

# Catalytic hydrogenation of nitrile-butadiene copolymers by cationic rhodium complexes

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## Abstract

The hydrogenation of nitrile-butadiene copolymers (NBR), catalyzed by a series of cationic rhodium complexes  $[\text{Rh}(\text{diene})(\text{L}_2)]^+$  (diene = norbornadiene (NBD) and 1,5-cyclooctadiene (COD);  $\text{L}_2 = (\text{PPh}_3)_2, \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 2, 3$  and 4);  $\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2$ ), was studied under 3.42 MPa hydrogen pressures at 140°C in monochlorobenzene. The general activity patterns found include: (1) the activity of complexes  $[\text{Rh}(\text{diene})(\text{PPh}_3)_2]^+$  is similar to that of Wilkinson catalyst  $\text{RhCl}(\text{PPh}_3)_3$ ; (2) with chelating diphosphines, the activity of complexes  $[\text{Rh}(\text{diene})(\text{L}_2)]^+$  increases with the increase of the chain length of the diphosphine; (3) complexes  $[\text{Rh}(\text{diene})(\text{PPh}_3)_2]^+$  are more active catalysts than those containing chelating phosphines. These results demonstrate that there are a number of similarities and remarkable differences between the hydrogenation of NBR and the hydrogenation of simple olefins reported, which is mainly attributed to the steric effect of olefins. In contrast to simple olefin hydrogenation where the coordination of olefin to a metal center is typically facile, this step becomes rate-determining in the case of the hydrogenation of large olefins such as NBR. In order to determine the effects of the factors on the reaction, such as catalyst concentration, polymer concentration, hydrogen pressure and temperature, a detailed kinetic study on the reaction catalyzed by complex  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+$  was carried out. On the basis of the kinetic results and the related statistical analysis, both a reaction pathway and a reaction rate law are proposed. The dilute solution viscosities of fully hydrogenated NBR were found to be independent of reaction conditions employed, suggesting that the properties of hydrogenated NBR are uniform. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Catalytic modifications of butadiene polymers have attracted much attention as they are among the most important approaches to the production of specialty elastomers with desirable chemical and physical properties which are generally unattainable by conventional polymerization methods [1,2]. In contrast to existing

polymers, the modified polymers usually exhibit enhanced stability towards thermal and oxidative degradation to meet the commercial demands for robust elastomers that can be used in severe environments [3].

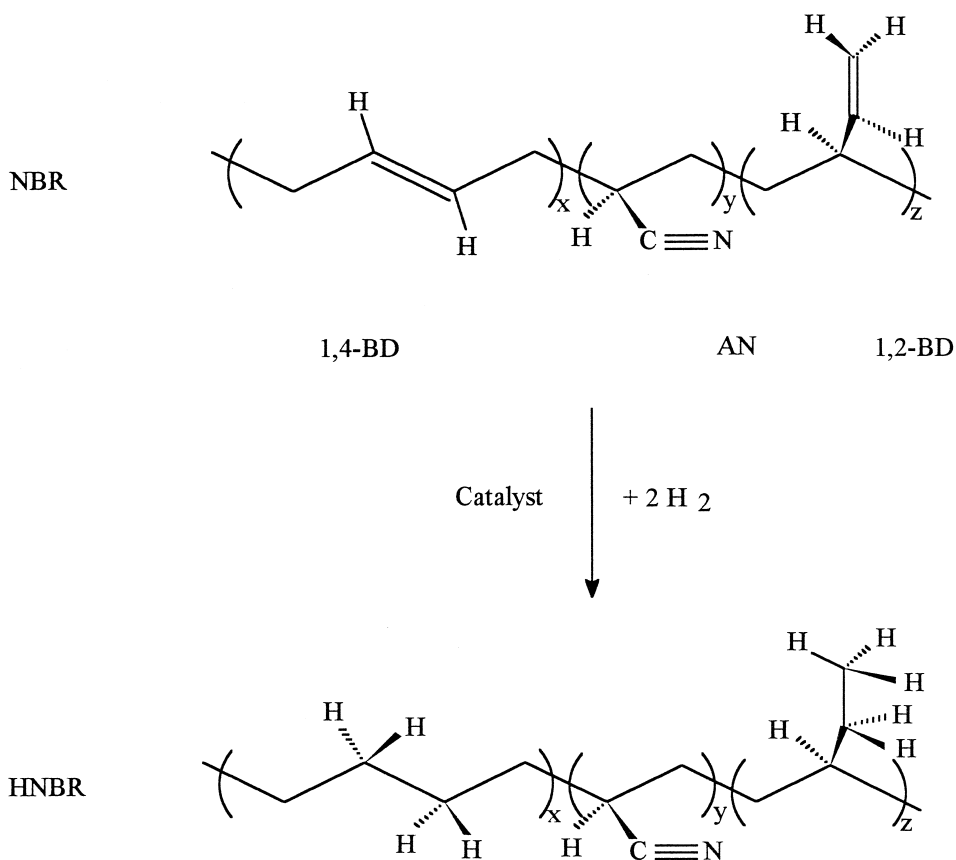
A most common method employed for polymer modifications is the catalytic hydrogenation reaction. Many examples have been listed in recent review articles [1,2]. In the case of nitrile butadiene rubber (NBR), there are two types of unsaturation present, namely, olefin and nitrile

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group (Scheme 1). The challenge of this process is, therefore, to selectively hydrogenate olefin with the nitrile group remaining intact as the reduction of nitrile group would reduce the oil resistant properties of the material. Many transition metal complexes, generally containing a group VIII transition metal from the second and third rows of the periodic table, are used as homogeneous catalysts for this process [1,2,4,13]. As for the hydrogenation of olefins, the Wilkinson catalyst,  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ , is the most popular catalyst employed for this process [1,2,5–7]. This is due to the fact that it is a highly active catalyst capable of achieving complete hydrogenation of olefin without any reduction of nitrile group [7]. In contrast, and to the best of our knowledge, there are no reports in the literature on the hydrogenation of NBR by

another closely related class of hydrogenation catalysts of the form,  $[\text{Rh}(\text{diene})(\text{L}_2)]^+$ , where diene is norbornadiene (NBD) or 1,5-cyclooctadiene (COD) and L is a triphenylphosphine ligand or  $\text{L}_2$  is a chelating phosphine ligand. As part of our ongoing studies on NBR modifications, it was of interest to investigate the catalytic hydrogenation reactions by these cationic rhodium complexes, which have also received considerable attention for simple olefin hydrogenation [8–11].

