CHAPTER 5

HYDROGENATION OF NATURAL RUBBER LATEX
CATALYZED BY Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$

The hydrogenation of elastomers in latex form would be of great interest and significant since many diene based polymers are produced in the latex form especially natural rubber. By applying the hydrogenation process to a polymer emulsion, the typical procedures for the polymer hydrogenation, such as the precipitation of polymer from its emulsion, the subsequent drying process, and the redissolution of the polymer into an organic solvent for the hydrogenation, can be avoided. This would represent economic and environmental advantages for the production of hydrogenated polymers.

The hydrogenation of NBR latex catalyzed by the water soluble complex, RhCl (DPM)$_3$ (DPM = diphenyl phosphino benzene m-sulphonate) provided about 60% hydrogenation at 75°C and atmospheric hydrogen pressure(Singha and Sivaram, 1995). Hydrogenation of PBD, SBR and NBR in aqueous/organic biphasic media using water soluble catalyst, [RhCl(HEXNa)$_2$]$_2$ (HEXNa =Ph$_2$P-(CH$_2$)$_5$-CO$_2$Na) was studied at 100°C and 5.5 MPa H$_2$ (Mudalige and Rempel, 1997). The rhodium complex showed a reasonable activity and enhanced selectivity for hydrogenation of 1,2 addition units over the 1,4 units in all polymers studied. Recently, Leube et al. (2002) revealed the selectively hydrogenation of unsaturated double bonds in polymer in the presence of rhodium and/or ruthenium compounds or their salts as catalysts at 150°C and 100 bar. NBR emulsion was hydrogenated in methyl ethyl ketone (MEK) with Ru based catalysts at 100 - 200°C and 2.5 - 10.0 MPa H$_2$ (Rempel and Guo, 1993). The results showed that addition of organic additives can minimize the gel formation during the NBR hydrogenation using Ru catalyst. Although there have been a number of studies on the hydrogenation of polymer in emulsion form using water soluble catalysts or oil soluble catalysts, there have been no reports on the kinetic of such a polymer hydrogenation processes.

In this chapter an attempt is made to provide insight into NR latex hydrogenation from an investigation of the kinetic reaction and the chemistry involved in this important process. The present work was focused on determining the

optimal conditions for the hydrogenation of natural rubber latex in terms of factors such as catalyst loading, double bond concentration, acid concentration, hydrogen pressure and temperature.

5.1   FTIR and NMR Spectroscopic Characterization

Figure 5.1 illustrates the IR spectra of both NR latex (NRL) and 90% hydrogenated NR latex (HNRL). The nonhydrogenated latex spectrum shows distinct peaks for the C=C unsaturation, i.e. at 1663 (C=C stretching) and 836 cm^{-1} (trisubstituted olefinic C-H bending). It can be noted that the transmittance peaks for the C=C unsaturation decrease after the hydrogenation.

