

# Hydrogenation of Natural Rubber Using Nickel 2-Ethylhexanoate Catalyst in Combination with Triisobutylaluminum

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## SYNOPSIS

Kinetic studies for the homogeneous hydrogenation of natural rubber, in the presence of nickel 2-ethylhexanoate and triisobutylaluminum, have been carried out by monitoring the change in hydrogen pressure in a Parr reactor of fixed volume. <sup>1</sup>H-NMR spectroscopy provides the measurements of the extent of hydrogenation. The reaction kinetics, in the presence of a fixed amount of catalyst, showed an overall second-order kinetic with respect to [H<sub>2</sub>] and [C=C]. The reaction has a relatively low apparent activation energy of 26.0 kJ mol<sup>-1</sup> and is therefore suitable for the hydrogenation of natural rubber at ambient conditions to minimize side reactions. The impurities in commercial rubbers have a slight effect on the catalyst activity. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Chemical modification of natural rubber has been an active field of research because of the technological importance of the modified products.<sup>1</sup> Hydrogenation is one of the important methods for improving and changing the properties of unsaturated elastomer toward greater stability against thermal, oxidative, and radiation-induced degradation. The conversion of an unsaturated polymer to a saturated one can be brought about by homogeneous and heterogeneous catalysts, as well as by noncatalytic hydrogenation.

Homogeneous hydrogenation uses a soluble catalytic complex to activate the reaction between molecular hydrogen and the carbon-carbon double bond. Generally, this method could be selective, does not yield high conversions, and is accompanied by chain scission and some structural changes, and the removal of catalyst at the end of the reaction could be a problem.<sup>2-6</sup> On the other hand, heterogeneous hydrogenation relies on an insoluble transition-

metal catalyst to promote hydrogen addition to the double bond. This technique yields high conversions and usually does not cause chain scission. Difficulty of preparation and ease of poisoning are the usual disadvantages. The reaction rates of the heterogeneous reactions are also slower than in homogeneous hydrogenations, and more vigorous reaction conditions are required.<sup>7-10</sup> Early catalytic hydrogenation of polyisoprene procedures involved reactions at high temperatures and pressures using platinum or nickel catalysts, resulting in considerable degradation or other side reactions.

The noncatalytic technique uses a hydrogenation reagent,<sup>11-13</sup> such as a diimide generated *in situ* from *p*-toluene-sulfonylhydrazide (TSH).<sup>11,12</sup> The reaction of polyisoprene with TSH at 140°C could only produce a low level of hydrogenation (< 40% conversion) despite using a large amount of TSH. In addition, the polymer was partially depolymerized and cyclized.<sup>12</sup>

Recently, it was shown that it is possible to hydrogenate natural rubbers catalytically under mild conditions which minimize concomitant side reactions. Both heterogeneous palladium-supported catalysts<sup>14</sup> and homogeneous two-component systems<sup>3</sup> have been reported. The latter catalyst is

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less susceptible to the impurities in natural rubber and was capable of achieving 100% hydrogenation of the natural rubber under optimum reaction conditions.<sup>15</sup> This article describes the use of a homogeneous catalyst prepared from nickel 2-ethylhexanoate and triisobutylaluminum in the hydrogenation of natural rubber. The kinetics of the reaction, effect of rubber concentration and cocatalyst level, and the apparent activation energy are reported.

## EXPERIMENTAL

### Chemicals

Nickel 2-ethylhexanoate and triisobutylaluminum were commercial products purchased from Alfa Products, U.S.A., and Fluka Chemicals, Switzerland, respectively. Hexane was purified by distilling over sodium metal and stored over activated molecular sieves under a nitrogen atmosphere. Hydrogen gas was supplied by Malaysian Oxygen Ltd. Co. and was used without purification.

### Rubber Samples

Purified rubber was isolated from freshly tapped rubber latex of a RRIM 600 clone by a procedure described elsewhere.<sup>16</sup> DPNR, SMRCV, and SMRL were commercial natural rubber samples obtained from the Rubber Research Institute of Malaysia.

