sumption of IPO by the various side reactions.

Bulk polymerization of IPOEDT adduct in the absence of the radical inhibitor BHA leads to cross-linking as detected by the formation of insoluble polymer. The obvious route to cross-linking is the polymerization of olefinic end groups and/or their copolymerization with IPO. The presence of BHA prevented cross-linking at all temperatures except 200 °C. Cross-linking did not occur in solution polymerization even in the absence of BHA.

The IPOH_2S system differs from the IPOEDT system in some quantitative aspects. Decomposition of the adduct is more extensive for IPOH_2S, occurring at all reaction temperatures. The elimination reaction is also more extensive for the IPOH_2S system. The greater volatility of H_2S relative to EDT is probably responsible for the greater extent of elimination and adduct decomposition. Liberated H_2S adds to oxazoline end grups to yield more thiol end groups than oxazoline end groups for solution polymerization at 160 °C. The thiol end groups are not detected due to their facile elimination to olefinic end groups. One observes the ratio of olefinic to oxazoline end groups to be greater than one. The outcome is somewhat different for bulk polymerizations. H_2S escapes the reaction system while the less volatile IPO remains and adds to thiol end groups. Oxazoline end groups constitute the major end groups at 100–120 °C. At higher reaction temperatures (140–160 °C), elimination of thiol end groups is favored over their reaction with IPO and the result is comparable amounts of oxazoline and olefinic end groups.

Small amounts of CH_2OH groups, identified in both the IPOEDT and IPOH_2S polymers, are most likely formed by the reaction of oxazoline end groups with trace amounts of water present in the reaction mixture. The mechanism for forming CSSH groups, found in minor amounts in the IPOH_2S polymer, is unclear.

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Registry No. IIIa, 32154-11-3; IIIa (homopolymer), 32070-33-0; IVa, 29920-38-5; IVa (homopolymer), 32070-18-1; Va, 28212-99-9; VIa, 110143-72-1; BHA, 489-01-0.

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Homogeneous Selective Catalytic Hydrogenation of C=C in Acrylonitrile–Butadiene Copolymer

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ABSTRACT: The chemical modification of unsaturated polymers via catalytic hydrogenation offers a potentially useful method for altering and optimizing the physical and mechanical properties of macromolecules. A study involving the hydrogenation of an acrylonitrile–butadiene copolymer has been carried out in the presence of $RhCl(P(C_6H_5)_3)_3$ which under mild reaction conditions provides quantitative hydrogenation of carbon–carbon unsaturation without any hydrogenation of the nitrile functionality. The selectivity of the catalyst for terminal versus internal double bonds present in the polymer is markedly influenced by the nature of the solvent media. In order to appreciate the important factors which influence the nature and extent of this reaction, a detailed kinetic study has been carried out under experimental conditions where the reaction is chemically controlled. The reaction kinetics exhibit unusual effects on substrate dependence and hydrogen dependence as well as solvent media. The kinetic results and spectral observations are consistent with a mechanism in which the active catalyst $RhClH_2(P(C_6H_5)_3)_2$ interacts with the carbon–carbon unsaturation within the copolymer in a rate-determining step. The nitrile functionality present in the copolymer also interacts with the active catalyst and inhibits the rate of hydrogenation.

Introduction

The development of new specialty polymers, from diene-based elastomers, with improved performance characteristics is of great importance in a number of product applications. This is primarily a result of the fact that the conditions to which well-established synthetic elastomers are currently being subjected to in the oil, nuclear power, and automotive industries have become much more severe in recent years.[1,2]

The chemical modification of unsaturated polymers via catalytic hydrogenation offers a potentially useful method for altering and optimizing the physical and mechanical properties of macromolecules. One of the major problems encountered, however, in such hydrogenation processes

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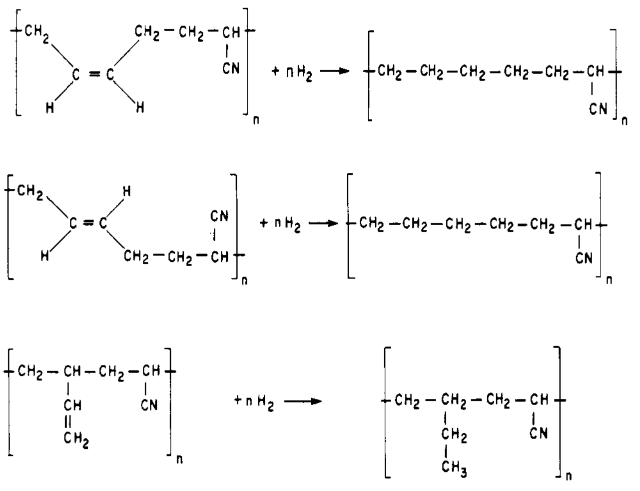


Figure 1. Acrylonitrile–butadiene copolymer hydrogenation reaction.

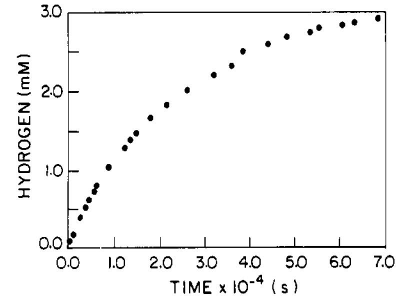


Figure 2. Representative hydrogen consumption plot for the hydrogenation of an acrylonitrile–butadiene copolymer: $[C{=}C]_0$ = 303 mM; $[Rh]_{total}$ = 1.958 mM; temperature = 40 °C; 2-butanone = 10 mL; $[H_2]$ = mM.