Although complexes of the type  $[\text{Rh}(\text{diene})(\text{L}_2)]^+$  are excellent catalysts for small olefin hydrogenation [8–11], their activity may not be directly extrapolated to the hydrogenation of larger olefins such as the carbon–carbon double bonds within diene based polymers. The rate of hydrogenation of carbon–carbon double



Scheme 1. Structures of NBR and hydrogenated NBR (HNBR).

bonds within such polymers is generally much slower than that within the small olefin analogs due to the steric inaccessibility of olefin to the metal coordination sphere. Thus, we have attempted to determine the catalytic activity of a series of complexes using screening experiments. This series of complexes include  $[\text{Rh}(\text{diene})(\text{L}_2)]^+$  where diene = NBD, COD;  $\text{L} = \text{PPh}_3$  or  $\text{L}_2 = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$  (dppe),  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$  (dppp),  $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$  (dppb);  $\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2$  (dcpe). Moreover, a detailed kinetic study on the catalyst,  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+$ , was carried out with a view to further appreciate the intimate catalytic process.

## 2. Experimental

### 2.1. General

All organometallic complexes were prepared under an atmosphere of nitrogen using standard Schlenk techniques. Infrared spectra were recorded on a Nicolet 520 FT-IR spectrophotometer over the range 400–4000  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectra were recorded on a Bruker 200 MHz or a Bruker 250 MHz spectrometer and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker 200 MHz spectrometer. The  $^1\text{H}$  NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) while  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shifts are reported relative to external 85%  $\text{H}_3\text{PO}_4$ .

### 2.2. Materials and reagents

Rhodium trichloride hydrate was purchased from Engelhard. The acrylonitrile-butadiene copolymer (NBR) was obtained from Bayer. This rubber (Krynac 38.50) had a molecular weight of 200 000 with 38% nitrile by weight. The following compounds were prepared by published procedures:  $[\text{Rh}(\text{diene})(\text{PPh}_3)_2]^+\text{PF}_6^-$  (diene = NBD, COD) [12],  $[\text{Rh}(\text{diene})(\text{L}_2)]^+\text{BF}_4^-$  (diene = NBD, COD;  $\text{L}_2 = \text{dppe}$ , dppp, dppb).

All reagent grade solvents were used as received and were thoroughly degassed prior to use. NBD and COD were obtained from Aldrich Chemical and distilled before use. The ligands, triphenylphosphine, bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)propane (dppp), and bis(diphenylphosphino)butane (dppb) were purchased from Aldrich. Bis(dicyclohexylphosphino)ethane (dcpe) was obtained from Strem Chemical. Oxygen-free hydrogen gas (99.99%) was obtained from Linde-Union Carbide Canada.

### 2.3. Synthesis of $\text{Rh}(\text{COD})(\text{dcpe})^+\text{BF}_4^-$

Fluoboric acid (48% in  $\text{H}_2\text{O}$ , 29  $\mu\text{l}$ , 0.2 mmol) was added to a yellow solution of 1,5-cyclooctadienerhodiumacetylacetonate (69 mg, 0.2 mmol) in 2 ml tetrahydrofuran at 0°C. The reaction mixture was stirred vigorously and allowed to warm to room temperature. A solution of bis(dicyclohexylphosphino)ethane (88 mg, 0.2 mmol) in 3 ml tetrahydrofuran was then added, resulting in rapid formation of an orange solution. The mixture was stirred for 2 h at room temperature. The solvent was then removed in vacuo. The residue was recrystallized from  $\text{CH}_2\text{Cl}_2$ /ether to give 97 mg (67%) of light orange powder.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.31 (br s, 4 H, olefin), 1.15–2.40 (56 H,  $4\text{C}_6\text{H}_{11}$ ,  $2\text{CH}_2$ ,  $4\text{CH}_2(\text{COD})$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  67.9 (d,  $J_{\text{Rhp}} = 145$  Hz).

### 2.4. Hydrogenation reactions

The hydrogenation reactions were carried out in a batch autoclave reactor. In a typical experiment, a polymer (1.55 g) was dissolved in 75 ml monochlorobenzene. This solution was then transferred into a glass liner, which was placed inside the autoclave reactor. After the reactor was assembled, the system was degassed by charging the reactor with hydrogen to about 3.42 MPa, stirring vigorously under hydrogen for a few minutes, and venting. After this cycle

was repeated three times, the system was further degassed by bubbling hydrogen through the solution for 30 min. The reactor was heated to 140°C. After equilibrium was reached, a solution of catalyst (0.02 mmol) in 25 ml monochlorobenzene was added into the reactor to initiate the hydrogenation reaction. The reaction was maintained at 140°C and the pressure of the system was adjusted to 3.42 MPa with hydrogen. In order to maintain constant reaction pressure of the system throughout the hydrogenation, hydrogen gas was introduced when required. The reaction was monitored by periodically withdrawing samples from the reactor and recording their IR spectra. After reaction, the system was quickly cooled to room temperature, followed by venting hydrogen. The hydrogenated polymer was precipitated with methanol and dried in vacuum.

### 2.5. Kinetic studies

The kinetic experiments were carried out in a batch reactor, which was interfaced to a computer system. Hydrogen gas consumption was continuously monitored and the pressure in the reactor was maintained constant throughout the hydrogenation. A detailed description of the experimental apparatus is given elsewhere [14].

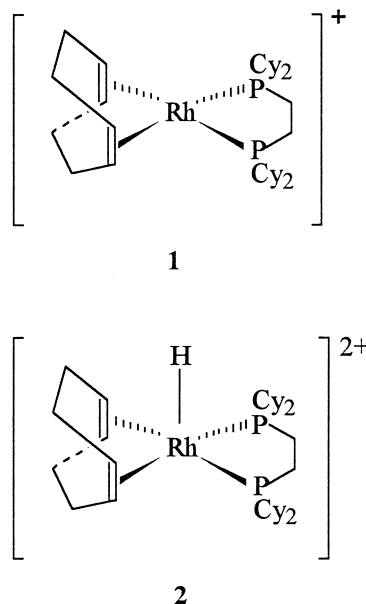
The experimental procedures are similar to those described previously [15]. The polymer was accurately weighed out and dissolved in 150 ml monochlorobenzene. When a known amount of catalyst was added into the polymer solution, the computer program recording reaction time, hydrogen gas uptake, and reaction temperature, was then started. The experiment was stopped when hydrogen gas uptake was no longer noticeable. Finally, the degree of hydrogenation was calculated based on an IR spectrum of the hydrogenated polymer, which was obtained from a thin film of the polymer on a NaCl plate [16]. The viscosity measurements of fully hydrogenated NBR solutions (0.250 g of HNBR/25 ml of 2-butanone) were performed

at 35°C in a Ubellohde capillary viscometer. The data reported are relative to pure solvent.

