\text{I}]} \quad (5)$$

Although the actual amount of impurities that have an effect on the catalyst activity is unclear, it is evident that the system sacrifices some amount of catalyst at a constant concentration of NR at a given temperature. The experimental results show that about 45 μM of the ruthenium catalyst was destroyed when the concentration of NR was 260 mM in 150 mL of chlorobenzene. Equation (6) provides a model for NR hydrogenation by assuming a constant concentration of impurities at a given temperature below 160°C:

$$k' = \frac{k_4P_{\text{H}_2}([\text{Ru}]_T - C)}{K_5 + [\text{PCy}_3]} \quad (6)$$

TABLE III
Summary of GPC Molecular Weight Data for NR and Hydrogenated Natural Rubber (HNR)

Polymer	[C=C] (mM)	Temperature (°C)	P_{H_2} (bar)	[Ru] (μM)	p-TsOH (equiv)	M_n	M_w	M_w/M_n
			Condition					
NR	—	—	—	—	—	512,000	974,400	1.90
HNR	260	160	40.3	200	8.8	474,600	939,600	1.98
HNR	260	160	67.9	200	8.8	562,200	962,900	1.71
HNR	260	140	40.3	200	8.8	538,600	1,094,000	2.03
HNR	260	180	40.3	200	8.8	415,700	752,600	1.81

M_n = number-average molecular weight; M_w = weight-average molecular weight.

The rate constant k_4 is a lumped constant containing k_{rds}, K_1 and K_2, and K_H, whereas the constant K_5 represents $K_1 + K_1K_3[I]$, and C is a correction factor for the presence of impurities, which is assumed to be constant for each concentration of NR.

Polymer chain length properties

Typically, a GPC analysis of NR shows a bimodal molecular weight distribution with high-molecular-weight and low-molecular-weight peaks. Table III summarizes the molecular weight data of NR and the hydrogenated product. The nonhydrogenated rubber is partially insoluble in THF. However, its soluble part displays a GPC chromatogram similar to that of its hydrogenated polymer, and the molecular weight distribution did not change significantly during hydrogenation. The hydrogenation of NR at a high temperature (180°C) led to a significant decrease in the molecular weight of the hydrogenated rubber.

Thermal analysis

The results in Table IV show that the T_g values of the hydrogenated products were close to those of the starting polymers. This suggests that the hydrogenated polymers still exhibited amorphous properties. T_{id} was determined from the intersection of two tangents at the onset of the decomposition temperature. T_{max} was calculated from the peak maximum of the derivative of the TGA curves. T_{id} and T_{max} of rubbers are also shown in Table IV. It is apparent that both T_{id}

and T_{max} increased as the degree of hydrogenation increased. Similar behavior in the thermal properties of hydrogenated products was observed by Singha.[13]

CONCLUSIONS

The quantitative hydrogenation of NR can be achieved with Ru[CH=CH(Ph)]Cl(CO)(PCy$_3$)$_2$ as the catalyst. The presence of impurities and the high molecular weight of NR may reduce the efficiency of the catalyst. The addition of a small amount of acid, that is, p-TsOH, appears to neutralize the poisonous effect of the system. The molecular weight and molecular weight distribution of NR are similar to those of the hydrogenated polymer. The hydrogenation reaction leads to an increase in the thermal stability of NR without affecting its T_g.

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TABLE IV
DSC and TGA Results of Hydrogenated Natural Rubber (HNR)

Polymer	Hydrogenation (%)	T_g (°C)	T_{id} (°C)	T_{max} (°C)
NR	0	−62	357	380
HNR-1	69	−59	397	441
HNR-2	80	−58	431	460
HNR-3	98	−57	439	468