

Hydrogenation of Natural Rubber in the Presence of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$: Kinetics and Mechanism

N. Hinchiranan,¹ P. Prasassarakich,¹ G. L. Rempel²

¹Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

²Department of Chemical Engineering, University of Waterloo, Ontario, N2L 3G1, Canada

Received 9 July 2004; accepted 13 January 2005

DOI 10.1002/app.22125

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The homogeneous catalyst precursor, $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$, was utilized for the hydrogenation of natural rubber to convert the unsaturated structure to a saturated form, providing an alternating ethylene-propylene copolymer. A detailed kinetic investigation was carried out by monitoring the amount of hydrogen consumption during the reaction using a gas-uptake apparatus. ^1H NMR spectroscopy was used to determine the final olefin conversion to the hydrogenated product. Kinetic data, collected according to a statistical design framework, defined the influence of catalyst and polymer concentration, hydrogen pressure, and reaction temperature on the catalytic activity. The kinetic results indicated that the hydrogenation rate exhibited a first- shifted to zero-order dependence on hydrogen at lower hydrogen pressure, which then decreased toward an inverse behavior at pressures higher than 41.4 bar. The hydrogenation was also observed to be first-order with respect to catalyst concentration, and an apparent inverse

dependence on rubber concentration was observed due to the impurities in the rubber. The hydrogenation rate was dependent on reaction temperature, and the apparent activation energy over the temperature range of 125–145°C was found to be 122.76 kJ/mol. Mechanistic aspects of the hydrogenation of natural rubber in the presence of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ were proposed on the basis of the observed kinetic results. The addition of some acids and certain nitrogen containing materials showed an effect on the hydrogenation rate. The thermal properties of hydrogenated natural rubber indicated that the thermal stability increased with increasing % hydrogenation of the rubber. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4499–4514, 2006

Key words: catalyst; hydrogenation; kinetics; natural rubber; osmium complex

INTRODUCTION

Natural rubber (NR) in the commercial market is totally dominated by *Hevea Brasiliensis*, which is an important industrial material utilized in many applications, such as tires, gloves, footwear, belts, cables, and so forth, because of its high resilience, tear resistance, low hysteresis (heat build-up), excellent dynamic properties, and general fatigue resistance.¹ The major component of NR identified from FTIR and NMR studies is polyisoprene in a *cis*-1,4 configuration ~ 94%. The unique composition of the NR structure involves proteins, which are believed to bring about its characteristic properties. The rubber chain is composed of unidentified initiating terminal groups, two trans isoprene units, and a long chain of *cis*-isoprene units terminated with unidentified chain end groups. The unidentified initiating and chain end groups are possibly an oligopeptide and a fatty acid ester, respectively.² Due to the unsaturation of the carbon–carbon double bonds of the isoprene backbone, NR degrades

when exposed to sunlight, ozone, oxygen, and long term heating. Chemical modification of unsaturated polymers continues to be an active research field for the improvement of the material properties of the polymer. It enables the production of new polymeric materials, which are often inaccessible or difficult to prepare via general polymerization processes. Hydrogenation is one type of chemical modification, which reduces the amount of unsaturation and thus changes the properties of the diene polymer toward greater stability against thermal and oxidative degradation.^{3,4}

Catalytic hydrogenation of unsaturated polymers has been increasingly studied since noncatalytic systems often tend to yield side reactions, such as *cis*-trans isomerization, depolymerization, cyclization, and crosslinking.^{5,6} Hydrogenation catalyzed by homogeneous catalysts is more favorable than heterogeneous catalysts since they exhibit higher selectivity and are not susceptible to macroscopic diffusion problems. In addition, the performance of homogeneous catalysts can be explained and understood at the molecular level.⁷ Homogeneous catalysis for hydrogenation of diene-based polymers, such as polybutadiene and nitrile rubber, has been traditionally dominated by ruthenium, rhodium, and palladium complexes.^{8–13} The potential reactivity of 5d metals, transition metals of the third row, for homogeneous

Correspondence to: G. L. Rempel (grempe@cape.uwaterloo.ca).

catalytic transformation, for the most part, has been overlooked in the past. Presumably, this has resulted from the belief that reactions comprising typical catalytic cycles, such as Lewis base addition-elimination, oxidative addition-reductive elimination, and insertion-deinsertion of third row metal complexes, are slower than their 4d congeners because 5d metals usually form more stable complexes.

Mononuclear osmium complexes, $\text{OsHCl}(\text{CO})(\text{PR}_3)_2$, have been shown to be efficient catalysts for olefin hydrogenation of substrates such as phenylacetylene and benzylideneacetone.^{14–16} The selection of the ligand is an important factor to affect the efficiency of the catalysts. Mao and coworkers¹⁷ reported the effect of various phosphine ligands of osmium complexes on the catalytic activity for NBR hydrogenation. It was found that the activity of $\text{OsHCl}(\text{CO})(\text{O}_2)\text{L}_2$ was increased when L was a bulky monophosphine with a cone angle of more than 160° , such as $P\text{-}i\text{-Pr}_3$, PCy_3 , and PCy_2Ph , due to the ease of dissociation of the ligand from an 18-electron complex to produce a 16-electron species. Unlike the $\text{RhCl}(\text{PPh}_3)_3$ system, a distinct advantage of the osmium complex is that no addition of phosphine is required to maintain the catalytic activity.¹⁸ $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ has been shown to be a very effective catalyst for the hydrogenation of acrylonitrile-butadiene copolymer (NBR)¹⁸ and synthetic *cis*-1,4-polyisoprene (PIP),¹⁹ with up to 99% conversion within 15–30 min at moderate conditions. However, NR and polyisoprene are rather difficult to hydrogenate using conventional catalysts due to the steric constraint of the isopropyl group in the rubber chain. Singha and colleagues³ reported the hydrogenation of NR in the presence of $\text{RhCl}(\text{PPh}_3)_3$. It was found that the quantitative hydrogenation was only obtained after 22 h using a very high loading of catalyst (1.91 mM/NR 0.50 g). This appears to be a rather ineffective catalyst system.

The purpose of the present work is to study the kinetics and optimize the process of NR hydrogenation catalyzed by $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$. The effect of catalyst concentration ($[\text{Os}]$), rubber concentration ($[\text{C}=\text{C}]$), hydrogen pressure (P_{H_2}), and reaction temperature were studied using two-level factorial design and univariate kinetic experiments. The results from univariate experiments were used to propose a catalytic mechanism for the hydrogenation process. The effects of the addition of some acids and nitrogen containing substances on the rate of hydrogenation and the thermal properties of hydrogenated natural rubber (HNR) were also investigated.

EXPERIMENTAL

Materials

Osmium (III) chloride trihydrate ($\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$) and tricyclohexylphosphine (PCy_3) were obtained from Strem Chemicals (Newburyport, MA, USA). 99.99%

oxygen-free hydrogen gas for the hydrogenation experiments was supplied by Praxair Inc. (Kitchener, ON, Canada). Monochlorobenzene from Fischer Scientific Ltd. (Fair Lawn, NJ, USA), toluene, xylene, hexane, and 2-methoxyethanol from EM Science (Darmstadt, Germany) and tetrahydrofuran from Calendon Laboratories Ltd. (Georgetown, ON, Canada) were all reagent grade and used as received. 3-Chloropropionic acid and *p*-toluenesulfonic acid were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA). Hexylamine was obtained from BDH Chemicals (Toronto, ON, Canada), and hexadecylacrylamide was synthesized in our laboratory. The natural rubber (STR-5L) was provided by Chalong Latex Industry Co., Ltd. (Songkhla, Thailand). High molecular weight *cis*-1,4-polyisoprene with 97% of *cis* configuration (Natsyn) was obtained from Bayer, Inc. (Sania, Canada).

Catalyst preparation

$\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$, which was used as the catalytic precursor for NR hydrogenation, was prepared by refluxing $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ with PCy_3 in 2-methoxyethanol under a nitrogen atmosphere to generate the active species, $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$, following the procedure of Esteruelas and Werner.²⁰ $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ was prepared by exposing a hexane suspension of the species $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$ to pure oxygen gas, as detailed by Esteruelas and colleagues.²¹ The catalytic complex was washed with cold hexane and then dried in vacuum. $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$: ^1H NMR (CD_2Cl_2): δ -33.06 (br.), $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 37.5 (s). $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$: ^1H NMR (CD_2Cl_2): δ -2.99 (t), $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 16.63 (s).

Kinetic study of NR hydrogenation

Kinetic data provided from hydrogen consumption profiles were obtained using the gas-uptake apparatus developed by Mohammadi and Rempel.²² This equipment can maintain isothermal ($\pm 1^\circ\text{C}$) and isobaric (± 0.02 bar) conditions throughout the hydrogenation process. The NR solutions were prepared by dissolving the desired amount of NR in 150 mL of monochlorobenzene in the dark. The catalyst was weighed into a small glass bucket and placed in a port of the reactor head. The rubber solution was degassed three times by charging with hydrogen gas at 13.8 bar, followed by continuously bubbling hydrogen gas through the reaction solution for 20 min at an agitation rate of 1200 rpm to ensure that oxygen was removed from the system. Once liquid-vapor equilibrium under the desired reaction conditions was established, the catalyst was released by using a slight overpressure of hydrogen. The amount of hydrogen consumed by the reaction as a function of time and the solution temperature were then recorded. Each experiment proceeded until

the reaction culminated, after which the reactor was cooled and the hydrogenated product was isolated by precipitation with ethanol and then dried in vacuum.

Characterization

The structure of NHR and the final conversion provided from the hydrogen consumption profile were confirmed by FTIR and ^1H NMR spectroscopy. Samples for FTIR analyses were prepared by casting films on NaCl plates. FTIR scans were obtained on a BIO-RAD Merlin FTS 3000X spectrometer. ^1H NMR spectra of samples dissolved in CDCl_3 were obtained on a Bruker 300 MHz spectrometer. The relative viscosity representative of the molecular weight of the HNR was also investigated. 0.12500 ± 0.00015 g of HNR samples were dissolved in 25 mL of toluene at 35°C and then transferred to an Ubblohde capillary viscometer through a coarse, sintered-glass filter to separate any insoluble gel in the rubber solution. The relative viscosity data (η_{rel}) was reported as the viscosity relative to pure solvent.

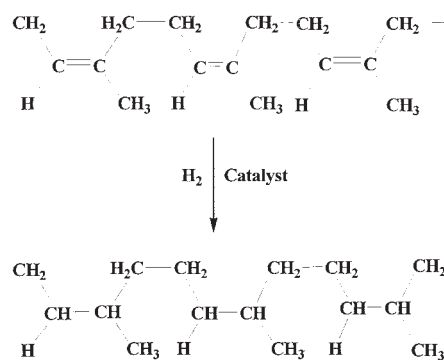
Thermogravimetric analysis (TGA) of the sample was performed on a Perkin-Elmer Pyris Diamond TG/DTA. The temperature was raised under a nitrogen atmosphere from room temperature to 700°C at a constant heating rate of $10^\circ\text{C}/\text{min}$. The flow rate of nitrogen gas was 50 mL/min. The initial decomposition temperature (T_{id}) and the temperature at the maximum of mass loss rate (T_{max}) were evaluated.