^{1}H-NMR spectra for the nonhydrogenated NR latex and 93% hydrogenated NR latex are provided in Figure 5.2. Major peaks are obtained in the aliphatic (1.7 and 2.2 ppm) regions. The signals of *cis* olefinic protons are centered at 5.2 ppm. As the hydrogenation progresses, the olefinic peak area decreases considerably, and new peaks appear at $\delta = 0.8 - 1.8$ ppm attributed to $-CH_3$ and saturated $-CH_2-$ units. The extent of hydrogenation has been calculated from ^{1}H-NMR spectra from the change in the integral of the peaks representing protons in hydrogenated rubber latex.
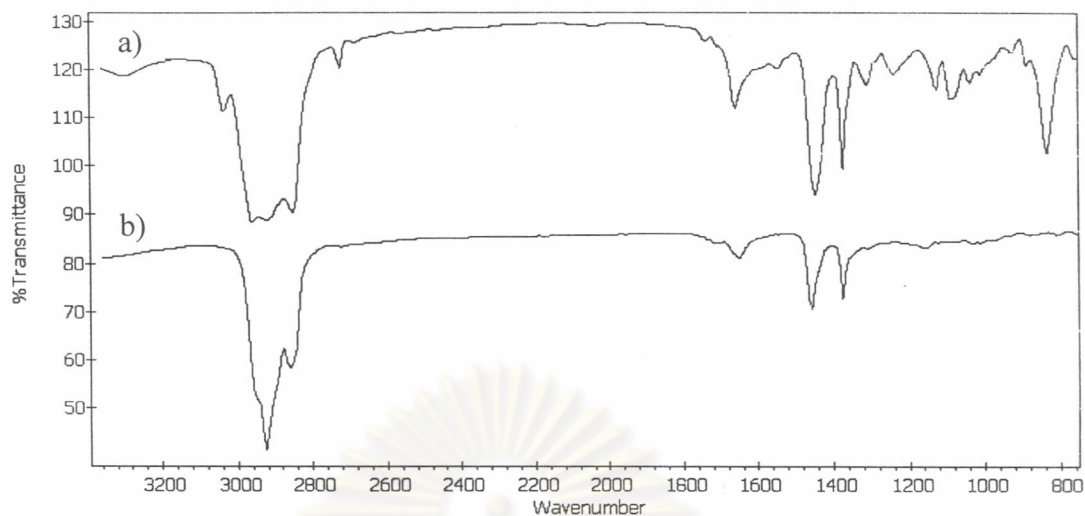
Figure 5.1: FTIR spectra of (a) NRL, (b) HNRL (90% hydrogenation),
[Ru] = 300 μM; [C=C] = 130 mM; P_{H2} = 40.3 bar; T = 140°C; [*p*-TsOH] = 44
equiv.
[*p*-TsOH] is defined as [acid]/[Ru]
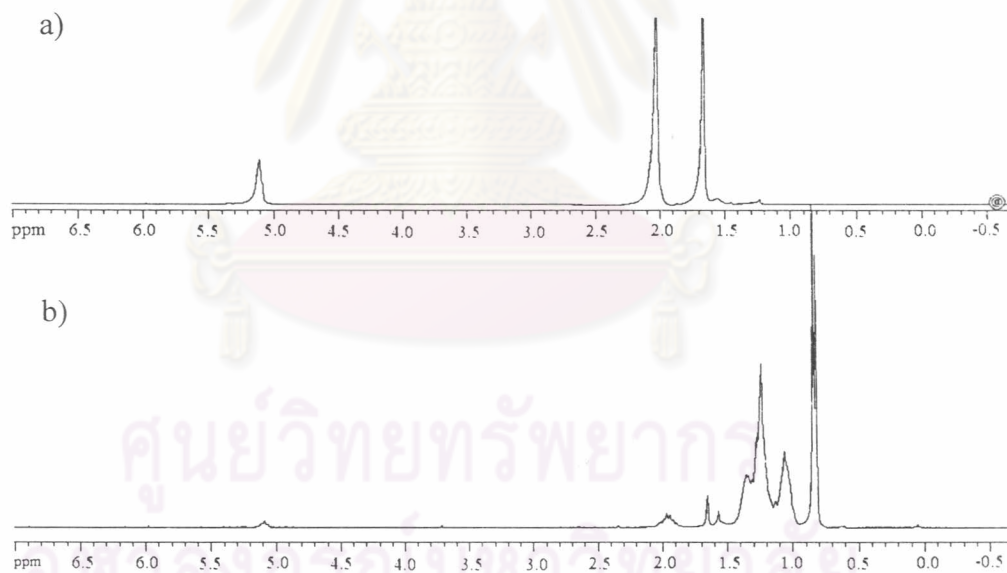
Figure 5.2: ^{1}H-NMR spectra of a) NRL b) HNRL (93% hydrogenation),
T = 140°C, P_{H2} = 40.3 bar, [C=C] = 130 mM; [Ru] = 200 μM; [*p*-TsOH] = 44
equiv.

