

A detailed study of the hydrogenation of nitrile–butadiene rubber and other substrates catalyzed by Ru(II) complexes

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Abstract

Development of a computer controlled apparatus for measurement of gas uptake at elevated temperatures and pressures has made possible a study of the kinetics of NBR hydrogenation at conditions approaching those that are used in commercial operations. Complexes of the form $\text{Ru}(\text{X})\text{Cl}(\text{CO})\text{L}_2$ where $\text{X} = \text{H}$ or β -styryl ($\text{CH}=\text{CH}(\text{Ph})$) and L is a bulky phosphine such as tricyclohexyl- or triisopropyl-phosphine are excellent catalysts for the hydrogenation of $\text{C}=\text{C}$ in a variety of polymers and are superior to other Ru complexes for the hydrogenation of $\text{C}=\text{C}$ in nitrile–butadiene rubber. This report describes comparative studies using these complexes for the hydrogenation of $\text{C}=\text{C}$ in various polymer and small molecule substrates. Also presented are complete details of an in depth mechanistic study into the hydrogenation of NBR catalyzed by the complex $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$. © 1997 Elsevier Science B.V.

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1. Introduction

Until recently there were few reports of catalytic studies using complexes of the form $\text{MHCl}(\text{CO})\text{L}_2$ where L is a bulky phosphine such as di-*t*-butylalkyl-, tricyclohexyl- or triisopropyl-phosphine [1–3]. The last few years has seen significant interest in these systems. It has been reported that $\text{MHCl}(\text{CO})(\text{L})_2$ ($\text{M} = \text{Ru}$, Os ; $\text{L} = \text{P}^i\text{Pr}_3$, and $\text{PMe}(\text{tBu})_2$) are effective catalysts for the hydrogenation of carbonyl groups, carbon–carbon double and triple bonds in a variety of organic substrates [4–8]. The complexes are also excellent catalysts for the

selective hydrogenation of carbon–carbon double bonds ($\text{C}=\text{C}$) in nitrile–butadiene rubber [9].

The hydrogenation of $\text{C}=\text{C}$ in butadiene polymers has been the subject of much research because it is a method to produce useful polymers which are inaccessible by standard polymerization methods. The topic has recently been the subject of review [10,11]. Over the past two decades the catalytic hydrogenation of nitrile–butadiene rubber (NBR) has been developed as a commercial process. The driving force for this work is that the hydrogenated rubber (HNBR) is more resistant than NBR towards chemical, oxidative and thermal degradation [12].

Studies have shown that Rh complexes, $\text{RhCl}(\text{PPh}_3)_3$ [13] and $\text{RhH}(\text{PPh}_3)_4$ [14], are

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amongst the best catalysts for the process. The high cost of Rh led to interest into the examination of catalysts based on less expensive metals. For instance some Pd complexes are useful for efficient hydrogenation of NBR but are limited to use in ketone solvents [15,16]. Our own research group and others have examined complexes of ruthenium as possible alternatives to the Rh systems. Initial work examined hydrogenation catalyzed by Ru–PPh₃ complexes. Thus the kinetics of the hydrogenation of NBR catalyzed by RuCl(CO)(RCO₂)(PPh₃)₂ under an atmospheric pressure of hydrogen and at moderate temperatures [17] has been studied and it was possible to achieve only 40% hydrogenation of C=C in NBR. Other work showed that the Ru–PPh₃ complexes are useful catalysts for achieving >90% hydrogenation of C=C in NBR using more forcing reaction conditions; however, these complexes also promoted cross-linking of the polymers during hydrogenation unless the reaction was carried out in ketone solvents [18,19]. Recent work examining the hydrogenation of styrene–butadiene rubber catalyzed by RuCl₂(PPh₃)₃ has not reported any problem with crosslinking [20]. These results suggest that the crosslinking maybe related to hydrogenation of the nitrile groups in NBR.

Different ligand environments on metals can dramatically alter catalytic behavior. This stimulated our initial examination of the activity of the five coordinate complexes: RuHCl(CO)(PR₃)₂ (R = cyclohexyl or isopropyl) and some derivatives. Screening studies showed these complexes to be excellent catalysts for NBR hydrogenation over a wide range of reaction conditions and substrate concentrations [9]. The activities of the Ru–PCy₃ complexes were far superior to those of similar Ru–PPh₃ complexes. A detailed mechanistic study of the hydrogenation of NBR using these complexes was an obvious extension to expand understanding of this important catalytic system. However, the procedure used in initial studies (i.e. sampling at intervals from a simple batch reactor) was inadequate for accurate kinetic measurements. A

better method was the monitoring of gas uptake during the reaction and this was made possible by the development of a gas uptake apparatus to operate at elevated temperatures and pressures [21]. The details of this apparatus and its use in extensive kinetic studies are described below. A preliminary report of some of this work has already appeared in the literature [22]. We now present new results which give important insights into the reaction mechanism and a detailed account of the complete study.

2. Experimental

2.1. Chemicals

RuCl₃.aq was obtained from Engelhard; PCy₃ and P^{*i*}Pr₃ from Strem Chemicals; triethylamine from Fisher; phenyl–acetylene, decene and hexene from Aldrich; Krynac 38.50 (NBR containing 38% acrylonitrile units) and Taktene 1203 (high *cis*-polybutadiene (PBD)) from Bayer Rubber (formerly Polysar Rubber); Finaprene 410 (SBR containing 68 mol% butadiene) from Petrofina; polyisoprene (PIP) from Polymer Sciences; 3-pentenitrile was from Dupont Chemicals. Solvents were degassed but used without further purification in the operations described. All synthetic operations were carried out under an inert atmosphere.

RuHCl(CO)(PR₃)₂ [23,24], Ru(CH=CH(Ph))Cl(CO)(P^{*i*}R₃)₂ (R = ^{*i*}Pr and Cy) [25], and Ru(Ph)Cl(CO)(PPh₃)₂ [26] were prepared by literature methods.

RuHCl(CO)(PCy₃)₂ was prepared by an improvement to the literature method [23]: RuCl₃.aq (2.54 g, 10 mmol) was dissolved in methoxyethanol (50 ml). After 5 min, PCy₃ (8.23 g, 29.4 mmol) was added. The solution was heated under reflux for 20 min, then triethylamine (6 ml) was added. The mixture was heated under reflux for a further 6 h and then cooled. The microcrystalline orange product was

filtered and then washed with toluene (2×15 ml) and dried in vacuo; yield 5.6 g (80%).

2.2. Characterization

NMR spectra were run on a Bruker AM 250 MHz spectrometer. IR spectra were recorded on a Nicolet 520 FT IR spectrometer. Gas chromatograms were obtained using a Perkin Elmer Sigma 2000 instrument using a 30×0.322 m capillary column with a $3 \mu\text{m}$ thick DB-1 liquid film (J&W Scientific, #109473). Gel permeation chromatography was performed using a Waters high pressure liquid chromatography system fitted with a Waters Ultrastaygel 10^4 Angstrom column and employing a differential refractive index (DRI) detector with an IBM PC/386 data acquisition system using customized software. Polymer viscosity measurements were made using a Fann Dressler rotating cup viscometer fitted with an F 0.2 spring. Kinetic studies were made using a high pressure gas uptake device developed in this laboratory.

2.3. Description of gas uptake apparatus

The basic design of the gas uptake apparatus was based on that of Mohammadi and Rempel [27,28]. Few modifications were needed for operation at high pressure (Fig. 1).

The reactor vessel was a 1 l Autoclave Engineers 'Zipperclave', with a maximum service of 138 bar at 200°C . The vessel was fitted with a magnetic drive agitator and a $1/3$ hp brushless motor. Five head ports were allocated as follows: gas feed, thermowell, dip tube (for degassing and liquid sampling), gas out and catalyst addition (see Fig. 2).