### Hydrogenation Procedure

Hydrogenation was carried out in a Parr reactor (Model 4842) equipped with mechanical stirrer, temperature controller, and pressure transducer. Typically, the specified amount of rubber sample was dissolved in 100 mL of hexane in a closed flask under a nitrogen atmosphere. The solution was then transferred into the Parr reactor. The catalyst, 0.75 mmol, and the designated amount of cocatalyst in hexane solutions were added. The apparatus was partially evacuated and purged several times with hydrogen before filling to the required pressure (usually at around 825 kPa) and cut off from the gas tank. During the course of hydrogenation, the mixture was agitated by stirring at constant speed of 200 rpm and the progress of the reaction monitored by the drop in hydrogen pressure. The hydrogenated rubber was isolated by precipitation in ethyl acetate containing 1% HCl, followed by washing with methanol, and, finally, the rubber was vacuum dried at 40°C overnight.

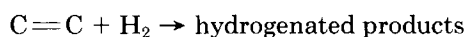
### Characterization of Product

Fourier transform infrared (FTIR) spectra of the rubber samples were run as cast films on NaCl discs using a Perkin-Elmer FTIR 1600 instrument. Films were prepared from a dilute rubber solution in chloroform, the solvent being removed with the help of a hot-air blower. NMR spectra were recorded on 3% w/v solutions of the rubber in CDCl<sub>3</sub> with a JOEL-JNM-GSX270 NMR spectrometer.

## RESULTS AND DISCUSSION

### General Kinetics of Hydrogenation and Effect of Rubber Concentration

The hydrogenation reaction can be represented by



Assuming that the reaction is second order, then the rate of reaction is given by

$$-\frac{d[H_2]}{dt} = k[C=C][H_2] \quad (1)$$

$$\ln \frac{[H_2]}{[C=C]} = k \{ [H_2]_0 - [C=C]_0 \} t + \ln \frac{[H_2]_0}{[C=C]_0} \quad (2)$$

where  $[H_2]$  and  $[C=C]$  are the concentration of hydrogen and double bond, respectively, at time  $t$ , and  $[H_2]_0$  and  $[C=C]_0$  are the corresponding initial concentrations (i.e., at  $t = 0$ ). By Henry's Law, the solubility of hydrogen gas in hexane is proportional to the hydrogen gas pressure. The following approximation can be used for expressing the dissolved hydrogen as mol dm<sup>-3</sup> in the solvent:

$$[H_2] = k'P \quad (3)$$

where  $k'$  represents the proportionality constant, and  $P$ , the pressure of hydrogen gas. Equation (2) can then be expressed in term of the hydrogen pressure as follows:

$$\ln \frac{P}{[C=C]} = k \{ [H_2]_0 - [C=C]_0 \} t + \ln \frac{P_0}{[C=C]_0} \quad (4)$$

A typical set of data is as shown in Table I.

**Table I** Kinetics of Hydrogenation Reaction, from the Drop in Hydrogen Gas Pressure with Reaction Time

Time (min)	$P, H_2$ Pressure (kPa)	$H_2$ Reacted (mol)	$[C=C]$ ( $mol\ dm^{-3}$ )	$P/[NR]$	$\ln \{P/[C=C]\}$
0.00	824.9	0.00000	0.142	5815	8.668
0.45	811.2	0.00088	0.133	6078	8.712
1.08	797.4	0.00176	0.125	6377	8.760
1.37	790.5	0.00220	0.121	6542	8.786
1.97	776.7	0.00308	0.112	6909	8.841
2.62	762.9	0.00396	0.104	7335	8.900
3.00	756.0	0.00440	0.100	7575	8.933
3.72	742.2	0.00528	0.091	8122	9.002
4.53	728.4	0.00616	0.083	8779	9.080
5.78	714.6	0.00704	0.075	9585	9.168
6.27	707.7	0.00748	0.070	10061	9.216
7.07	700.8	0.00792	0.066	10596	9.268
8.00	693.9	0.00836	0.062	11205	9.324
8.63	687.0	0.00880	0.058	11902	9.384
9.27	680.2	0.00924	0.054	12709	9.450
10.00	673.3	0.00968	0.049	13654	9.522
12.00	652.6	0.01100	0.037	17787	9.786
13.00	645.7	0.01144	0.032	19879	9.897
15.00	638.8	0.01188	0.028	22593	10.025

