

Kinetics of the Hydrogenation of NBR by Hydrazine and Oxygen, Using Selenium as a Catalyst

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ABSTRACT: The kinetics of hydrogenation of the acrylonitrile-polybutadiene (NBR) rubber by the action of hydrazine in the presence of selenium and oxygen was studied by varying reaction parameters such as latex and catalyst concentrations. The method of initial rates gives a reaction order of 0.91 and a rate constant of $3.2 \times 10^1 \text{ L mol}^{-1} \text{ h}^{-1}$ in relation to the NBR latex concentration, and an order of 0.86 and a rate constant of $3.3 \times 10^1 \text{ L mol}^{-1} \text{ h}^{-1}$ in relation to the catalyst concentration. Based on these values, a first-order mechanism with the formation

of a diimide intermediate is suggested, which is formed through the oxidation of hydrazine in an oxygen atmosphere in the presence of selenium catalyst. This diimine species reacts rapidly, reducing the carbon-carbon double bonds of NBR resulting in the formation of HNBR rubber. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3605–3609, 2012

Key words: NBR latex; hydrogenation; diimide; selenium; rate velocity

INTRODUCTION

The carbon-carbon double bonds hydrogenation has been largely used to obtain elastomers with improved resistance compared to the original materials.^{1–3} This is the case of hydrogenated nitrile rubber (HNBR), which is commercialized for use in diversified sectors of the petrochemical industry, especially in the automotive field.^{4–6}

The NBR hydrogenation has been classically performed using homogeneous transition metal catalysts and molecular hydrogen in a process that suffers from cost associated with the dissolution of NBR, the use of organic solvents and the use of expensive hydrogenation conditions, which are mostly associated with high pressure reactors and expensive catalysts. The direct NBR hydrogenation has been showed as an attractive alternative,^{1,2} particularly in the case in which the hydrogenation is performed by diimide (diazene, $\text{NH}=\text{NH}$). The diimide is generated by oxidation of hydrazine in an oxidizing atmosphere. Previous studies showed that diimide is extremely efficient in the reduction of the carbon-carbon double bonds in NBR, even in aqueous solu-

tions including the latex originally synthesized in the industrial production of NBR.

The partial NBR hydrogenation by diimide was reported by Wideman⁷ in 1984. After that, Parker performed similar studies with hydrazine, reporting crosslinking problems of these systems.^{8–10} Several hydrogenation experiments have been described using the diimide method (i.e., reacting hydrazine (diazane) and an oxidative agent like hydrogen peroxide) and have also examined the effects of ions copper, silver nitrate and boric acid as catalytic precursors.^{11,12}

Herein is described the kinetics of the process of the NBR latex hydrogenation using hydrazine, oxygen and selenium as the catalyst,¹³ and the determination of the kinetic equation to understand aspects of the hydrogenation process and to control the gel formation.