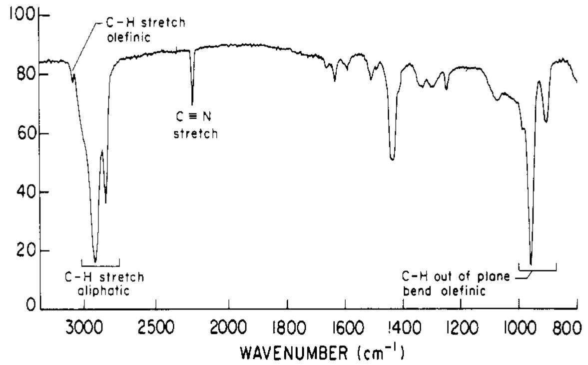


Figure 3. Infrared spectrum of acrylonitrile–butadiene copolymer (polymer film on NaCl plate).

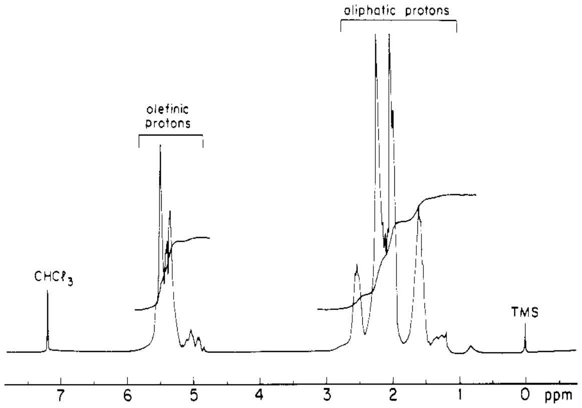


Figure 4. Nuclear magnetic resonance (^1H) spectrum of acrylonitrile–butadiene copolymer (polymer solution in chloroform-d_1).

involves the activity and selectivity offered by the catalyst for removing carbon–carbon unsaturation in the presence of other potentially reducible functional groups also present in the parent material. Although a variety of homogeneous organometallic catalysts have been reported to offer selectivity for various functional monomeric olefins, reports on their utilization for polymer hydrogenation are indeed scarce. The well-known homogeneous hydrogenation catalyst $RhCl(P(C_6H_5)_3)_3$ has however recently received some attention in this regard.[3,4]

Acrylonitrile–butadiene copolymers are reported[4] to undergo selective quantitative C=C hydrogenation without C≡N reduction in the presence of $RhCl(P(C_6H_5)_3)_3$ to provide polymeric materials with greatly improved performance characteristics. There have been no reports however on the kinetic and mechanistic aspects of such polymer hydrogenation processes. This paper attempts to provide some insight into the reaction details and the chemistry involved in this important process.

Experimental Section

$RhCl(P(C_6H_5)_3)_3$ was prepared from commercially available rhodium trichloride trihydrate (Engelhard Industries Ltd.) according to a procedure based on that given by Wilkinson and co-workers.[5]

Reagent grade chemicals and solvents were used throughout. Solvents used in the kinetic experiments were freshly distilled before use.

The acrylonitrile–butadiene copolymer used in this investigation which contained 34% acrylonitrile content was obtained from Polysar Ltd. (Sarnia, Ontario, Canada). The copolymer was used as received without purification.

UV–visible spectra were recorded on a Varian-Cary 219 spectrophotometer. GLC analysis was carried out by using a Perkin-Elmer Sigma 2000 chromatograph equipped with a flame ionization detector. Separations were accomplished with a Porapak Q, 6 ft × 0.125 in. o.d. S.S. column supplied by Chromatographic Specialties Ltd. Infrared measurements were carried out with a Perkin-Elmer 1330 infrared spectrophotometer. NMR spectra were obtained by using a Bruker 250-MHz NMR spectrophotometer. Kinetic measurements were made by following the consumption of hydrogen at constant pressure using a computer-controlled batch reactor described earlier.[6] The solubility of hydrogen in 2-butanone was determined, using the Perkin-Elmer Sigma 2000 chromatograph equipped with a hot wire detector, as 3.25×10^{-3} mol/L at a total pressure of 101.32 kPa and 25 °C, Henry's law being obeyed at least up to 1 atm.

Results and Discussion

Stoichiometry of Copolymer Hydrogenation. Under mild reaction conditions (<101.32 kPa hydrogen pressure, 20–50 °C), $RhCl(P(C_6H_5)_3)_3$ functions as an efficient catalyst in 2-butanone for the hydrogenation of the carbon–carbon unsaturation present in acrylonitrile–butadiene copolymers. Since the copolymer contains both internal and terminal carbon–carbon unsaturation, the three distinct hydrogenation reactions shown in Figure 1 are required for complete hydrogenation of the carbon–carbon unsaturation in the copolymer. Hydrogen consumption ceases at an amount equal to that required for complete hydrogenation of the carbon–carbon double bonds present in the copolymer and the formation of a dihydride rhodium species, $H_2RhCl(P(C_6H_5)_3)_3$. In the absence of the copolymer substrate, $RhCl(P(C_6H_5)_3)_3$ in 2-butanone takes up 1 mol of hydrogen/mol of $RhCl(P(C_6H_5)_3)_3$ present. Under the reaction conditions employed in this investigation for copolymer hydrogenation, no reduction of the keto group of the 2-butanone solvent is observed. This was confirmed by carrying out a hydrogenation run in the absence of the copolymer.