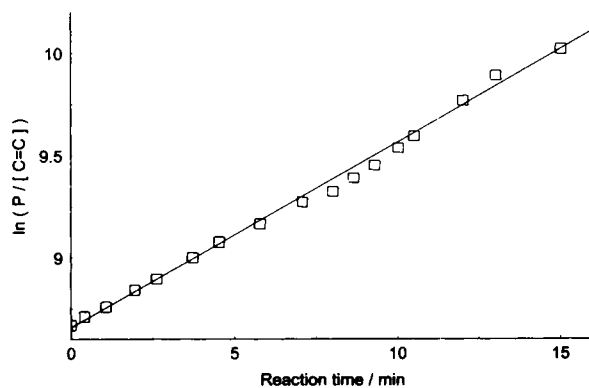
[Ni catalyst] = 7.20 mmol dm<sup>-3</sup>; Al/Ni = 3.0, total volume of solution = 104.6 cm<sup>3</sup>; weight of rubber sample = 1.0091 g, containing 0.0148 mol C=C bond, thus the initial [C=C] = 0.142 mol dm<sup>-3</sup>; temperature = 30°C; stirring speed = 200 rpm; closed volume of reactor = 265.4 cm<sup>3</sup>.

Natural rubber consists of *cis*-1,4-polyisoprene and would contain 68 g mol<sup>-1</sup> of the repeating unit, —CH<sub>2</sub>C(CH<sub>3</sub>)=CHCH<sub>2</sub>—. The concentration of the unhydrogenated isoprene unit is expressed as [C=C] in the fourth column. Since the Parr reactor has a closed volume, and assuming the hydrogen gas behavior ideally, the pressure drop can be expressed as the number of moles of hydrogen consumed,  $\Delta n = V \Delta p / RT$ , and, consequently, the same number of moles of the isoprene unit would be hydrogenated. A plot of  $\ln P/[C=C]$  vs.  $t$ , as shown in Figure 1, is, in fact, linear. The gradient of the graph is equal to  $k \{ [H_2]_0 - [C=C]_0 \}$  and intercept  $\ln P_0/[C=C]_0$ .

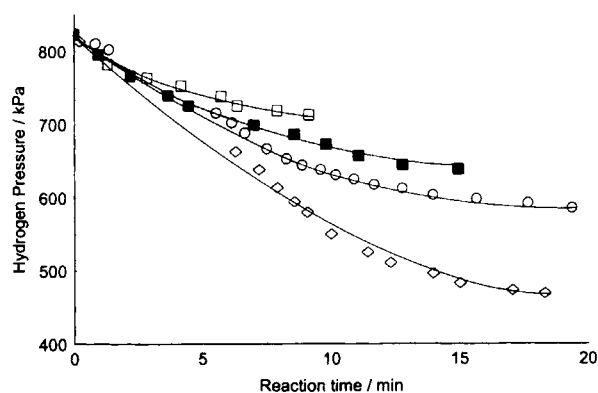
As shown in Figure 2, at a fixed catalyst concentration, the rate of hydrogen pressure drop increases with the concentration of the rubber solution. However, it was noted that the viscosity of the solution increases rapidly with the rubber concentration. This could affect the amount of hydrogen gas which could dissolve in the solvent as well as the stirring from being uniform. At a concentration of higher than 2.5 g rubber in 100 mL hexane, it would take more than 48 h of stirring and some undissolved gels were still observable. Thus, for the kinetic studies, the concentration was maintained at around 1 g rubber in 100 mL hexane.