5.2 Initial Studies of Natural Rubber Latex Hydrogenation in Various Solvents

In an attempt to gain insight into the effect of solvent on the hydrogenation of the NRL system, two different types of solvents were used i.e. tetrahydrofuran (THF) and monochlorobenzene (MCB). THF may be a good solvent for homogeneous catalytic hydrogenation of latex, being miscible with the emulsion phase and capable of dissolving the polymer and catalyst. THF can destroy the surface interaction of the polymer particles in the emulsion and dissolve the polymer particle into the resulting solvent-latex mixture. MCB involves a heterogeneous catalytic system for latex hydrogenation, since MCB is not miscible with the emulsion phase. The organic solvent can only swell the polymer particles in the emulsion; however, this solvent is capable of dissolving the catalyst. In both reaction systems, certain additives i.e. p-toluenesulfonic acid (p-TsOH) were added in order to improve the activities of Ru catalysts. The effect of polymer concentration, catalyst concentration, additive loading, temperature, and hydrogen pressure were investigated and listed in Table 5.1. The results show that the homogeneous hydrogenation system yielded a much slower rate than the heterogeneous reaction system for the conditions used. The effect of polymer concentration showed that the hydrogenation rate is reduced significantly by increasing the polymer loading. This may be due to the poisoning effect of the NR latex such as water, protein, or lipids, etc. From our previous studies, the addition of acid played an important role for the reduction of the poisonous effect in NR (Section 4.3). It is also effective for the hydrogenation of NR in the latex stage. Since it is evident from that the results increasing p-TsOH loading by about 50% increased the degree of hydrogenation from 17% to 43% for THF and from 27% to 97% for MCB. This is consistent with the observations of Guo and Rempel (1997) for NBR emulsion hydrogenation in the presence of a small amount of added carboxylic acid. Moreover, the optimum amount of acid addition depends on the concentration of catalyst. The results show that the degree of hydrogenation increased from 17% to 39% for THF and from 27% to 99% for MCB when the Ru concentration was increased from 200 μM to 300 μM. It is interesting that increasing the temperature from 140°C to 160°C seems to reduce the hydrogenation rate. Degradation of polymer particles in the system due to the higher temperature used may explain these results. The influence of high hydrogen pressure was found to increase the degree of hydrogenation.

From these initial experimental results, the heterogeneous catalytic hydrogenation system, which used MCB as solvent, was selected a detailed kinetic study of the hydrogenation of natural rubber latex (60% dry rubber content).

Table 5.1: Initial Studies of Hydrogenation of Natural Rubber Latex Catalyzed by Ru(CH=CH)(Ph)Cl(CO)(PCy₃)₂.

Entry	Solvent	$[C=C]_0$ (mM)	[Ru] (μM)	[p-TsOH] (equiv)[b]	Temp (°C)	P_{H2}[a] (bar)	% Hydrogenation
1	THF	130[c]	200	44	160	40.3	82.3
2	THF	260[d]	200	44	160	40.3	16.7
3	THF	260[d]	300	44	160	40.3	39.0
4	THF	260[d]	200	66	160	40.3	42.9
5	THF	260[d]	200	44	140	40.3	20.0
6	THF	260[d]	200	44	160	54.1	24.8
7	MCB	130[c]	200	44	160	40.3	100.0
8	MCB	260[d]	200	44	160	40.3	26.5
9	MCB	260[d]	300	44	160	40.3	99.1
10	MCB	260[d]	200	66	160	40.3	96.7
11	MCB	260[d]	200	44	140	40.3	60.0
12	MCB	260[d]	200	44	160	54.1	49.5

Condition: reaction time 4 hours, Total volume = 150 ml
[a] Partial pressure of H_2.
[b] [p-TsOH]/[Ru]
[c] Latex volume = 2.7 ml.
[d] Latex volume = 5.4 ml
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5.3 Kinetics of NRL Hydrogenation using Ru(CH=CH(Ph))Cl(CO)(PCy₃)₂

Over the range of process conditions studied Ru(CH=CH(Ph))Cl(CO)(PCy₃)₂ functioned as a promising catalyst system for the quantitative hydrogenation of natural rubber latex as well as for CPIP and NR. A representative hydrogenation uptake profile corresponding to the saturation of olefin is presented in Figure 5.3. The conversion profile is represented by a simple first order with respect to olefin as shown in Equation 5.1.
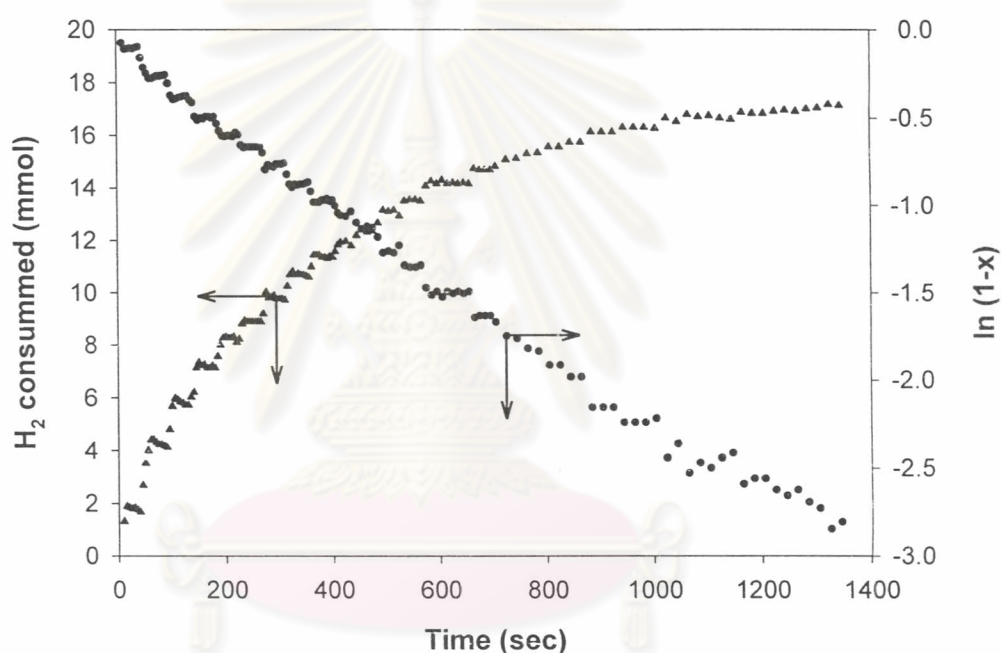
Figure 5.3: Hydrogen consumption plot for NRL hydrogenation, [Ru] = 200 μM; [C=C] = 130 mM; [p-TsOH] = 44 equiv; P$_{H2}$ = 40.3 bar; T = 140°C; Latex volume = 2.7 ml; Total volume = 150 ml, Solvent = MCB.