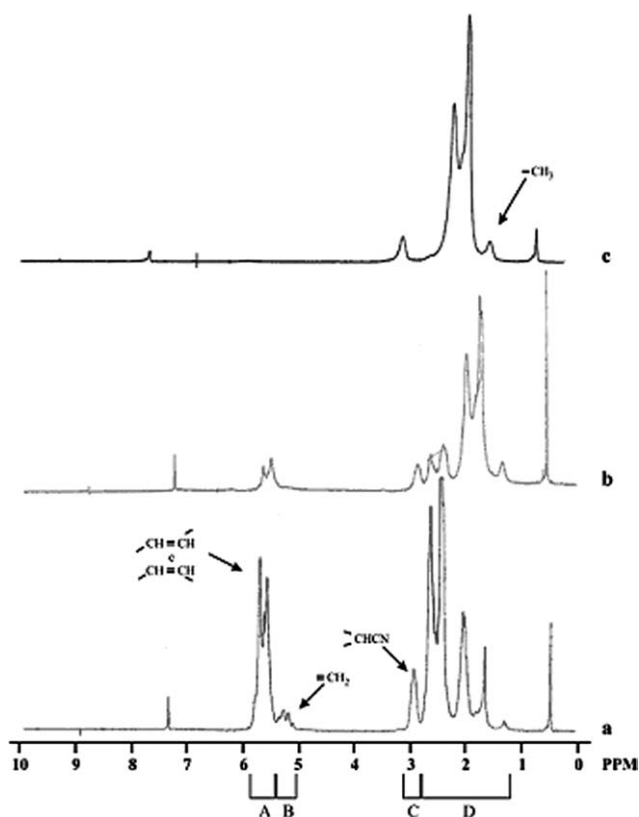
EXPERIMENTAL

Materials and methods

The NBR latex hydrogenation runs were performed in a 0.5 L mechanically stirred glass reactor with three entries, two of which were equipped with a condenser and an addition funnel.

In a typical run, the reactor was charged with 23 mL of NBR latex [33% of acrylonitrile, 56% of 1,4 *cis*-trans C=C double bonds and 11% of vinyl C=C double bonds, NBR 3350 from Petroflex], 8.05 mL of hydrazine [64% aqueous solution from Acros Organics] and 5.5 mg of selenium (100 mesh powder, from

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Scheme 1 ^1H NMR spectra of the NBR containing 33 wt % acrylonitrile and (a) 0%, (b) 61%, and (c) 100% hydrogenated.

Aldrich). The temperature was raised to 60°C using a thermostatic circulation bath, and a flow of 1 L min^{-1} of oxygen (99.99% purity, Air Liquide) was fed during a 4-h period. At the end of the reaction, the

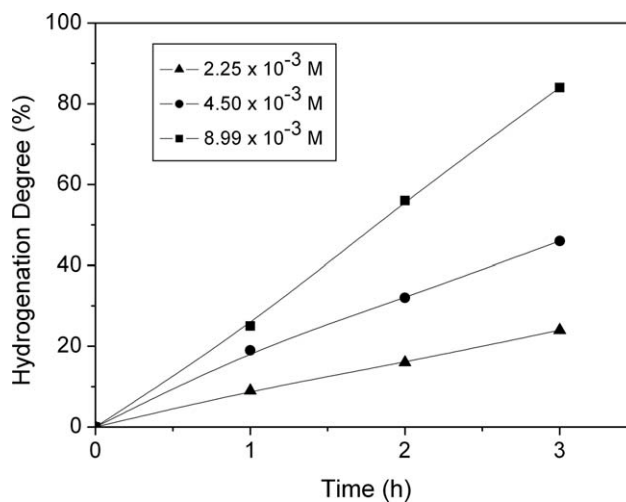
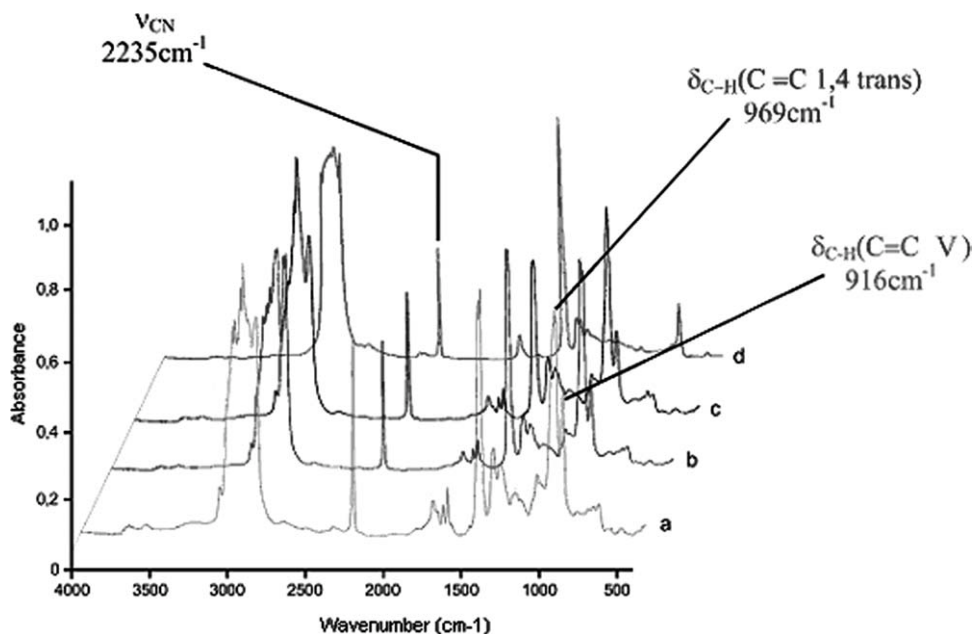