Differential scanning calorimetry (DSC) of the sample was carried out on a Mettler Toledo DSC 822. The instrument signal is derived from the temperature difference between the sample and the reference. The rubber samples in a crimped aluminum pan were cooled to -100°C with liquid nitrogen and then heated at a constant rate of $20^\circ\text{C}/\text{min}$ to 0°C . The glass transition temperature was calculated from the midpoint of the base-line shift of the DSC thermogram.

RESULTS AND DISCUSSION

The hydrogenation reaction of NR can be represented as shown in Scheme 1. The structure of HNR is similar to the structure of an alternating ethylene-propylene copolymer.^{3,23} FTIR spectra of NR before and after hydrogenation are illustrated in Figure 1. The characteristic FTIR spectrum of HNR indicated that the $\text{C}=\text{C}$ stretching (1660 cm^{-1}) and olefinic C-H bending (836 cm^{-1}) disappeared, while the intensity of the peak at 735 cm^{-1} attributed to $-(\text{CH}_2)_3-$ increased. For NR and HNR with impurities (proteins), the weak transmittance bands at 3280 cm^{-1} and 1530 cm^{-1} , which are characteristic vibrations of $>\text{N}-\text{H}$ and $>\text{N}-\text{C}=\text{O}$,²⁴ remained after the hydrogenation process.

Figure 2 shows a comparison of the ^1H NMR spectra of NR and HNR. The characteristic ^1H NMR signal attributed to $-\text{CH}_3$ (1.6 ppm), $-\text{CH}_2-$ (2.0 ppm), and



Scheme 1 Natural rubber hydrogenation converted to alternating ethylene-propylene copolymer.

olefinic protons (5.1 ppm), disappeared; and new signals, saturated $-\text{CH}_3$ (0.8 ppm) and $-\text{CH}_2-$ (1.2 ppm), were observed after the hydrogenation process. The actual degree of hydrogenation for each experiment could be calculated from the peak area at 5.1 ppm and the summation of peak areas between 0.8 and 2.0 ppm.

Kinetic experiments for NR hydrogenation

All the kinetic data for the NR hydrogenation using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ as catalyst were obtained using the gas-uptake apparatus. The initial experimental work was conducted by using a factorial design of experiments to find the main effects for the system, and then univariate experiments were carried out to investigate the effect of each factor individually. Figure 3 shows the olefin conversion profiles and corresponding \ln plots for the NR hydrogenation carried out in the gas-uptake apparatus. The reaction rate equation corresponds to a first order reaction rate model with respect to double bond concentration, $[\text{C}=\text{C}]$, as shown in eq. (1).

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

where k' , the pseudofirst-order rate constant, was calculated from the slope of the straight line portion of the first order \ln plot of the gas-uptake data where x was the olefin conversion. The $\ln(1 - x)$ versus time curves for NR hydrogenation exhibited good straight line behavior during the initial stages of the reaction and then deviated as the rate decreased. This result was different from the data observed for the hydrogenation of synthetic *cis*-1,4-polyisoprene (PIP),¹⁹ where the $\ln(1 - x)$ versus time curves were linear to very high conversions. Presumably, the impurities in NR played a role in reducing the catalytic activity as the reaction progressed; therefore, the \ln plot data deviated from the linear model. However, the reaction data was close to the linear model for hydrogenation when higher catalyst concentrations were used as the

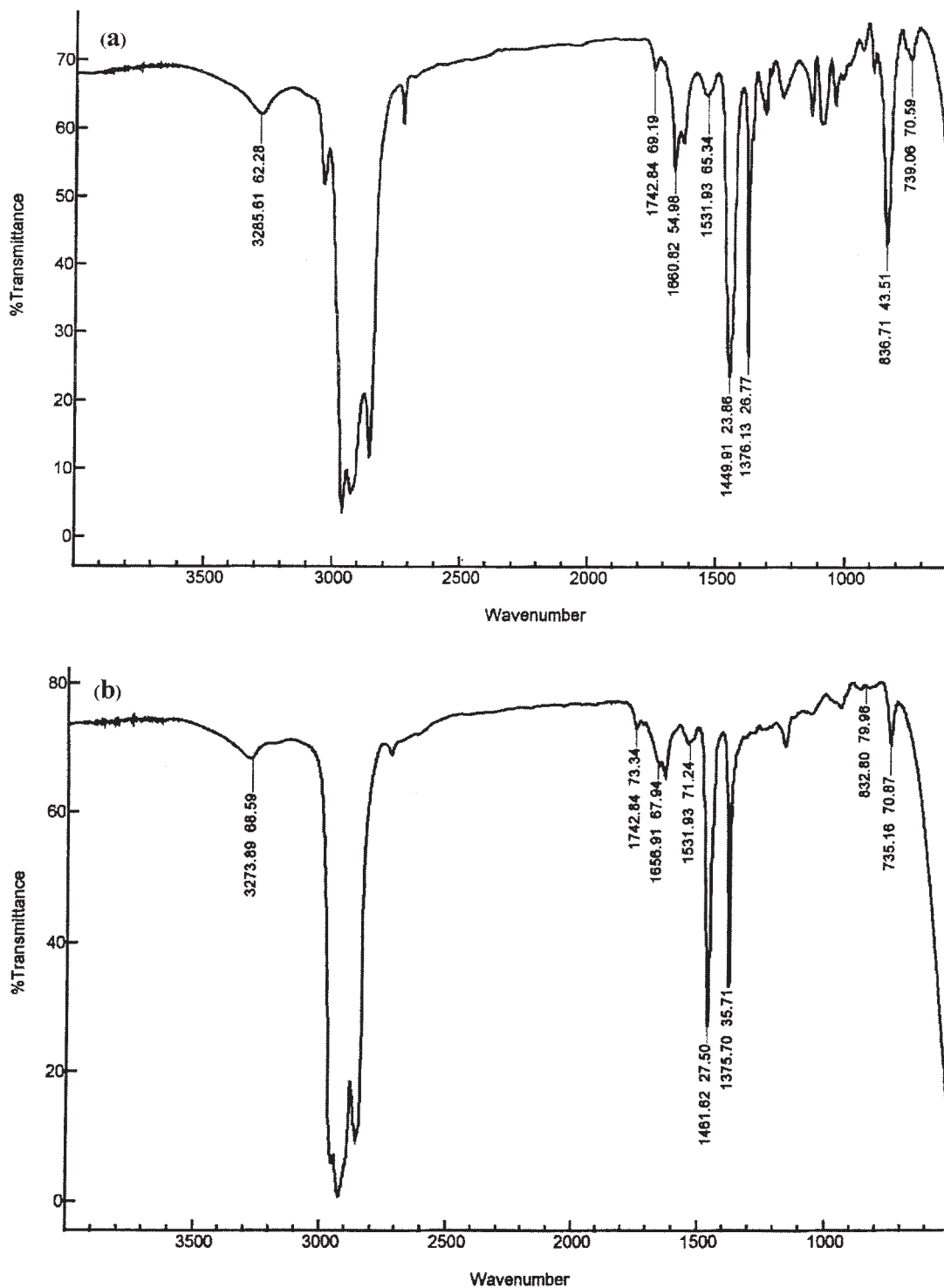


Figure 1 FTIR spectra of (a) NR and (b) HNR.

relative amount of the catalyst deactivated to overcome the effect of impurities was not that significant compared to the total amount of catalyst used.

Two-level factorial design experiments

Factorial designs are generally used for experimental systems involving several factors to study the main ef-

fects and joint effects of factors on the response.²⁵ Two-level factorial design experiments are widely used to screen the influence of each reaction factor. In this work, the principal factors that had an effect on the k' and catalytic cycle of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ were $[\text{Os}]$, $[\text{C}=\text{C}]$, and P_{H_2} . When two-level factorial design was applied to calculate the effect of parameters in the experiment, the levels of factors may be arbitrarily called "low

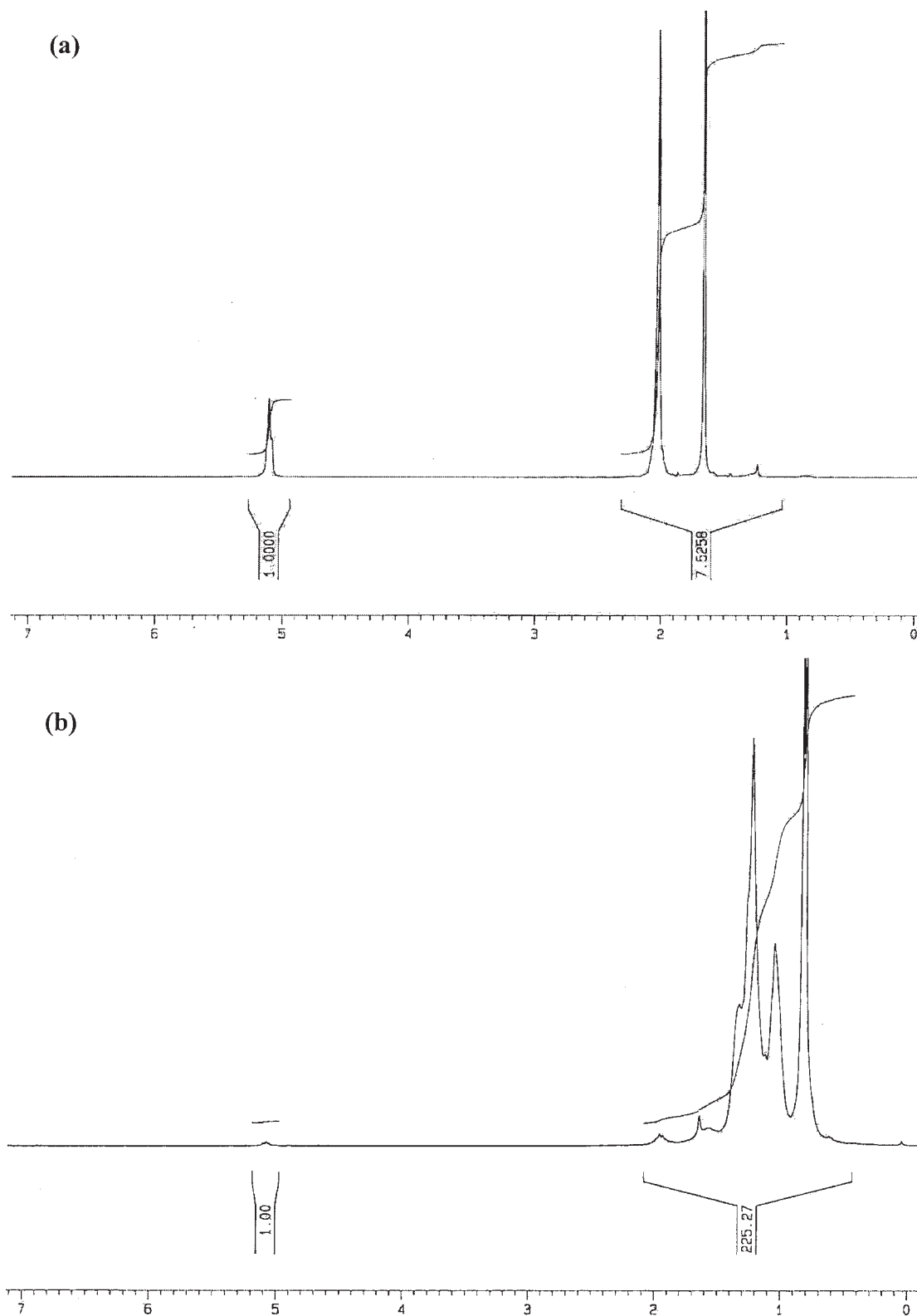


Figure 2 ^1H NMR spectra of (a) NR and (b) HNR.