$$\frac{-d[C=C]}{dt} = k'[C=C] \tag{5.1}$$

Regression estimates of k′, the pseudo-first order rate constant, summarize the essential information regarding the hydrogenation rate. A summary of results, for a series of experiments, showing the effect of hydrogenation variables on the rate constant is provided in Table 5.2.

Table 5.2: Summary of Kinetic Data from the Study of NRL Hydrogenation Catalyzed by Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$

Expt.	[C=C][a] (mM)	[Ru] (μM)	[p-TsOH][c] (equiv)	P$_{H2}$[c] (bar)	Temp (°C)	k'x10^3 (s^{-1})	Hydrogenation %	Time (h)
1	130[b]	200	44	12.8	140	1.07	58.7	0.46
2	130	200	44	26.6	140	1.79	91.1	0.37
3	130	200	44	40.3	140	2.52	91.1	0.33
4	130	200	44	54.1	140	3.63	97.0	0.30
5	130	200	44	40.3	100	0.86	94.7	0.72
6	130	200	44	40.3	120	1.73	96.7	0.52
7	130	200	44	40.3	160	3.21	93.7	0.28
8	100[d]	200	44	40.3	140	5.87	93.8	0.20
9	160	200	44	40.3	140	0.31	52.8	0.86
10	180	200	44	40.3	140	0.00	0.0	0.36
11	190	200	44	40.3	140	0.00	0.0	0.28
12	130	200	22	40.3	140	0.16	12.3	0.23
13	130	200	66[d]	40.3	140	3.21	99.0	0.28
14	130	100	44	40.3	140	0.00	0.0	0.17
15	130	150	44	40.3	140	0.00	0.0	0.18
16	130	170	44	40.3	140	1.10	47.9	0.22
17	130	250[d]	44	40.3	140	4.16	98.5	0.31
18	130	300[d]	44	40.3	140	4.68	89.9	0.16

[a] NRL contains 60% dry rubber content, [b] latex volume = 2.7 ml, [c] partial pressure of H$_2$, [d] gel observation in hydrogenated product, Solvent = chlorobenzene, Total volume = 150 ml.

5.3.1 Effect of the Ruthenium Concentration

In order to investigate the effect of catalyst loading on the initial rate of hydrogenation, a series of hydrogenation experiments in which the ruthenium concentration was varied over the range of $100 - 300$ μM were carried out in 150 ml of chlorobenzene. The results shown in Figure 5.4 suggest that the hydrogenation reaction occurs when the concentration of Ru catalyst is over 150 μM. It is suspected that some of the additive and the large amount of water in the NR latex could have a poisonous effect on the hydrogenation catalysts. The reaction is likely first order with respect to the total [Ru] below 250 μM catalyst concentration. Above this, the rate tends to a zero order dependence on $[Ru]_T$. At high concentration of catalyst, gel in polymer product was observed. The shift in $[Ru]_T$ order can be explained on the basis that the ruthenium catalyst may be entrapped in the gel phase.

A comparison of the hydrogenation rate of NR with NRL at 130 mM of [C=C] is illustrated in Figure 5.4. For the hydrogenation of NR a smaller amount of catalyst is sacrificed with the impurities in the natural polymer than for the reaction of NR emulsion. At the 200 μM of [Ru], the reaction rate of NRL is faster than that of NR although the temperature of NR hydrogenation used is higher than that of NRL reaction. This may be due to the greater amount of acid addition in the NRL hydrogenation.