A representative hydrogen consumption plot for the hydrogenation of the copolymer in 2-butanone is shown in Figure 2. These results indicate that the catalyst system

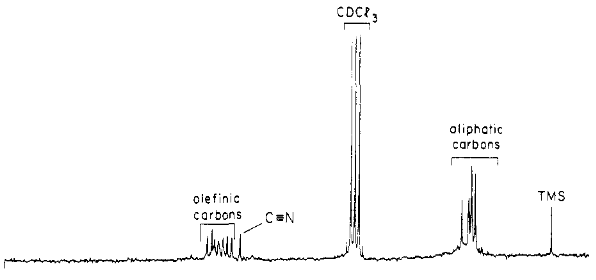


Figure 5. Nuclear magnetic resonance (^{13}C) spectrum of acrylonitrile-butadiene copolymer (polymer solution in chloroform-d_1 (with TMS as reference)).

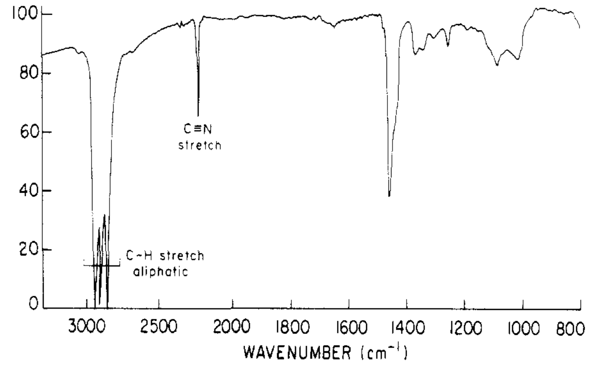


Figure 6. Infrared spectrum of hydrogenated acrylonitrile–butadiene copolymer (polymer film on NaCl plate).

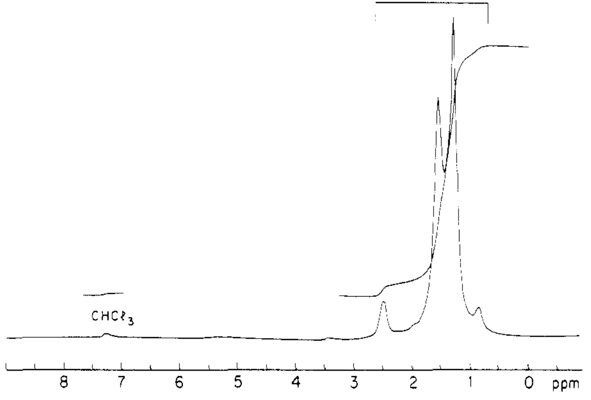


Figure 7. Nuclear magnetic resonance (^{1}H) spectrum of hydrogenated acrylonitrile–butadiene copolymer (polymer solution in chloroform-d_1).

in 2-butanone does not exhibit selectivity for the hydrogenation of terminal over internal carbon–carbon double bonds present in the copolymer. After completion of the hydrogenation reaction, the hydrogenated copolymer obtained was analyzed by IR and NMR spectroscopy. The IR and ^{1}H and ^{13}C NMR spectra are shown for the original copolymer in Figures 3, 4, and 5, respectively, and for the hydrogenated copolymer in Figures 6, 7, and 8, respectively. Upon termination of the hydrogen consumption, no residual carbon–carbon double-bond unsaturation remains and the IR and ^{13}C NMR spectra indicate no hydrogenation of the nitrile group present in the copolymer. When the copolymer was fully hydrogenated, the catalyst still retained its activity for the hydrogenation of additional copolymer added in the form of a 2-butanone solution.

The results are of particular interest in view of the earlier report of Oppelt et al.[3] in which only partial hydrogenation of the trans configuration of the double bonds was claimed when 2-butanone was employed as the reaction solvent. It is likely that quantitative hydrogenation was not observed in this earlier work due to catalyst deactivation by impurities in the ketone solvent.

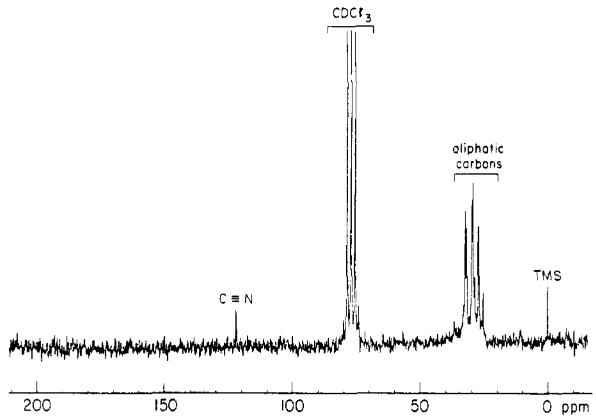


Figure 8. Nuclear magnetic resonance (^{13}C) spectrum of hydrogenated acrylonitrile–butadiene copolymer (polymer solution in chloroform-d_1 (with TMS as reference)).

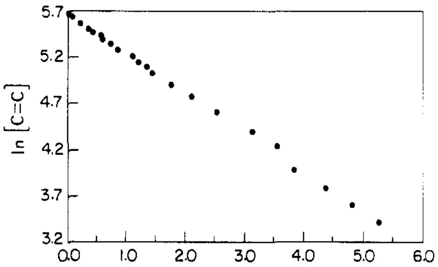


Figure 9. Logarithmic plot of ln [C=C] vs. time for the hydrogenation of copolymer: $[C{=}C]_0$ = 303 mM; $[Rh]_{total}$ = 1.958 mM; temperature = 40 °C; 2-butanone = 10 mL, $[H_2]$ = 0.445 mM.