(-1)" and "high (+1)." The range of $[\text{Os}]$, $[\text{C}=\text{C}]$, and P_{H_2} were 60–120 μM , 260–392 mM, and 6.9–41.3 bar, respectively, as shown in Table I. The reaction temperature was kept constant at 140°C. Yate's algorithm was applied to investigate the main effects and interaction

effects on the rate constant derived from the experimental data.²⁶ Tables II and III represent the results of the Yate's algorithm calculation and the calculation of effects and standard errors for the 2^3 factorial design. The results in Table III indicate that $[\text{Os}]$ and $[\text{C}=\text{C}]$ had a

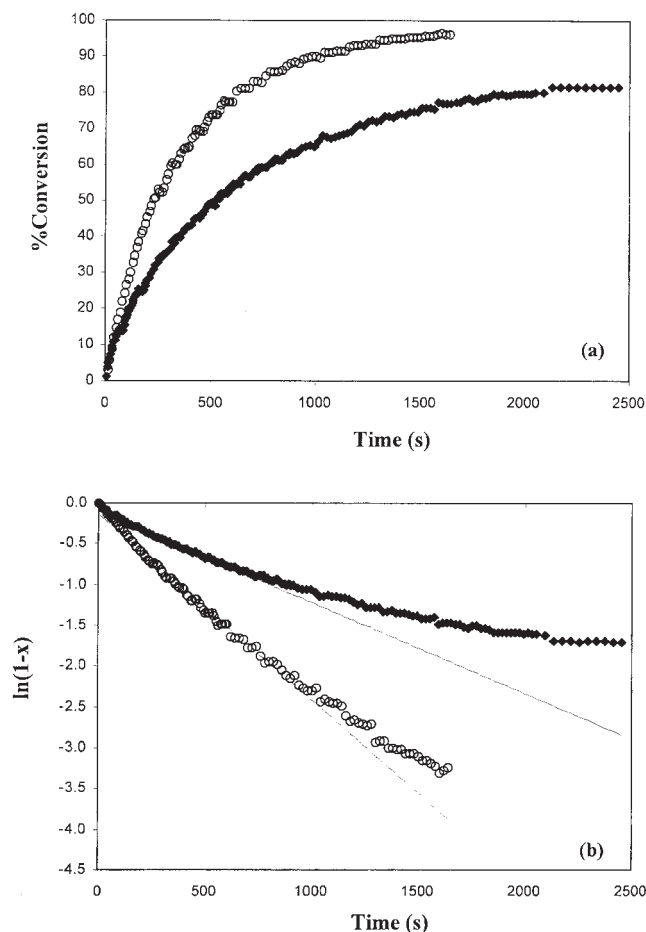


Figure 3 Hydrogenation profile of NR obtained from gas-uptake apparatus: (a) olefin conversion profiles, and (b) first-order \ln plot (— model from linear regression). $[\text{Os}]_T = 60 \mu\text{M}$ (\blacklozenge), and $100 \mu\text{M}$ (\circ); $[\text{C}=\text{C}] = 260 \text{ mM}$; $P_{\text{H}_2} = 6.9 \text{ bar}$; $T = 140^\circ\text{C}$ in monochlorobenzene.

profound influence on the rate of hydrogenation, while the effect of P_{H_2} was moderate on the system over the selected range. Due to the fact that the low level of the hydrogen pressure selected was still relatively high for this catalyst system as seen from univariate experiments presented later, it became an important factor for NR hydrogenation when the hydrogen pressure was lower than 6.9 bar. This finding is discussed later for the univariate experiments. The $[\text{Os}]$ and P_{H_2} had a positive effect, which implies that the rate of hydrogenation increased with an increase in the $[\text{Os}]$ and P_{H_2} . In contrast, $[\text{C}=\text{C}]$ showed a large negative effect on the rate constant. It can be postulated that the impurities in the rubber might be giving rise to this effect on the rate of hydrogenation. The binary interactions, $[\text{Os}][\text{C}=\text{C}]$, $[\text{Os}]P_{\text{H}_2}$, and $[\text{C}=\text{C}]P_{\text{H}_2}$, also affected the hydrogenation rate, but the three-factor interaction ($[\text{Os}][\text{C}=\text{C}]P_{\text{H}_2}$) was not highly significant.

Univariate kinetic experiments

The statistical experiments described above provide only information on the significance of the factors. To

determine how each variable affects the hydrogenation rate, univariate experiments of the central composite design of the parameters were carried out individually to determine their influence on the hydrogenation rate, as shown in Figures 4–7. The results of these experiments are summarized in Table IV.

Dependence on catalyst concentration

To study the influence of catalyst concentration on the rate of hydrogenation, the range of $[\text{Os}]$ was varied between 40 and 120 μM at three levels of hydrogen pressure, 6.9, 27.6, and 41.4 bar. The rubber concentration was 260 mM at 140°C in monochlorobenzene. The influence of catalyst loading charged into the reaction system is illustrated in Figure 4. It can be seen that the reaction rate is linearly proportional to the total catalyst concentration at every hydrogen pressure. This implies that the NR hydrogenation exhibits a first-order behavior with respect to $[\text{Os}]$. This observation is consistent with the work of Andriollo and coworkers¹⁵ and J. S. Parent and colleagues,¹⁸ who suggested that the active complex is a mononuclear species. This figure also shows that the rate of PIP hydrogenation¹⁹ was higher than that of NR hydrogenation, which required higher loading of the catalyst. It appears that impurities in NR decrease the activity of the catalyst. Furthermore, the plots of NR hydrogenation exhibit a positive intercept on the $[\text{Os}]$ -axis, while such was not the case for PIP hydrogenation. This suggests that in the case of NR hydrogenation some portion of the catalyst, about 25 μM , is sacrificed during the reaction to quench impurities in the rubber.

Dependence on rubber concentration

The influence of NR concentration on the hydrogenation rate was studied over the range of 65–440 mM, for

TABLE I
Results from 2^3 Factorial Design Experiment for NR Hydrogenation

Exp.	$[\text{Os}]$ (μM)	$[\text{C}=\text{C}]$ (mM)	P_{H_2} (bar)	Temperature ($^\circ\text{C}$)	$k' \times 10^3$ (s^{-1})
1	60	259.9	6.8	140	1.12
2	60	259.8	6.8	140	0.96
3	120	259.8	6.8	140	3.13
4	120	259.8	6.8	140	2.86
5	60	392.4	7.0	140	0.72
6	60	392.3	6.9	140	0.56
7	120	392.3	6.9	140	0.98
8	120	392.3	6.9	140	1.18
9	60	259.8	41.4	140	1.08
10	60	259.8	41.4	140	1.26
11	120	259.7	41.4	140	3.71
12	120	259.8	41.4	140	3.83
13	60	392.4	41.2	140	1.02
14	60	392.3	41.0	140	1.04
15	120	392.2	41.2	140	1.83
16	120	392.2	41.3	140	2.04

Conditions: $T = 140^\circ\text{C}$ in monochlorobenzene.

TABLE II
Yate's Algorithm Calculation of the 2³ Factorial Experiment

Exp.	Design matrix variables			Ave. k' (s ⁻¹)	Algorithm			Divisor	Estimate	Identification
	[Os]	[C=C]	P _{H₂}		(1)	(2)	(3)			
1	-1	-1	-1	0.00104	0.00404	0.00576	0.01366	8	0.00171	Average
2	1	-1	-1	0.00300	0.00172	0.00791	0.00590	4	0.00148	[Os]
3	-1	1	-1	0.00064	0.00494	0.00240	-0.00429	4	-0.00107	[C=C]
4	1	1	-1	0.00108	0.00297	0.00351	-0.00321	4	-0.00080	[Os]*[C=C]
5	-1	-1	1	0.00117	0.00196	-0.00232	0.00215	4	0.00054	P _{H₂}
6	1	-1	1	0.00377	0.00044	-0.00198	0.00111	4	0.00028	[Os]*P _{H₂}
7	-1	1	1	0.00103	0.00260	-0.00152	0.00034	4	0.00009	[C=C]*P _{H₂}
8	1	1	1	0.00194	0.00091	-0.00170	-0.00018	4	-0.00005	[Os]*[C=C]*P _{H₂}

which the initial catalyst concentration (100 μM), reaction temperature (140°C), and hydrogen pressure (27.6 bar) were kept constant. The results of these experiments are displayed in Figure 5. These results indicate that the reaction rate decreased with an increase in rubber concentration. This figure also shows that the rate of PIP hydrogenation is constant when the rubber concentration is increased.¹⁹ In general, the hydrogenation rates of PIP¹⁹ and styrene-butadiene rubber (SBR)¹⁸ are independent of the rubber concentration. In contrast, the hydrogenation rate of NBR decreased with increasing rubber concentration. The nitrile functional group within NBR is known to reversibly coordinate to OsHCl(CO)(PCy₃)₂. Through σ-donation from the nitrogen lone pair, nitrile coordinates trans to the hydride to bind the metal center.¹⁸ This behavior has also been observed for NBR hydrogenation catalyzed by [Rh(diene)(NBD₂)]⁺,²⁷ RhCl(PPh₃)₃,¹¹ RhH(PPh₃)₄,¹¹ and RuCl(CO)(styryl)(PCy₃)₂.⁹ However, since NR does not contain any other complexing functional group, the reduction of the hydrogenation rate of NR is attributed to the influence of some impurities in the rubber. From Figure 1, the FTIR spectrum of NR shows that proteins (bands 3280 and 1530 cm⁻¹) are the main impurities. These might compete with olefin for the metal coordination sites during the catalytic hydrogenation, re-

sulting in a certain level of catalytically inactive forms of the Os complex.