## 3. Results and discussion

### 3.1. Synthesis and characterization of $Rh(COD)(dcpe)^+BF_4^-$

The effect of phosphine on the hydrogenation activity of transition metal complexes is a well known phenomenon [17,18]. In order to expand the scope of complexes  $[Rh(\text{diene})(L_2)]^+BF_4^-$  (diene = NBD, COD;  $L_2$  = dppe, dppp, dppb), we attempted to prepare  $[Rh(COD)(dcpe)]^+BF_4^-$ . The synthesis of this complex was initially attempted in a similar way to those of  $[Rh(\text{diene})(L_2)]^+BF_4^-$  (diene = NBD, COD;  $L_2$  = dppe, dppp, dppb) [19]. Unexpectedly, addition of dcpe to a mixture of  $Rh(COD)(\text{acac})$  and excess of  $HBF_4$  (3.8 equivalents) in THF resulted in the formation of two complexes, **1** and **2**, in a ratio of 3:2.



Both compound **1** and **2** were characterized by  $^1H$  and  $^{31}P\{^1H\}$  NMR spectroscopy. The

$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CD}_2\text{Cl}_2$  showed a doublet at  $\delta$  99.4 ( $J_{\text{RhP}} = 137$  Hz), indicating that two phosphines are equivalent. In the corresponding  $^1\text{H}$  NMR spectrum a doublet of triplets at  $\delta$  – 22.4 ( $J_{\text{RhH}} = 28.7$  Hz,  $J_{\text{PH}} = 22.6$  Hz) was observed, which is assigned to the hydride. The possibility of a trigonal–bipyramidal structure, where one of the phosphines occupies an in-plane equatorial position and the other takes up an axial position, can be ruled out since it would generate two unequivalent phosphines. Thus, the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopic data are in accord with the structure as shown. The  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of complex **1** are very similar to those of  $[\text{Rh}(\text{COD})(\text{dppe})]^+\text{ClO}_4^-$  [12] and therefore an analogous structure is assigned to it.

Although the mechanism of formation of complex **2** was not investigated, one can envision that species **1** is a very possible intermediate. Since  $[\text{Rh}(\text{COD})(\text{dppe})]^+\text{ClO}_4^-$  is resistant to protonation, the ease of protonation of complex **1** is due to the fact that a dcpe ligand is a much better donor than a dppe ligand, which stabilizes cationic species **2**. Based on this premise, the method for the preparation of compound **1** is modified and only one equivalent of  $\text{HBF}_4$  was used. Indeed, as described in the experimental section, the complex **1** was prepared in good yield.

### 3.2. Catalytic hydrogenation

The catalytic activity of a series of  $[\text{Rh}(\text{diene})(\text{L}_2)]^+$  complexes was studied at  $140^\circ\text{C}$  and a hydrogen pressure of 3.42 MPa. The results are shown in Table 1. Consistent with the hydrogenation of simple olefins, all complexes are active catalysts for NBR hydrogenation. The general features of the results are summarized as follows.

- The catalytic activity of complexes of the type  $[\text{Rh}(\text{diene})(\text{L}_2)]^+$  is mainly dependent on the nature of phosphine. Interestingly, the complexes containing monophosphine ligands such

as  $\text{PPh}_3$  are the most active catalysts. In the case of diphosphines including dppe, dppp, dppb, the catalytic activities increase with the increase of the backbone length of phosphines, namely, in the following order:  $[\text{Rh}(\text{diene})(\text{dppb})]^+ > [\text{Rh}(\text{diene})(\text{dppp})]^+ > [\text{Rh}(\text{diene})(\text{dppe})]^+$ . This trend is consistent with that found for simple olefins [18]. Since the electronic properties of dppe, dppp, and dppb are similar, their activity differences are attributed to the steric effect of the ligands. In contrast to a short chain phosphine, a phosphine having a longer chain length is more flexible to accommodate structure changes during the catalytic process thereby facilitating the reaction.

- With the same phosphine ligand, a complex containing a NBD ligand is more reactive at the early stage of the reaction than that containing a COD ligand. This is attributed to the fact that the reduction of norbornadiene is faster than that of 1,5-cyclooctadiene to generate a catalytic active species [20].

- The catalytic activity of  $[\text{Rh}(\text{diene})(\text{PPh}_3)_2]^+$  is similar to that of  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ .

- The  $[\text{Rh}(\text{COD})(\text{dppe})]^+$  is more active than  $[\text{Rh}(\text{COD})(\text{dcpe})]^+$  catalyst.

- In contrast to simple olefin hydrogenation where the activities of  $[\text{Rh}(\text{diene})(\text{L}_2)]^+$  ( $\text{L}_2 = \text{dppe}, \text{dppp}, \text{dppb}$ ) are higher than those observed for  $[\text{Rh}(\text{diene})(\text{PPh}_3)_2]^+$ , the complexes of type  $[\text{Rh}(\text{diene})(\text{PPh}_3)_2]^+$  are more active than complexes of the type  $[\text{Rh}(\text{diene})(\text{L}_2)]^+$  ( $\text{L}_2 = \text{dppe}, \text{dppp}, \text{dppb}$ ).

As described above, the hydrogenation of NBR using  $[\text{Rh}(\text{diene})\text{L}_2]^+$  exhibit some similarities to that observed for small olefins [18]. The catalyst activity increases as the chain length of the diphosphine increases. The activity of  $[\text{Rh}(\text{diene})(\text{PPh}_3)_2]^+$  is similar to  $\text{RhCl}(\text{PPh}_3)_3$ . Thus the hydrogenation processes of NBR with  $[\text{Rh}(\text{diene})\text{L}_2]^+$  appear to be similar to those of small olefins. Halpern [18] reported that, in the hydrogenation of small olefins, the cationic rhodium complexes  $[\text{Rh}(\text{diene})\text{L}_2]^+$  containing a chelating diphosphine have much higher activity than complexes containing monophosphines

Table 1  
The hydrogenation of NBR with cationic rhodium complexes<sup>a</sup>

| Catalyst  | % Hydrogenation <sup>b</sup> | Turnover rate <sup>c</sup><br>(mol (mol Rh) <sup>-1</sup> h <sup>-1</sup> ) |
|---|------------------------------|---|
| Rh(COD)(dppe) <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                           | 20                           | 178   |
| Rh(NBD)(dppe) <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                           | 22                           | 196   |
| Rh(COD)(dcpe) <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                           | 7                            | 62  |
| Rh(COD)(dppp) <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                           | 35                           | 312   |
| Rh(NBD)(dppp) <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                           | 40                           | 356   |
| Rh(COD)(dppb) <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                           | 91                           | 810   |
| Rh(NBD)(dppb) <sup>+</sup> BF <sub>4</sub> <sup>-</sup>                           | 91                           | 810   |
| Rh(COD)(PPh <sub>3</sub> ) <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup> | 97                           | 863   |
| Rh(NBD)(PPh <sub>3</sub> ) <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup> | 97                           | 863   |
| RhCl(PPh <sub>3</sub> ) <sub>3</sub>  | 99                           | 881   |

<sup>a</sup>Reaction conditions: Catalyst =  $2 \times 10^{-5}$  mol, olefin in NBR (Krynac 38.50) =  $1.78 \times 10^{-2}$  mol, solvent = 100 ml monochlorobenzene, temperature = 140°C,  $P_{H_2}$  = 3.42 MPa.