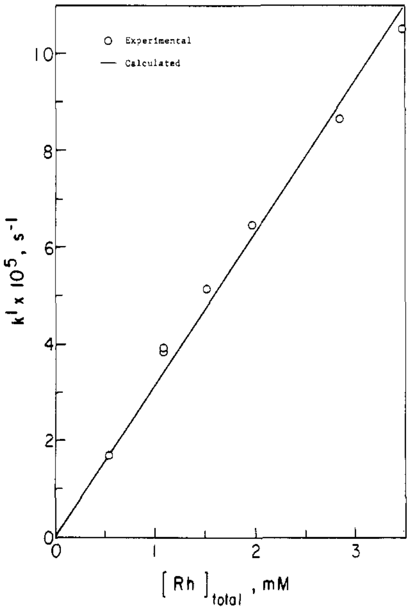


Figure 10. Effect of catalyst concentration on the rate of acrylonitrile–butadiene copolymer hydrogenation: $[C{=}C]_0$ = 303 mM; $[H_2]$ = 3.14 mM; temperature = 40 °C; 2-butanone = 10 mL.

Kinetics of Copolymer Hydrogenation. Detailed kinetics of the hydrogenation of the acrylonitrile–butadiene copolymer (34% acrylonitrile content) in the presence of the homogeneous hydrogenation catalyst $RhCl(P(C_6H_5)_3)_3$ were investigated in 2-butanone by using a computer-controlled constant pressure batch reactor.[6] A representative hydrogen consumption plot for the hydrogenation of the copolymer is shown in Figure 2. Such uptake

Table I
Summary of Kinetic Data[a]

[Rh], mM	[H_2], mM	[C=C]$_0$, mM	[CN], mM	[$P(C_6H_5)_3$] added, mM	$10^5k'$(expt), L/s	$10^5k'$(pred), L/s	$10^6(k' - k'')$, L/s
0.541	3.142	303.0	173.0	0.000	1.678	1.709	−0.315
1.082	3.142	303.0	173.0	0.000	3.856	3.419	4.369
1.082	3.142	303.0	173.0	0.000	3.920	3.419	5.009
1.515	3.142	303.0	173.0	0.000	5.141	4.787	3.537
1.958	3.142	303.0	173.0	0.000	6.470	6.187	2.828
2.834	3.142	303.0	173.0	0.000	8.660	8.955	−2.953
3.462	3.142	303.0	173.0	0.000	10.540	10.939	−3.997
1.958	0.117	303.0	173.0	0.000	1.676	1.922	−2.459
1.958	0.445	303.0	173.0	0.000	4.120	4.070	0.501
1.958	0.445	303.0	173.0	0.000	4.210	4.070	1.401
1.958	1.236	303.0	173.0	0.000	5.487	5.464	0.231
1.958	2.141	303.0	173.0	0.000	6.167	5.948	2.186
1.958	3.046	303.0	173.0	0.000	6.558	6.170	3.875
1.958	3.142	303.0	173.0	0.000	6.470	6.187	2.828
1.958	4.063	303.0	173.0	0.000	5.958	6.309	−3.519
1.958	4.063	303.0	173.0	0.000	6.365	6.309	0.550
1.958	5.194	303.0	173.0	0.000	6.674	6.404	2.696
1.958	5.680	303.0	173.0	0.000	6.384	6.434	−0.499
1.958	3.142	303.0	173.0	0.967	4.660	4.536	1.241
1.958	3.142	303.0	173.0	1.958	3.660	3.562	0.983
1.958	3.142	303.0	173.0	3.970	2.400	2.480	−0.803
1.958	3.142	303.0	173.0	5.880	1.790	1.925	−1.353
1.958	3.142	56.0	32.0	0.000	19.840	19.585	2.549
1.958	3.142	112.3	64.1	0.000	12.340	13.125	−7.853
1.958	3.142	207.6	118.5	0.000	8.480	8.410	0.698
1.958	3.142	303.0	173.0	0.000	6.472	6.187	2.848
1.958	3.142	381.4	217.8	0.000	4.767	5.083	−3.159
1.958	3.142	448.9	256.3	0.000	4.210	4.406	−1.961

[a] T = 40 °C; solvent (2-butanone) = 10 mL.

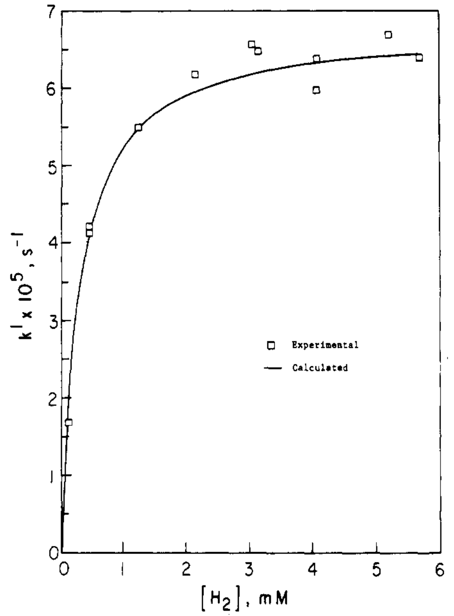


Figure 11. Effect of hydrogen concentration on the rate of acrylonitrile–butadiene copolymer hydrogenation: [C=C]$_0$ = 303 mM; [Rh]$_{total}$ = 1.958 mM; temperature = 40 °C; 2-butanone = 10 mL.

plots suggest that the reaction is apparently first order in the olefinic substrate according to eq 1.

