



# Hydrogenation of natural rubber latex in the presence of $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$

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## ABSTRACT

Natural rubber latex (NRL) is comprised of *cis*-1,4-polyisoprene as the major component which has poor resistance to oxidation and degradation by ozone and long-term heating due to the presence of carbon–carbon double bonds in the polymer backbone. Hydrogenation is a useful method, for improving the oxidative and thermal degradation resistance of diene-based polymers. Hydrogenation of NRL was carried out and the degree of hydrogenation was determined via a <sup>1</sup>H NMR spectroscopic technique. Kinetic data were collected using a computer controlled gas-uptake apparatus in terms of hydrogen consumption as a function of time. The kinetic results indicated that the hydrogenation of NRL catalyzed by  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  exhibited a first-order dependence on hydrogen pressure and first-order dependence with respect to catalyst concentration and an apparent inverse behavior with respect to rubber concentration due to the effect of impurities present in the NRL. Acid addition helped to suppress the poisoning of the catalyst by impurities. The apparent activation energy of the hydrogenation of NRL was calculated to be 31.8 kJ/mol. A mechanism for the hydrogenation of the NRL was also proposed.

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## 1. Introduction

Natural rubber latex (NRL) is a milk like substance derived from *Hevea Brasiliensis*. The hydrogenation of elastomers in latex form is of great interest and significance since many diene-based polymers are produced in latex form, especially natural rubber. By applying the hydrogenation process to a polymer emulsion, the typical procedures for the polymer hydrogenation, such as the precipitation of polymer from its emulsion, the subsequent drying process, and the redissolution of the polymer into an organic solvent for the hydrogenation, can be avoided. This would represent economic and environmental advantages for the production of hydrogenated polymers. Hydrogenation of rubber latex can be performed by both catalytic and non-catalytic methods. Hydrogenation of unsaturated polymers via a homogeneous catalyst is a favorable method. Many of the new developments in the field of catalytic hydrogenation of relatively high molecular weight polymers have involved the use of homogeneous catalysts because they have higher selectivity and are not prone to macroscopic diffusion problems encountered with heterogeneous catalysts. In addition, the performance of homogeneous catalysts are more easily explained and understood on the molecular level [1]. Mahittikul et al. [2] have also reported on the effective hydrogenation of NRL using an osmium complex catalyst.

Many homogeneous hydrogenation catalysts share one shortcoming—i.e., hindered olefins are not reduced at efficient rates. Normally, a homogeneous hydrogenation solution contains either coordinating solvents or dissociated ligands which compete with the olefin for catalytically active metal sites, preventing hydrogenation of highly hindered olefins. An exception is the Crabtree's catalyst. Crabtree and Morris [3] discovered that the cationic iridium catalysts,  $[\text{Ir}(\text{cod})\text{L}_2]\text{PF}_6$  and  $[\text{Ir}(\text{cod})\text{L}(\text{py})]\text{PF}_6$ , were effective catalysts for hindered alkene hydrogenation in the presence of non-coordinating chlorinated solvents,  $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_5\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$ . Presumably, they all have high polarity but negligible coordinating power. Normally,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  can oxidize and deactivate other low valent catalysts involved in hydrogenation. Nevertheless, both iridium catalytic precursors were later found to be stable to oxidizing reagents such as oxygen or ethyl iodide.

There have been some previous reports on the hydrogenation of diene-based polymers catalyzed by iridium catalysts. Gilliom studied the catalytic hydrogenation of polybutadiene and a butadiene–styrene block copolymer by using polymer entrained  $[\text{Ir}(\text{cod})(\text{PMePh}_2)_2]\text{PF}_6$  as a catalyst in the absence of solvent under moderate reaction conditions [4]. Hu et al. studied the kinetics of the hydrogenation of nitrile–butadiene rubber using  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  in solution form [5]. Hinchiranan et al. [6] have also used this iridium complex to hydrogenate natural rubber (NR) in solution form and proposed a catalytic mechanism for this system.