To gain further understanding about the effect of the inherent impurities in NR on the hydrogenation process, an attempt was made to model NR by using PIP with addition of hexylamine (CH₃(CH₂)₄CH₂NH₂) or hexadecylamide (H₂C=CH(CO)NHC₁₆H₃₃), both of which have nitrogen containing functional groups akin to the functional groups present in proteins. Table V shows the effect of added nitrogen substances on the catalytic activity in PIP hydrogenation. The reaction conditions were 260 mM of rubber concentration, 40 μM of catalyst concentration, and 13.8 bar of hydrogen pressure at 130°C in toluene. It was found that hexylamine caused a drastic decrease in activity of OsHCl(CO)(O₂)(PCy₃)₂. Hexylamine has an amine group, which is an electron donating species, so hexylamine can form bonds easily with the osmium center. However, for hexadecylamide, the lone pair of electrons of the nitrogen atom can be delocalized between nitrogen and -C=O; therefore, hexadecylamide does not easily coordinate with the osmium center. The results of the

TABLE III
Calculation of Effects and Standard Errors for 2³ Factorial Design Experiment

Effect	Estimate ± Standard Error
Average	0.00171 ± 3.16E-05
Main effects	
Catalyst concentration, [Os]	0.00148 ± 6.32E-05
Rubber concentration, [C=C]	-0.00107 ± 6.32E-05
Hydrogen pressure, P _{H₂}	0.00054 ± 6.32E-05
Two-Factor interaction	
[Os]*[C=C]	-0.00080 ± 6.32E-05
[Os]*P _{H₂}	0.00028 ± 6.32E-05
[C=C]*P _{H₂}	0.00009 ± 6.32E-05
Three-Factor interaction	
[Os]*[C=C]*P _{H₂}	-0.00005 ± 6.32E-05

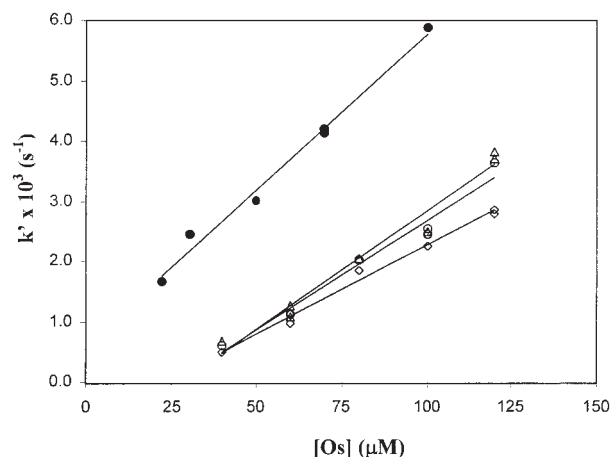


Figure 4 Effect of catalyst concentration on the rate of NR hydrogenation compared with PIP hydrogenation.¹⁹ For NR: [C=C] = 260 mM; P_{H₂} = 6.9 (◇), 27.6 (○), and 41.4 (Δ) bar; T = 140°C in monochlorobenzene. For PIP (●): [C=C] = 260 mM, P_{H₂} = 20.7 bar, and T = 130°C in toluene.

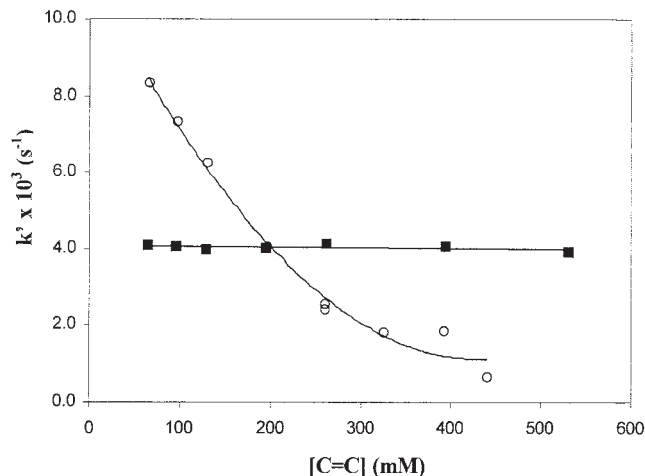


Figure 5 Effect of rubber concentration on the rate of NR hydrogenation compared with PIP hydrogenation.¹⁹ For NR (○): $[\text{Os}]_T = 100 \mu\text{M}$, $P_{\text{H}_2} = 27.6$ bar, $T = 140^\circ\text{C}$ in monochlorobenzene. For PIP (■): $[\text{Os}]_T = 70 \mu\text{M}$, $P_{\text{H}_2} = 20.7$ bar, $T = 130^\circ\text{C}$ in toluene.

addition of nitrogen containing substances agree with the results of the factorial study and the univariate experiments, which indicate that the hydrogenation rate decreased due to the increase with rubber loading and impurities.

Dependence on hydrogen pressure

According to the unique behavior of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ to form multiple hydride species, the hydrogenation of diene polymers, such as NBR¹⁸ and PIP,¹⁹ catalyzed by $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ was found to exhibit a second-order dependence on the hydrogen pressure, which then tended to a zero-order behavior at high hydrogen pressure. However, for NBR hydrogenation in the presence of the $\text{RhCl}(\text{PPh}_3)_3$ system, it was found that the order of reaction with respect to hydrogen pressure shifted from a first- to zero-order behavior with increasing hydrogen pressure,¹¹ while a first-order behavior in hydrogen pressure is maintained over a considerable range of hydrogen pressure for the Ru complex, the $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ system.⁹ For NR hydrogenation catalyzed with $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)$, the rate of reaction is a function of hydrogen pressure. To investigate the dependence of the hydrogenation rate on the hydrogen pressure, a series of experiments was carried out from 2.1 to 68.9 bar at 140°C in monochlorobenzene. The catalyst concentration and rubber concentration were $100 \mu\text{M}$ and 260 mM , respectively. The results shown in Figure 6a demonstrate that the rate of NR hydrogenation exhibited first order with respect to the hydrogen pressure from 2.1 to 6.9 bar and then shifted toward zero order dependence when the hydrogen pressure was 13.8 to 41.4 bar. The reaction rate of NR hydrogenation was diminished when the hydrogen pressure was higher

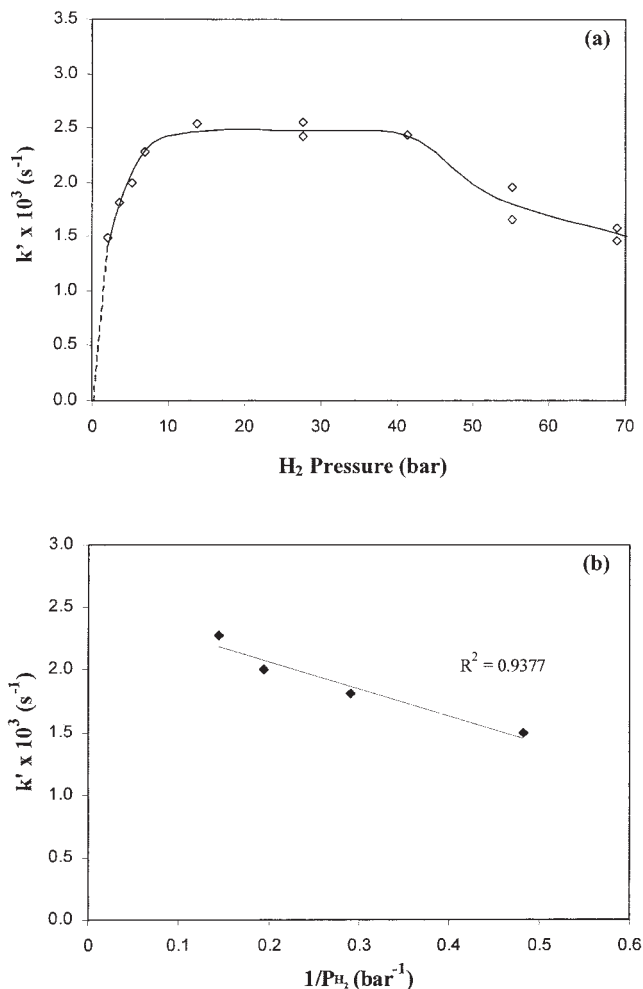


Figure 6 (a) Effect of hydrogen pressure on the rate of NR hydrogenation, and (b) the plot of $1/P_{\text{H}_2}$ versus the rate constant (2.1–6.9 bar). $[\text{Os}]_T = 100 \mu\text{M}$, $[\text{C}=\text{C}] = 260 \text{ mM}$, $T = 140^\circ\text{C}$ in monochlorobenzene.

than 41.4 bar. This first-order dependence at low hydrogen pressure (2.1–6.9 bar) was shown by plotting $1/P_{\text{H}_2}$ versus the hydrogenation rate, as illustrated in

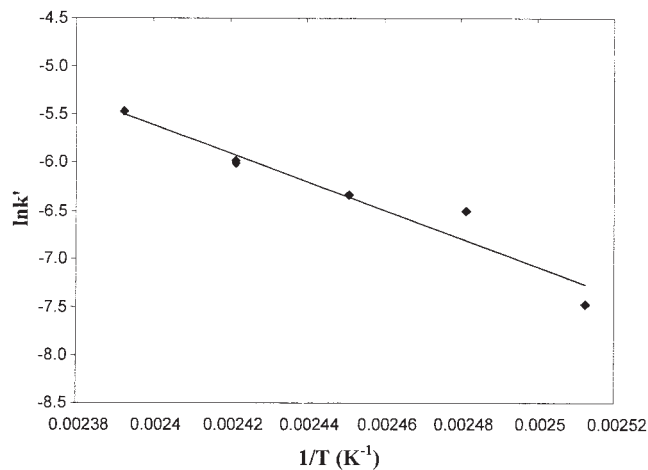


Figure 7 Arrhenius plots for the NR hydrogenation. $[\text{Os}]_T = 100 \mu\text{M}$, $[\text{C}=\text{C}] = 260 \text{ mM}$, and $P_{\text{H}_2} = 27.6$ bar.