5.3.2 Effect of Hydrogen Pressure

The dependence of the initial hydrogenation rate on the hydrogen pressure was studied over the range of $12.8 - 54.1$ bar at 140°C in 150 ml chlorobenzene. The initial concentration of C=C was 130 mM, concentration of catalyst was 200 mM and [p-TsOH]/[Ru] was 44. Under these conditions a plot of initial hydrogenation rate versus hydrogen pressure is fairly linear as shown in Figure 5.5. It can be concluded from this plot that the reaction is first order with respect to hydrogen concentration. This first order behavior implied that a single mechanistic pathway is probably involved in the reaction of the polymer with hydrogen as was the case for NR hydrogenation (Section 4.4.2). Otherwise, it might be expected that the relative contribution of each pathway would change as the hydrogen pressure changed, and then the dependence would deviate from the first order behavior.
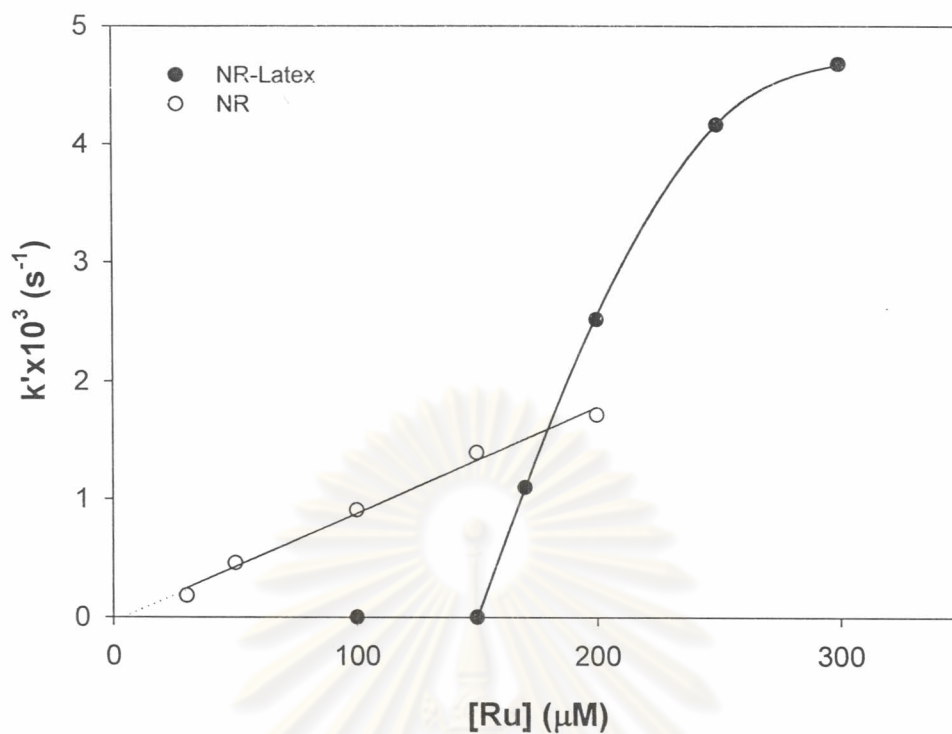
Figure 5.4: Effect of [Ru] on rate constant,
For NRL: [C=C] = 130 mM; P_{H2} = 40.3 bar; T = 140°C; [p-TsOH] = 44 equiv.
For NR: [C=C] = 130 mM; P_{H2} = 40.3 bar; T = 160°C; [p-TsOH] = 8.8 equiv.
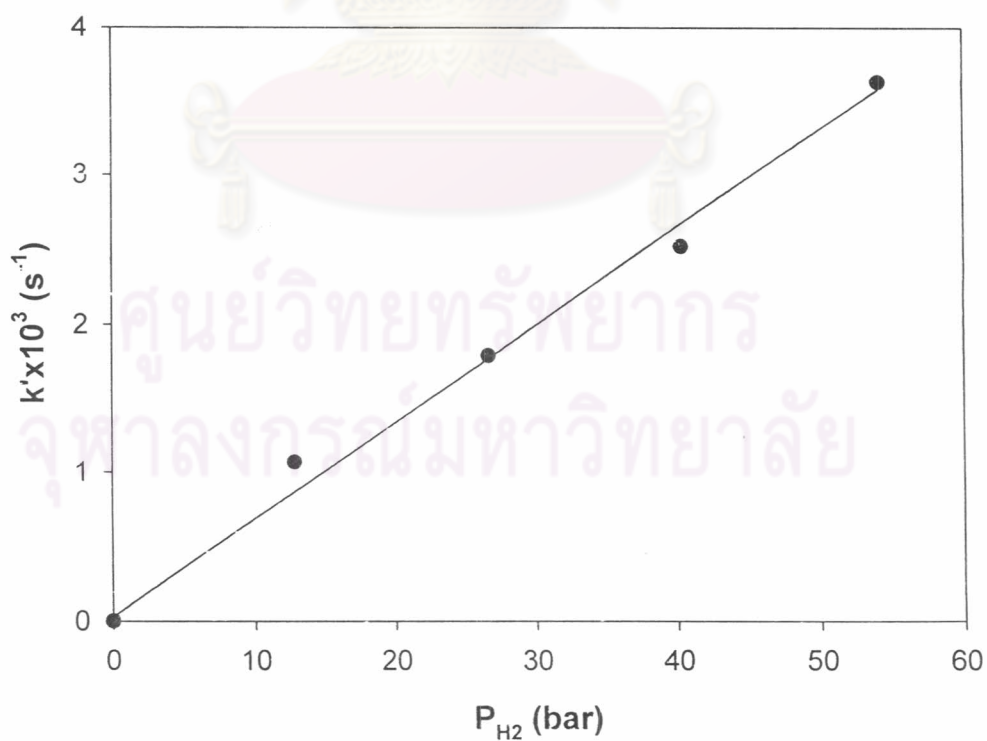
Figure 5.5: Effect of P_{H2} on the rate constant,
[C=C] = 130 mM; [Ru] = 200 μM; T = 140°C; [p-TsOH] = 44 equiv.