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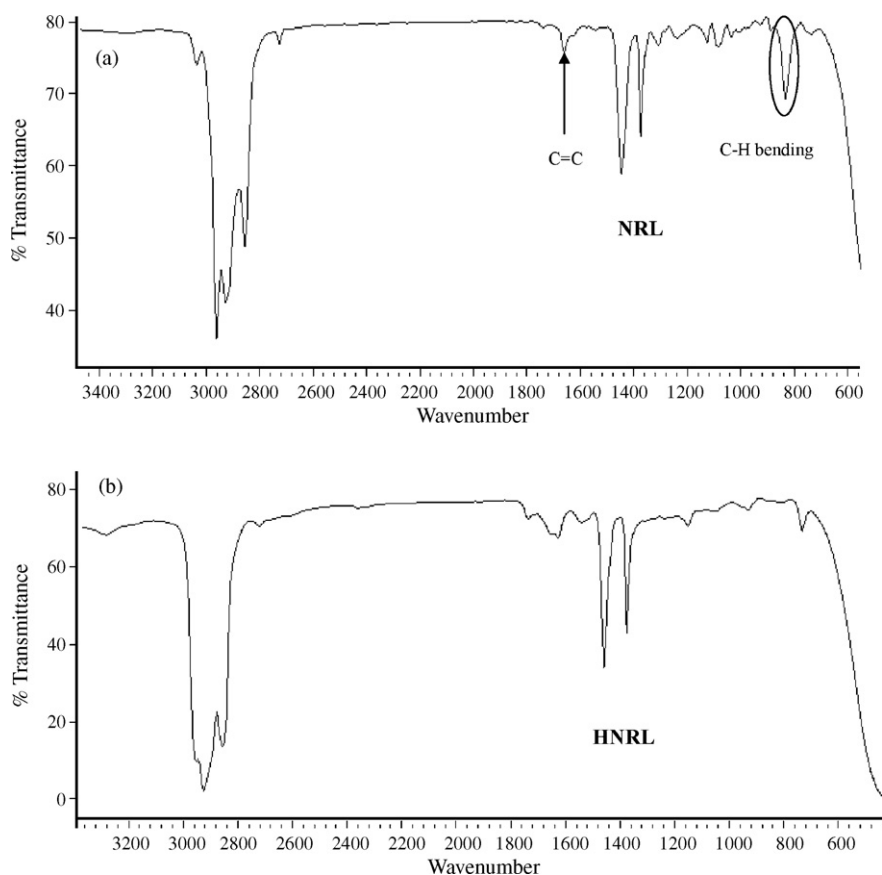


Fig. 1. FTIR spectra of NRL before and after hydrogenation catalyzed by  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ .

In the present investigation, the goal of the research was to study the hydrogenation of NRL catalyzed by  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ . The effect of reaction parameters on the hydrogenation rate such as catalyst concentration, rubber concentration, hydrogen pressure, acid concentration and reaction temperature were investigated. A reaction mechanism for the NRL hydrogenation was proposed.

## 2. Experimental

### 2.1. Materials

$[\text{Ir}(\text{cod})\text{py}(\text{PCy}_3)]\text{PF}_6$  was 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). Solvents (reagent grade monochlorobenzene (MCB) from Fischer Scientific Ltd. (Fair Lawn, NJ, USA), dichlorobenzene (DCB) and trichlorobenzene (TCB) from EM Science (Darmstadt, Germany) and tetrahydrofuran (THF) from Caledon Laboratories Ltd. (Georgetown, ON, Canada) were used as received. *p*-Toluenesulfonic acid (*p*-TSA) was purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA). Natural rubber latex with high ammonia content was provided by Thai Rubber and Latex Co. Ltd. (Bangkok, Thailand).

### 2.2. Kinetic study of NRL hydrogenation

Kinetic data were obtained from hydrogen consumption profiles obtained using a gas-uptake apparatus developed by Mohammadi and Rempel [7]. This equipment can maintain isothermal ( $\pm 1$  °C)

and isobaric ( $\pm 0.02$  bar) conditions throughout the hydrogenation process. The NRL mixtures were prepared by dissolving the desired amount of NRL in 150 mL of monochlorobenzene. Catalyst was weighed into a small glass bucket and placed in a catalyst addition device within the reactor head. For experiments performed with added acid, the desired amount of acid was added to the latex/solvent mixture. The rubber latex mixture was degassed by charging with hydrogen gas at 13.8 bar followed by evacuation three times. Hydrogen gas was then passed through the reactor for 20 min while stirring the mixture at 1200 rpm. The reactor was then heated to the desired temperature and the pressure adjusted to the reaction pressure. Once liquid/vapor equilibrium at the desired conditions was established, the catalyst was released from a catalyst addition device by using an overpressure of hydrogen. The amount of hydrogen consumed by the reaction as a function of time and the solution temperature were recorded over the course of the reaction. Each experiment proceeded until no further hydrogen uptake was recorded, after which the reactor was cooled and the hydrogenated product was isolated by precipitation with ethanol and then dried in vacuum.

### 2.3. Characterization

The structure of the hydrogenated NRL and the exact final conversion provided from the hydrogen consumption profiles were confirmed by FTIR and  $^1\text{H}$  NMR spectroscopy. The samples were prepared by casting a rubber film on NaCl plates for FTIR scans obtained on a BIO-RAD Merlin FTS 3000X spectrometer.  $^1\text{H}$  NMR spectra of NRL and HNRL samples dissolved in  $\text{CDCl}_3$  were obtained using a Bruker 300 MHz spectrometer.