### Effect of Hydrogen Pressure

Keeping the reaction temperature, catalyst, and initial rubber concentrations constant, the hydrogenation was repeated with different initial hydrogen pressure. As expected, when  $\ln P/[C=C]$  was plotted against reaction time, the gradient increases with the higher initial hydrogen pressure as shown in Figure 3. The values of the gradients at different initial hydrogen pressure  $P_0$  are summarized in



**Figure 1** Graph of  $\ln (P/[C=C])$  vs. reaction time. [Ni catalyst] = 7.2 mmol dm<sup>-3</sup>; Al/Ni = 3.0; temperature = 30°C; initial hydrogen pressure 825 kPa.



**Figure 2** Effect of rubber concentration on the rate of hydrogenation. Weight of rubber samples: (□) 0.500 g; (■) 1.00 g; (○) 2.00 g; (◇) 2.50 g. [Ni catalyst] = 7.2 mmol dm<sup>-3</sup>; Al/Ni = 3.0; temperature = 30°C; initial pressure = 825 kPa.

Table II. As  $k\{[\text{H}_2]_0 - [\text{C}=\text{C}]_0\} = k\{k'P_0 - [\text{C}=\text{C}]_0\}$ ,

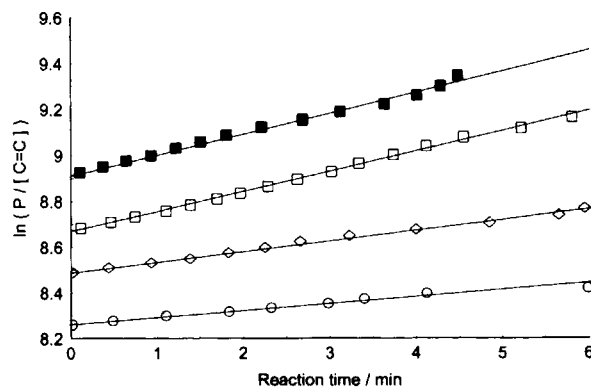
$$kk'P_0 = k\{[\text{H}_2]_0 - [\text{C}=\text{C}]_0\} + k[\text{C}=\text{C}]_0 \quad (5)$$

Figure 4 shows that a plot of  $P_0$  vs.  $k\{[\text{H}_2]_0 - [\text{C}=\text{C}]_0\}$  gives a straight line. The intercept of the straight line is equal to  $[\text{C}=\text{C}]_0/k' = 288.4$ . Since this series of hydrogenation was done at constant initial  $[\text{C}=\text{C}]_0 = 0.141$  mol dm<sup>-3</sup>, the proportional constant,  $k'$ , is thus estimated to be 0.000489 mol dm<sup>-3</sup> kPa<sup>-1</sup>. The gradient of the graph is equal to  $1/kk' = 7687$ ; thus, the second-order rate constant  $k = 0.266$  mol<sup>-1</sup> dm<sup>3</sup> min<sup>-1</sup>.

The original form of Henry's Law is  $P = k_H X_H$ , where  $k_H$  is the Henry's constant and  $X_H$  is the mol fraction of hydrogen gas in the solvent.  $k_H$  is related to  $k'$  as follows:

$$k_H = d_{hx}/(k'M_{hx}) \quad (6)$$

where  $M_{hx}$  = molecular weight of hexane and  $d_{hx}$  is the density of hexane. Substituting  $k' = 0.000489$



**Figure 3** Effect of initial hydrogen pressure. [Ni catalyst] = 7.2 mmol dm<sup>-3</sup>; Al/Ni = 3.0; temperature = 30°C; weights of rubber sample 1.0001–1.0091 g; initial hydrogen pressure: (■) 1032 kPa; (□) 825 kPa; (◇) 687 kPa; (○) 548 kPa.

mol dm<sup>-3</sup> × 10<sup>-3</sup> Pa<sup>-1</sup>,  $M_{hx} = 86$  g mol<sup>-1</sup>, and  $d_{hx} = 0.66$  g × 10<sup>3</sup> dm<sup>-3</sup>, the Henry's constant works out to be  $k_H = 1.57 \times 10^7$  Pa at 30°C. In the case of hydrogen gas in pure hexane at 25°C, the Henry's constant was reported<sup>17</sup> to be  $1.60 \times 10^8$  Pa. This result shows that the solubility of hydrogen in hexane is lower at higher temperature and also in the presence of a catalyst and natural rubber.