Figure 1 Conversion versus time with different catalyst concentrations to obtained r_0 in the conditions of 5.52 g of latex (0.067 mol de C=C), 5.15 g de N_2H_4 (0.1 mol), oxygen stream of 1 L min^{-1} , 60°C and 4 h of reaction.

hydrogenated product was coagulated by adding 5.5 mg of a 1 wt % solution of Irganox antioxidant (IB215 from Ciba) in 23 mL of methanol and 4.6 mL of an aqueous 20 wt % NaCl solution, under stirring. Afterward, a 3.5 wt % sulfuric acid solution was added until a pH of 4 was reached. The product was filtered and dried at 90°C .

The hydrogenation degree obtained in each experiment was determined by infrared spectroscopy (IR) using an ABB INC. model FTLA 2000-100 spectrometer operating in a range of $4000\text{--}600\text{ cm}^{-1}$. The NBR film was prepared through the evaporation of the NBR latex in a rectangular window of zinc



Scheme 2 IR Spectra of the NBR containing 33 wt % acrylonitrile and (a) 0%, (b) 17%, (c) 31%, and (d) 100% hydrogenated.

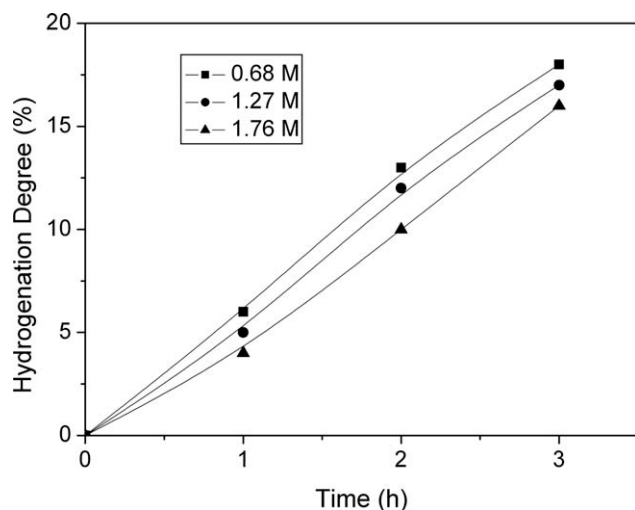


Figure 2 Conversion versus time with different NBR latex concentrations to obtained r_0 in the condition of 0.0055 g of catalyst, 5.15 g de N_2H_4 (0.1 mol), oxygen stream of 1 $L\ min^{-1}$, 60°C and 4 h of reaction.

selenide. The hydrogenation degree was also confirmed and measured by 1H NMR using a Varian VXR 200 NMR, operating at a frequency of 200 MHz. By using 1H NMR, the hydrogenation degree, or conversion of the C=C double bonds, was calculated using the ratio of the integrals of the area indicative of the olefinic protons in the region from 5.0 to 6.0 ppm and the area indicative of the aliphatic protons in the region from 1.2 to 2.8 ppm. Schemes 1 and 2 illustrate the 1H NMR and IR spectra, respectively, wherein magnetic resonance (Scheme 1) shows a decrease in size for the peaks indicative of the olefinic protons in the region between 5.0 and 6.0 ppm and a similar increase in the size of the peaks in the aliphatic protons in the region between 1.2 and 2.8 ppm. In the IR spectra (Scheme 2) show a decrease of the bands of axialdeformation indicative of the 1,4-trans C—H bonds at $969\ cm^{-1}$ and of the 1,2-vinylc bonds at $916\ cm^{-1}$ was observed and compared to the absorption of nitrile groups (ν_{CN}) at $2235\ cm^{-1}$, which remained constant during the NBR hydrogenation.