The vessel was heated using clamp on ceramic band heaters. Heating control used an Autoclave Engineers time PID digital self tuning temperature controller. The controller used a type K thermocouple in a thermowell to measure temperature.

CV-1 was a Kammer pneumatically actuated valve with integral positioner, with a C_v of 0.000016. The valve trim has a equal percent

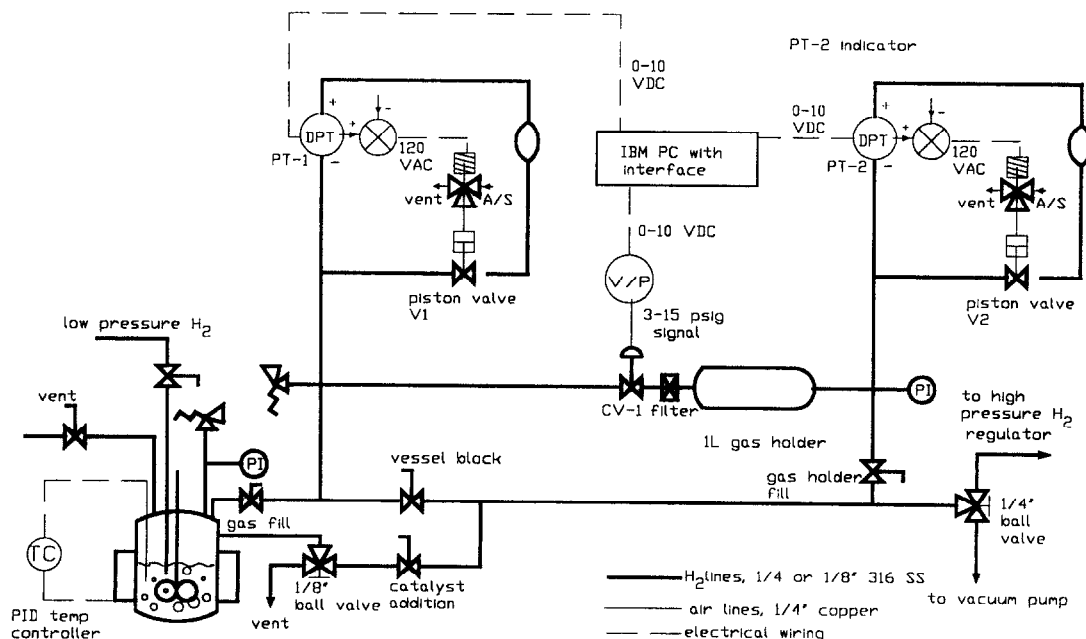


Fig. 1. Schematic of gas uptake apparatus.

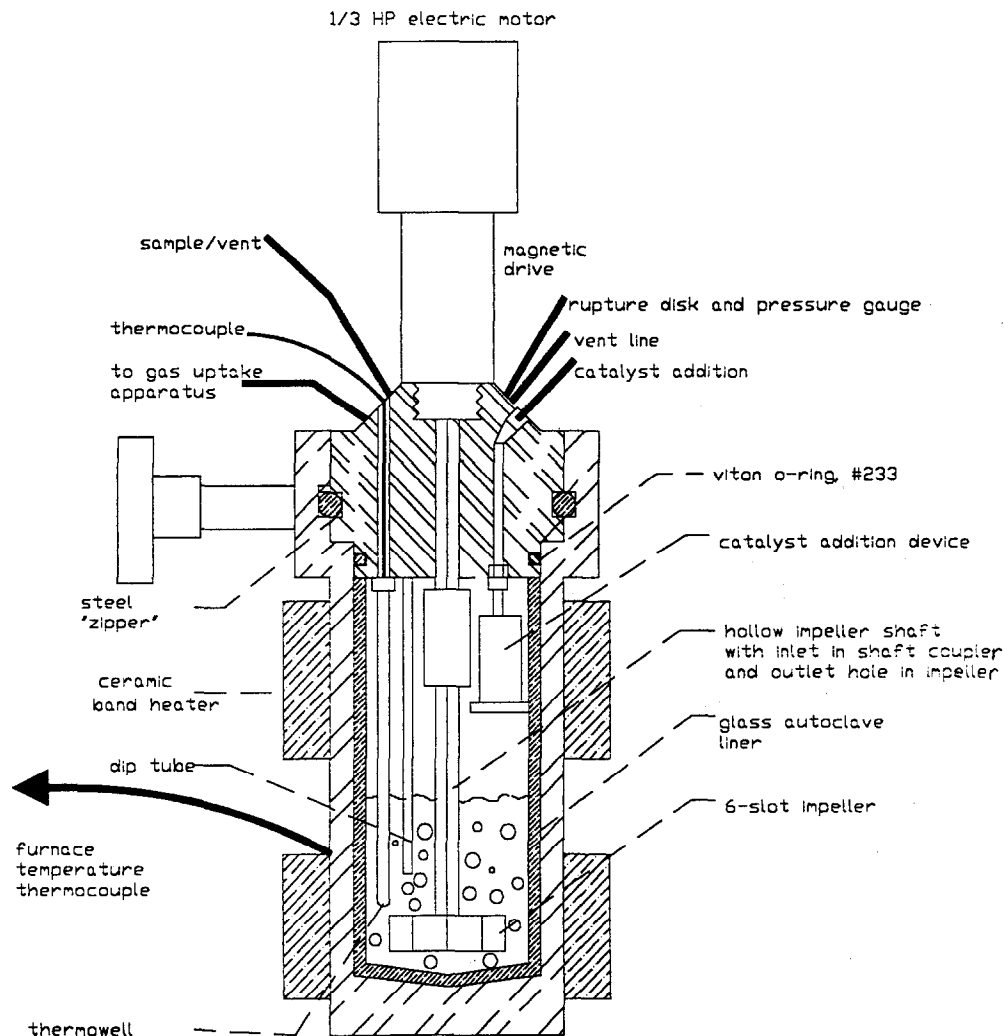


Fig. 2. Schematic of reactor.

flow/ percent open flow characteristic. The valve driver consisted of a Sampson electropneumatic (*V/P*) converter which converted a 0–10 V electric signal from D/A converter to 0.2–1 bar pneumatic signal required by the valve.

PT-1 and PT-2 were Validyne variable reluctance differential pressure transducers with maximum service pressures of 207 bar. PT-1 was rated for ± 2.1 bar differential and PT-2 was rated for 3.4 bar differential. The transducers were protected by simple comparators A1 and A2 (high level alarms) connected to their outputs; the comparators opened solenoid valves

which actuated pneumatic diaphragm valves V1 and V2, which equalized pressure across PT-1 and PT-2 for about 0.5 s (re-zeroing the transducer output). PT-2 was equalized at 9 V or 3.1 bar output, while PT-1 was equalized at 5 V or 1 bar output. Reference pressures were stored in vessels A and B, which were 150 ml steel sample cylinders rated for 124 bar. All piping components were constructed of 316 stainless steel (1/4 inch).

Pressure control and gas uptake monitoring were performed by an IBM PC resident control program via a Labmaster interface. One 12 bit D/A converter was used to supply the 0–10 V

input signal for the valve driver and two channels of 12 bit successive approximation A/D conversion were used, one for each transducer. The program was coded in structured BASIC compiled using Turbo Basic.