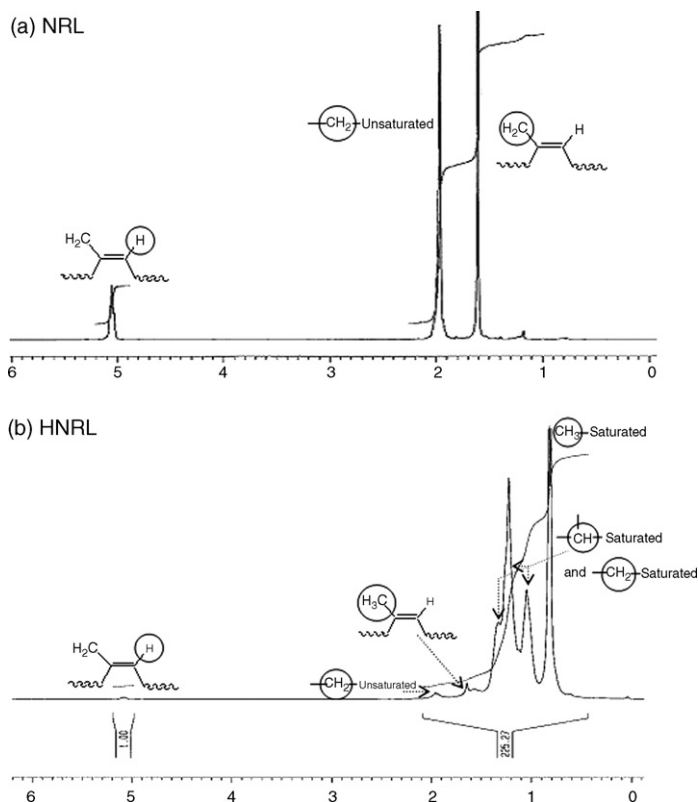


Fig. 2.  $^1\text{H}$  NMR spectra of NRL before and after hydrogenation catalyzed by  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ .

### 3. Results and discussion

#### 3.1. Structure characterization using FTIR and NMR spectroscopy

The structure of NRL before and after the hydrogenation process was characterized by Fourier transform infrared spectroscopy (FTIR) as shown in Fig. 1a and b. The structure of hydrogenated natural rubber is similar to an alternating ethylene–propylene copolymer (EPDM). The FTIR spectrum of hydrogenated natural rubber latex (HNRL) shows that the absorption bands corresponding to the C=C stretching, olefinic C–H bending and  $-(\text{CH}_2)_3-$  are located at 1664, 836 and 739  $\text{cm}^{-1}$ , respectively. The characteristic signals of unsaturation, 1664 and 836  $\text{cm}^{-1}$ , disappeared in the hydrogenated rubbers while an intense signal appeared at 739  $\text{cm}^{-1}$  due to saturated carbon formed through hydrogenation.  $^1\text{H}$  NMR spectroscopy was used to examine the actual degree of hydrogenation in each sample. The structure of both NRL and HNRL were previously investigated by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy [2]. The  $^1\text{H}$  NMR spectra of NRL before and after the hydrogenation reaction are shown in Fig. 2a and b. Fig. 2b shows that the intensity of the olefinic proton, unsaturated methylene and unsaturated methyl signal at 5.17, 1.95 and 1.67 ppm, respectively, was reduced. The remaining signals show very low intensity which confirms that most carbon–carbon double bonds in NRL were hydrogenated. HNRL shows new strong signals in the range 0.8–1.4 ppm which are attributed to methine, methylene and methyl groups.

#### 3.2. Kinetic experiments of natural rubber latex hydrogenation

All the kinetic data for NRL hydrogenation in the presence of the homogeneous catalyst,  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ , were obtained using an automated gas-uptake apparatus. The univariate experiments

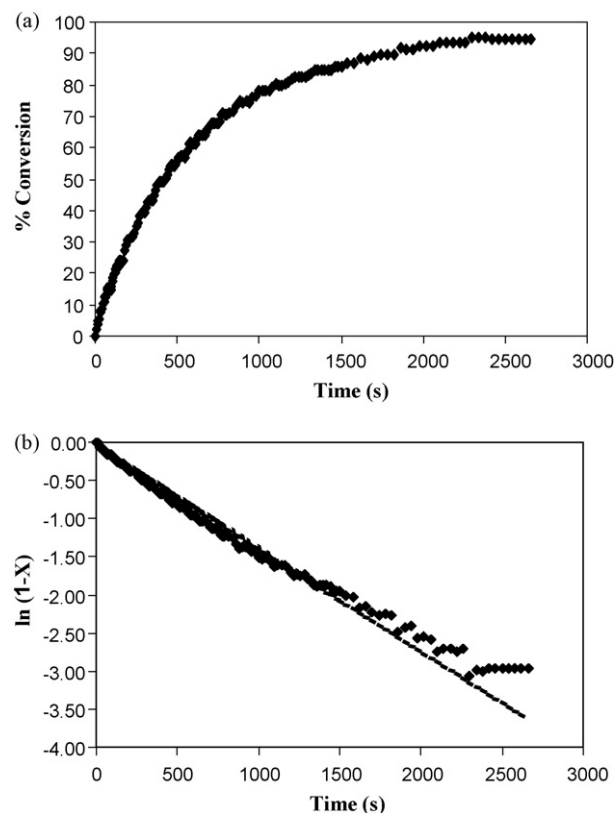


Fig. 3. NRL hydrogenation profile obtained from gas-uptake apparatus: (a) olefin conversion profile and (b) first-order  $\ln$  plot (---: model from linear regression) of NRL hydrogenation.  $[\text{Ir}] = 120 \mu\text{M}$ ;  $[\text{C}=\text{C}] = 100 \text{ mM}$ ;  $p_{\text{H}_2} = 41.4 \text{ bar}$ ;  $[p\text{-TSA}] = 10 \text{ mM}$ ;  $T = 150^\circ\text{C}$  in monochlorobenzene.