<sup>b</sup>Reported for 1 h reaction period.

<sup>c</sup>Turnover rate were calculated based on the number of moles of olefin reduced per mole of rhodium in the first 1-h interval of the experiment.

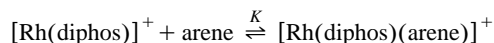
such as [Rh(diene)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. However, the rate of NBR hydrogenation with [Rh(diene)L<sub>2</sub>]<sup>+</sup> (L<sub>2</sub> = dcpe, dppe, dppp, dppb) is significantly *slower* than that with [Rh(diene)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> catalysts. In the case of small olefin hydrogenation, the rate determining step is usually either the oxidative addition of H<sub>2</sub> or the reductive elimination of the final products. In contrast, with macromolecules such as NBR, the step of the coordination of olefin to the metal center becomes rate determining [5,7,21,22]. Thus the following discussion will focus on the rate determining step of the reaction and show that the olefin is coordinated to the two types of metal centers.

The catalytic hydrogenation of simple olefins with [Rh(diene)(L<sub>2</sub>)]<sup>+</sup> complexes have been extensively studied [11,23]. It is generally accepted that there are two distinct reaction pathways associated with this type of catalysts, which are dependent on the nature of phosphine ligands. In the case of a monophosphine such as triphenylphosphine, the reaction follows a hydride pathway. With diphosphines, the reaction proceeds by an olefin route. Consequently, in the case of complexes of the form [Rh(diene)-L<sub>2</sub>]<sup>+</sup> (L<sub>2</sub> = dcpe, dppe, dppp, dppb) as catalysts,

an olefin is coordinated to a rhodium (I) complex [Rh(L<sub>2</sub>)(NC)<sub>2</sub>]<sup>+</sup> where NC stands for the nitrile group present in NBR. With complexes [Rh(diene)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> as catalysts, an olefin is coordinated to a rhodium (III) complex [Rh(H)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(NC)]<sup>+</sup> as required by a hydride pathway. As an olefin is prone to attack the more electrophilic rhodium (III) center instead of attacking the rhodium (I) center, the catalytic reactions with [Rh(diene)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> are expected to be faster than those carried out with diphosphine complexes. This is also consistent with the observations that the complex [Rh(COD)(dcpe)]<sup>+</sup> is a less efficient catalyst compared to [Rh(COD)(dppe)]<sup>+</sup>. Since the dppe ligand is a poorer  $\sigma$ -donor than the dcpe ligand, the Rh metal in the complex [Rh(dppe)(NC)<sub>2</sub>]<sup>+</sup> derived from the latter complex is a better electrophilic center than that from the former complex thereby speeding up the reaction. Although the steric effect in these catalytic processes is not obvious, a steric bulky dcpe ligand could prohibit the coordination of a bulky olefin in NBR thereby retarding the reaction.

Halpern et al. [24] reported that [Rh-(NBD)(diphos)]<sup>+</sup> reacts with hydrogen to give the species [Rh(diphos)]<sup>+</sup>. This species can un-

dergo dimerization to form  $[\text{Rh}_2(\text{diphos})_2]^{2+}$ . More importantly, it is found to react with arenes to form adducts such as:



The parameter  $K$  was determined with a variety of arenes and olefins in methanol [24]. They include benzene ( $18 \text{ M}^{-1}$ ); toluene ( $97 \text{ M}^{-1}$ ); *o*-, *m*-, or *p*-xylene ( $\sim 500 \text{ M}^{-1}$ ); 1-hexene ( $2 \text{ M}^{-1}$ ); methyl acrylate ( $3 \text{ M}^{-1}$ ). Clearly, arenes are much better ligands to form the adducts than olefins, indicating that in the case of NBR hydrogenation in monochlorobenzene (MCB), MCB is an effective ligand to compete with olefins for the vacant sites of  $[\text{Rh}(\text{diphos})]^{+}$  thereby retarding the catalytic hydrogenation of NBR. In contrast, analogous arene adducts were not observed in the hydrogenation of olefins with complex  $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]^{+}$ , suggesting that MCB does not com-

pete with olefins for vacant sites at the metal [9].

### 3.3. Kinetics of the hydrogenation

A series of experiments was carried out to investigate the effects of variables, such as, catalyst concentration, carbon-carbon unsaturation, temperature, hydrogen pressure, on the rate of NBR hydrogenation with  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^{+}$ . The reason that this catalyst was chosen is that it showed the highest activity of hydrogenation among the complexes described earlier and resulted in near quantitative olefin hydrogenation, which made it suitable for measuring hydrogen gas uptake accurately using a computer controlled gas uptake apparatus [14]. A summary of kinetic results is given in Table 2. A representative gas uptake profile is shown

Table 2

The summary of kinetic data for the hydrogenation of NBR (Krynac 38.50) catalyzed by  $\text{Rh}(\text{NBD})(\text{PPh}_3)_2\text{PF}_6$  in monochlorobenzene