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

Good linear plots of ln [C=C] vs. time such as that shown in Figure 9 were obtained for more than 85% completion of the reaction and the slopes of such plots provide values of k'. At different reagent concentrations and temperatures, the values of k' were estimated as shown in Table I and used to elucidate the overall kinetics of the reaction.

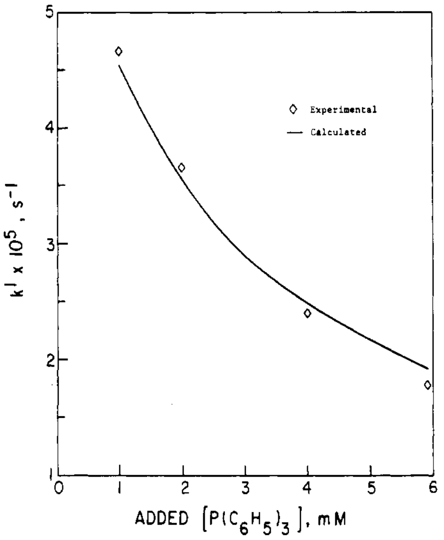


Figure 12. Effect of added $P(C_6H_5)_3$ concentration on the rate of acrylonitrile–butadiene copolymer hydrogenation: [C=C]$_0$ = 303 mM; [Rh]$_{total}$ = 1.958 mM; temperature = 40 °C; 2-butanone = 10 mL; [H_2] = 3.14 mM.

A first-order dependence of the hydrogenation rate on [Rh] total is apparent from a plot of k' vs. [Rh] total as shown in Figure 10. Figure 11 suggests that the rate of hydrogenation is first order in [H_2] at low hydrogen pressures and that the rate tends to a zero-order dependence on [H_2] at higher hydrogen pressures. The calculations for hydrogen concentrations were based on solubility measurements carried out at atmospheric pressure and by assuming the validity of Henry's law.

A series of experiments were carried out in which triphenylphosphine was added to the reaction solution over the concentration range of 0–5.88 mM. The plot of k' vs. the concentration of added triphenylphosphine shown in Figure 12 indicates a definite inverse dependence of re-

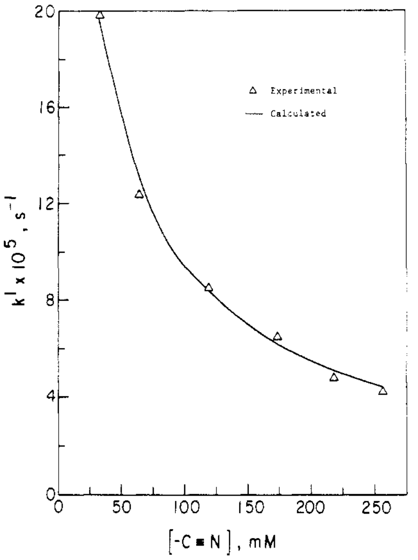


Figure 13. Effect of [CN] (total copolymer concentration) on the rate of acrylonitrile-butadiene copolymer hydrogenation: $[Rh]_{total}$ = 1.958 mM; $[H_2]$ = 3.14 mM; temperature = 40 °C; 2-butanone = 10 mL.

action rate on added $[P(C_6H_5)_3]$.

As already mentioned, plots of ln [C=C] vs. time are linear, when 2-butanone is used as the solvent media, indicating an apparent first-order dependence on the copolymer concentration. This would seem to suggest that a series of experiments carried out with different initial copolymer concentrations would be expected to provide essentially the same value of k' as defined by eq 1. A number of experiments were conducted in which the initial concentration of the acrylonitrile–butadiene copolymer was varied in the range of 56–499 mM [C=C]. Although the independent ln [C=C] vs. time plots exhibited excellent linearity, the k' values deduced from such plots indicated an inverse dependence of reaction rate on polymer concentration. This result is obviously the result of inhibition by nitrile concentration as indicated by the plot of k' vs. [C≡N] shown in Figure 13.

Mechanistic Considerations

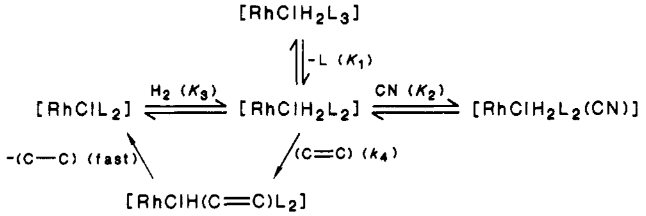
Mechanistic studies of the homogeneous hydrogenation of alkenes in the presence of $RhCl(P(C_6H_5)_3)_3$ have revealed the complexity of the system.[7-9] Several intermediates are thought to be present in the reaction mixtures, and the concentrations of these species are very sensitive to reaction conditions.[7-9] However, probable mechanisms can be proposed utilizing results from kinetic studies and spectroscopic techniques.

The mechanism illustrated by Scheme I is proposed as the most significant pathway for hydrogenation of the acrylonitrile–butadiene copolymer.