were carried out to investigate the effect of each factor individually. All kinetic data were collected under a constant pressure of hydrogen, with vigorous mixing. Therefore,  $[\text{H}_2]$  was assumed to be in equilibrium with the gaseous pressure and remained constant during the course of the reaction. Consequently, the reaction could be approximated as a pseudo-first-order reaction:

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

where  $k'$  is the pseudo-first-order rate constant. Fig. 3a shows a typical plot of conversion versus reaction time for the NRL hydrogenation reaction. The hydrogen consumption plot indicates that the reaction was apparently first-order in the olefinic substrate, which according to Eq. (1) can be expressed in terms of the conversion of unsaturated double bonds (extent of hydrogenation),  $x$ , as:

$$\ln(1-x) = -k't \quad (2)$$

where  $t$  is the reaction time. Fig. 3b shows a linear plot of  $\ln(1-x)$  versus time ( $t$ ) for the NRL hydrogenation. The pseudo-first-order rate constant is then readily determined from the slope of the corresponding line. A summary of results for the effect of hydrogenation variables such as catalyst concentration, rubber concentration, acid concentration and hydrogen pressure on the experimental rate constant is presented in Table 1. Table 1 also presents the effect of reaction parameters on the degree of hydrogenation.

#### 3.3. Effect of catalyst concentration

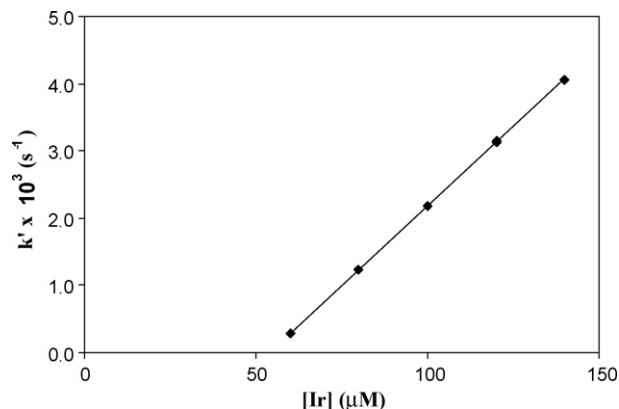
To investigate the influence of catalyst concentration on NRL hydrogenation, the catalyst concentration was varied. The range of

**Table 1**  
Kinetic results of univariate experiments for NRL hydrogenation catalyzed by  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ .

Experiment	[Ir] ( $\mu\text{M}$ )	[C=C] (mM)	$P_{\text{H}_2}$ (bar)	Temp ( $^\circ\text{C}$ )	[Acid] (mM)	Solvent	$k' \times 10^3$ ( $\text{s}^{-1}$ )	% hydrogenation at 30 min	$\eta_{(\text{rel})}$
1	60	100	41.4	150	10	MCB	0.29	22.5	–
2	80	100	41.4	150	10	MCB	1.23	52.6	8.23
3	100	100	41.4	150	10	MCB	2.19	79.4	8.41
4	120	100	41.4	150	10	MCB	3.13	89.9	8.67
5	120	100	41.4	150	10	MCB	3.14	90.1	8.69
6	140	100	41.4	150	10	MCB	4.06	95.4	8.82
7	120	80	41.4	150	10	MCB	4.56	97.6 (25.5 min)	–
8	120	100	41.4	150	10	MCB	3.14	90	8.67
9	120	100	41.4	150	10	MCB	3.15	90	8.68
10	120	120	41.4	150	10	MCB	2.3	66.5	8.41
11	120	150	41.4	150	10	MCB	1.56	46.9	8.13
12	120	200	41.4	150	10	MCB	1.02	21.5	7.73
13	120	100	6.9	150	10	MCB	0.89	25.4	–
14	120	100	13.8	150	10	MCB	1.35	48.7	8.56
15	120	100	27.6	150	10	MCB	2.27	66.7	8.67
16	120	100	41.4	150	10	MCB	3.12	89.9	8.7
17	120	100	41.4	150	10	MCB	3.11	90	8.68
18	120	100	55.1	150	10	MCB	3.85	93.7 (28.6 min)	8.72
19	120	100	69.2	150	10	MCB	4.48	92.4 (25.5 min)	8.73
20	120	100	41.4	150	0	MCB	0.02	4.5	–
21	120	100	41.4	150	3	MCB	0.09	15.9	–
22	120	100	41.4	150	5	MCB	0.42	34.6	–
23	120	100	41.4	150	7	MCB	2.65	63.6	8.56
24	120	100	41.4	150	10	MCB	3.13	90	8.69
25	120	100	41.4	150	12	MCB	2.96	80.7	6.05
26	120	100	41.4	150	15	MCB	2.65	70.6	5.12
27	120	100	41.4	120	10	MCB	1.55	45.8	–
28	120	100	41.4	130	10	MCB	2.06	56.9	–
29	120	100	41.4	140	10	MCB	2.78	76.7	–
30	120	100	41.4	150	10	MCB	3.23	88.4	–
31	120	100	41.4	160	10	MCB	3.79	90.3 (23.7 min)	–
32	120	100	41.4	150	10	MCB	3.14	90.1	–
33	120	100	41.4	150	10	DCB	3.26	91.5	–
34	120	100	41.4	150	10	TCB	3.54	94.2	–
35	120	100	41.4	150	10	THF	1.23	38.7	–