### Effect of Cocatalyst-to-Catalyst Ratio

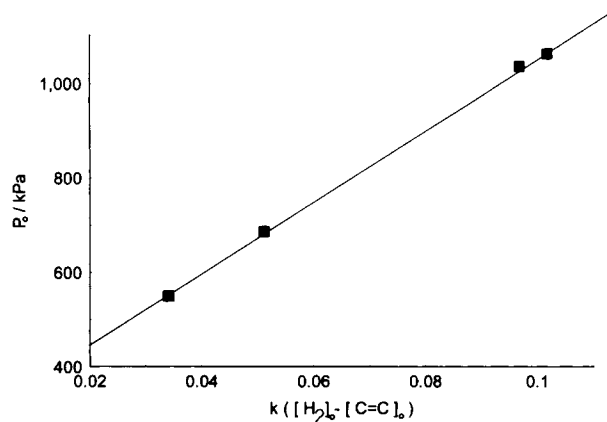
The activity of the two-component Ziegler–Natta type of catalyst systems is known to be dependent on the ratio of cocatalyst to catalyst.<sup>3</sup> The hydrogenation activity at various Al/Ni ratios was investigated by reacting the same weight of natural rubber at the same initial hydrogen pressure at constant temperature. At each chosen ratio,  $\ln(P/[\text{C}=\text{C}])$  was plotted against time; the gradient of the linear portion and the intercept was determined graphically. The results are summarized in Table III.

As expected, since this series of reactions were carried out at a constant initial hydrogen pressure

**Table II** Effect of Different Initial Hydrogen Pressure

$P_0$ (kPa)	Gradient $k\{[\text{H}_2]_0 - [\text{C}=\text{C}]_0\}$	Intercept from Graph	$\ln \frac{P_0}{[\text{C}=\text{C}]_0}$ by Calculation
549.2	0.0344	8.26	8.27
687.1	0.0513	8.49	8.49
826.9	0.0887	8.67	8.67
1038.7	0.0970	8.92	8.91
1066.3	0.1019	8.93	8.93

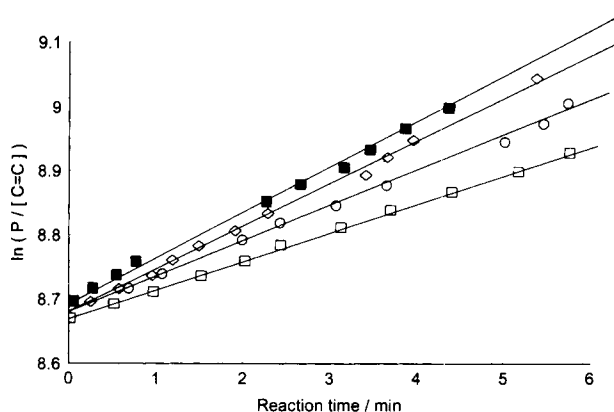
[Ni catalyst] = 7.2 mmol dm<sup>-3</sup>; Al/Ni = 3.0; temperature = 30°C. Rubber used = 1.0001–1.0091 g in 100 mL hexane.



**Figure 4** Plot of initial hydrogen pressure,  $P_0$ , vs.  $k\{[H]_0-[C=C]_0\}$  for the determination of the proportionality constant  $k'$  and the second-order rate constant  $k$ .

of 824.9 kPa and rubber concentration equivalent to 0.142 mol double bond per  $\text{dm}^3$ , the intercepts converge at the same value of  $\ln(824.9/0.1422) = 8.67$ . The catalyst activity appears to be maximum at  $\text{Al/Ni} = 3.0$ .