TABLE IV
Univariate Kinetic Data of NR Hydrogenation Catalyzed by OsHCl(CO)(O₂)(PCy₃)₂

Exp.	[Os] (μ M)	[C=C] (mM)	P _{H₂} (bar)	Temp. (°C)	% hydrogenation		k' $\times 10^3$ (s ⁻¹)	η_{rel}
					10 min	20 min		
1	40	259.8	6.9	140	37.1	54.5	0.58	-
2	60	259.9	6.9	140	53.6	70.7	1.12	-
3	60	259.8	6.9	140	50.9	69.7	0.96	-
4	80	259.9	6.9	140	69.8	86.7	1.83	-
5	100	259.8	6.9	140	77.5	93.0	2.28	8.50
6	120	259.8	6.9	140	84.5	94.6	2.79	-
7	120	259.8	6.9	140	83.1	90.2	2.86	-
8	40	259.8	27.6	140	38.6	55.1	0.60	7.12
9	60	259.9	27.6	140	49.4	70.0	1.01	7.65
10	80	259.8	27.6	140	68.8	85.8	2.02	7.63
11	100	259.9	27.6	140	79.1	92.7	2.53	8.18
12	100	259.9	27.6	140	77.9	91.4	2.45	-
13	120	259.9	27.6	140	87.1	97.5	3.64	8.43
14	40	259.9	41.4	140	38.8	56.7	0.62	-
15	60	259.8	41.4	140	52.1	72.1	1.08	-
16	60	259.8	41.4	140	59.6	76.4	1.26	-
17	80	258.9	41.4	140	68.2	86.3	1.99	-
18	100	259.7	41.4	140	78.5	92.7	2.49	8.52
19	120	259.7	41.4	140	87.7	97.3	3.71	-
20	120	259.8	41.4	140	88.5	98.2	3.83	-
21	100	259.9	2.1	140	61.6	75.5	1.46	-
22	100	259.8	3.4	140	69.0	81.2	1.79	7.26
23	100	259.7	5.2	140	74.2	89.5	1.99	6.57
24	100	259.8	13.8	140	78.0	92.3	2.53	7.40
25	100	259.9	55.2	140	69.0	86.6	1.96	7.57
26	100	259.7	55.2	140	63.2	82.5	1.66	-
27	100	259.8	68.9	140	68.2	86.2	1.58	-
28	100	259.7	68.9	140	66.1	84.5	1.47	-
29	100	64.9	27.6	140	94.1 (7.5 min)	-	8.34	9.21
30	100	97.6	27.6	140	96.7	97.0 (10.8 min)	7.72	9.88
31	100	129.9	27.6	140	96.3	97.5 (12.3 min)	6.28	9.25
32	100	194.9	27.6	140	92.0	97.6	4.06	8.70
33	100	326.0	27.6	140	68.2	85.2	1.84	8.39
34	100	392.2	27.6	140	72.7	88.0	1.88	-
35	100	441.2	27.6	140	35.8	55.5	0.64	-
36	100	259.8	27.6	125	34.6	53.1	0.58	-
37	100	259.7	27.6	130	63.4	82.0	1.49	-
38	100	259.7	27.6	135	68.2	87.1	1.78	-
39	100	259.8	27.6	145	90.5	97.2	4.19	-

Relative viscosity (η_{rel}) of NR = 7.54

Figure 6b. It can be seen that the curve in this figure is linearly proportional to $1/P_{H_2}$. This shift in $[H_2]$ order in NR hydrogenation showed a different behavior

TABLE V
The Effect of Nitrogenous Substances on the Hydrogenation Rate of Synthetic *Cis*-1,4-Polyisoprene (PIP)

Exp.	Substance	[Substance] ^a (mM)	[Substance]/[Os]	k' $\times 10^3$ (s ⁻¹)
1	None	-	-	2.96
2	Hexylamine	1.29	32.3	0.37
3	Hexadecylacrylamide	1.05	26.3	2.44

Conditions: [Os] = 40 μ M, [C=C] = 260 mM, and P_{H₂} = 13.8 bar at 130°C in toluene.

^a The substance concentration was based on the maximum of nitrogen content in NR in grade STR-5L (0.60%).

from the hydrogenation of NBR¹⁸ and PIP.¹⁹ The reason for the reduction of the NR hydrogenation rate dependence on hydrogen pressure will be discussed later in the section of mechanistic interpretation of the kinetic data.

Dependence on reaction temperature

A series of experiments was carried out over the range of 125 to 145°C. The reaction conditions remained constant at 100 μ M of catalyst concentration, 260 mM of rubber concentration, and 27.6 bar of hydrogen pressure. The Arrhenius plot is shown in Figure 7. The apparent activation energy calculated from a least squares regression analysis of $\ln(k')$ versus $1/T$ was 122.76 kJ/mol, providing evidence that the experiments were performed without mass-transfer limitation. The activation energy of NR

TABLE VI
Effect of Solvent on the NR Hydrogenation

Solvent	$k' \times 10^3$ (s^{-1})	Time for 60% conversion (min)
Tetrahydrofuran	2.54	4.7
Monochlorobenzene	2.50	5.8
Toluene	0.55	30.0
Xylene	0.49	35.3

Conditions: $[Os] = 100 \mu M$, $[C=C] = 260 \text{ mM}$, and $P_{H_2} = 27.6 \text{ bar}$ at $140^\circ C$.

hydrogenation is higher than that of PIP hydrogenation (109.32 kJ/mol).¹⁹

Dependence on solvents

The effect of different solvents on the NR hydrogenation was investigated at $100 \mu M$ of catalyst concentration, 260 mM of rubber concentration, and 27.6 bar of hydrogen pressure at $140^\circ C$. The results of these experiments are presented in Table VI. It is obvious that the solvent plays an important role in the hydrogenation reaction. Thus, the solvent should have sufficient coordinating power to facilitate dissociation of a tricyclohexylphosphine ligand in the catalytic cycle of the hydrogenation, but it should not be too strong to obstruct displacement by alkene. Ketone solvents, such as methyl ethyl ketone (MEK) and butanone, were not used since $OsHCl(CO)(O_2)(PCy_3)_2$ has been reported to be not active in these solvents.¹⁸ From Table VI, it was found that the rate constant increased with increasing solvating power of the solvent in the order: tetrahydrofuran \cong chlorobenzene $>$ toluene $>$ xylene.

Effect of acid addition on the catalytic activity

There have been some research reports on acid addition to improve the catalytic activity for olefinic type hydrogenation reactions. Guo and coworkers²⁸ discovered that carboxylic acids increased the catalytic activity for the hydrogenation of an NBR emulsion catalyzed by $RuCl(CO)(styryl)(PCy_3)_2$. It was suggested that carboxylic acids were very effective in preventing the poisoning of the catalyst by impurities in emulsion systems. Yi and colleagues²⁹ also reported that the addition of acids with weakly coordinating anions, such as trifluoromethanesulfonic acid (HOTf) and tetrafluoroboric acid–dimethyl ether complex ($HBF_4 \cdot OEt_2$), enhanced the reaction rate of alkene hydrogenation catalyzed by $RuH(CO)(Cl)(PCy_3)_2$. They found that the increase in catalytic activity of the $RuH(CO)(Cl)(PCy_3)_2$ /acid system might be due to selective entrapment of the phosphine ligand and the formation of a highly active 14-electron ruthenium-monophosphine species. However, $HBF_4 \cdot OEt_2$ cannot be employed in the gas-uptake apparatus because of its low flash point ($-42^\circ F$) and flammability. In this work, the role of the acids, 3-chloropropionic acid (3-

CPA) and *p*-toluenesulfonic acid (*p*-TSA), on NR and PIP hydrogenation were studied, and the results obtained are presented in Tables VII and VIII and Figures 8 and 9.

The conversion profiles in Figure 8 indicate that the addition of 3-CPA increased the rate of NR hydrogenation. Figure 9a shows the effect of 3-CPA concentration on the rate of hydrogenation. It was found that this acid was effective when NR was dissolved in toluene. The rate of hydrogenation increased when the acid concentration was increased from 0.30 to 6.39 mM , then diminished and leveled off at an acid concentration above 6.39 mM . When monochlorobenzene was used as the solvent, the rate of hydrogenation decreased with increase in the acid concentration and also leveled off. It is possible that the acid can easily dissociate to an anion in a more polar solvent, which may cause the decrease in catalytic activity.

The effect of *p*-TSA on the rate of NR hydrogenation is illustrated in Figure 9b. The results are different from the 3-CPA system in that the rate of hydrogenation increased with increasing acid concentration in both solvents and the hydrogenation rates tended to decrease when the *p*-TSA concentration was more than 3.01 mM in toluene and 2.00 mM in monochlorobenzene. The drastic decrease in hydrogenation rate at high loading of *p*-TSA can be explained in that *p*-TSA is a stronger acid than 3-CPA and can easily dissociate to the *p*-toluenesulfonic anion, which may decrease the efficiency of the catalyst.

The results obtained from addition of these acids in the hydrogenation of PIP in toluene and monochlorobenzene are represented in Table VIII. It was found that the addition of these acids has an adverse effect on the hydrogenation rate. For hydrogenation in toluene, the rates decreased slightly; and in monochlorobenzene, the rates decreased drastically. Although this result cannot be explained for PIP hydrogenation, the role of acids in the NR hydrogenation may partially be due to the possible neutralization of the impurities in the rubber.

Mechanistic interpretation of the kinetic data

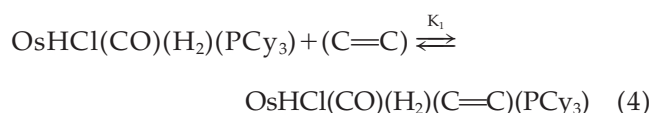
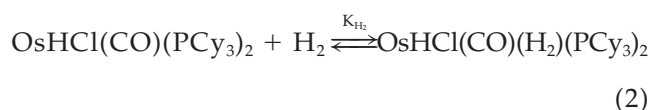
A catalytic pathway is developed from inferences on the kinetic data and electron counting schemes. The catalytic cycle of $OsHCl(CO)(O_2)(PCy_3)_2$ for NR hydrogenation illustrated in Scheme 2 is inferred from the observed kinetic data. The catalytic cycle for polymer hydrogenation catalyzed by $OsHCl(CO)(O_2)(PCy_3)_2$ has been proposed in an earlier work on NBR and PIP hydrogenation.^{18,19}

When the O_2 adducted catalyst precursor complex is employed in the hydrogenation system, $OsHCl(CO)(O_2)(PCy_3)_2$ is activated by O_2 dissociation to produce the five-coordinate analogue, $OsHCl(CO)(PCy_3)_2$, which is an active species. According to its coordinative unsaturation, a molecule of H_2 coordinates to $OsHCl(CO)(PCy_3)_2$ by η^2 coordination, as shown in eq.(2).