Solvent: 150 mL. Relative viscosity ( $\eta_{\text{rel}}$ ) of NR and NRL in toluene are 7.42 and 4.45, respectively.

catalyst concentration was 60–140  $\mu\text{M}$  in monochlorobenzene. The hydrogen pressure (41.4 bar) and temperature (150  $^\circ\text{C}$ ) were kept constant for all experiments. The influence of catalyst concentration on the pseudo-first-order rate constant is illustrated in Fig. 4. The results suggest a first-order dependence on catalyst concentration, which implied that the active complex is a mononuclear species. The NRL hydrogenation system requires a relatively high loading of catalyst (750  $\mu\text{M}$ ). It can be presumed that impurities in NRL might reduce the catalytic activity; thus, some portion of catalyst about 50  $\mu\text{M}$  appeared to be sacrificed due to the impurities present within the NRL. This behavior with respect to catalyst



**Fig. 4.** Effect of catalyst concentration on NRL hydrogenation rate.  $P_{\text{H}_2} = 41.4$  bar;  $[\text{C}=\text{C}] = 100$  mM;  $[p\text{-TSA}] = 10$  mM;  $T = 150$   $^\circ\text{C}$ .

concentration is similar to that observed for the NRL hydrogenation catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  which also exhibited a decrease in catalytic activity with an increase in the rubber concentration [2].

#### 3.4. Effect of hydrogen pressure

A series of experiments was carried out over the hydrogen pressure range of 6.9–69.2 bar ( $[\text{Ir}] = 120$   $\mu\text{M}$ ,  $[\text{C}=\text{C}] = 100$  mM,  $[p\text{-TSA}] = 10$  mM) at 150  $^\circ\text{C}$  in monochlorobenzene. The results from Table 1 suggested that the rate of hydrogenation was first-order with respect to the hydrogen pressure. This first-order rate dependence implies that primarily a single reaction pathway is probably involved in the reaction of the unsaturation of the polymer with hydrogen. If more than one process were involved, the relative contribution of each pathway should change with varying hydrogen pressure, and thus the dependence might deviate from the first-order behavior observed. A similar behavior of the first-order rate dependence on hydrogen pressure was also observed from NBR hydrogenation using this iridium complex [5]. Hinchiranan et al. [6] reported that the first-order rate dependence on hydrogen pressure was also observed in the solution hydrogenation of NR using this iridium complex. In contrast, the hydrogenation of natural rubber latex (NRL) in the presence of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  showed a second- to zero-order dependence as the system pressure increased [2].

#### 3.5. Effect of rubber concentration

The effect of rubber concentration on the hydrogenation rate was studied over the range of 80–200 mM ( $[\text{Ir}] = 120$   $\mu\text{M}$ ,  $[p\text{-$

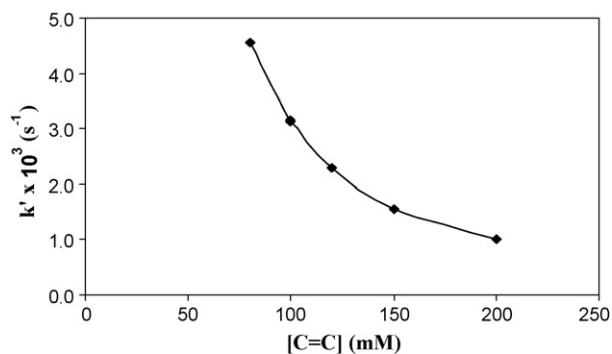


Fig. 5. Effect of rubber concentration on NRL hydrogenation rate:  $[\text{Ir}] = 120 \mu\text{M}$ ;  $P_{\text{H}_2} = 41.4 \text{ bar}$ ;  $[p\text{-TSA}] = 10 \text{ mM}$ ;  $T = 150^\circ\text{C}$ .

TSA) = 10 mM,  $P_{\text{H}_2} = 41.4 \text{ bar}$ ,  $T = 150^\circ\text{C}$  in monochlorobenzene). The results shown in Fig. 5 indicate that the reaction rate has an inverse rate behavior with an increase in the rubber loading. The iridium complexes,  $[\text{Ir}(\text{cod})\text{L}(\text{py})]\text{PF}_6$  and  $[\text{Ir}(\text{cod})\text{L}_2]\text{PF}_6$ , are sensitive to a number of functional groups such as amines, which totally deactivate the catalysts via deprotonation reactions. Proteins in NRL likely lower the catalytic activity of  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  due to the amine content in the protein structure. The influence of impurities in NRL drastically decreased the efficiency of the Ir complex. The effect of rubber concentration on the reaction rate of NRL hydrogenation was similar to the hydrogenation of natural rubber and rubber with an interacting functional group such as the nitrile group in NBR. There are a number of reports showing that the activity of rhodium, ruthenium, osmium and iridium complexes were inhibited by coordination of the nitrile functional group with the metal center of the complexes [5,8–11].