In other Ziegler-Natta catalysts such as Ti salts in combination with aluminum alkyls, an optimum activity is usually obtained for cocatalyst/catalyst molar ratios in the region of 10–50. The aluminum alkyl could be involved in a number of important functions: alkylation and reduction of the transition metal, dynamic exchange reactions between the transition metal and aluminum ligands, adsorption on the active center, and, finally, scavenger activity for the impurities present in the reaction medium. The correct Al/Ti is needed to reduce the Ti to the right oxidation state so that it became active. However, a greater excess of aluminum alkyl might produce an overreduction of Ti to a valence state which



**Figure 5** Effect of temperature on the rate of hydrogenation.  $[\text{Ni catalyst}] = 7.2 \text{ mmol dm}^{-3}$ ;  $\text{Al/Ni} = 3.0$ ; initial hydrogen pressure 825 kPa; weight of rubber sample 1.00 g; temperatures: (■) 60°C; (◇) 50°C; (○) 42°C; (□) 33°C.

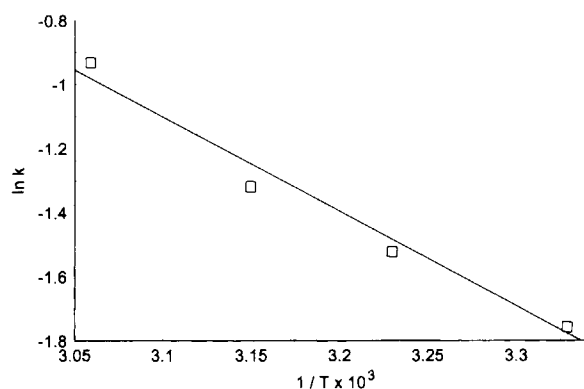
was inactive. Reversible adsorption of the excess cocatalyst on the active center could also reduce the rate of reaction.

In the present case, on addition of the cocatalyst to the nickel 2-ethylhexanoate, there was an instant change in color from green to black. The active species for hydrogenation was formed probably through the reduction of the nickel 2-ethylhexanoate by the triisobutylaluminum. At very low ratios of Al/Ni, the triisobutylaluminum is insufficient to produce the complete reduction of the Ni(II). The maximum number of active species was generated at an Al/Ni ratio of 3.0. At a higher Al/Ni ratio, the excess aluminum alkyl could have interacted with the active species to give an inactive product. In addition, we have noted that the aluminum alkyl concentration above  $0.04 \text{ mol dm}^{-3}$  could cause gelation of the rubber solution and greatly affect the rate of hydrogenation.

**Table III** Effect of Al/Ni Ratio

Al/Ni	Gradient $k\{[H_2]_0-[C=C]_0\}$	Intercept	Rate Constant ( $k/\text{mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ )	Initial Rate $k[H_2]_0[C=C]$ ( $\text{mol dm}^{-3} \text{ min}^{-1}$ )
2.0	0.0652	8.66	0.250	0.0143
2.5	0.0856	8.67	0.327	0.0187
3.0	0.0887	8.67	0.338	0.0194
3.5	0.0711	8.67	0.270	0.0153
4.0	0.0682	8.67	0.259	0.0147
5.0	0.0688	8.70	0.261	0.0147

$[\text{Ni catalyst}] = 7.2 \text{ mmol dm}^{-3}$ ; temperature = 30°C. Rubber used = 1.0022–1.0091 g in 100 mL hexane.