The reaction of $RhCl(P(C_6H_5)_3)_3$ with hydrogen to give first the complex $RhClH_2(P(C_6H_5)_3)_3$ has been well established and is represented by eq 2.[10,11]

$$[RhCl(P(C_6H_5)_3)_3] + H_2 \rightleftharpoons [RhClH_2(P(C_6H_5)_3)_3] \tag{2}$$

Scheme I
Mechanism for the Hydrogenation of an Acrylonitrile-Butadiene Copolymer Using $[RhClL_3]$[a]



[a] L = $P(C_6H_5)_3$; CN = nitrile group in the copolymer; (C=C) = carbon–carbon unsaturation in the copolymer; (C—C) = saturated polymer product.

The hydrogenation of the acrylonitrile–butadiene copolymer with $RhCl(P(C_6H_5)_3)_3$ under a hydrogen atmosphere was carried out in DMF-d_7 at 25 °C. The ^1H NMR spectrum of the reaction mixture contains signals typical of saturated and unsaturated copolymers and also signals due to the complex $RhClH_2(P(C_6H_5)_3)_3$. The presence of $RhClH_2(P(C_6H_5)_3)_3$ in solution has also been confirmed by visible spectroscopy. The visible spectrum of the reaction mixture in 2-butanone at 25 °C under an atmosphere of hydrogen is identical with the visible spectrum of $RhClH_2(P(C_6H_5)_3)_3$ under the same conditions. These spectra are also identical with the published spectrum of $RhClH_2(P(C_6H_5)_3)_3$.[12] When the hydrogenation of the copolymer was monitored at constant pressure by using a computer-controlled batch reactor, an extremely fast consumption of hydrogen was observed when the catalyst was added and at the same time, the solution changed from brown to yellow.[13] The molar ratio of the uptake of hydrogen to the catalyst is 1:1; this confirms that for the present system eq 2 is a fast equilibrium and lies far to the right.[11] Under a hydrogen atmosphere, the complex $RhClH_2(P(C_6H_5)_3)_3$ dissociates according to eq 3 to give the intermediate $RhClH_2(P(C_6H_5)_3)_2$.

$$[RhClH_2(P(C_6H_5)_3)_3] \overset{K_1}{\rightleftharpoons} [RhClH_2(P(C_6H_5)_3)_2] + P(C_6H_5)_3 \tag{3}$$

The complex $RhClH_2(P(C_6H_5)_3)_2$ can either react with nitrile functions within the copolymer (eq 4) or with carbon–carbon double bonds within the copolymer chain (eq 5).

$$[RhClH_2(P(C_6H_5)_3)_2] + CN \overset{K_2}{\rightleftharpoons} [RhClH_2(CN)(P(C_6H_5)_3)_2] \tag{4}$$

$$[RhClH_2(P(C_6H_5)_3)_2] + (C{=}C) \overset{k_4}{\rightleftharpoons} [RhClH_2(P(C_6H_5)_3)_2(C{=}C)] \tag{5}$$

In the presence of the nitrile group, eq 4 competes with the hydrogenation reaction described by eq 5. This has been illustrated by the decrease of observed rate constant with increasing copolymer concentration shown as Figure 13. Added acetonitrile also is found to inhibit the hydrogenation of the copolymer. In addition, the presence of nitrile appears to prevent significant formation of the dimer $[Rh(\mu\text{-}Cl)(P(C_6H_5)_3)_2]_2$. The ^1H NMR spectrum of the reaction mixture under hydrogen with 50% hydrogenation shows no signals at 25 °C due to $(P(C_6H_5)_3)_2Rh(\mu\text{-}Cl)_2RhH_2(P(C_6H_5)_3)_2$. However, hydrogenation of polybutadiene ($\bar{M}_n$ 20000) under the same reaction conditions gives a significant amount of $[Rh(\mu\text{-}Cl)(P(C_6H_5)_3)_2]_2$ (i.e., 70% of $RhCl(P(C_6H_5)_3)_3$) as an orange precipitate after only about 30% hydrogenation. The ability of the acrylonitrile–butadiene copolymer to prevent the formation of $[Rh(\mu\text{-}Cl)(P(C_6H_5)_3)_2]_2$ in the present system is very advantageous since no active rhodium-containing intermediate is lost through the precipitation of the slightly soluble dimer $[Rh(\mu\text{-}Cl)(P(C_6H_5)_3)_2]_2$. The rate-determining step in the hydrogenation of simple alkenes using $RhCl(P(C_6H_5)_3)_3$ is thought to be the insertion of the alkene into the hydrido–rhodium bond to give the alkyl–rhodium intermediate,[8] since the initial coordination of the alkene to the complex $RhClH_2(P(C_6H_5)_3)_2$ is fast. However, coordination of carbon–carbon double bonds to rhodium centers is expected to be more difficult with

Table II
Analysis of Variance

source	degree of freedom	sum of squares	mean square
regression	4	1.381×10^{-7}	3.452×10^{-8}
residual	24	2.413×10^{-10}	1.005×10^{-11}
uncorrected total	28	1.383×10^{-7}	
corrected total	27	3.640×10^{-8}	

Table III
Estimates of Reaction Parameters

parameter	estimate	std error	95% confidence interval	
			lower	upper
K_1, mM	1.98×10^{-1}	4.00×10^{-2}	1.15×10^{-1}	2.80×10^{-1}
K_2, L/mM	6.50×10^{-2}	1.14×10^{-2}	4.16×10^{-2}	8.85×10^{-2}
K_3, L/mM	2.76×10^{-1}	7.86×10^{-2}	1.14×10^{-1}	4.39×10^{-1}
k_4, L/(mM s)	4.23×10^{-4}	7.11×10^{-5}	2.76×10^{-4}	5.70×10^{-4}

polymeric substrates. This can be attributed to the steric bulk of polymers. Since it is not possible at this time to identify if the slowest step is the insertion of the carbon–carbon double bond into the hydrido–rhodium bond or the coordination of the double bond, the rate-determining step is expressed as eq 5.