Figure 3 Formation of diimide by hidrazine and selenium.

RESULTS AND DISCUSSION

The kinetics of the reaction of the NBR latex hydrogenation using selenium as a catalyst has been investigated using the method of initial rates. The reaction rate has been measured at the initial stages of the reaction and with different concentrations of reagents such as NBR and selenium. The catalyst concentration has been studied in the range of 1.79×10^{-3} to $8.99 \times 10^{-3}\ M$ and the NBR latex concentration in the range of 0.68–2.22 M .

For low conversions, the reaction rate, $-dx/dt$, can be estimated by $-\Delta x/\Delta t$, giving the basis for the method of initial rates. In these studies, the results were cast using the hydrogenation degree (HD) versus the time, in which $dHD/dt \cong \Delta HD/\Delta t$. The initial rate was obtained by a linear fit.

Figure 1 shows the dependence of the conversion on the catalyst concentration, and Figure 2 shows the effect on the NBR latex concentration.

Figures 1 and 2 illustrate graphically the calculation of $\Delta x/\Delta t$ obtained by a linear fit on the hydrogenation degree experimental data. The Table I shows, the hydrogenation degree, the initial rate r_0 (column $\Delta x/\Delta t$ multiplied by the column of initial concentration of the reactant and the estimative of the rate constant.

The simplest reaction law for a chemical process can be written as

$$r = kC_A^{n_1}C_B^{n_2}C_C^{n_3} \quad (1)$$

in which,

r = reaction rate

k = rate constant

C_A, C_B, C_C = NBR, catalyst and hydrazine concentration, respectively.

n_1, n_2, n_3 = reaction order in relation to their reagents A, B, and C.

TABLE I
Kinetic Data for the Hydrogenation of NBR with Se Catalysts at Different Reaction Conditions

Concentration		Hydrogenation degree (%)			Initial rate		Rate constant
Catalyst ($10^{-3}\ M$)	C=C (M)	At 1 h	At 2 h	At 3 h	$(\Delta x/\Delta t)\ h^{-1}$	$r_0\ (mol\ L^{-1}\ h^{-1})$	$k'\ (L\ mol^{-1}\ h^{-1})$
2.25	2.22	9	16	24	0.079	0.175	3.51×10^1
4.50	2.22	19	32	46	0.151	0.335	3.35×10^1
8.99	2.22	25	56	84	0.283	0.628	3.15×10^1
1.79	0.68	6	13	18	0.061	0.041	3.41×10^1
1.79	1.27	5	12	17	0.058	0.074	3.24×10^1
1.79	1.76	4	10	16	0.054	0.095	3.01×10^1

Reaction conditions: 5.15 g de N_2H_4 (0.1 mol), oxygen stream of 1 $L\ min^{-1}$, 60°C, and 4 h of reaction.

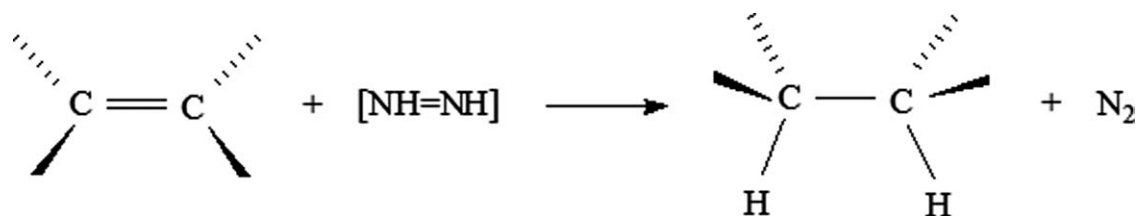


Figure 4 Hydrogenation of double bonds by diimide.

therefore,

$$\ln r_0 = \ln k + n_1 \ln C_A + n_2 \ln C_B + n_3 \ln C_C \quad (2)$$

or

$$\ln r_0 = \ln k' + n_1 \ln C_A \quad (3)$$

When the concentration of B and C are constant and thus, the order (n_1) can be calculated:

At $t = 0$ and $C_{Se} = cte$,

$$r_0 = \frac{dC=C}{dt} = kC_{NBR}^{n_1} \quad (4)$$

where, $d(C=C)/dt$ = disappearance rate of carbon-carbon double bonds

r_0 = initial rate

k = rate constant

C_{NBR} = NBR latex concentration

n_1 = reaction order in relation to NBR latex concentration.