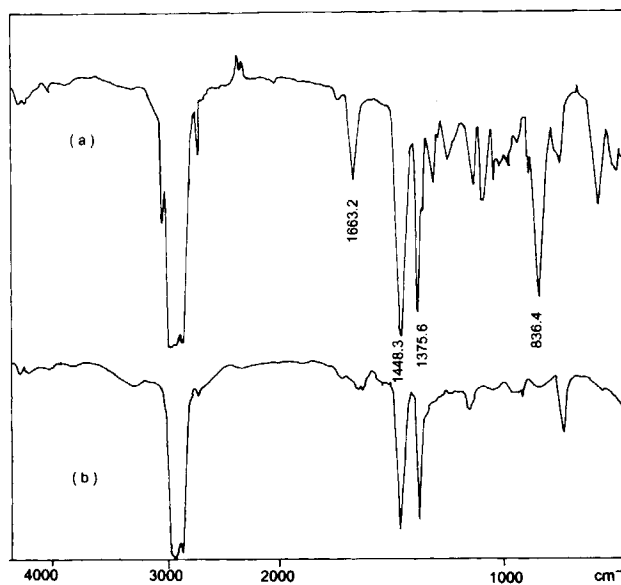
**Figure 6** Arrhenius plot for the determination of apparent activation energy.

### Apparent Activation Energy

The apparent activation energy of the reaction could be determined by carrying out the hydrogenation at different temperatures. The results (Fig. 5) show that the plots have the same intercept when the initial hydrogen pressure and rubber concentration was maintained. Although the rubber solution was prepared at room temperature, the value of  $[C=C]_0$  has not changed significantly in the temperature range of 30–60°C.

The rate constants at the different temperatures were calculated and are shown in Table IV. The Arrhenius plot of  $k$  vs.  $1/T$  is shown in Figure 6. The apparent activation energy of hydrogenation is 26.0  $\text{kJ mol}^{-1}$ . This is generally much lower than the apparent activation energies of the homogeneous  $\text{RhCl}(\text{PPh}_3)_3$  catalyst, which was 102  $\text{kJ/mol}$  for the hydrogenation of polybutadiene in toluene,<sup>17</sup> 74.8  $\text{kJ/mol}$  for the hydrogenation of the styrene-butadiene-styrene triblock copolymer, and 60.8  $\text{kJ/mol}$  for the hydrogenation of the styrene-butadiene diblock copolymer.<sup>18</sup>

The typical FTIR and NMR spectra of the hydrogenated products are shown in Figures 7 and 8, respectively. The most apparent changes in the IR spectra were the reduction in the peaks at 1663 and



**Figure 7** FTIR spectra of (a) 0% and (b) 100% hydrogenated rubber.

836  $\text{cm}^{-1}$  as the extent of hydrogenation of  $C=C$  increased (Fig. 7). The major H-NMR peaks of  $-\text{CH}_3$ ,  $-\text{CH}_2-$ , and  $=\text{CH}$  groups of the rubber before and after 100% hydrogenation are shown in Figure 8. The reaction led to the reduction in the peaks of the isoprene unit of natural rubber at 1.7, 2.2, and 5.2 ppm and the increase in the peaks of the propylene-ethylene block of the hydrogenated product at 0.89 and 1.1–1.3 ppm.

### Effect of Rubber Purity

It should be pointed out that the results discussed above were based on the hydrogenation of purified rubber, as natural rubber from different sources which were processed differently might contain impurities that could affect the performance of the catalyst. One of the readily measurable impurity in natural rubber is the nitrogen content of the sample which reflects the amount of protein and amino acids

**Table IV** Effect of Different Temperature

Temp	Gradient	Intercept	Rate Constant ( $k/\text{mol}^{-1} \text{dm}^3 \text{min}^{-1}$ )	Initial Rate ( $\text{mol dm}^{-3} \text{min}^{-1}$ )
306 K	0.0450	8.67	0.172	0.00983
315 K	0.0568	8.68	0.216	0.01226
323 K	0.0702	8.68	0.267	0.01517
333 K	0.1040	8.68	0.396	0.02243

[Ni catalyst] = 7.2  $\text{mmol dm}^{-3}$ ; Al/Ni = 3.0. Rubber used = 1.0001–1.0091 g in 100 mL hexane.

in the rubber. A series of commercial natural rubbers was hydrogenated under the same conditions, and the rate of reaction was correlated with the nitrogen content determined by a procedure described elsewhere.<sup>16</sup> The results are summarized in Table V.