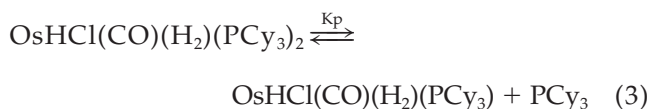
TABLE VII
The Effect of Acid Types and Acid Concentration on the Rate of NR Hydrogenation

Solvent	Acid	[Acid] (mM)	[Acid]/[Os]	$k' \times 10^3$ (s ⁻¹)	% Hydrogenation		η_{rel}
					10 min	20 min	
Toluene	-	-	-	0.63	32.6	49.5	-
	3-CPA	0.30	3	1.06	51.8	70.6	-
		0.83	8	1.64	68.2	87.5	-
		1.16	12	1.83	68.6	88.7	-
		2.06	21	2.16	77.4	91.1	-
		6.39	64	2.36	77.0	94.3	-
		10.07	101	2.10	77.2	92.0	-
	p-TSA	15.03	150	2.03	73.9	90.4	-
		0.19	2	1.09	51.9	72.2	-
		0.53	5	3.49	90.8	96.5	7.84
		1.03	10	3.52	87.1	97.1	8.03
		3.01	30	3.77	88.4	97.8	7.82
		5.96	60	2.93	76.4	93.3	7.47
-		-	-	2.51	80.3	92.8	8.18
Monochlorobenzene	3-CPA	0.73	7	2.21	77.6	92.7	-
		1.02	10	1.79	68.7	89.3	-
		3.07	31	1.82	69.6	89.1	-
		9.77	98	1.95	72.4	92.0	-
		16.11	161	1.99	72.8	91.6	-
	p-TSA	0.20	2	2.97	84.1	97.1	-
		0.50	5	3.95	92.0	98.9	-
		1.06	11	4.03	92.1	97.6	-
		2.00	20	4.00	91.9	98.1	-
		4.00	40	1.75	78.6	90.5	-
		6.00	60	0.87	57.1	71.4	-

Conditions: [Os] = 100 μ M, [C=C] = 260 mM, and P_{H_2} = 27.6 bar at 140°C.



The complex formed in eq. (2) subsequently dissociates into a monophosphine complex,¹⁸ and then the insertion of the carbon-carbon double bond of NR participates to $\text{OsHCl}(\text{CO})(\text{H}_2)(\text{PCy}_3)$ to generate the hydrogenated product, as shown in eqs. (3) and (4), respectively.



According to the inverse behaviors with respect to the rubber concentration and high hydrogen pressure (> 41.4 bar), this shows that there are effective competitions between the carbon-carbon double bond and impurities coordination or a second hydrogen molecule. The effect of impurities (X) in NR on the hydrogenation rate can be compared to the effect of the nitrile functional group, which inhibits the catalytic activity in NBR hydrogenation. Whereas the impurities inside NR are dominated by

TABLE VIII
Effect of Acid Addition on the Hydrogenation Rate of Synthetic *Cis*-1,4- Polyisoprene

Solvent	Acid	[Acid] (mM)	[Acid]/[Os]	$k' \times 10^3$ (s ⁻¹)	% Hydrogenation	
					10 min	20 min
Toluene	-	-	-	2.96	80.4	96.6
	3-CPA	0.82	20	2.46	73.2	93.8
	p-TSA	0.80	20	2.50	76.2	93.8
Monochlorobenzene	-	-	-	3.03	83.1	95.7
	3-CPA	0.82	20	1.69	72.5	87.6
		3.36	84	1.59	64.6	82.6
		6.33	158	1.00	55.2	74.1
	p-TSA	0.80	20	0.96	65.8	80.8

Conditions: [Os] = 40 μ M, [C=C] = 260 mM, and P_{H_2} = 13.8 bar at 130°C.

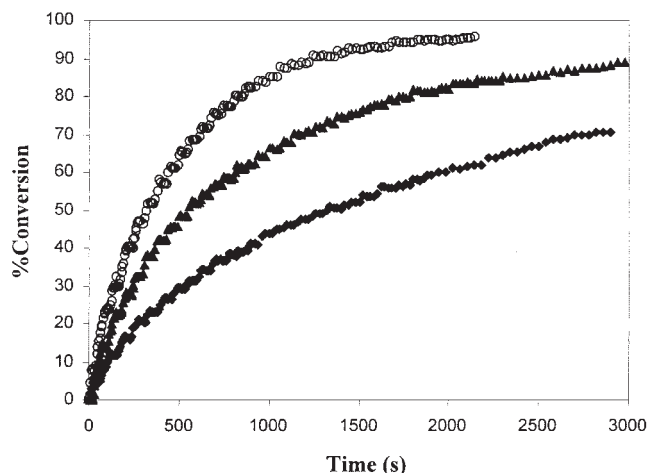
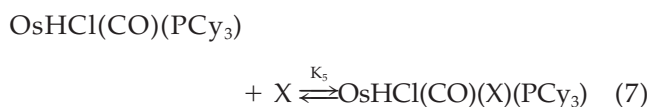
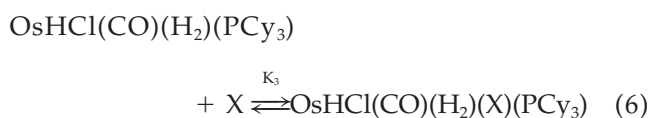
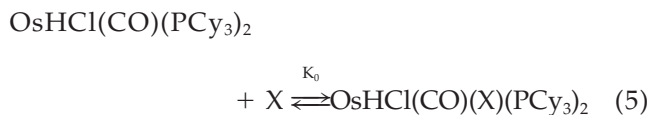


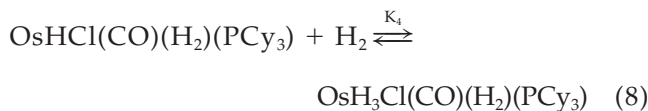
Figure 8 NR hydrogenation conversion profiles of non-acid addition (◆) and acid addition systems: [3-CPA]/[Os]_T = 3/1 (▲) and [3-CPA]/[Os]_T = 12/1 (○). [Os]_T = 100 μM, [C=C] = 260 mM, P_{H₂} = 27.6 bar, T = 140°C in toluene.

proteins, the amine group of proteins is an electron donating species that may react with intermediate species, OsHCl(CO)(PCy₃)₂, OsHCl(CO)(H₂)(PCy₃), or OsHCl(CO)(PCy₃), and then deactivate the catalysts. Equations (5), (6), and (7) illustrate three possible pathways of impurities coordination that could inhibit the catalytic activity:



Unlike the shift in second- to zero-order behavior dependence on hydrogen pressure in the hydrogenation of NBR¹⁸ or PIP¹⁹ catalyzed by OsHCl(CO)(O₂)(PCy₃)₂, the kinetic data of NR hydrogenation in the presence of this Os catalytic precursor showed the shift in first- to zero-order dependence on low hydrogen pressure and then the inverse behavior appeared when the hydrogen pressure exceeded 41.4 bar. It is possible that NR hydrogenation required only 1 molecule of H₂ to generate the hydrogenated product. The second hydrogen molecule may react with OsHCl(CO)-

(H₂)(PCy₃) to form the stable 18-electron catalytic species, OsH₃Cl(CO)(H₂)(PCy₃), as illustrated in eq. (8).



Parent and coworkers¹⁸ reported that the observed kinetic isotope effect is involved with the cleavage of a bond to hydrogen in the rate-determining reaction. The rate expression for olefin hydrogenation is assumed from the coordination of olefin onto an Os-H bond or by a reductive elimination of an osmium-alkyl to produce the saturated product, as shown in eq. (9).

$$-\frac{d[\text{C}=\text{C}]}{dt} = k_{\text{rds}}[\text{OsHCl(CO)(H}_2\text{)(C}=\text{C)(PCy}_3)] \quad (9)$$

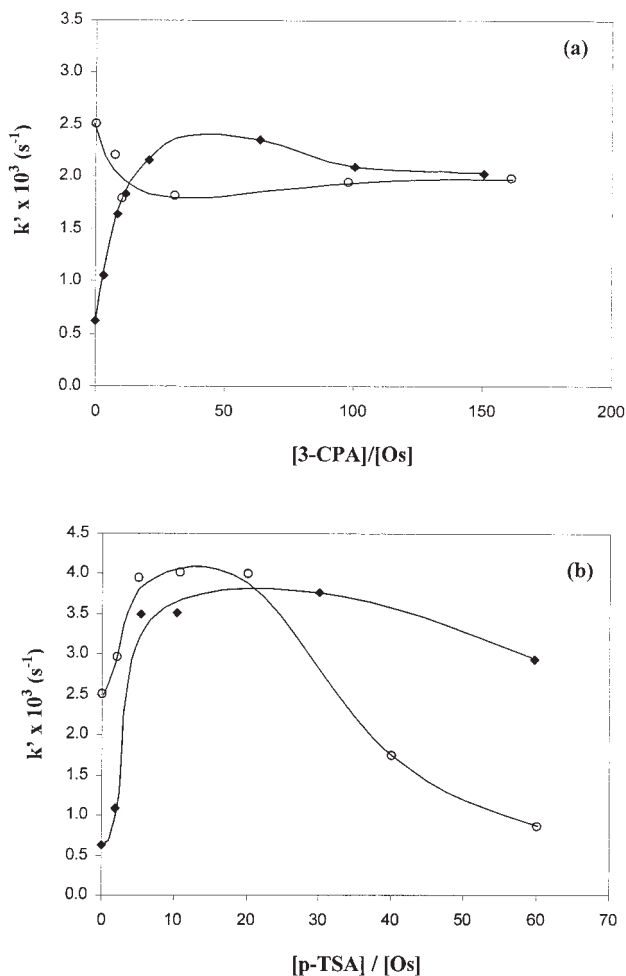
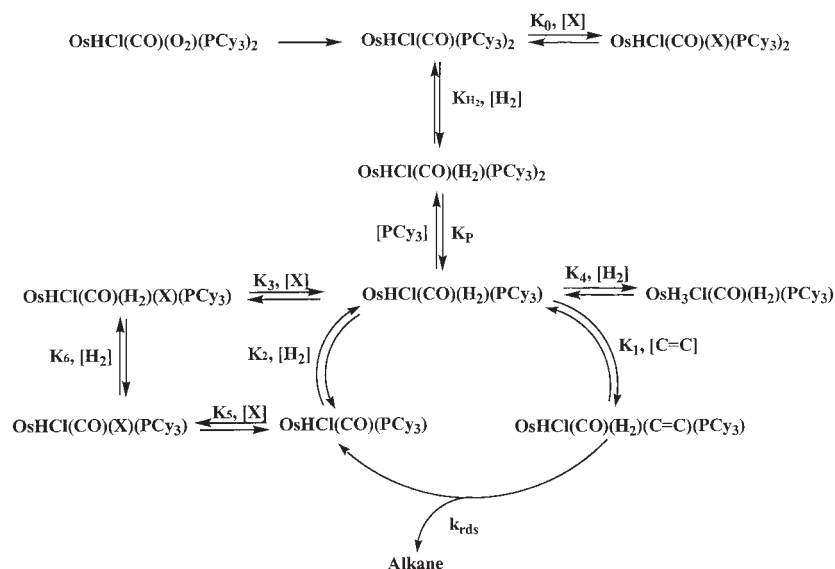


Figure 9 Effect of acid type and acid concentration on the NR hydrogenation: (a) the effect of 3-chloropropionic and (b) the effect of p-toluenesulfonic acid in toluene (◆) and monochlorobenzene (○). [Os]_T = 100 μM, [C=C] = 260 mM, and P_{H₂} = 27.6 bar.