Similarly maintaining a and C constant, n_2 can be calculated:

At $t = 0$ and $C_{NBR} = cte$,

$$r_0 = \frac{dC=C}{dt} = kC_{Se}^{n_2} \quad (5)$$

where,

$d(C=C)/dt$ = disappearance rate of carbon-carbon double bonds

r_0 = initial rate

k = rate constant

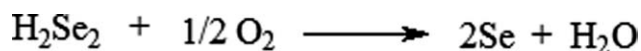


Figure 5 Regeneration of selenium.

C_{Se} = selenium catalyst concentration

n_2 = reaction order in relation to selenium concentration.

We obtain the general equation,

$$\ln r_0 = \ln k' + n_1 \ln C_{NBR} + n_2 \ln C_{Se} \quad (6)$$

Particularly, in this study, the variation in the concentrations of catalyst (selenium) and double bonds ($C=C$ of NBR latex) was investigated, keeping constant the concentration of hydrazine, where the term C^{n_3} of the eq. (1) is incorporated by an effective reaction constant k' ($k' = k \times C^{n_3}$). So, the eq. (6) was used for the rate constant calculations.

From previous studies,^{1,2} it is known that the process of the hydrogenation of $C=C$ double bonds of the NBR latex using hydrazine is dependent on the formation of the intermediary diimide, which occurs in two stages: the reaction between hydrazine and selenium to produce diimide in atmosphere of oxygen (Fig. 3) and the reaction between diimide and the $C=C$ double bonds to obtain a hydrogenated polymer (Fig. 4).

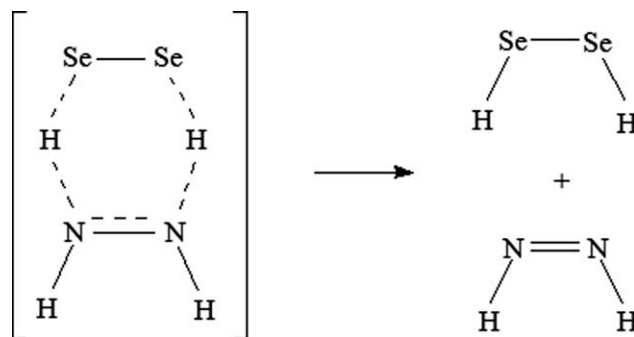


Figure 7 Formation of diimide.

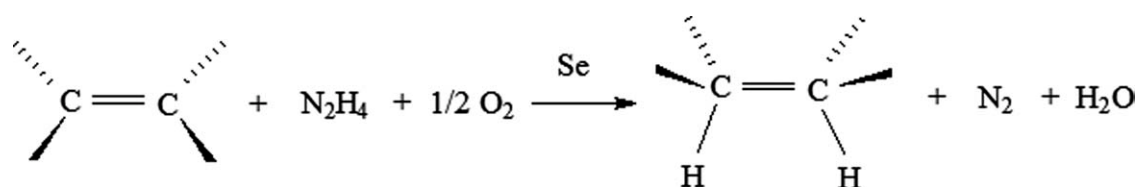


Figure 6 Global reaction.