2.4. Hydrogenation of $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$

The reaction of $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$ with H_2 was followed using a low pressure gas uptake reactor. 0.033 mmol of complex were dissolved in chlorobenzene (50 ml) and this solution was treated with 0.99 bar (743 mm Hg) of H_2 at 60°C. The uptake of hydrogen was monitored. After reaction gc analysis of the solution was carried out to confirm the presence of ethylbenzene.

2.5. High pressure gas uptake experiment

In a typical experiment 310 ml of polymer solution (376 mmol/l w.r.t. C=C content) was measured out and poured into a glass liner. Catalyst was weighed into a small glass bucket which was placed in a port in the reactor head which was fitted with a trap door. The liner, containing the solution, was then placed in the lower part of the pressure reactor and the reactor was subsequently assembled. The polymer solution was deoxygenated by bubbling hydrogen through the reactor dip tube for ca. 10 min. The reactor was pressurized to 31 bar and then stirring was commenced. The reactor was warmed to 3°C below reaction temperature and the system pressure was adjusted to 41.3 bar and then allowed to stabilize for ca. 1 h. When the system had stabilized the gas uptake program was initialized. The catalyst was then added by exerting an overpressure of H_2 to the catalyst addition port. The pressure was readjusted to 41.3 bar and then gas uptake monitoring was initiated. Following reaction, a sample was taken and the level of hydrogenation was

measured from an IR spectrum of a thin film of the polymer [29].

2.6. The isomerization of high *cis*-polybutadiene

A solution of high *cis*-polybutadiene (10 g) in chlorobenzene (310 ml) was stirred at 25°C and deoxygenated by sparging with argon. $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ (40 mg) was added to the solution. The solution was maintained at 25–27°C and samples were taken at intervals up to 137 h. The infra red spectra of the polymer from the samples were recorded from films on NaCl plates.

3. Results and discussion

3.1. Initial studies in the gas uptake apparatus

The hydrogenation of NBR and other diene polymers catalyzed by various Ru(II) complexes was followed using the gas uptake apparatus described in the experimental section. The results are summarized in Table 1. In all cases the reactions gave rise to typical first order plots up to high levels of conversion (see Fig. 3). First order rate constants were calculated from straight line first order plots (Fig. 4) of the gas

Table 1
Activity of Ru(II) catalysts towards the hydrogenation of polymers

Catalyst	Substrate	$k' \times 10^3 \text{ (s}^{-1}\text{)}$
$\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$	NBR	2.70
$\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$	NBR	2.60
$\text{RuHCl}(\text{CO})_2(\text{PCy}_3)_2$	NBR	0.72
$\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$	NBR	2.70
$\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$	NBR	^a
$\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$	PBD	3.50
$\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$	PBD	3.50
$\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$	PIP	0.09

Conditions: hydrogenations were carried out in chlorobenzene (310 ml). $[\text{Ru}]_T = 0.078 \text{ mmol/l}$, $[\text{C}=\text{C}] = 376 \text{ mmol/l}$, temperature = 160°C, H_2 partial pressure (p_{H_2}) = 40.3 bar.

^aGel formation occurred after ca. 50% conversion.

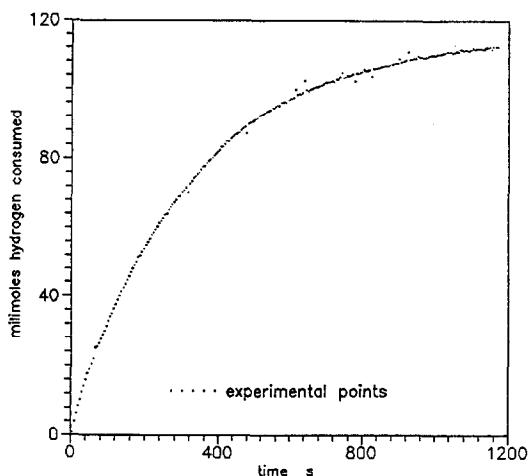


Fig. 3. Gas uptake profile for NBR hydrogenation. $[\text{Ru}] = 0.078$ mmol/l; temperature = 160°C ; pressure = 40.3 bar; $[\text{CN}] = 231$ mmol/l; total $\text{C}=\text{C} = 118$ mmol.

uptake data in accordance with Eq. (1) (where k' is the pseudo first order rate constant).

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

It can be seen from the results in Table 1 that $\text{Ru}-\text{PCy}_3$ and $-\text{P}^i\text{Pr}_3$ complexes had more or less the same activity towards the hydrogenation of NBR, except for $\text{RuHCl}(\text{CO})_2(\text{PCy}_3)_2$ which was significantly less active than the other complexes. In all cases essentially quantitative hydrogenation of the $\text{C}=\text{C}$ was observed as confirmed by IR analysis of the products which showed the virtual disappearance of the band due to $\text{C}=\text{C}$ at ca. 970 cm^{-1} .

Complexes containing PPh_3 ligands were found to be as active as the bulky phosphine complexes for the hydrogenation of PBD but led to rapid gel formation when used in conjunction with NBR. This suggested that the crosslinking reaction in the NBR system involved reduction of the nitrile group.

These results indicate that the choice of phosphine has little effect on rates of hydrogenation but has a significant influence towards selectivity of the catalysts for hydrogenation of $\text{C}=\text{C}$ over nitrile hydrogenation. This is presumably related to a balance of steric and electronic characteristics for the different phosphines [30].

Hydrogenation of $\text{C}=\text{C}$ in polyisoprene was far slower than for NBR and PBD. This indicates the strong effect caused by steric hindrance related to the extra methyl group on the polymer chain which presumably impedes $\text{C}=\text{C}$ complexation at the catalyst center.

From the results of these preliminary experiments, the preferred complexes for examination in a detailed mechanistic study of NBR hydrogenation were $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ and $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PR}_3)_2$; of the two, $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$ was chosen because it was easiest to handle due to its stability in air as a solid.

3.2. Hydrogenation of $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$

The hydrogenation of $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$ was followed at relatively mild reaction conditions using a manual gas uptake apparatus. The results of this study are shown in Fig. 5. The total hydrogen uptake corresponded to 2 mol per mol of catalyst. The formation of ethylbenzene confirmed that the styryl group is hydrogenated and indicated that $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ is formed. This strongly suggested that the hydrogenation of

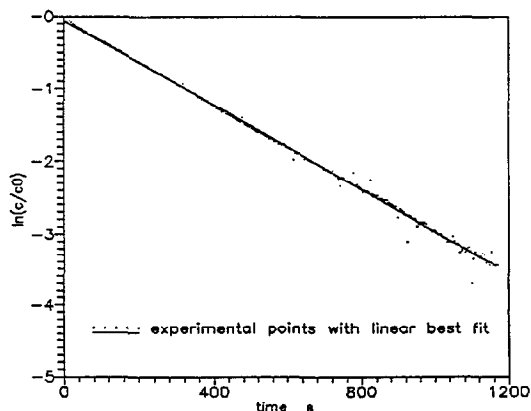


Fig. 4. First order plot for NBR hydrogenation. $[\text{Ru}] = 0.078$ mmol/l; temperature = 160°C ; pressure = 40.3 bar; $[\text{CN}] = 231$ mmol/l.

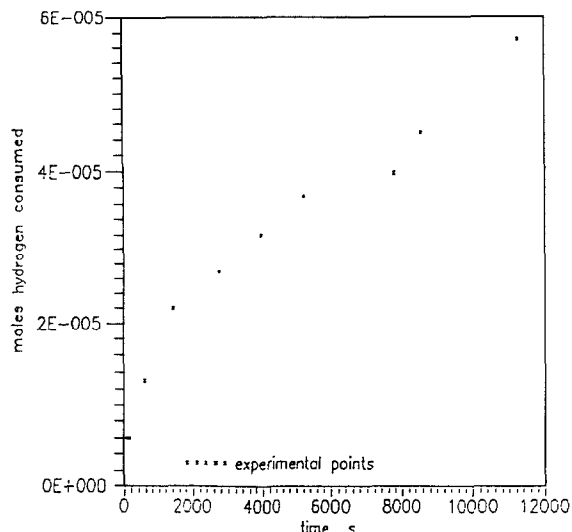


Fig. 5. Gas uptake plot for hydrogenation of $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$. Temperature = 60°C ; pressure = 0.99 bar; $[\text{Ru}] = 0.663 \text{ mmol/l}$.