| $[\text{Rh}]_{\text{T}}$<br>( $\mu\text{M}$ ) | $[\text{C}=\text{C}]_0$<br>(mM) | $[\text{CN}]$<br>(mM) | $P_{\text{H}_2}$<br>(MPa) | $[\text{H}_2]$<br>(mM) | Temperature<br>(K) | $k \times 10^4$ ,<br>$\text{s}^{-1}$ | $\eta_{\text{rel}}$ |
|---|---------------------------------|-----------------------|---------------------------|------------------------|--------------------|--------------------------------------|---------------------|
| 80.1  | 153.0                           | 95.5                  | 2.46                      | 107                    | 388.2              | 4.51                                 |                     |
| 80.1  | 153.0                           | 95.5                  | 2.46                      | 107                    | 388.2              | 4.39                                 |                     |
| 160.2   | 152.9                           | 95.5                  | 2.46                      | 107                    | 388.2              | 8.12                                 | 4.32                |
| 160.2   | 153.0                           | 95.5                  | 2.46                      | 107                    | 388.2              | 9.25                                 | 3.87                |
| 240.4   | 153.0                           | 95.5                  | 2.46                      | 107                    | 388.2              | 12.6                                 | 4.13                |
| 239.8   | 152.9                           | 95.5                  | 2.46                      | 107                    | 388.2              | 13.4                                 |                     |
| 319.9   | 153.0                           | 95.5                  | 2.46                      | 107                    | 388.2              | 15.5                                 |                     |
| 320.3   | 153.0                           | 95.5                  | 2.46                      | 107                    | 388.2              | 16.3                                 | 3.89                |
| 239.8   | 76.5                            | 47.8                  | 2.46                      | 107                    | 388.2              | 19.8                                 |                     |
| 240.3   | 107.3                           | 67.0                  | 2.46                      | 107                    | 388.2              | 14.3                                 |                     |
| 240.0   | 137.6                           | 85.9                  | 2.46                      | 107                    | 388.2              | 13.6                                 |                     |
| 239.9   | 137.8                           | 86.0                  | 2.46                      | 107                    | 388.2              | 15.1                                 |                     |
| 239.9   | 191.2                           | 119.4                 | 2.46                      | 107                    | 388.2              | 11.7                                 | 3.88                |
| 240.2   | 229.6                           | 143.4                 | 2.46                      | 107                    | 388.2              | 10.8                                 | 4.05                |
| 240.4   | 275.4                           | 172.0                 | 2.46                      | 107                    | 388.2              | 8.79                                 |                     |
| 240.1   | 153.1                           | 95.6                  | 1.36                      | 61.7                   | 388.2              | 6.56                                 |                     |
| 240.2   | 153.0                           | 95.6                  | 3.72                      | 159                    | 388.2              | 17.1                                 |                     |
| 240.0   | 153.0                           | 95.6                  | 4.86                      | 205                    | 388.2              | 20.8                                 | 4.54                |
| 240.0   | 153.0                           | 95.5                  | 5.97                      | 250                    | 388.2              | 24.1                                 |                     |
| 240.1   | 153.0                           | 95.5                  | 5.97                      | 250                    | 388.2              | 23.5                                 |                     |
| 240.1   | 153.0                           | 95.5                  | 6.96                      | 284                    | 388.2              | 29.9                                 |                     |
| 240.4   | 152.9                           | 95.5                  | 7.01                      | 285                    | 388.2              | 31.0                                 |                     |
| 240.0   | 153.0                           | 95.6                  | 2.46                      | 107                    | 373.2              | 5.94                                 |                     |
| 239.8   | 153.0                           | 95.6                  | 2.46                      | 107                    | 378.2              | 8.17                                 |                     |
| 240.3   | 153.0                           | 95.6                  | 2.46                      | 107                    | 383.2              | 9.26                                 |                     |
| 239.8   | 153.0                           | 95.6                  | 2.46                      | 107                    | 393.2              | 16.6                                 |                     |

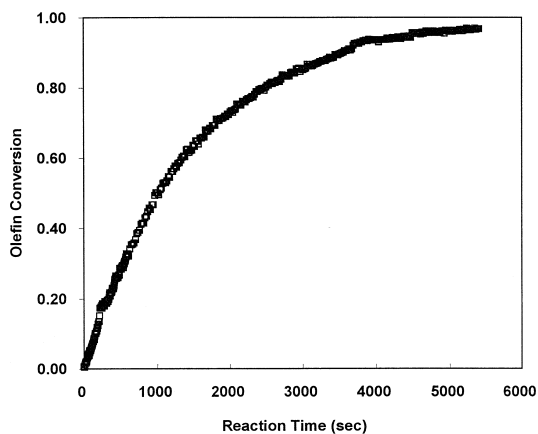


Fig. 1. Representative olefin conversion profiles for the hydrogenation of NBR in monochlorobenzene.  $[\text{Rh}]_{\text{T}} = 240 \mu\text{M}$ ;  $[\text{CN}] = 95.6 \text{ mM}$ ;  $P_{\text{H}_2} = 1.36 \text{ MPa}$ ;  $T = 388.2 \text{ K}$ .

in Fig. 1. The catalytic reaction follows a first-order regression model indicating that there is no preference for the hydrogenation of vinyl/*cis*/*trans* butadiene isomerization of NBR under the reaction conditions. This is in accord with the observations found for  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  and  $\text{RhH}(\text{PPh}_3)_4$  systems investigated under similar conditions [7]. The relative viscosities ( $\eta_{\text{rel}}$ ) reported in Table 2 are in the range from 3.87 to 4.54, which are somewhat higher than those found for  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  and

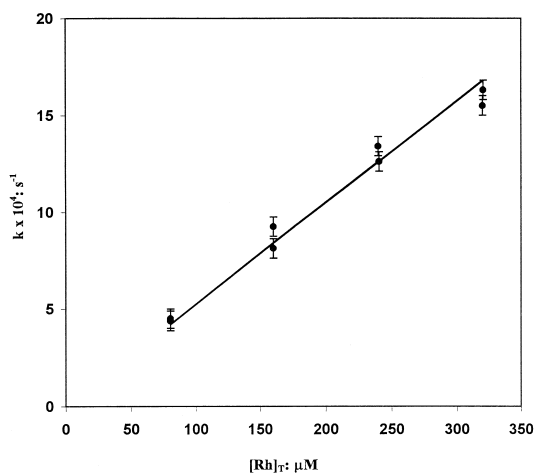


Fig. 2. Effect of  $[\text{Rh}]_{\text{T}}$  on the rate of hydrogenation.  $[\text{CN}] = 95.5 \text{ mM}$ ;  $P_{\text{H}_2} = 2.46 \text{ MPa}$ ;  $T = 388.2 \text{ K}$ . (·) Observed data; (—) model.

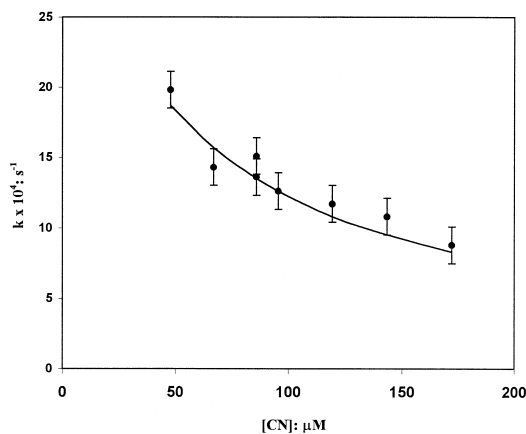


Fig. 3. Effect of  $[\text{CN}]$  on the rate of hydrogenation.  $[\text{Rh}]_{\text{T}} = 240 \mu\text{M}$ ;  $P_{\text{H}_2} = 2.46 \text{ MPa}$ ;  $T = 388.2 \text{ K}$ . (·) Observed data; (—) model.