The kinetic results obtained for the acrylonitrile–butadiene copolymer hydrogenation are in accord with the mechanism shown by Scheme I. The rate law for the mechanism shown in Scheme I is given as follows:

$$-\frac{d[C{=}C]}{dt} = k_4[RhClH_2(P(C_6H_5)_3)_2][C{=}C] \quad (6)$$

If the total rhodium concentration is expressed as shown by eq 7

$$[Rh] = [RhClH_2(P(C_6H_5)_3)_3] + [RhClH_2(P(C_6H_5)_3)_2] + [RhCl(P(C_6H_5)_3)_2] + [RhClH_2(P(C_6H_5)_3)_2(CN)] \quad (7)$$

then

$$[RhClH_2(P(C_6H_5)_3)_2] = \{[Rh]K_1K_3[H_2]\}/\{K_3[H_2] \times [P(C_6H_5)_3] + K_1 + K_1K_3[H_2] + K_1K_2K_3[CN][H_2]\} \quad (8)$$

When eq 8 is substituted into eq 6, the rate law has the form of eq 9.

$$-\frac{d[C{=}C]}{dt} = \frac{k_4K_1K_3[Rh][H_2][C{=}C]}{K_3[H_2][P(C_6H_5)_3] + K_1 + K_1K_3[H_2] + K_1K_2K_3[CN][H_2]} \quad (9)$$

A comparison of eq 9 with (1) leads to the relation given by eq 10.

$$k' = \{k_4K_1K_3[Rh][H_2]\}/\{K_3[H_2] \times [P(C_6H_5)_3] + K_1 + K_1K_3[H_2] + K_1K_2K_3[CN][H_2]\} \quad (10)$$

In order to test the validity of the model given by eq 10 with the observed kinetic data, a least-squares method for model discrimination is employed.[14] Results of 28 hydrogenation experiments with varying reaction conditions are tabulated in Table I. The Gauss–Newton[15] method for nonlinear least-squares regression is used for the computation of reaction parameters K_1, K_2, K_3, and k_4. The nonlinear least-squares summary statistics thus obtained are listed in Tables II and III. Table II shows the analysis of variance. Table III gives the estimates of reaction parameters along with the 95% confidence interval.

A very low value for the mean sum of squares of residuals shown in Table II confirms the consistency of the observed kinetic data with eq 10. Figures 10 through 13 show the observed experimental points along with the k' values predicted by eq 10. This also confirms the consistency of the kinetic data with eq 10.

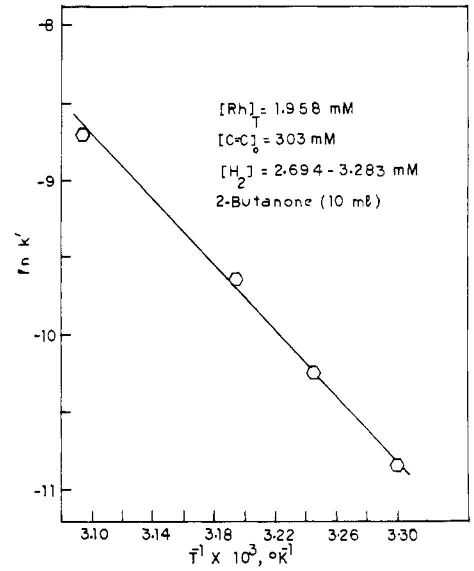


Figure 14. Arrhenius plot for the hydrogenation of the copolymer: $[C{=}C]_0$ = 303 mM; $[Rh]_{total}$ = 1.958 mM; 2-butanone = 10 mL; total pressure = 98.26 kPa.

One other possible pathway, namely, the "unsaturation route" where hydrogen is oxidatively added to a preformed alkene–rhodium complex (i.e., $RhCl(P(C_6H_5)_3)_2(C{=}C)$), has previously been proposed for the hydrogenation of simple alkenes.[5,9,16] This particular mechanism is considered insignificant in the hydrogenation of polymers mainly due to the rapid formation of $RhClH_2(P(C_6H_5)_3)_2$ which is observed in the presence of the copolymer and the barriers to carbon–carbon double-bond coordination described earlier.

The effect of temperature on the reaction rate provides the activation parameters associated with the experimental rate constant which is a composite of the rate-determining step k_4 (i.e., the formation of copolymer complex with the metal hydride) and equilibrium constants K_1, K_2, and K_3. Under the set of reaction conditions used for the temperature dependence the fourth term in the denominator of eq 10 predominates. Consequently, for the temperature dependence, eq 10 can be written in simplified form as shown in eq 11

$$k' \simeq (k_4/K_2)([Rh]/[CN]) \quad (11)$$

Since the temperature dependence is carried out at constant [Rh] and [CN], a plot of ln k' vs. $1/T$ is expected to be linear. A good linear Arrhenius plot as shown in Figure 14 is indeed obtained for the values of k' obtained at temperatures in the range of 30–50 °C. The apparent activation energy obtained from this plot had a value of 87.28 kJ/mol. At 40 °C the apparent activation enthalpy (i.e., $\Delta H_4^{\ddagger} - \Delta H_2^{\circ}$) is estimated to be 84.67 kJ/mol and the apparent activation entropy (i.e., $\Delta S_4^{\ddagger} - \Delta S_2^{\circ}$) is calculated as −8.3 J/(mol K).