Scheme 2 Proposed catalytic mechanism for NR hydrogenation in the presence of $\text{OsHCl(CO)(O}_2\text{)(PCy}_3\text{)}_2$.

A material balance on the osmium complex charged into the system given by eq. (10) is a function of the

total amount of osmium ($[\text{Os}]_T$).

$$\begin{aligned}
 [\text{Os}]_T = & [\text{OsHCl(CO)(H}_2\text{)(C=C)(PCy}_3\text{)}] + [\text{OsHCl(CO)(H}_2\text{)(PCy}_3\text{)}] + [\text{OsHCl(CO)(PCy}_3\text{)}_2] \\
 & + [\text{OsHCl(CO)(H}_2\text{)(PCy}_3\text{)}_2] + [\text{OsHCl(CO)(X)(PCy}_3\text{)}_2] + [\text{OsHCl(CO)(PCy}_3\text{)}] \\
 & + [\text{OsHCl(CO)(H}_2\text{)(X)(PCy}_3\text{)}] + [\text{OsHCl(CO)(X)(PCy}_3\text{)}] + [\text{OsH}_3\text{Cl(CO)(H}_2\text{)(PCy}_3\text{)}] \quad (10)
 \end{aligned}$$

Every osmium complex species concentration term in eq. (10) can be converted in terms of $\text{OsHCl(CO)(H}_2\text{)(C=C)(PCy}_3\text{)}$ using the equilibria defined in

Scheme 2, and then can be substituted into eq. (9) to provide the resulting rate law, as shown in eq. (11).

$$\begin{aligned}
 -\frac{d[\text{C=C}]}{dt} &= \frac{k_{\text{rds}}K_1K_2K_pK_{\text{H}_2}[\text{Os}]_T[\text{H}_2][\text{C=C}]}{K_2K_pK_{\text{H}_2}[\text{H}_2](1 + K_1[\text{C=C}]) + K_pK_{\text{H}_2}(1 + K_2K_3[\text{X}][\text{H}_2] + K_5[\text{X}] + K_2K_4[\text{H}_2]^2) + K_2[\text{PCy}_3](1 + K_{\text{H}_2}[\text{H}_2] + K_0[\text{X}])} \quad (11)
 \end{aligned}$$

The rate law equation of NR hydrogenation catalyzed by catalyst precursor $\text{OsHCl(CO)(O}_2\text{)(PCy}_3\text{)}_2$ indicates that the reaction exhibits a first-order dependence on osmium concentration and an inverse behavior with respect to rubber concentration due to the impurities in NR. According to the observed kinetic data, the rate of NR hydrogenation exhibited a first-order dependence at low hydrogen pressure. The order of the reaction with respect to hydrogen shifted to a zero-order dependence when the hydrogen pressure was varied over the range of 13.8 to 41.4 bar. Above 41.4 bar, the term of $K_2K_4[\text{H}_2]^2$ in eq. (11) was more significant, so that the rate of NR hydrogenation showed an inverse behavior on hydrogen.

Relative viscosity of HNR

Although FTIR or NMR spectroscopy can detect the level of hydrogenation, these techniques are not sensitive enough to investigate side reactions, such as degradation and crosslinking during the hydrogenation reaction. Dilute solution viscometry is used to monitor the shifts of molecular weight, which are related to the morphology and microstructure of the polymer chains. The viscosity of a dilute NR and HNR solution relative to pure solvent (η_{rel}) provides a simple and effective means of measuring the consequences of crosslinking and degradation of the samples. Over the range of conditions investigated ($[\text{Os}] = 20\text{--}40 \mu\text{M}$, $P_{\text{H}_2} = 3.5\text{--}55.2 \text{ bar}$,

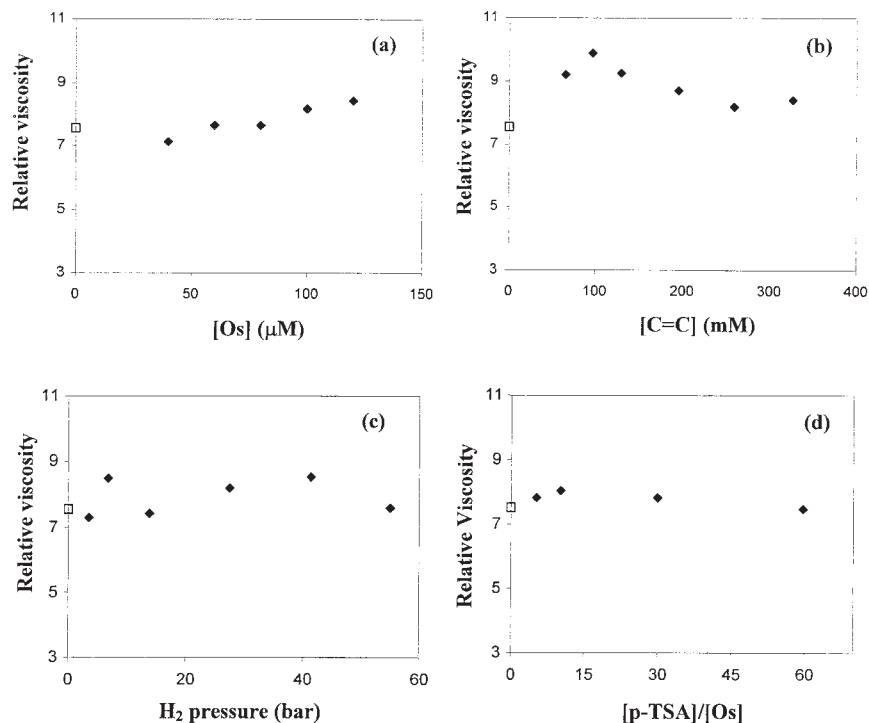


Figure 10 (a) Relative viscosity (η_{rel}) of HNR as a function of total metal loading (72.7–98.3% hydrogenation): $P_{H_2} = 27.6$ bar, $[C=C] = 260$ mM, $T = 140^\circ\text{C}$; (b) Relative viscosity of HNR as a function of rubber concentration (95–98% hydrogenation): $[Os]_T = 100\ \mu\text{M}$, $P_{H_2} = 27.6$ bar, $T = 140^\circ\text{C}$; (c) Relative viscosity of HNR as a function of hydrogen pressure (93–96% hydrogenation): $[Os]_T = 100\ \mu\text{M}$, $[C=C] = 260$ mM, $T = 140^\circ\text{C}$; (d) Relative viscosity of HNR as a function of acid-catalyst ratio (95–98% hydrogenation): $[Os]_T = 100\ \mu\text{M}$, $[C=C] = 260$ mM, $P_{H_2} = 27.6$ bar, $T = 140^\circ\text{C}$ in toluene (relative viscosity of NR (\square) = 7.54).

$[C=C] = 64.9$ – 326.0 mM, and $[p\text{-TSA}]/[Os] = 5$ – 60 at 140°C), the results of the relative viscosity of some HNR samples are summarized in Tables IV and VII. Figures 10a–10d illustrate the effect of $[Os]$, $[C=C]$, P_{H_2} , and the molar ratio of $[p\text{-TSA}]/[Os]$ on the relative viscosity of HNR. It was found that the relative viscosity of NR was 7.54, while the relative viscosity of HNR varied over the range of 7.12–9.88, showing dependence on the reaction condition, degree of hydrogenation, and reaction time.

The relative viscosity results of HNR are different from that of hydrogenated PIP,¹⁹ which has a fairly constant relative viscosity with varying $[Os]$, $[C=C]$, and P_{H_2} . Figures 10a, 10c, and 10d show that the relative viscosity of HNR samples was not changed significantly when $[Os]$, P_{H_2} , and $[p\text{-TSA}]/[Os]$ increased.

For the effect of rubber concentration (Fig. 10b), the relative viscosity of samples hydrogenated at low rubber concentration (64.9–129.9 mM) were greater than that of samples hydrogenated at higher rubber loading. This might be explained on the basis that when the catalyst loading is relatively high to the amount of polymer present, a higher degree of crosslinking occurs. Similar results were observed for NBR hydrogenation catalyzed by $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$.³⁰

Thermal properties of HNR

Thermal analysis is used to investigate the physical properties of substrates as a function of temperature. These experiments are carried out using a differential scanning calorimeter (DSC) and thermogravimetric analysis apparatus (TGA) to find the glass transition temperature (T_g) and decomposition temperature, respectively. The results of decomposition temperature and T_g of HNR are shown in Figures 11 and 12 and Table IX.

Thermogravimetric analyses of NR, HNR, PIP, and an ethylene-propylene copolymer (EPDM) were conducted under a nitrogen atmosphere. The T_g curves for HNR samples at various % hydrogenations are shown in Figure 11. It can be seen that the polymer degradation is an overall one-step reaction because the T_g curve of the samples is a one-step and provides smooth weight loss curves. The initial decomposition temperature (T_{id}) was determined from the intersection of two tangents at the onset of the decomposition temperature. The maximum decomposition temperature (T_{max}) of each sample was obtained from the peak maxima of the derivative of TG curves. The results in Table IX show that both T_{id} and T_{max} of HNR samples increased with an increase in the reduction of the carbon–carbon double bond in NR. Therefore, hydro-