$\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PR}_3)_2$ would be virtually instantaneous under the reaction conditions generally used for polymer hydrogenation and other kinetic studies described below.

3.3. Kinetics of NBR hydrogenation

A thorough examination of the kinetics of NBR hydrogenation catalyzed by $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$ was carried out with varying substrate concentrations and reaction conditions. The results of the main study are presented in Table 2. The following observations were made from the data obtained.

3.4. Dependence on C=C concentration

As mentioned above the hydrogenation of NBR followed pseudo first order kinetics to greater than 90% conversion of the double bonds (Figs. 3 and 4). This behavior was observed at all sets of reagent concentrations and reaction conditions. The first order behavior implies that under the conditions used there is no selectivity towards hydrogenation of the various isomeric

forms of C=C in the base polymer, i.e., *cis*, *trans* or vinyl.

3.5. Dependence on ruthenium concentration

The range of catalyst concentrations used in the present study was between 0.0097 and 0.116 mmol/l (2.5–30 mg in 310 ml). In experiments with varying catalyst concentration all other variables were kept constant. The results displayed in Fig. 6 showed that the reaction followed a first order dependence on the catalyst concentration.

3.6. Dependence on hydrogen pressure

The partial pressure of chlorobenzene was estimated at 160°C in order to obtain more accurate values of the true hydrogen pressures in the reactor under the reaction conditions used. This was done by using the Harlecher correlation, assuming that the polymer and hydrogen pressure did not significantly affect the vapor pressure. This gave a P^* for chlorobenzene of 2.06 bar. This value was corroborated by measurement in the gas uptake apparatus in the absence of hydrogen at 160°C (2.04 bar). This value was used in the studies described in calculation of the hydrogen pressure in the reactor: i.e. the absolute hydrogen pressure = gauge hydrogen pressure — $P^* + 1$ bar. Dissolved H_2 concentrations were calculated using the constants described by Parent and Rempel [31].

Two sets of experiments were performed to determine the influence of hydrogen concentration on the rate of hydrogenation. The first set investigated the effect of varying hydrogen pressures from 5.8 to 54.1 bar using a Ru concentration of 0.078 mmol/l. The second set of experiments used a Ru concentration of 0.019 mmol/l.

Fig. 7 shows the first order rate dependence at both levels of catalyst concentration. The first order rate dependence implies that a single reaction pathway is involved in the reaction of the polymer with hydrogen. If more than one pro-

cess was involved, the relative contributions of each pathway should change with varying hydrogen pressure, and thus the dependence would deviate from first order behavior.

Infra red spectra of the products of experiments carried out at 5.8 bar showed an extra shoulder at 2214 cm^{-1} with the main CN stretch being at 2236 cm^{-1} . This results from isomer-

Table 2

Kinetic data from detailed study of the hydrogenation of NBR catalyzed by $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$

[Ru] (mmol/l)	[CN] ₀ (mmol/l)	p_{H_2} (bar) ^a	[H ₂] (mmol/l)	Experimental rate constant $k' \times 10^3$ (s ⁻¹)
0.0776	231	40.3	176	2.71
0.0782	231	40.3	176	2.73
0.0777	231	40.3	176	2.91
0.0780	231	40.3	176	2.91
0.0779	231	40.3	176	3.23
0.0780	231	40.3	176	2.91
0.0786	231	40.3	176	2.63
0.0779	231	40.3	176	2.79
0.0778	231	54.1	236	3.70
0.0779	231	26.5	116	2.35
0.0779	231	12.8	55.9	0.71
0.0780	231	26.5	116	1.57
0.0778	231	5.86	27.1	0.34
0.0781	231	54.1	236	4.06
0.0779	231	26.5	116	1.79
0.0195	231	40.3	176	0.67
0.0192	231	81.7	357	1.43
0.0192	231	40.3	176	0.62
0.0194	231	26.5	116	0.42
0.0196	231	12.8	55.9	0.13
0.0195	231	54.1	236	1.17
0.0199	231	54.1	236	1.19
0.0197	231	67.9	296	1.13
0.0197	231	67.9	296	1.38
0.0199	231	26.5	116	0.60
0.0199	231	81.7	357	1.60
0.0392	231	40.3	176	1.20
0.0195	231	40.3	176	0.64
0.0393	231	40.3	176	1.78
0.0585	231	40.3	176	2.31
0.0585	231	40.3	176	2.01
0.0389	231	40.3	176	1.74
0.0199	231	40.3	176	1.14
0.0779	116	40.3	176	3.30
0.0781	173	40.3	176	2.97
0.0778	462	40.3	176	2.16
0.0781	462	40.3	176	1.52
0.0781	231	40.3	176	2.50
0.0779	58	40.3	176	4.30
0.0780	346	40.3	176	1.93
0.0777	346	40.3	176	1.73
0.0778	185	40.3	176	2.62
0.0777	139	40.3	176	3.36

Solvent was chlorobenzene; temperature = 160°C.

^apartial pressure of H₂

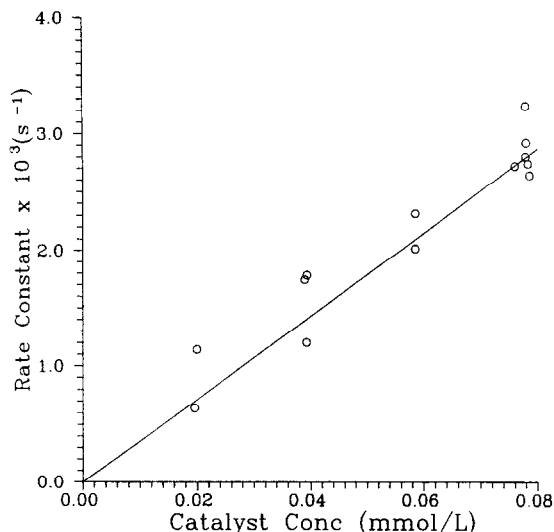


Fig. 6. Rate constants for hydrogenation of NBR: Ru concentration dependence. \circ Experimental data; — model. Temperature = 160°C; pressure = 40.3 bar; [CN] = 231 mmol/l.

ization within the polymer chain to give C=C conjugated with CN. No attempt was made to measure the proportion of isomerized product within the sample. This isomerization was only observed at reaction conditions which combined relatively high catalyst concentrations and low pressures.

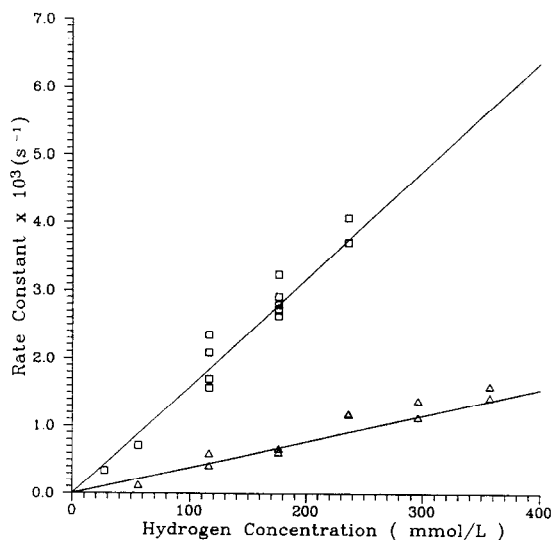


Fig. 7. Rate constants for hydrogenation of NBR: H_2 concentration dependence. Experimental data: \square [Ru] = 0.078 mmol/l; Δ [Ru] = 0.019 mmol/l; — model. Temperature = 160°C; [CN] = 231 mmol/l.