5.3.3 Effect of Double Bond Concentration

The range of polymer loadings used in the present study was between 100 - 190 mM (1.7 - 3.2 g in 150 ml). In experiments with varying catalyst concentration all other variables were kept constant. Conversion profiles for latex hydrogenation that exhibit a first order dependence on concentration of unsaturated carbon-carbon double bonds are independent of the amount of olefin charged to the reactor by definition. Thus, the activity of catalyst is expected to be unaffected by the amount of olefin. The hydrogenation of CPIP showed independence on the hydrogenation rate constant on [C=C] in the polymer (Section 3.3.4). However, for the case of NR latex hydrogenation a lower hydrogenation activity was observed as the concentration of NRL was increased (Figure 5.6). This behavior was also observed for hydrogenation of NR (Section 4.4.3) and hydrogenation of NBR emulsion (Guo and Rempel, 1997). No hydrogenation was observed for concentration of latex over 160 mM. A comparison for the reaction rate constant versus [C=C] of NR with NRL hydrogenation was provided in Figure 5.6. The reaction rate of NR hydrogenation is faster than that of NRL at the same concentration of carbon-carbon double bonds. This evidence confirms that the non-rubber constituents in the NR latex such as proteins, carbohydrates, etc. reduced the reactivity of Ru catalyst. Similar results of the effect of polymer concentration on the heterogeneous catalytic hydrogenation of NBR emulsion were observed (Guo and Rempel, 1997). In this case some polymer precipitated out from the solution at high polymer concentration due to the reduction of solubility of the hydrogenated product in the presence of water.
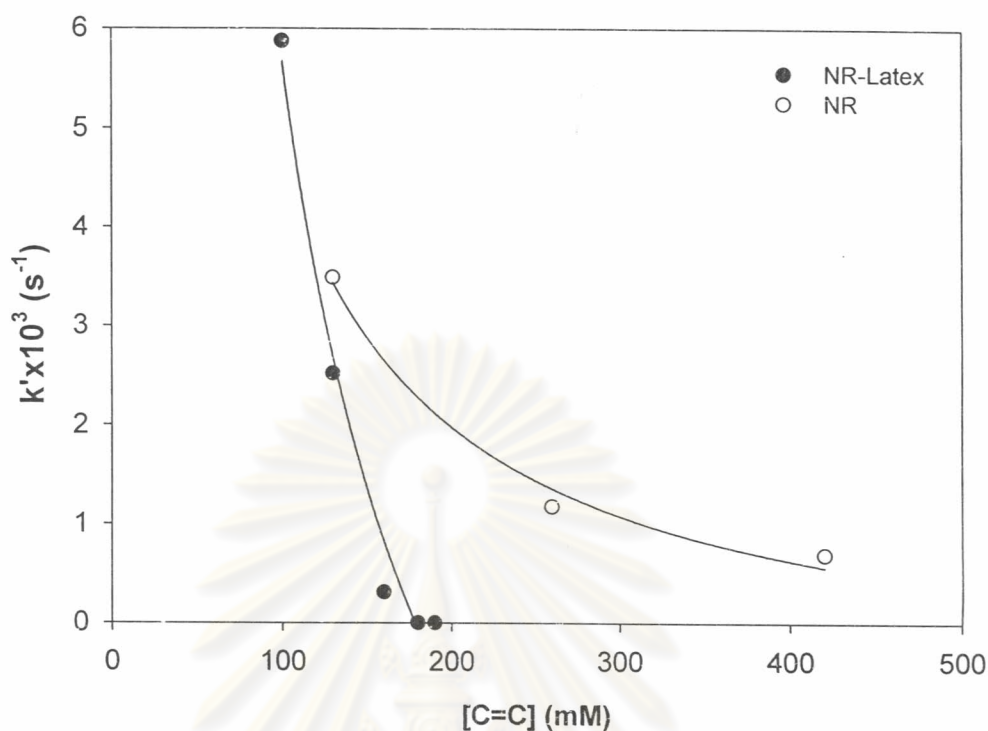
Figure 5.6: Effect of [C=C] on the rate constant,
For NRL: [Ru] = 200 μM; P_{H2} = 40.3 bar; T = 140°C; [p-TsOH] = 44 equiv.
For NR: [Ru] = 200 μM; P_{H2} = 40.3 bar; T = 160°C; [p-TsOH] = 8.8 equiv.