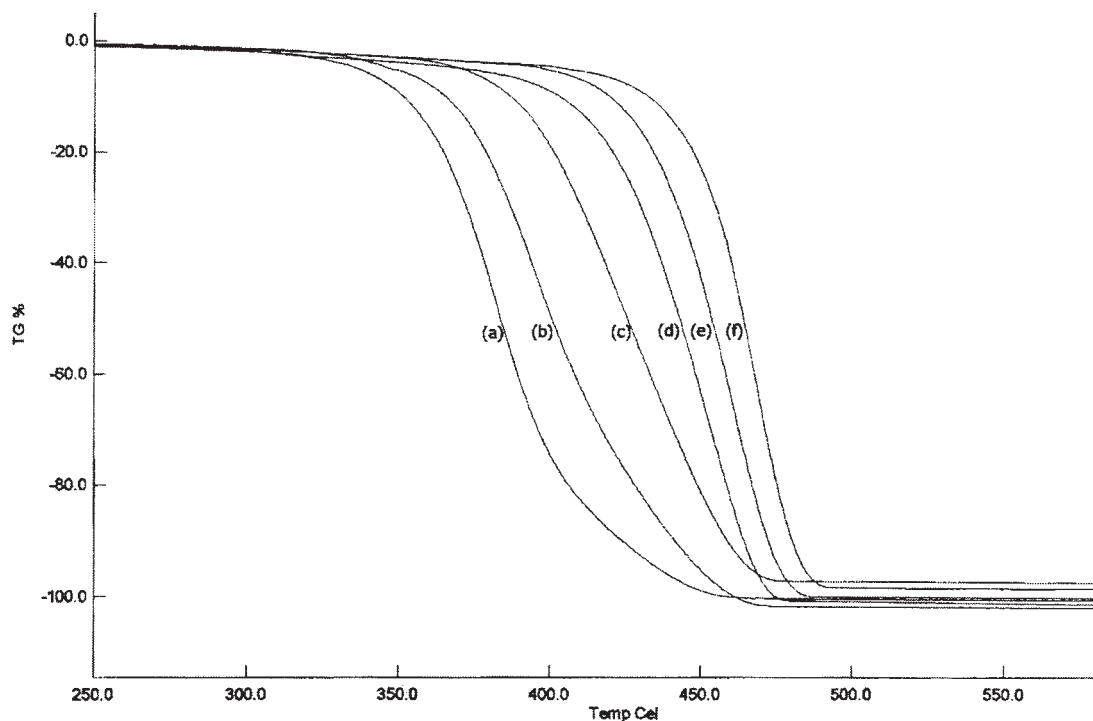


Figure 11 TGA thermograms of NR and HNR at various % hydrogenation: (a) NR, (b) 37.9%, (c) 52.2%, (d) 79.1%, (e) 91.9%, and (f) 99.7%.

generation can improve the thermal stability of NR by converting the weak π bond within NR to the stronger C-H σ bond.³¹ On comparison with standard EPDM, it was found that T_{id} and T_{max} of the completely hydrogenated NR were close to those of EPDM. It can be concluded that the structure of HNR provides a facile entry and alternative method to alternating ethylene-propylene copolymers.

The glass transition temperature, T_g , is one of the most important parameters for characterization of the

polymer structure. The T_g is a transition related to the motion in the amorphous sections of the polymer. It is determined from the midpoint of the base-line shift of the DSC thermogram. The DSC thermograms of HNR samples at various degrees of hydrogenation are presented in Figure 12. All DSC thermograms of HNR samples indicate a one-step base-line shift. This suggests that the HNR sample has a single glass transition temperature. It can also suggest that no side reactions occurred during the catalytic hydrogenation process.

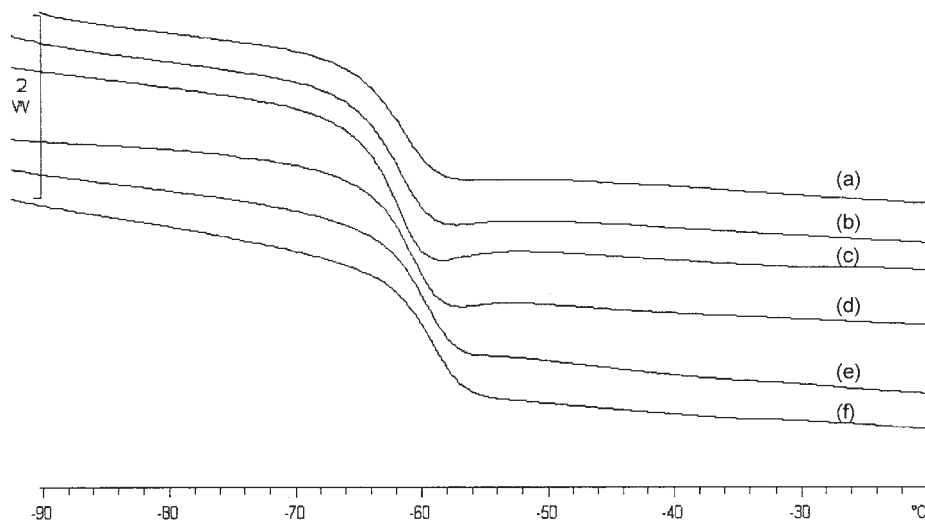


Figure 12 DSC thermograms of NR and HNR at various % hydrogenation: (a) NR, (b) 37.9%, (c) 52.2%, (d) 79.1%, (e) 91.9%, and (f) 99.7%.

TABLE IX
Analysis of Glass Transition Temperature and
Decomposition Temperature of Rubber Samples

Rubber	% Hydrogenation	T_g (°C)	T_{id} (°C)	T_{max} (°C)
EPDM ^a	-	-44.6	452.7	470.7
PIP	-	-58.9	359.2	384.1
NR	-	-62.3	357.2	380.9
HNR	37.9	-63.2	366.5	392.5
	52.2	-63.0	390.4	423.3
	79.1	-61.9	420.5	451.2
	91.9	-60.5	433.5	462.1
	99.7	-59.6	447.5	469.2

^aThe ethylene-propylene copolymer (EPDM) has the ratio of ethylene/propylene as 50/50 and 9.5% of diene content.

In addition, the glass transition temperature of HNR was slightly increased with an increase in the level of hydrogenation. The standard EPDM (ethylene/propylene = 50/50, diene = 9.5%) having the higher T_g (-44.6°C) shows a higher degree of crystallization within the polymer structure compared to that of HNR. It can be concluded that the hydrogenation does not affect the glass transition temperature of NR; consequently, the HNR product still has a high rubbery property. A similar observation was also made by Singha and coworkers for HNR obtained using the $RhCl(PPh_3)_3$ catalytic hydrogenation system.³

CONCLUSIONS

$OsHCl(CO)(O_2)(PCy_3)_2$ was found to be an efficient catalyst precursor for natural rubber hydrogenation in chlorobenzene. Kinetic studies showed that the hydrogenation reaction was first order with respect to catalyst concentration, which implied that the active complex was a mononuclear species. In contrast, the increase in rubber concentration reduced the catalytic activity. It is possible that impurities in NR could coordinate to the metal center to produce the inverse dependence on rubber concentration. The unique behavior of NR hydrogenation catalyzed by $OsHCl(CO)(O_2)(PCy_3)_2$ was first-order with respect to hydrogen pressure, which diminished to an inverse behavior dependence at high hydrogen pressure. The hydrogenation rate was dependent on reaction temperature, and the activation energy of this process was 122.76 kJ/mol. In addition, the role of carboxylic acid and sulfonic acid in rubber hydrogenation suggested that these acids could assist in helping to prevent the poisoning of $OsHCl(CO)(O_2)(PCy_3)_2$ by the impurities present in NR. The present hydrogenation method disclosed in this investigation results in the improvement of the thermal stability of natural rubber without affecting its glass transition temperature.

We gratefully acknowledge the support of the Thailand Research Fund (The Royal Golden Jubilee Project) and the Natural Sciences and Engineering Research Council of Canada (NSERC). We thank Dr. Neil T. McManus and Dr. Kitikorn Charmondusit for their assistance throughout the course of this work.

References

- Morton, M. *Rubber Technology*; Van Nostrand Reinhold Company: New York, 1973; 2nd ed, p 169.
- Tanaka, Y. *Rubber Chem Tech* 2001, 74, 355.
- Singha, N. K.; De, P. P.; Sivaram, S. *J Appl Polym Sci* 1997, 66, 1647.
- Sarkar, M. D.; Mukunda, P. G.; De, P. P.; Bhowmick, A. K. *Rubber Chem Tech* 1997, 70, 855.
- Schulz, D. N.; Turner, S. R. *Rubber Chem Technol* 1982, 55, 809.
- Nang, T. D.; Katabe, Y.; Minoura, Y. *Polymer* 1976, 17, 117.
- Bhaduri, S.; Mukesh, D. *Homogeneous Catalysis Mechanisms and Industrial Applications*; Wiley & Sons: New York, 2000; p. 8.
- Rao, P. V. C.; Upadhyay, V. K.; Pillai, S. M. *Eur Polym Mater* 2001, 37, 1159.
- Martin, P.; McManus, N. T.; Rempel, G. L. *J Mol Catal A* 1997, 126, 115.
- Mohammadi, N. A.; Rempel, G. L. *J Mol Catal A* 1989, 50, 259.
- Parent, J. S.; McManus, N. T.; Rempel, G. L. *Ind Eng Chem Res* 1996, 35, 4417.
- Bhattacharjee, S.; Bhowmick, A. K.; Avasthi, B. N. *J Polym Sci* 1992, 30, 471.
- Bhattacharjee, S.; Bhowmick, A. K.; Avasthi, B. N. *Polymer* 1993, 34, 5168.
- Delgado, R. A. S.; Rosales, M.; Esteruelas, M. A.; Oro, L. A. *J Mol Catal A* 1995, 96, 231.
- Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Delgado, R. A. S.; Sola, E.; Velero, C.; Werner, H. *J Am Chem Soc* 1989, 111, 7431.
- Esteruelas, M. A.; Oro, L. A.; Velero, C. *Organometallics* 1992, 11, 3362.
- Mao, T. F.; Rempel, G. L. *J Mol Catal A* 2000, 153, 63.
- Parent, J. S.; McManus, N. T.; Rempel, G. L. *Ind Eng Chem Res* 1998, 37, 4253.
- Charmondusit, K.; Prasassarakich, P.; McManus, N. T.; Rempel, G. L. *J Appl Polym Sci* 2003, 89, 142.
- Esteruelas, M. A.; Werner, H. *J Organometallic Chem* 1986, 303, 221.
- Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew Chem Int Ed Engl* 1988, 27, 1563.
- Mohammadi, N. A.; Rempel, G. L. *Comput Chem Eng* 1987a, 11, 27.
- Brydson, J. A. *Rubber Materials and Their Compounds*; Elsevier Applied Science: New York, 1988; p 86.
- Aik-Hwee, E.; Tanaka, Y.; Seng-Neon, G. *J Nat Rubber Res* 1992, 7, 152.
- Montgomery, D. C. *Design and Analysis of Experiments*; John Wiley & Sons: New York, 2001; 5th ed, p 228.
- Mason, R. L.; Gunst, R. F.; Hess, L. H. *Statistical Design and Analysis of Experiments*; John Wiley & Sons: New York, 1989.
- Mao, T. F.; Rempel, G. L. *J Mol Catal A* 1998, 135, 121.
- Guo, X. Y.; Rempel, G. L. *J Appl Polym Sci* 1997, 65, 667.
- Yi, C. S.; Lee, D. W.; He, Z. *Organometallics* 2000, 19, 2909.
- Hu, J. M. Eng. Thesis, University of Waterloo, Waterloo, Ontario, Canada, 2000.
- Charmondusit, K. Ph.D. Thesis, Chulalongkorn University, Bangkok, Thailand, 2001.