### 3.6. Effect of acid concentration

Acid addition in a number of hydrogenation systems has been found to improve the catalytic activity of olefinic hydrogenation catalysts. Guo and Rempel [11] established that carboxylic acids increased the catalytic activity for the hydrogenation of a NBR emulsion using  $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$ . They reported that the carboxylic acids were very effective in preventing the poisoning of the catalyst by impurities in the emulsion system. Yi et al. [12] also found that the addition of acids increased the rate of alkene hydrogenation catalyzed by  $\text{RuH}(\text{CO})(\text{Cl})(\text{PCy}_3)_2$ . They suggested that the increase in catalytic activity of this Ru catalytic species might be due to the selective entrapment of the phosphine ligand and the formation of a highly active 14-electron ruthenium-monophosphine species. For the system of NRL hydrogenation catalyzed by  $[\text{Ir}(\text{cod})(\text{py})(\text{PCy}_3)]\text{PF}_6$ , the role of acid on the NRL hydrogenation was studied and the results are presented in Fig. 6. The effect of acid addition on the NRL hydrogenation rate in the presence of Crabtree's catalyst was carried out at base conditions:  $[\text{Ir}] = 120 \mu\text{M}$ ,  $P_{\text{H}_2} = 41.4 \text{ bar}$ ,  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $T = 150^\circ\text{C}$ . It was found that the acid addition could increase the rate of NRL hydrogenation. Therefore, it is possible that the acid addition might promote the catalytic activity of  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  by preventing the poisoning of the catalyst due to proteins present in NRL. Hu et al. [5] reported that a peak for free  $\text{PCy}_3$  ligand dissociated from the catalyst precursor at 10 ppm was not present in the  $^{31}\text{P}$  NMR spectrum at  $70^\circ\text{C}$ , which indicated that no appreciable dissociation of the  $\text{PCy}_3$  ligand occurred and it can be concluded that the role of acid addition was not the entrapment of dissociated  $\text{PCy}_3$ . However, carboxylic acids have been known to increase the catalytic activity of the catalyst for NRL hydrogenation in the presence

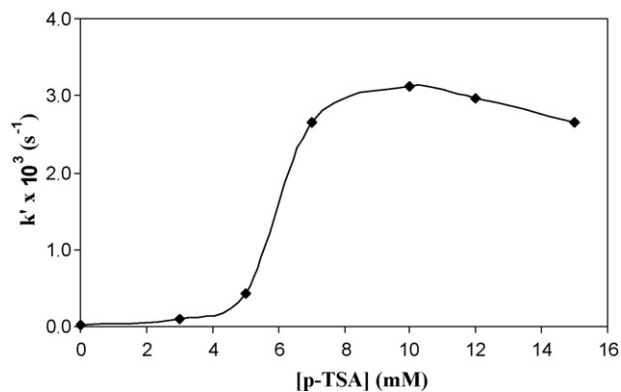


Fig. 6. Effect of acid concentration on NRL hydrogenation rate:  $[\text{Ir}] = 120 \mu\text{M}$ ;  $P_{\text{H}_2} = 41.4 \text{ bar}$ ;  $[\text{C}=\text{C}] = 100 \text{ mM}$ ;  $T = 150^\circ\text{C}$ .

of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  [2]. However, a high concentration overload of these acids in the system might partially or totally deactivate the Ir complex, presumably by coordination [4].

### 3.7. Effect of reaction temperature

A series of experiments were carried out over the temperature range of  $120\text{--}160^\circ\text{C}$  ( $[\text{Ir}] = 120 \mu\text{M}$ ,  $[\text{C}=\text{C}] = 100 \text{ mM}$  and  $P_{\text{H}_2} = 41.4 \text{ bar}$  in monochlorobenzene). The effect of temperature on the rate constant is shown in Table 1 and is represented by a good linear Arrhenius plot. The activation energy calculated from a least squares regression analysis of a plot of  $\ln(k')$  versus  $1/T$  was  $31.79 \text{ kJ/mol}$ . This suggests further evidence that the kinetic data were obtained without severe mass transfer limitation and the diffusion of the reactants was not the main rate-determining factor under these conditions.