Overall, the rates of hydrogenation of commercial rubbers were marginally lower than that of the purified rubber. For example, the SMR L which has the highest nitrogen content, which is almost nine times that of the purified rubber, has a rate which is 80% of that of the purified rubber. On the other hand, the commercial DPNR with a nitrogen content of only 2.3 times that of the purified rubber was

**Table V Hydrogenation of Commercial Natural Rubbers—Effect of Nitrogen Content**

Sample	Nitrogen Content (%)	Rate of Hydrogenation $\times 10^2$
Purified rubber	0.040	2.71
DPNR	0.090	2.33
SMR CV	0.302	2.22
SMR L	0.338	2.18

[Ni catalyst] = 7.2 mmol dm<sup>-3</sup>; Al/Ni = 3.0; temperature = 30°C. Rubber used = 1.0001–1.0091 g in 100 mL hexane.

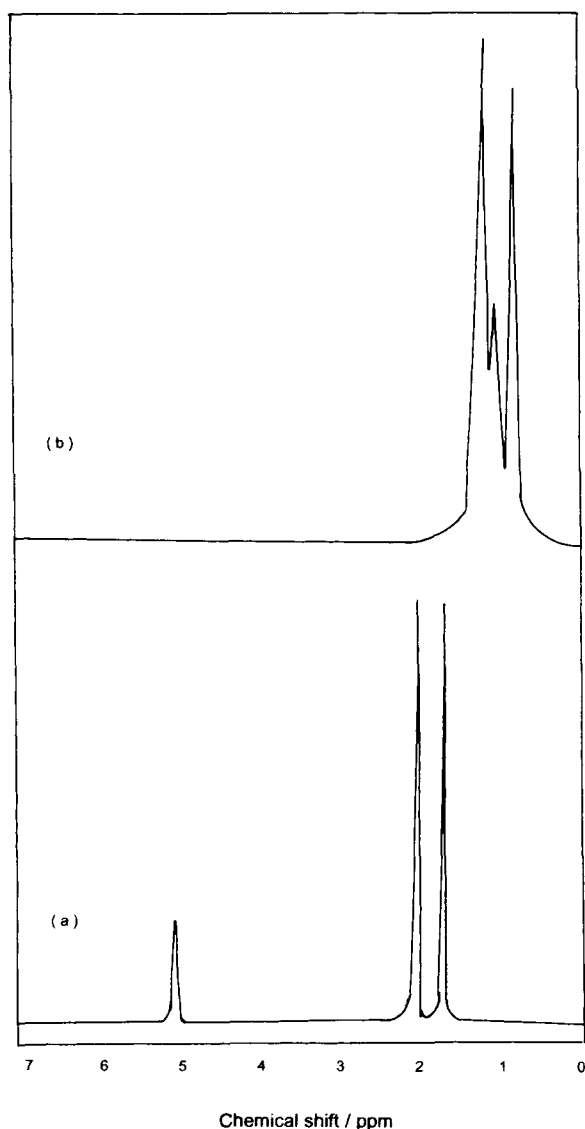
hydrogenated at a rate about 82% of that of the purified rubber.

In conclusion, this article confirms the possibility of solution hydrogenation of natural rubber under mild conditions using nickel 2-ethylhexanoate in combination with triisobutylaluminum. Kinetics studies showed that the reaction is of second order. The highest catalytic activity was attained at a Al/Ni ratio of 3.0. The apparent activation energy was found to be 26.0 kJ/mol. The results also showed that the commercial rubber samples could also be hydrogenated readily, but at a slightly slower rate.

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**Figure 8**  $^1\text{H-NMR}$  spectra of (a) 0% and (b) 100% hydrogenated rubber.

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