Effect of Solvent on Catalytic Activity and Selectivity. As mentioned above, the acrylonitrile–butadiene copolymer employed in this study contains three types of carbon–carbon bonds (see Figure 1). During polymerization, 1,4-*cis*- and 1,4-*trans*-butadiene addition results in the formation of internal double bonds whereas 1,2-butadiene addition results in the formation of terminal double bonds. The acrylonitrile–butadiene copolymer used in this study contained about 30% terminal and 70% internal

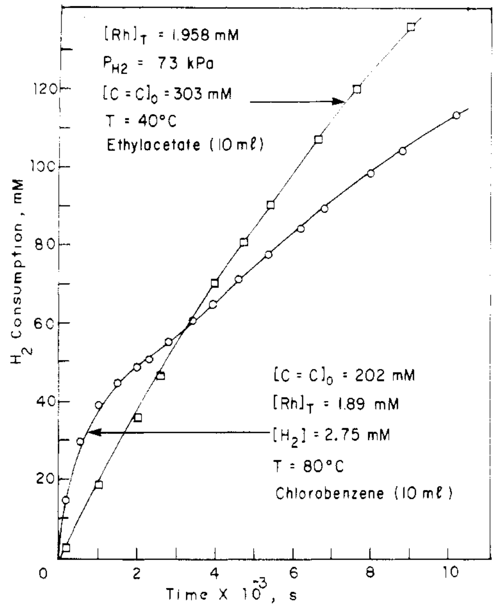


Figure 15. Hydrogen consumption plot for the hydrogenation of the copolymer in chlorobenzene and ethyl acetate.

carbon–carbon unsaturation.

The results presented above for the hydrogenation of the acrylonitrile–butadiene copolymer in the presence of $RhCl(P(C_6H_5)_3)_3$ in 2-butanone (Figure 2) indicates that this catalyst system exhibits no selectivity for the hydrogenation of terminal vs. internal carbon–carbon unsaturation.

When chlorobenzene was employed as the solvent for hydrogenation of the copolymer in the presence of $RhCl(P(C_6H_5)_3)_3$, it was necessary to increase the reaction temperature to 80 °C in order to achieve quantitative hydrogenation in a time comparable to that required for the reaction in 2-butanone at only 40 °C. However, an even more striking difference for the reaction in chlorobenzene was the selectivity exhibited by the $RhCl(P(C_6H_5)_3)_3$ catalyst in chlorobenzene for terminal vs. internal carbon–carbon double-bond hydrogenation as suggested by the nature of the hydrogen consumption plot shown in Figure 15. The initial relatively rapid consumption of hydrogen can be attributed to hydrogenation of the terminal olefinic unsaturation and the subsequent slower consumption of hydrogen for hydrogenation of the internal olefinic unsaturation. Furthermore, the inflection in the hydrogen consumption curve at approximately 60 mM corresponds closely to the approximate 30% terminal carbon–carbon unsaturation (i.e., 62 mM in this case) present in the original copolymer. Additional confirmation for this selectivity was obtained from an infrared analysis of the polymer product at 40% completion of the hydrogenation process. An IR spectra of 40% hydrogenated acrylonitrile–butadiene copolymer is shown in Figure 16. As seen from this figure, the lack of any distinct absorption at 910 cm^{-1}, characteristic of terminal unsaturation, indicated that the catalyst is indeed selective in the chlorobenzene media.

The hydrogenation of the copolymer was also carried out by using ethylacetate as solvent. The hydrogen consumption plot shown in Figure 15 for the reaction in ethylacetate at 40 °C shows nonselectivity and a catalytic activity similar to that observed in 2-butanone (Figure 2).

It is of interest to note however that when the $RhCl(P(C_6H_5)_3)_3$ catalyst is used for the hydrogenation of monomeric unsaturated nitriles in 2-butanone, a selectivity pattern does indeed appear to result. For hydrogenation reactions carried out at 40 °C in the presence of 2 mM [Rh], 3.14 mM [H_2], and 51 mM [C=C]$_0$, acrylonitrile:methacrylonitrile:3,3-dimethylacrylonitrile hydrogenation rates are in the ratio of 65:5:1, respectively.

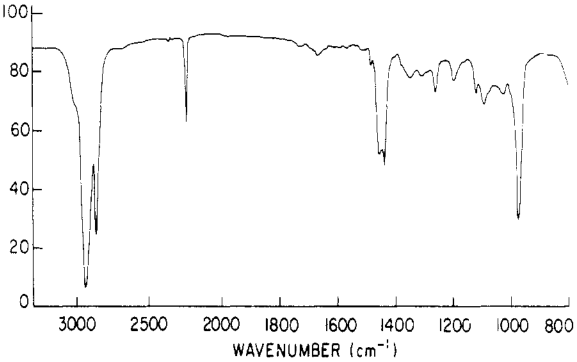


Figure 16. Infrared spectrum of partially hydrogenated acrylonitrile–butadiene copolymer (polymer film on NaCl).

Consequently, the results presently available on solvent effects suggests that the interaction of the solvent with the copolymer is extremely important in influencing both the nature and the rate of the catalytic process. Work is currently underway to gain a better understanding of this interesting aspect of the catalytic hydrogenation of polymers.

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Registry No. $P(C_6H_5)_3$, 603-35-0; $PhCl(P(C_6H_5)_3)_3$, 14694-95-2; (acrylonitrile)(butadiene) (copolymer), 9003-18-3.

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