### 3.8. Effect of solvents

The effect of different solvents on the hydrogenation rate of NRL in the presence of Crabtree's catalyst was investigated at base conditions:  $[\text{Ir}] = 120 \mu\text{M}$ ,  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $P_{\text{H}_2} = 41.4 \text{ bar}$ ,  $T = 150^\circ\text{C}$ . The effect of solvent on the hydrogenation is also summarized in Table 1 (Experiment no. 5, 33, 34 and 35). It seems that chlorinated solvents are viable solvents for catalytic hydrogenation with this cationic iridium catalyst. Toluene, hexane and xylene were not used as solvents since they could not completely dissolve the cationic iridium catalyst. Crabtree et al. [13] studied alkene hydrogenation catalyzed by  $[\text{Ir}(\text{cod})\text{L}_2]\text{PF}_6$  and  $[\text{Ir}(\text{cod})\text{L}(\text{py})]\text{PF}_6$  where (cod) was 1,5-cyclooctadiene and L was a tertiary phosphine and found that non-coordinating solvents such as toluene, benzene or hexane also were inappropriate solvents since only catalytically inactive precipitates were formed under a hydrogen atmosphere. However, these Ir complexes were very active in solvents containing a chlorine atom except for 1,1-dichloroethylene and carbon tetrachloride since they failed to dissolve the Ir catalysts under a hydrogen atmosphere [3]. The strong coordinating solvent (tetrahydrofuran) was found to be an efficient solvent for the hydrogenation of *cis*-1,4-polyisoprene (CPIP) and NR using an Os catalyst, but it was not a good solvent for the hydrogenation of CPIP and NR using Crabtree's catalyst [6]. Thus, higher activity of Crabtree's catalyst was obtained in non-coordinating solvents. This is consistent with the hydrogenation of acrylonitrile-butadiene copolymers using Crabtree's catalyst [5]. In addition, the results shown in Table 1 indicate that the hydrogenation of NRL showed a slight difference in reaction rate with different amounts of chlorine atoms in the chlorinated solvents.

**Table 2**  
Effect of impurity on degree of NRL hydrogenation.

Rubber type	% nitrogen content	% conversion (4 h)
NRL	0.20	91.2
DPNRL	0.02	98.9

Conditions:  $[\text{Ir}] = 120 \mu\text{M}$ ,  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $[p\text{-TSA}] = 10 \text{ mM}$ ,  $P_{\text{H}_2} = 41.4 \text{ bar}$ ,  $T = 150^\circ\text{C}$  in monochlorobenzene.

**Table 3**  
Effect of dry rubber content on degree of NRL hydrogenation.

%DRC	% conversion (4 h)
60	91.3
50	57.6
40	44.5
30	38.7

Conditions:  $[\text{Ir}] = 120 \mu\text{M}$ ;  $P_{\text{H}_2} = 41.4 \text{ bar}$ ;  $[\text{C}=\text{C}] = 100 \text{ mM}$ ;  $[p\text{-TSA}] = 10 \text{ mM}$ ;  $T = 150^\circ\text{C}$  in monochlorobenzene.

### 3.9. Effect of impurity

The presence of impurities in NRL was suspected to decrease the hydrogenation rate. To support this, the hydrogenation of deproteinized NRL was investigated. The deproteinized rubber latex (DPNRL) was prepared using a proteolytic enzyme method [14]. The experiments were carried out in a Parr reactor for 4 h:  $[\text{Ir}] = 120 \mu\text{M}$ ,  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $[p\text{-TSA}] = 10 \text{ mM}$ ,  $P_{\text{H}_2} = 41.4 \text{ bar}$ ,  $T = 150^\circ\text{C}$  in monochlorobenzene. Table 2 shows the effect of impurity on the degree of hydrogenation. For comparison between DPNRL and NRL, DPNRL exhibited a higher degree of hydrogenation than NRL. This is attributed to the lower amount of impurity in the system. A similar result was obtained for NRL hydrogenation using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  [2].

### 3.10. Effect of dry rubber content

Since Crabtree's catalyst is sensitive to moisture, the effect of water in the system was studied. The hydrogenation at varying water contents in the system was performed in a Parr reactor under the base condition:  $[\text{Ir}] = 120 \mu\text{M}$ ;  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $P_{\text{H}_2} = 41.4 \text{ bar}$ ,  $[p\text{-TSA}] = 10 \text{ mM}$ ,  $T = 150^\circ\text{C}$  in monochlorobenzene. The range of %DRC was varied between 60 and 40%. From Table 3, it can be seen that the degree of hydrogenation decreased with decreasing dry

rubber content (or increasing water content). This might be due to the presence of water in the system acting as an inhibitor during hydrogenation.

### 3.11. Reaction mechanism and rate law

Previous studies of Crabtree's catalyst and its analogues have provided plausible pathways involved in the catalytic hydrogenation of olefins. Hydrogenation of diene polymers catalyzed by homogeneous catalysts often involved many intermediate complexes. The preferred catalytic pathway is developed from inferences from the kinetic data and electron counting schemes. The plausible catalytic cycle of  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  for the NRL hydrogenation is illustrated in Fig. 7.