$\text{RhH}(\text{PPh}_3)_4$  systems where the viscosities are in the range from 3.35 to 3.93 [7]. The random viscosities indicate that the product properties are independent of the reaction conditions employed.

### 3.3.1. Effect of catalyst concentration

To determine the dependence of the rate of hydrogenation on catalyst concentration, a series of experiments was carried out in which the catalyst concentration was varied from  $80 \mu\text{M}$

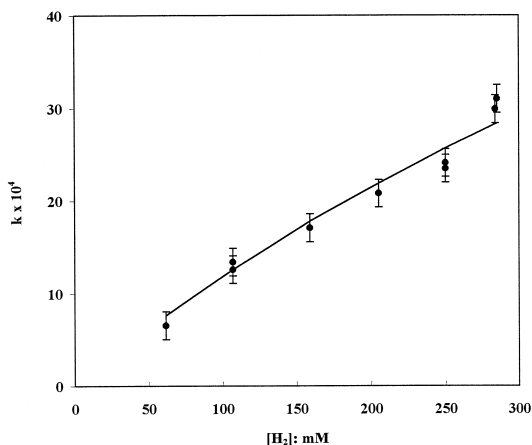
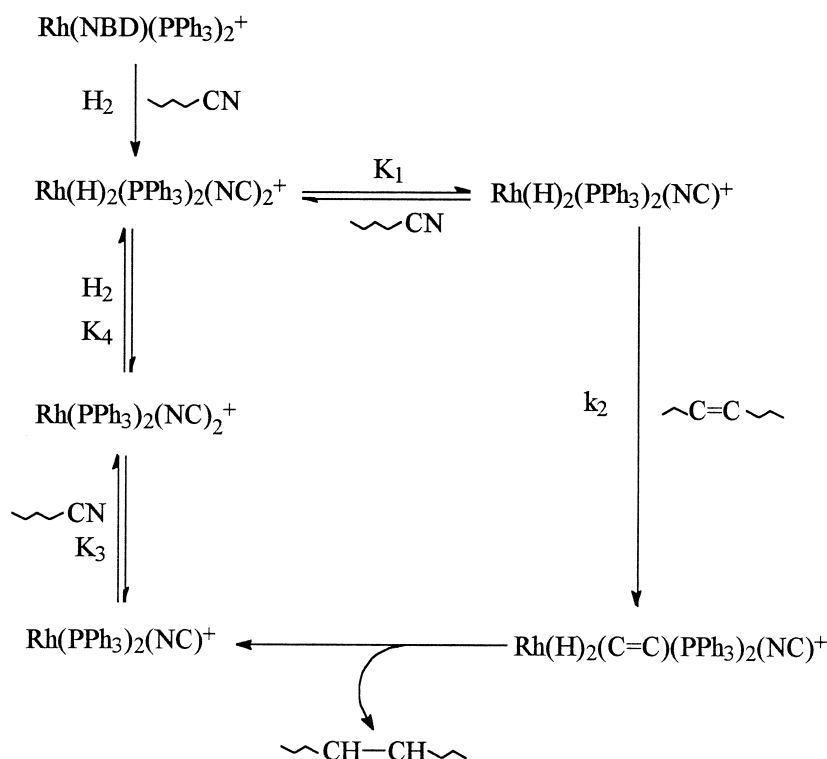


Fig. 4. Effect of hydrogen pressure on the rate of hydrogenation.  $[\text{Rh}]_{\text{T}} = 240 \mu\text{M}$ ;  $[\text{CN}] = 95.5 \text{ mM}$ ;  $T = 388.2 \text{ K}$ . (·) Observed data; (—) model.



Scheme 2. Proposed mechanism for the hydrogenation of NBR with  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+$ .

to 320  $\mu\text{M}$  while the polymer concentration (153 mM), hydrogen pressure (2.46 MPa), and temperature (388.2 K) were maintained unchanged. Fig. 2 shows the resulting rate constants and their regression value. The linear relationship between the reaction rates and the catalyst concentrations indicates that the reaction is first order in catalyst concentration.

### 3.3.2. Effect of polymer concentration

When the catalyst concentration (240  $\mu\text{M}$ ), reaction temperature (388.2 K), and hydrogen pressure (2.46 MPa) were held constant, the

effect of NBR concentration on the rate of the reaction can be studied by varying NBR concentration. Fig. 3 shows that the reaction rate decreases with increase of NBR concentration. This is due to the presence of nitrile group in NBR, which can compete with olefin for the metal coordination sites during the catalytic process. Schrock and Osborn [8] reported that acetonitrile strongly inhibits the hydrogenation of simple olefins, such as 1-hexene, by  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+$ . This is attributed to the facile reaction of  $[\text{RhH}_2(\text{PPh}_3)_2\text{S}_2]^+$

Table 3  
Model analysis of variance results

| Source     | Sum of squares         | df | Mean square            |
|------------|------------------------|----|------------------------|
| Regression | $6.400 \times 10^{-5}$ | 4  | $1.600 \times 10^{-5}$ |
| Residual   | $3.314 \times 10^{-7}$ | 18 | $1.742 \times 10^{-8}$ |
| Total      | $6.132 \times 10^{-5}$ | 22 |                        |
| Corrected  | $1.148 \times 10^{-5}$ | 21 |                        |

Table 4  
Estimates of model parameters

| Parameter                    | Estimate              | ASE                   | $\langle 95\% \rangle$ |                       |
|------------------------------|-----------------------|-----------------------|------------------------|-----------------------|
|                              |                       |                       | Lower                  | Upper                 |
| $k_2$ ( $\text{mM s}^{-1}$ ) | 1.34                  | 0.397                 | 0.505                  | 2.17                  |
| $K_1$ (mM)                   | 3.47                  | 1.04                  | 1.29                   | 5.65                  |
| $K_3$ ( $\text{mM}^{-1}$ )   | $1.67 \times 10^{-2}$ | $3.73 \times 10^{-3}$ | $8.87 \times 10^{-3}$  | $2.45 \times 10^{-2}$ |
| $K_4$ ( $\text{mM}^{-1}$ )   | $1.85 \times 10^{-3}$ | $7.23 \times 10^{-5}$ | $1.70 \times 10^{-3}$  | $2.00 \times 10^{-3}$ |

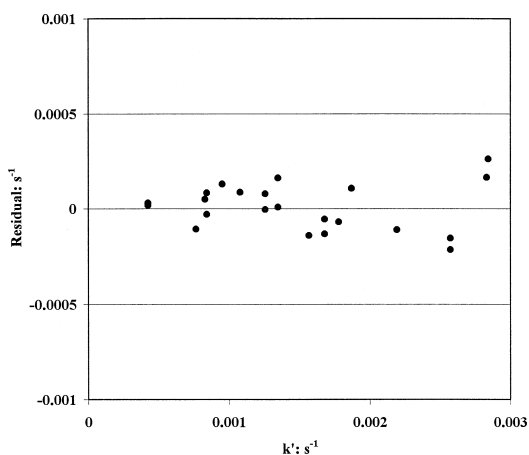


Fig. 5. Residual plot of  $(k'_{\text{actual}} - k'_{\text{model}})$  versus  $k'$ .