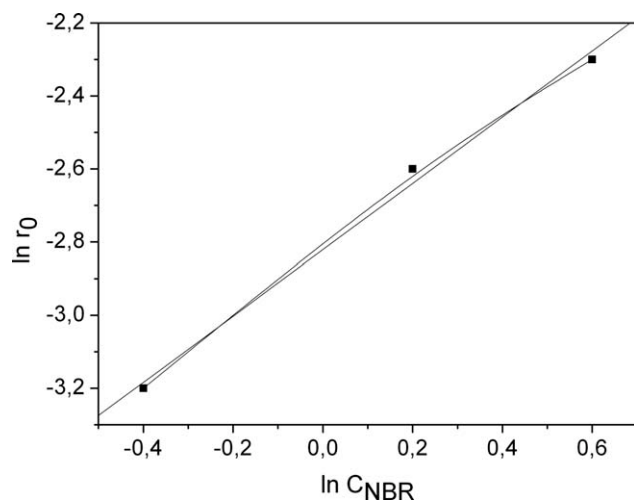


Figure 8 Graphic representation of the natural logarithm of the initial velocity (column r_0) versus the natural logarithm of the NBR latex concentration.

The Figure 5 show that the selenium catalyst is regenerated and Figure 6 represent the global reaction.

It was also reported that the oxidation of hydrazine with selenium during the formation of the intermediary diimide leads predominantly to the formation of diimide in its cis form¹³ (Fig. 7):

Using the data of Figures 1 and 2 shown also in Table I, the reaction order through the method of initial velocity was determined: $n_1 = 0.91$ for the NBR latex (Fig. 8) and $n_2 = 0.86$ for the catalyst (Fig. 9). Within the errors of the measurements, it can be assumed that both partial orders are equal to 1.

The values found for the reaction order in the hydrogenation reactions of the NBR latex using

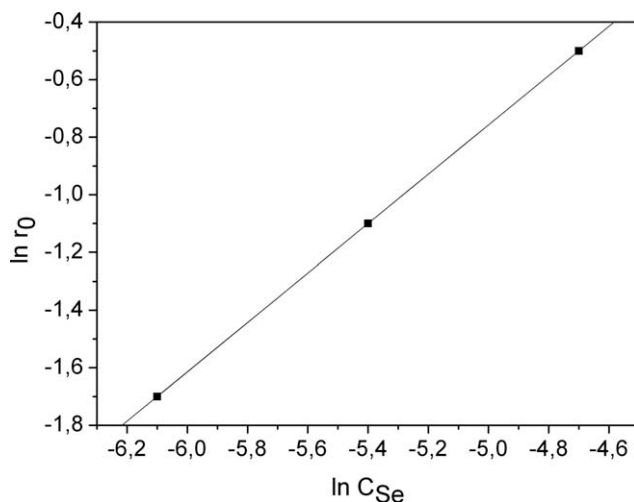


Figure 9 Graphic representation of the natural logarithm of the initial velocity (column r_0) versus the natural logarithm of the catalyst concentration.

diimide and the selenium catalyst show that the reaction is first-order in relation to the catalyst concentration and first-order in relation to the NBR latex concentration. The values of k' were obtained for different concentrations of catalyst and NBR latex, were determined according to the general eq. (6) described previously and are shown in Table I.

The average value of k' for the different concentrations of selenium C_1 ($2.25 \times 10^{-3} M$), C_2 ($4.50 \times 10^{-3} M$), and C_3 ($8.99 \times 10^{-3} M$) was of $3.3 \times 10^1 L mol^{-1} h^{-1}$ and for the different concentrations of NBR latex, C_1 (0.68 M), C_2 (1.27 M), and C_3 (1.76 M), the average value was of $3.2 \times 10^1 L mol^{-1} h^{-1}$. There is a good agreement between these both values, supporting the used method.

CONCLUSIONS

The kinetic study in this article suggests that the reaction of the NBR latex hydrogenation through the oxidation of hydrazine catalyzed with selenium is of first-order on both NBR and catalyst. The effective rate constant k' was determinate to be $3.2 \times 10^1 L mol^{-1} h^{-1}$ at $60^\circ C$. The selenium catalyst proved to be a new and efficient alternative in the hydrogenation reaction of NBR latex.¹ We report in our study a in which the change in the concentration of selenium catalyst from $8.99 \times 10^{-3} M$ to $1.79 \times 10^{-3} M$ and the NBR latex concentration from $2.22 M$ to $0.68 M$ for 4 h at $60^\circ C$ which resulted in a straight slope when we plot the hydrogenation degree versus time.

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