5.3.4 Effect of Temperature

Experiments were carried out from 100 – 160°C. The effects of temperature listed in Table 5.2 showed that the the hydrogenation rate increase with increasing temperature. This is in contrast to behavior observed on initial studies (Section 5.2) at temperature 140 – 160°C where the degree of hydrogenation decreased with increasing temperature. The reaction time for NRL hydrogenation of the initial studies (4 hours) is longer than that of kinetic studies in gas uptake apparatus (by about 30 minutes). Possibly the presence of latex at high temperature for a longer time would cause chain scission, which is a side reaction in the polymer hydrogenation.

The Arrhenius plot provided in Figure 5.7 illustrates the influence of temperature on the hydrogenation rate. The apparent activation energy is 29.2 kJ/mol. This is similar to a value of 25.3 kL/mol for NR hydrogenation (Section 4.4.5).
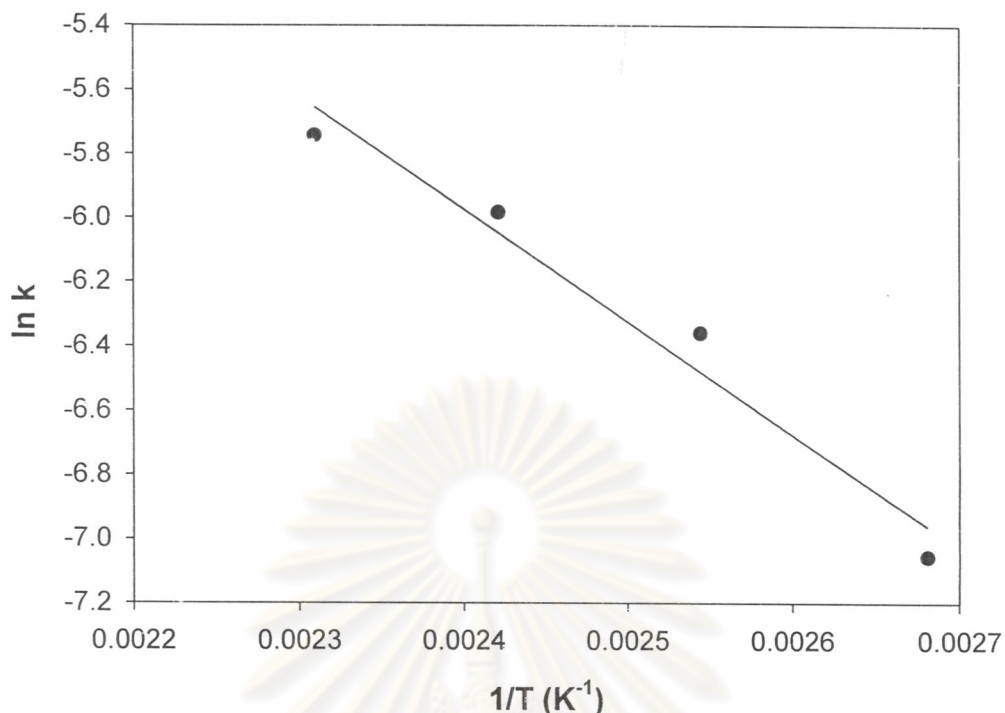
Figure 5.7: Arrhenius plot for NRL hydrogenation,
[C=C] = 130 mM; P_{H2} = 40.3 bar; [Ru] = 200 μM; [*p*-TsOH] = 44 equiv.