Table 3

Kinetic data for the hydrogenation of SBR catalyzed by $Ru(CH=CH(Ph))Cl(CO)(PCy_3)_2$

p_{H_2} (bar)	$[H_2]$ (mmol/l)	$k' \times 10^3$ (s^{-1})
40.6	177	4.56
19.4	84.7	2.96
61.5	269	8.56
30.3	132	4.09

Solvent was chlorobenzene, [C=C] = 379 mmol/l, [Ru] = 0.039 mmol/l, reaction temperature = 160°C.

A limited investigation examining hydrogen concentration dependence in the hydrogenation of SBR was made to ascertain if different behavior would be observed in the absence of nitrile. The results are presented in Table 3 and illustrated in Fig. 8. This study showed that the rates of hydrogenation for SBR were also first order with respect to hydrogen concentration under the chosen reaction conditions.

3.7. Mass transfer dependence

To ensure that mass transport was not limiting the rate of hydrogen uptake, an experiment was performed at conditions which would gen-

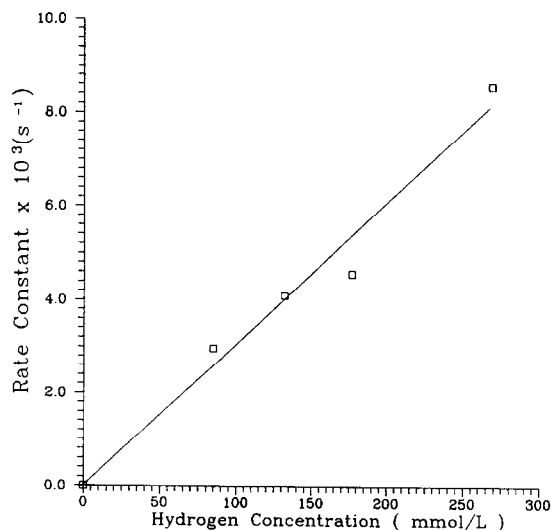


Fig. 8. Rate constants for hydrogenation of SBR: H_2 concentration dependence. Experimental data \square . — linear best fit. Temperature = 160°C; [Ru] = 0.038 mmol/l.

erate fast gas uptake (the same order of magnitude to most of the reaction conditions reported in Table 2). During this experiment, the stirrer speed was doubled after approximately 30–50% conversion of C=C. No significant change in first order rate constant was observed during this experiment, despite significantly higher energy input per unit volume. Mass transport of hydrogen into solution was therefore assumed to have an insignificant effect on the rate of reaction under the conditions studied.

Experiments performed at high [Ru], high polymer concentrations and high hydrogen pressures were tested for the onset of mass transport limitation using the method described above. Any experiments where the pseudo first order rate constant was greater by more than the normal run to run variability (ca. 10–15%) were rejected and not used for mathematical modelling. Only those experiments at high polymer concentrations (0.7 mol/l C=C) were rejected on this basis. A more thorough and quantitative examination of the mass transport factors was not undertaken.

3.8. Deuteration studies

The results of deuteration experiments are presented in Table 4. A comparison with equivalent hydrogenation experiments showed no difference in the observed rates of reaction. Thus there was no kinetic isotope effect for this system under the chosen set of reaction conditions.

3.9. Dependence on nitrile group concentration

Table 4
Isotope effect studies

Gas used	$k' \times 10^3 \text{ (s}^{-1}\text{)}$
D ₂	2.25
D ₂	2.14
H ₂	2.34
H ₂	2.09

Reaction parameters: solvent was chlorobenzene; [Ru]_T = 0.078 mmol/l; [CN] = 231 mmol/l; [C=C] = 379 mmol/l; p_{H_2} = 26.5 bar; temperature = 160°C.

A series of experiments were carried out at varying polymer concentrations to examine the effect of different nitrile concentrations. The nitrile concentration range was 460–58 mmol/l (20–2.5 g of Krynac 38.50 in 310 ml). At the high end of the concentration range problems associated with control and mass transfer were noted. Concentrations of less than 58 mmol/l were not practical because the low amount of gas consumed resulted in relatively high errors in measurement.

As can be seen from Fig. 9 the rate constants show an inverse dependence on nitrile concentration. This behavior was also observed when fully hydrogenated NBR was added to the reaction mixture. An experiment was also carried out with added octylcyanide and a significant drop in rate was recorded thus confirming that the drop in rate constants observed at higher nitrile concentrations in the polymer experiments was not the result of mass transport limitation. Quantitative assessment of nitrile coordination constants with such complexes at the conditions used for the hydrogenation experiments will be the subject of a subsequent study.

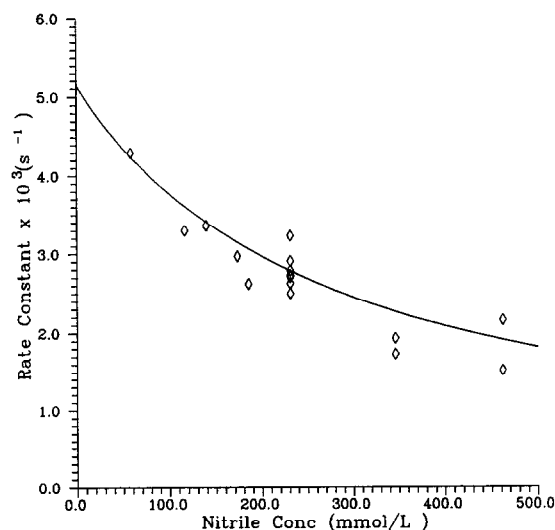


Fig. 9. Rate constants for hydrogenation of NBR: CN concentration dependence. Experimental data ◇; — model. Temperature = 160°C; pressure = 40.3 bar; [Ru] = 0.078 mmol/l.

Table 5
Effect of added PCy₃ on *k'*

Mole equivalents of added PCy ₃	<i>k'</i> × 10 ³ (s ⁻¹)
1	1.10
4	0.28
2	0.56
0.5	1.91
3	0.32
2	0.53
1	0.087

Reaction parameters: solvent was chlorobenzene; [Ru]_T = 0.078 mmol/l; [CN] = 231 mmol/l; [C=C] = 379 mmol/l; *p*_{H₂} = 40.3 bar; temperature = 160°C.

3.10. Dependence on added PCy₃

A series of experiments were made in the presence of added PCy₃ in order to understand the role of the complexed PCy₃ ligands in the catalytic process. The results of these experiments are presented in Table 5 and Fig. 10. There is a clear inverse dependence on the concentration of added phosphine. This may be due to inhibition of phosphine dissociation or by competitive coordination of PCy₃ with the active catalyst species.

3.11. Dependence on temperature

Experiments were carried out from 130 to 160°C. The results of these studies are presented in Table 6 and resulted in a good Arrhenius plot of the data. The activation energy calculated from least squares regression analysis of ln(*k'*) versus 1/*T* was 78 kJ mol⁻¹. An Eyring plot was used to estimate the enthalpy of activation (74.8 kJ mol⁻¹) and entropy of activation (-10.6 J mol⁻¹ K⁻¹).