(S = acetone or ethanol), which is a catalytic active species, with acetonitrile to generate  $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NCCH}_3)_2]^+$ . That nitrile inhibits the hydrogenation of NBR with  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  was also observed from this laboratory [5,7].

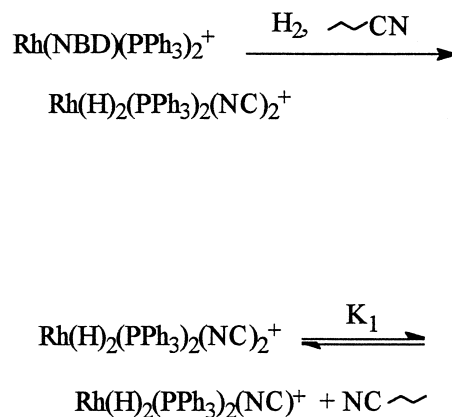
### 3.3.3. Effect of hydrogen pressure

The rate of NBR hydrogenation with  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  and  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  catalysts is a function of the hydrogen pressure, and the former one exhibits the first to zero order dependence on the hydrogen pressure while a second order dependence on the hydrogen pressure is observed in the case of osmium catalyst [7,25]. Thus, to determine the dependence of the hydrogenation rate on the hydrogen pressure, a series of experiments was carried out where the hydrogen pressure was varied over the range of 1.36–7.01 MPa. The initial polymer concentration, catalyst concentration and reaction temperature were kept constant. The hydrogen concentration in chlorobenzene was calculated based on the hydrogen solubility in chlorobenzene reported by Parent and Rempel [26]. The results shown in Fig. 4 demonstrate that the rate of hydrogenation is pseudo-first order with respect to the hydrogen pressure.

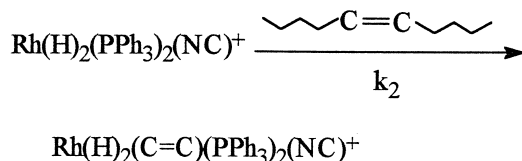
### 3.3.4. Reaction mechanism and rate law

It is well known that complexes  $[\text{Rh}(\text{diene})(\text{PPh}_3)_2]^+$  as catalyst precursors readily react

with  $\text{H}_2$  in coordinated solvents such as methanol and acetonitrile to generate the solvated species  $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2\text{S}_2]^+$  [20,24]. These complexes also react readily with  $\text{H}_2$  in the solvents of low coordinating power such as  $\text{CH}_2\text{Cl}_2$  and benzene to generate catalytically active species [9]. The exact nature of this species is not known as it has defied identification by  $^1\text{H}$  NMR spectroscopy at low temperature, presumably the concentrations of these active species are too low to be observed [9]. Thus, as illustrated in Eq. (1), we propose that the reaction of  $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+$  with  $\text{H}_2$  in the presence of NBR and chlorobenzene generates a putative species  $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})_2]^+$ , where NC stands for the nitrile group present in NBR. Complex  $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})_2]^+$  subsequently dissociates into a sixteen-electron species  $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})]^+$  [Eq. (2)].



The  $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})]^+$  species then reacts with olefin to form compound  $[\text{Rh}(\text{H})_2(\text{C}=\text{C})(\text{PPh}_3)_2(\text{NC})]^+$  [Eq. (3)]. This complex can undergo further intramolecular addition of a hydride to the coordinated olefinic bonds and the reductive elimination of hydrogenated NBR to give species  $[\text{Rh}(\text{PPh}_3)_2(\text{NC})]^+$ , which subsequently reacts with nitrile and  $\text{H}_2$  to regenerate the species,  $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})_2]^+$  (Scheme 2).



Halpern [23] and Landis and Halpern [27] have demonstrated that, in the catalytic hydrogenation of simple olefins using cationic rhodium complexes, the rate-determining step depends on the reaction conditions. When the catalytic reaction is carried out at low hydrogen pressure (1 atm) and room temperature, the oxidative addition of  $\text{H}_2$  is rate determining. However, the reductive elimination of final product becomes rate determining at temperature lower than  $-40^\circ\text{C}$ . In contrast to small olefin hydrogenation, Rempel and coworkers [5,7,21,22,28] have demonstrated that, in the hydrogenation of diene polymers at elevated temperatures and hydrogen pressures by  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ , the olefin coordination step is typically rate determining, which is attributed to the steric demands of the polymer that inhibits an olefin double bond from accessing the metal center. Thus, the olefin coordination step shown in Eq. (3) is assumed as the rate-determining

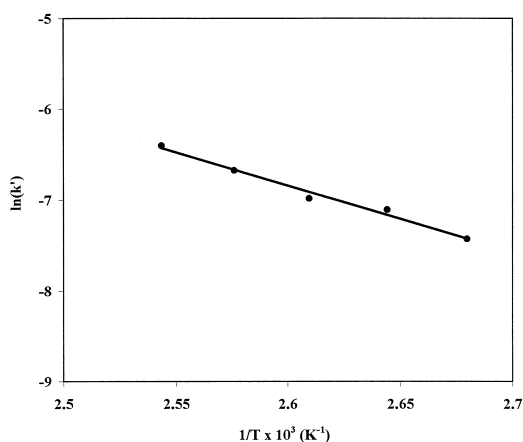


Fig. 6. Arrhenius plot.  $[\text{Rh}]_T = 240 \mu\text{M}$ ;  $[\text{CN}] = 95.5 \text{ mM}$ ;  $P_{\text{H}_2} = 2.46 \text{ MPa}$ ;  $T = 373.2 \text{ K} - 393.2 \text{ K}$ . (•) Observed data; (—) regression value.

step in this case and the corresponding rate law is given in Eq. (4).

$$\begin{aligned} \frac{d[\text{C}=\text{C}]}{dt} &= k'[\text{C}=\text{C}] \\ &= k_2[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})^+][\text{C}=\text{C}] \end{aligned} \quad (4)$$