5.3.5 Effect of Acid Concentration

Our previous studies on NR hydrogenation showed that the addition of a small amount of acid increased the reactivity of the Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$ catalyst (Section 4.4.6). This method was also applied in hydrogenation of NRL in an attempt to neutralize the poisons present in the emulsion system. The results were summarized in Table 5.2 and Figure 5.8. The hydrogenation of NRL was observed when the reaction was carried out by using the number of moles of *p*-TsOH of more than 20 times the number of moles of the ruthenium catalyst. The amount of acid used in the hydrogenation of NRL is greater than that of NR. The increase in acid concentration resulted in improving the hydrogenation rate. The gel formation was noticed if the molar ratio of acid to polymer was more than 7:100. In contrast, the adding of special additives such as citric acid, succinic acid, etc. suppressed the formation of crosslinked polymers in the hydrogenation of NBR emulsion catalyzed by this ruthenium catalyst (Rempel and Guo; 1993).
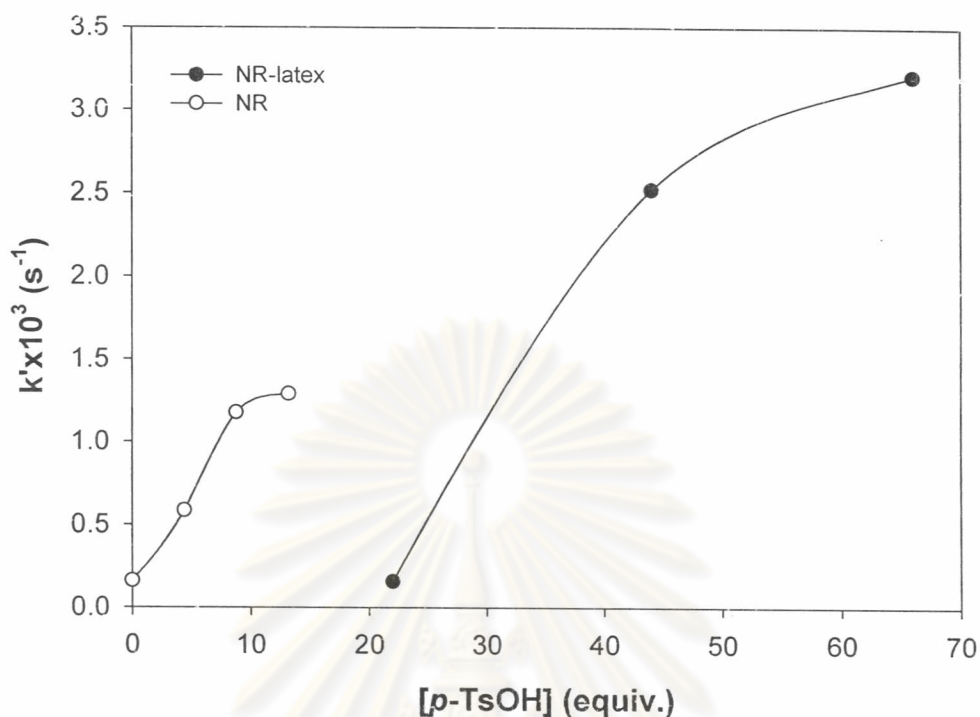
Figure 5.8: Effect of [*p*-TsOH] on the rate constant,
[C=C] = 130 mM; [Ru] = 200 μM; P_{H2} = 40.3 bar; T = 140°C.

5.4 Mechanistic Considerations

In monochlorobenzene, Ru(CH=CH(Ph))Cl(CO)(PCy$_3$)$_2$ is an efficient catalyst precursor for the hydrogenation of unsaturated double bonds within NR latex. An experimental rate law based on the kinetic results showed a first order dependence on the [Ru], [C=C] and hydrogen pressure over the range of studies. The presence of impurities in the latex rubber reduces the catalyst activity. These results show similarities to the NR hydrogenation catalyzed by this ruthenium catalyst. Therefore, it is expected that the mechanism of NR latex is probably quite similar to the NR mechanism (Section 4.6).