An additional experiment at 70°C was performed. The rate constant was 0.000025 s⁻¹, demonstrating that Ru(CH=CH(Ph))Cl(CO)(PCy₃)₂ is still an active and efficient NBR hydrogenation catalyst under relatively mild conditions.

3.12. Dependence on solvent

A series of experiments was undertaken using different solvents for NBR hydrogenation

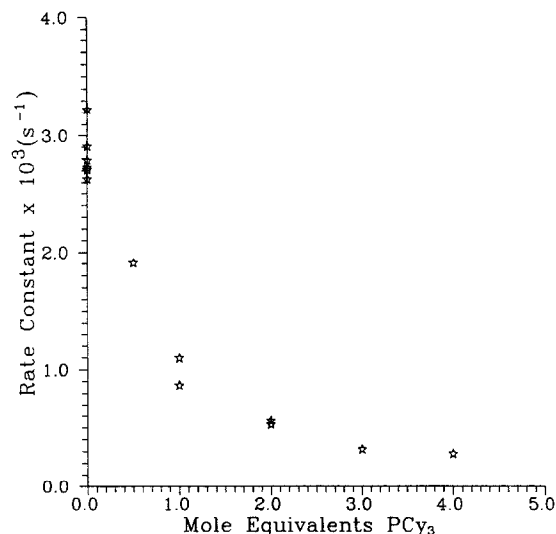


Fig. 10. Rate constants for hydrogenation of NBR: dependence on added PCy₃. Temperature = 160°C; pressure = 40.3 bar; [CN] = 231 mmol/l; [Ru] = 0.078 mmol/l.

under identical reaction conditions. The results of these studies are shown in Table 7. Experiments where toluene and xylene were used as the solvents did not result in complete hydrogenation of the polymer because hydrogenated NBR is not very soluble in these solvents and thus precipitation of partially hydrogenated product occurred during the course of the hydrogenation, thereby limiting the ultimate conversion achieved.

Using MEK or THF as the solvents led to significantly slower rates than observed when the chlorinated benzenes were used as solvents. This is probably the result of competitive coordination of the solvents with the active catalyst.

Table 6
Temperature dependence of *k'* for NBR hydrogenation

<i>T</i> (°C)	<i>T</i> (K)	<i>k'</i> × 10 ³ (s ⁻¹)
160	433.15	2.79
155	428.15	2.04
150	423.15	1.68
145	418.15	1.37
140	413.15	0.93
135	408.15	0.81
130	403.15	0.51

Conditions: solvent was chlorobenzene; [Ru] = 0.078 mmol/l; [CN] = 231 mmol/l; [C=C] = 379 mmol/l; *p*_{H₂} = 40.3 bar.

Table 7
Solvent dependence of k'

Solvent	$k' \times 10^3$ (s ⁻¹)
Monochlorobenzene	2.70
Dichlorobenzene	2.80
Methylethylketone	2.10
Tetrahydrofuran	2.20

Reaction parameters: [Ru] 0.078 mmol/l; [CN] = 231 mmol/l; [C=C] = 379 mmol/l; p_{H_2} = 40.3 bar; temperature = 160°C.

It was noted when MEK was used that a small amount of the solvent was hydrogenated to 2-butanol. Given that the hydrogenation of carbonyl compounds catalyzed by similar Ru complexes has been reported [3], this was to be expected. The result of our experiment however shows that the Ru catalyst is far more active as a catalyst for the hydrogenation of C=C than C=O.

3.13. Polymer chain length properties

Although the main concern of our work was to examine the kinetics and mechanism of NBR hydrogenation, there was some need to check that the process did not radically alter the polymer chain length. One of the key aspects of a useful polymer modification process is that it should not significantly alter the integrity of the polymer skeleton.

Results from gel permeation chromatography (Table 8) indicated that the polymer molecular weight distribution was not altered greatly during hydrogenation. However, solution viscosity measurements did significantly increase during hydrogenation. Some increase in polymer viscosity is expected on hydrogenation due to the reduced solubility of the hydrogenated polymer,

Table 8
Summary of GPC molecular weight data for normal and hydrogenated NBR

Polymer	M_n	M_w	Polydispersity	Solution viscosity (Pa ⁻¹)
Krynac 38.50	118 000	606 000	5.132	0.0113
99% hydrogenated Krynac 38.50 ^a	127 000	546 000	4.301	0.0433

^aHydrogenated polymer was obtained from an experiment using: [Ru] 0.078 mmol/l; [CN] = 231 mmol/l; temperature = 160°C; p_{H_2} = 40.3 bar in chlorobenzene.

but the fourfold increase suggested that some crosslinking may have occurred. Other studies have shown that these complexes do cause some increase in polymer molecular weight and the effect can be counteracted by the addition of primary amines which implies that the increase may be due to the formation of secondary amine linkage [32] between polymer chains. It is possible that the contradictory results seen from the two techniques are due to the fact that solutions for gpc are filtered before analysis and this may remove high molecular weight fractions from the sample.

3.14. Small molecule hydrogenation

The hydrogenation of some olefins catalyzed by Ru(CH=CH(Ph))Cl(CO)(PCy₃)₂ under conditions similar to those used for polymer hydrogenation was examined. The results of these experiments are presented in Table 9. As might be expected, for steric reasons, the hydrogenations occurred at far higher rates than the analogous reactions with polymers. Reaction rates were so rapid at 160°C that accurate measurements could not be made and so a temperature of 130°C was used for the studies. The hydrogenation of primary olefins was far more rapid than that of secondary olefins as evidenced by the comparative rates of hydrogenation for 1-decene and 2-hexene. This is not unusual for Ru; such selectivity has been observed for olefin hydrogenation catalyzed by various complexes [33–35]. The hydrogenation of the 3-pentenenitrile was observed to be much slower than that for 2-hexene, confirming that nitrile groups inhibit C=C hydrogenation. The prod-

Table 9
Small molecule hydrogenation catalyzed by Ru(PhCH=CH)Cl(CO)(PCy₃)₂

Olefin	Rate constant $k' \times 10^3$ (s ⁻¹)
1-decene	too fast for accurate measurement
Styrene	too fast for accurate measurement
2-hexene	7.90
3-pentenitrile	4.00 ^a

Reaction conditions: solvent chlorobenzene; [Ru] = 0.078 mmol/l; [C=C] = 376 mmol/l; p_{H_2} = 40.3 bar; temperature = 130°C.

^aNo amine from nitrile hydrogenation was detected during course of C=C hydrogenation. After 70 h at 160°C, 3% conversion to dipentylamine.

ucts of this reaction were analyzed by gc, after 100% hydrogenation of the C=C was achieved (ca. 10 min). No trace of amine products was detected by gc, indicating that little if any –CN hydrogenation had occurred by this point. Maintaining the reaction mixture at 160°C and 41.3 bar for 70 h yielded 3% conversion to dipentylamine as measured by gc.

3.15. The isomerization of high *cis*-polybutadiene

The isomerization of high *cis*-polybutadiene was followed by monitoring the IR spectra of the polymer at intervals. It was apparent that the characteristic bands for the out of plane deformation for C–H in a *cis*-C=C (at 720 cm⁻¹) diminished as the reaction progressed and the band characteristic for the same vibration in a *trans*-C=C (at 980 cm⁻¹) increased. A similar control experiment, with no added Ru, showed no change after a period of 2 months, demonstrating that RuHCl(CO)(PCy₃)₂ catalyses the isomerization reaction. Therefore the isomerization process presumably must proceed via a Ru–alkyl intermediate. It is likely that such a species is a key intermediate in the hydrogenation reaction catalyzed by the Ru catalysts.