In combination of the following Eqs. (5)–(8), the concentration of  $[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})^+]$  can be converted to the total concentration of rhodium  $[\text{Rh}]_T$ , nitrile concentration  $[\text{CN}]$ , and hydrogen concentration  $[\text{H}_2]$  and, by substituting it into Eq. (4), the pseudo-first-order rate constant ( $k'$ ) is obtained (Eq. (9)).

$$\begin{aligned} [\text{Rh}]_T &= [\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})_2^+] \\ &\quad + [\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})^+] \\ &\quad + [\text{Rh}(\text{PPh}_3)_2(\text{NC})^+] \\ &\quad + [\text{Rh}(\text{PPh}_3)_2(\text{NC})_2^+] \end{aligned} \quad (5)$$

$$K_1 = \frac{[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})^+][\text{CN}]}{[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})_2^+]} \quad (6)$$

$$K_3 = \frac{[\text{Rh}(\text{PPh}_3)_2(\text{NC})^+]}{[\text{Rh}(\text{PPh}_3)_2(\text{NC})^+][\text{CN}]} \quad (7)$$

$$K_4 = \frac{[\text{Rh}(\text{H})_2(\text{PPh}_3)_2(\text{NC})_2^+]}{[\text{Rh}(\text{PPh}_3)_2(\text{NC})_2^+][\text{H}_2]} \quad (8)$$

$$k' = \frac{k_2 K_1 K_3 K_4 [\text{H}_2][\text{Rh}]_T}{1 + K_3[\text{CN}] + K_1 K_3 K_4 [\text{H}_2] + K_3 K_4 [\text{CN}][\text{H}_2]} \quad (9)$$

The Gauss–Newton method for nonlinear least-squares regression is used for the statistical analysis of variance to verify the validity of the model [29]. The results obtained are listed in Table 3 and the reaction parameters  $K_1$ ,  $K_3$ ,  $K_4$ , and  $k_2$  generated are given in Table 4 along with the 95% confidence ranges. The values of parameters  $K_1$ ,  $K_3$ ,  $K_4$  and  $k_2$  are comparable to the similar parameters found for the NBR hydrogenation with  $\text{RhCl}(\text{PPh}_3)_3$  catalyst [7]. The residual plot is given in Fig. 5. Both a low value for the mean sum of squares of residues

shown in Table 3 and the random scattering of errors shown in Fig. 5 indicates that the observed kinetic data are consistent with the model.

### 3.3.5. Temperature dependence

A series of experiments were carried out over the temperature range of 100–120°C, where the catalyst concentration (0.240 mM), the polymer concentration (153 mM), and hydrogen pressure (2.46 MPa) remained constant. Fig. 6 shows an Arrhenius plot, from which the activation energy  $E_A$  of 60.7 kJ mol<sup>-1</sup> was obtained. This value is in good agreement with those found for Rh(PPh<sub>3</sub>)<sub>3</sub>Cl (73.5 kJ mol<sup>-1</sup>) and RhH(PPh<sub>3</sub>)<sub>4</sub> (57.4 kJ mol<sup>-1</sup>), indicating that the reaction is under chemical control and the diffusion of the reactants is not a rate determining factor under these reaction conditions. Based on the corresponding Eyring plot, the apparent activation enthalpy and entropy obtained are 57.5 kJ mol<sup>-1</sup> and -154.5 J mol<sup>-1</sup> K<sup>-1</sup>.

### Acknowledgements

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### References

- [1] N.T. McManus, G.L. Rempel, J. Macromol. Sci. Rev. Macromol. Chem. Phys. C 35 (1995) 239.
- [2] M.P. McGrath, E.D. Sall, S.J. Tremont, Chem. Rev. 95 (1995) 381.
- [3] K. Hashimoto, N. Watanabe, A. Yoshioka, Rubber World 190 (1984) 32.
- [4] G.L. Rempel, N.T. McManus, J.S. Parent, U.S. Patent 5561 197 (1996).
- [5] N.A. Mohammadi, G.L. Rempel, Macromolecules 20 (1987) 2362.
- [6] S. Bhattacharjee, A.K. Bhowmick, B.N. Avasthi, Ind. Eng. Chem. Res. 30 (1991) 1086.
- [7] J.S. Parent, N.T. McManus, G.L. Rempel, Ind. Eng. Chem. Res. 35 (1996) 4417.
- [8] R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 98 (1976) 2134.
- [9] R.H. Crabtree, A. Gautier, G. Giordano, T. Khan, J. Organomet. Chem. 141 (1977) 113.
- [10] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, Wiley-Interscience, New York, 1992, pp. 25–39.
- [11] R.S. Dickson, Homogeneous Catalysis with Compounds of Rhodium and Iridium, D. Reidel Publishing, Dordrecht, 1985, pp. 62–67.
- [12] R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 93 (1971) 2397.
- [13] D.C. Mudalige, G.L. Rempel, J. Mol. Catal. 116 (1997) 309.
- [14] N.A. Mohammadi, G.L. Rempel, Comput. Chem. Eng. 11 (1987) 27.
- [15] P. Martin, N.T. McManus, G.L. Rempel, J. Mol. Catal. A 126 (1997) 115.
- [16] A.J. Marshall, I.R. Jobe, T. Dee, C. Taylor, Rubber Chem. Technol. 63 (1990) 244.
- [17] R. Ugo, in: C. Manfredi (Ed.), Aspects of Homogeneous Catalysis, Milano, 1970, pp. 3–75.
- [18] J. Halpern, Phosphorus Sulfur 18 (1983) 307.
- [19] J.M. Brown, P.A. Chaloner, A.G. Kent, B.A. Murrer, P.N. Nicholson, D. Parker, P.J. Sidebottom, J. Organomet. Chem. 216 (1981) 263.
- [20] J.R. Shapley, R.R. Schrock, J.A. Osborn, J. Am. Chem. Soc. 91 (1971) 2816.
- [21] X.Y. Guo, G.L. Rempel, J. Mol. Catal. 63 (1990) 279.
- [22] N.A. Mohammadi, G.L. Rempel, J. Mol. Catal. 50 (1989) 259.
- [23] J. Halpern, Inorg. Chim. Acta 50 (1981) 11.
- [24] J. Halpern, D.P. Riley, A.S.C. Chan, J.J. Pluth, J. Am. Chem. Soc. 99 (1977) 8055.
- [25] J.S. Parent, PhD Thesis, University of Waterloo, 1996.
- [26] J.S. Parent, G.L. Rempel, J. Chem. Eng. Data 41 (1996) 192.
- [27] C.R. Landis, J. Halpern, J. Am. Chem. Soc. 109 (1987) 1746.
- [28] X.Y. Guo, P.J. Scott, G.L. Rempel, J. Mol. Catal. 72 (1992) 193.
- [29] SAS (Statistical Analysis System) User's Guide, SAS Institute, Cary, NC, 1985.