According to the proposed reaction mechanism, the NRL hydrogenation catalyzed by Crabtree's iridium complex may be represented by the following rate expression:

$$-\frac{d[\text{C}=\text{C}]}{dt} = k_3[\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)]^+ \quad (3)$$

The effect of impurities (X) in NRL on the hydrogenation rate can be compared to the effect of the nitrile functional group, which inhibits the catalytic activity in NBR hydrogenation [5] and NR hydrogenation [6]. It is possible that impurities in NRL might coordinate with unsaturated active species of the catalyst to reduce the hydrogenation activity. A material balance on the active species of the Ir catalyst is expressed in the following equation:

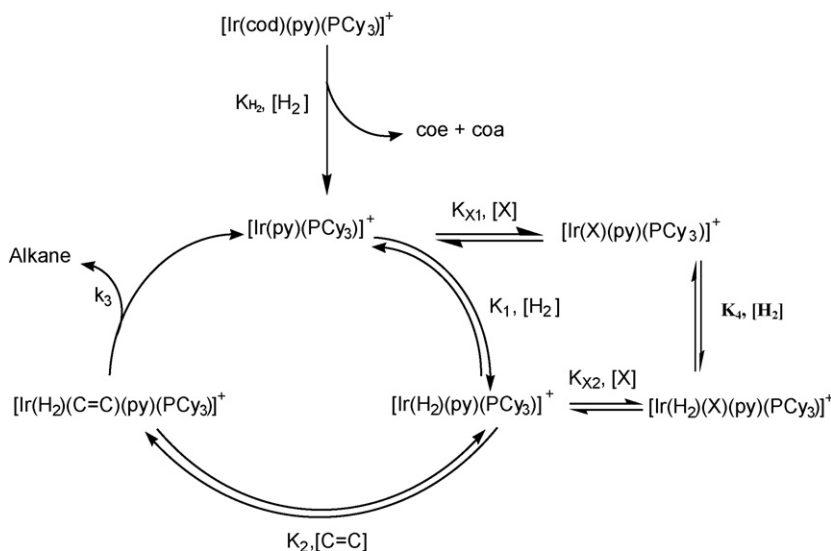
$$[\text{Ir}]_T = [\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)]^+ + [\text{Ir}(\text{H}_2)(\text{py})(\text{PCy}_3)]^+ + [\text{Ir}(\text{py})(\text{PCy}_3)]^+ + [\text{Ir}(\text{X})(\text{py})(\text{PCy}_3)]^+ + [\text{Ir}(\text{H}_2)(\text{X})(\text{py})(\text{PCy}_3)]^+ \quad (4)$$

where (X) represents an impurity.

All the iridium complex species within the concentration terms in Eq. (4) can be expressed in terms of  $[\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)]^+$  using the equilibria defined in Fig. 7 and then can be substituted into Eq. (3) to provide the resulting rate law:

$$-\frac{d[\text{C}=\text{C}]}{dt} = \frac{k_3 K_1 K_2 [\text{Ir}]_T [\text{C}=\text{C}] [\text{H}_2]}{1 + K_{X1} [\text{X}] + K_1 [\text{H}_2] (1 + K_2 [\text{C}=\text{C}] + K_{X2} [\text{X}])} \quad (5)$$

The rate expression is consistent with the behavior of the iridium system observed throughout the kinetic investigations. The kinetic



**Fig. 7.** Proposed catalytic mechanism for NRL hydrogenation in the presence of  $[\text{Ir}(\text{cod})(\text{py})(\text{PCy}_3)]\text{PF}_6$  (X = impurity).

observation indicated that the hydrogenation rate was first-order with respect to hydrogen pressure. It can be assumed that  $K_1$ ,  $K_2$  and  $K_{X_2}$  are very small and then the terms in which they appear in Eq. (5) become negligible for the range of the reaction conditions and substrate concentrations used in this study. The reaction was found to exhibit a first-order response of  $k'$  on [Ir]. In the case of hydrogenation of NR and CPIP in solution form, Hinchiranan et al. [6] reported that the reaction was found to exhibit a first-order response of  $k'$  with respect to [Ir] at low catalyst concentration and shift to zero-order at a high level of catalyst concentration due to the possible dimerization of the catalyst. The rate of NRL hydrogenation decreased with increasing rubber concentration due to an increase in the amount of impurities in the NRL.

#### 4. Conclusions

$[\text{Ir}(\text{COD})(\text{PCy}_3)(\text{py})]\text{PF}_6$  was found to be an effective catalyst for the hydrogenation of natural rubber latex in monochlorobenzene. The kinetic results indicated that the hydrogenation was first-order with respect to hydrogen pressure and first-order with respect to catalyst concentration over the ranges studied. These first-order dependencies suggest that the active complex is mononuclear over the catalyst concentration range investigated. Impurities present in the NRL caused the hydrogenation rate to have an inverse behavior with respect to increasing rubber concentration. The presence of a sulfonic acid in the hydrogenation process helped to prevent the poisoning of the iridium catalyst by impurities present in the emulsion system. The apparent activation energy of the hydrogenation

of NRL was calculated to be 31.8 kJ/mol. The proposed mechanism and the rate expression for hydrogenation of NRL in the presence of  $[\text{Ir}(\text{COD})(\text{PCy}_3)(\text{py})]\text{PF}_6$  were fairly consistent with the kinetic data.

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