3.16. Mechanism of hydrogenation

The observed kinetic dependencies of the pseudo first order rate constant for the hydro-

genation of C=C in NBR may be summarized by the expression shown in Eq. (2).

$$k' = \frac{k[H_2][Ru]}{(a + b[CN])} \quad (2)$$

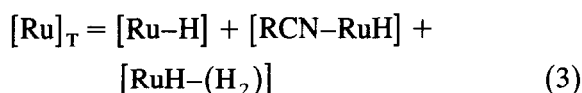
The rate of hydrogenation was first order in C=C concentration from 0 to 90% in every experiment involving both NBR and small molecules. This was shown by the fact that the pseudo first order rate constant k' determined from the gas uptake data had a single value throughout the course of the reactions (all plots of ln[C=C] versus t were linear). The experiments also showed that the rate of reaction had a first order dependence on both hydrogen concentration ([H₂]) and total ruthenium concentration ([Ru]_T) and an inverse dependence on the nitrile concentration ([CN]). In addition deuteration experiments suggest that the rate determining step does not involve C–H bond formation.

Our preliminary interpretation of the data [21,22] assumed that the rate limiting step was hydrogenolysis of a Ru–alkyl (formed from insertion of C=C into the Ru–H bond), with coordination of the olefin being a primary step in the catalytic cycle; previous studies have also reported such a mechanism for hydrogenation of small molecules by Ru complexes [20,35]. Such a mechanism fits the kinetic data but it also suggested that a primary kinetic isotope effect should be observed.

An alternative mechanism is now proposed and is shown in Scheme 1. The first stage in the process is the rapid hydrogenation of the styryl group in Ru(CH=CH(Ph))Cl(CO)(PCy₃)₂ to give the active species RuHCl(CO)(PCy₃)₂ (**1**) and ethyl benzene. The coordination of olefin is the likely rate determining step given the absence of a deuterium isotope effect. This implies that coordination of H₂ to (**1**) would be the initial step in the catalytic cycle. It has been shown previously that H₂ coordination to RuHCl(CO)(P^{*i*}Pr₃)₂ may be observed by ¹H NMR at low temperatures [36]. This would be

followed by coordination of olefin before the final rapid elimination of products and regeneration of (1). The method of hydrogenolysis cannot be ascertained with certainty but it likely involves η_2 coordinated H_2 interacting with a Ru-alkyl species which would be formed by insertion of olefin into the Ru-H bond. Concerted elimination of the hydrogenated olefin and reformation of (1) or possibly oxidative addition of H_2 followed by rapid elimination of the product are possible final steps of the cycle.

It is possible to derive a detailed rate law on the basis of the proposed mechanism. Firstly the total Ru concentration in the system may be defined as in Eq. (3).



Ru-H is the active catalyst (1), [RCN-RuH] is the adduct formed by the coordination of $\text{RuHCl(CO)(PCy}_3)_2$ with nitrile and $\text{RuH-(H}_2)$ is the product of dihydrogen coordination with (1). A term for $\text{Ru(CH=CH(Ph))Cl(CO)(PCy}_3)_2$ is not included because it is assumed that under the conditions used for the hydrogenation its concentration would be negligible if not zero. This has been confirmed by hydrogenation of the complex to form ethyl benzene and $\text{RuHCl(CO)(PCy}_3)_2$.

Assuming that the coordination of olefin to $[\text{Ru-H-(H}_2)]$ is the rate limiting step, the rate of reaction can be expressed as follows.

$$\begin{aligned} \text{rate} &= \frac{-d[\text{C=C}]}{dt} = k'[\text{C=C}] \\ &= k_2[\text{Ru-H-(H}_2)][\text{C=C}] \end{aligned} \quad (4)$$

It can also be assumed that the equilibria between (1) and the nitrile, and (1) and the hydrogen are rapidly established and these can be expressed by Eqs. (5) and (6).

$$K_N = \frac{[\text{RCN-RuH}]}{[\text{Ru-H}][\text{RCN}]} \quad (5)$$

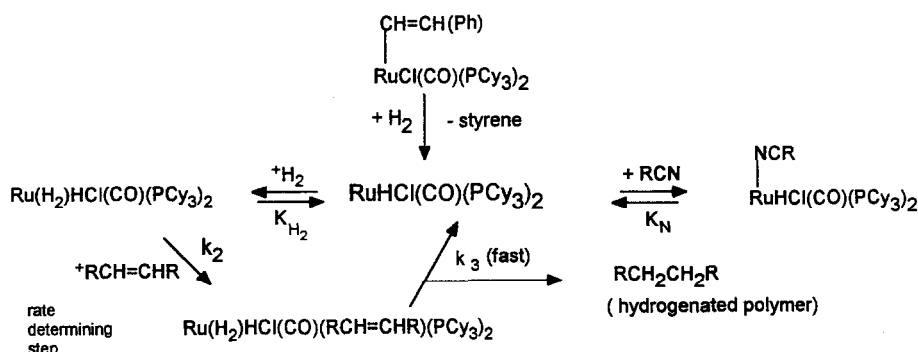
$$K_{H_2} = \frac{[\text{Ru-H}][\text{H}_2]}{[\text{Ru-H}][\text{H}_2]} \quad (6)$$

Rearranging Eqs. (3), (5) and (6) and substituting into Eq. (4) gives the rate law relating the observed pseudo first order rate constant to the kinetic parameters.

$$k' = \frac{k_2 K_H [\text{H}_2] [\text{Ru}]_T}{1 + K_H [\text{H}_2] + K_N [\text{RCN}]} \quad (7)$$

Given this expression it would be expected that there would be a zero order dependence on $[\text{H}_2]$ (if the product of $K_H[\text{H}_2]$ is large relative to (1) at least in the absence of nitrile). The fact that we observe rigorous first order behavior with respect to $[\text{H}_2]$ suggests that the parameter $K_H[\text{H}_2]$ is negligible for the range of reaction conditions and substrate concentrations used in this study. This simplifies the rate law to Eq. (8).

$$k' = \frac{k_1 [\text{Ru}]_T [\text{H}_2]}{1 + K_N [\text{RCN}]} \quad (8)$$



Scheme 1. Mechanism of C=C hydrogenation in NBR catalyzed by $\text{Ru(CH=CH(Ph))Cl(CO)(PCy}_3)_2$

Table 10
Results of non-linear best fit using SAS parameter estimate results

	Parameter $k_1 \times 10^3$ (mmol/l ² s ⁻¹)	Parameter $K_N \times 10^3$ (mmol/l)
Estimate	0.375	3.67
Asymptotic standard error	0.017	0.34
Asymptotic 95% confidence interval		
Lower limit	0.341	4.09
Upper limit	0.297	4.36

The constant k_1 is a lumped constant containing the limiting rate constant k_2 and the equilibrium constant K_H .

Table 11
Analysis of variance results for dependent variable k'

Source	Degrees of freedom	Sum of squares	Mean square
Regression model	2	0.00022	0.00011
Residual	43	0.0000029	6.7×10^{-8}
Uncorrected total	45	0.00022	

The proposed mechanism fits the experimental data but there is still some ambiguity attached to the interpretation of the results with regards the detailed chemistry. Further work is underway in an attempt to better understand what may be a more complex system than originally assumed.

3.17. Statistical analysis

A statistical analysis of the rate law in relation to the data obtained was undertaken to

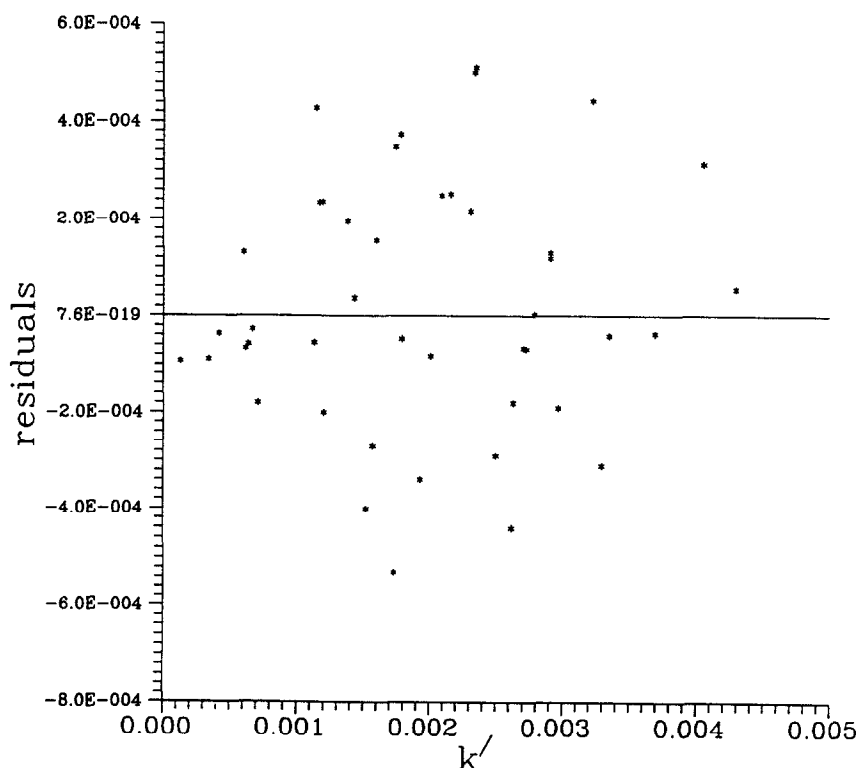


Fig. 11. Residual plot from non linear model regression.

obtain some support for the model that was derived for the reaction mechanism and to estimate values for k_1 and K_N . The abbreviated form of the rate law (Eq. (8)) was fitted to the observed pseudo first order rate constant data shown in Tables 2 and 4 using the Marquardt non linear least squares regression technique in SAS [37] (a statistical analysis package).

The results of the regression analysis are shown in Table 10. Analysis of the variance table (Table 11) shows the significance of the model; a large amount of the variability in k' is explained by a relatively simple two parameter model. The solid curves provided in Figs. 6, 7 and 9 show how well the model predictions fit the observed pseudo first order rate constants. Fig. 11 is the residual plot from the regression showing the random distribution of residual values with respect to the measured rate constant with a few outliers.

4. Conclusions

Development of equipment to accurately measure gas uptake at elevated temperatures and pressures has allowed the study of hydrogenation kinetics of an active Ru catalyst system at conditions approaching those used for the commercial hydrogenation of NBR. The advent of this equipment allows for studies of homogeneous hydrogenation at conditions beyond the normal limited range of previous studies. It has led to a better understanding of effects of process variables for the hydrogenation of olefins (particularly in selective hydrogenation of NBR) catalyzed by Ru complexes.

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References

- [1] W. Stroheimer, M. Michel, L. Weigelt, Z. Naturforsch. (B) 35 (1980) 648.
- [2] B. Graser, H. Steigerwald, J. Organomet. Chem. 193 (1980) 648.
- [3] R.A. Sanchez-Delgado, N. Valencia, R.-L. Marquez-Silva, A. Andriollo, M. Medina, Inorg. Chem. 25 (1986) 1106.
- [4] M.A. Esteruelas, E. Sola, L.A. Oro, H. Werner, U. Meyer, J. Mol. Catal. 45 (1988) 1.
- [5] M.A. Esteruelas, E. Sola, L.A. Oro, U. Meyer, H. Werner, Angew. Chem. Int. Ed. Engl. 27 (1988) 1563.
- [6] A. Andriollo, M.A. Esteruelas, U. Meyer, L.A. Oro, R.A. Sanchez-Delgado, E. Sola, C. Valero, H. Werner, J. Am. Chem. Soc. 111 (1989) 7431.
- [7] M.A. Esteruelas, E. Sola, L.A. Oro, H. Werner, U. Meyer, J. Mol. Catal. 53 (1989) 43.
- [8] M.A. Esteruelas, L.A. Oro, C. Valero, Organometallics 11 (1992) 3362.
- [9] G.L. Rempel, N.T. McManus, N.A. Mohammadi, US Patent, 5,057,581 (1991).
- [10] N.T. McManus, G.L. Rempel, J. Macromol. Sci. Rev. Macromol. Chem. Phys. C35 (1995) 239.
- [11] M.P. McGrath, E.D. Sail, S.J. Tremont, Chem. Rev. 95 (1995) 381.
- [12] J.R. Dunn, Elastomerics (1991) 15.
- [13] N.A. Mohammadi, G.L. Rempel, Macromolecules 20 (1987) 2362.
- [14] G.L. Rempel, H. Azizian, US Patent, 4,464,515 (1984).
- [15] S. Bhattacharjee, A.K. Bhowmick, B.N. Avasthi, J. Polym. Chem. A: Polym. Chem. 30 (1992) 471.
- [16] S. Bhattacharjee, A.K. Bhowmick, B.N. Avasthi, J. Appl. Polym. Sci. 41 (1990) 1357.
- [17] X.Y. Guo, G.L. Rempel, Prog. Catal. 73 (1992) 135.
- [18] G.L. Rempel, R. Farwaha, N.A. Mohamaddi, US Patent, 4,816,525 (1989).
- [19] P. Fiedler, H. Buding, R. Braden, German Patent, DE 3540918 (1987).
- [20] N.K. Singha, S. Sivaram, Polym. Bull. 35 (1995) 121.
- [21] P. Martin, M.A.Sc. thesis, University of Waterloo (1991).
- [22] P. Martin, G.L. Rempel, N.T. McManus, Prog. Catal. 73 (1992) 161.
- [23] F.G. Moers, J.P. Langhout, Rec. Trav. Pays Bas 91 (1972) 591.
- [24] M.A. Esteruelas, H. Werner, J. Organomet. Chem. 303 (1986) 221.
- [25] H. Werner, M.A. Esteruelas, H. Otto, Organometallics 5 (1986) 2295.
- [26] D.S. Bohle, G.R. Clark, C.E.F. Rickard, W. Roper, L.J. Wright, J. Organomet. Chem. 338 (1988) 411.
- [27] N.A. Mohammadi, G.L. Rempel, Comput. Chem. Eng. 11 (1987) 27.
- [28] G.L. Rempel, N.A. Mohammadi, US Patent, 4,858,637 (1989).
- [29] A.J. Marshall, I.R. Jobe, T. Dee, C. Taylor, Rubber Chem. Tech. 63 (1990) 244.
- [30] C. Tolman, Chem. Rev. 77 (1977) 313.
- [31] J.S. Parent, G.L. Rempel, J. Chem. Eng. Data 41 (1996) 192.
- [32] G.L. Rempel, N.T. McManus, US Patent 5,075,388 (1992).

- [33] P. Legdzins, R.W. Mitchell, G.L. Rempel, J.D. Ruddick, G. Wilkinson, *J. Chem. Soc. A* (1970) 3322.
- [34] P.S. Hallman, B.R. McGarvey, G. Wilkinson, *J. Chem. Soc. A* (1968) 3143.
- [35] R.W. Mitchell, A. Spencer, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* (1973) 846.
- [36] D.G. Gusev, A.B. Vymenits, V.I. Bakhmutov, *Inorg. Chem.* 31 (1992) 2.
- [37] SAS User's guide, SAS Inst. Inc., Cary, NC (1985).