

Kinetics of the hydrogenation of 1-octene catalyzed by [Ni(*o*-MeO-dppp)(OAc)₂]

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Abstract

The kinetics of the nickel-catalyzed hydrogenation of 1-octene have been studied using nickel(II) acetate in combination with the ligand 1,3-bis(di(*o*-methoxyphenyl)phosphanyl)propane (*o*-MeO-dppp). The effects of temperature and dihydrogen pressure, as well as the influence of the nickel and substrate concentrations have been studied ($T = 30\text{--}60^\circ\text{C}$, $p(\text{H}_2) = 30\text{--}60$ bar, $[\text{Ni}] = 0.35\text{--}2.81$ mM, $[1\text{-octene}] = 0.98\text{--}3.91$ M, ligand/Ni = 1.1 in a mixture of dichloromethane and methanol). The kinetic study results in the surprisingly simple rate law $r = k_{\text{cat}}[\text{Ni}][1\text{-octene}]p(\text{H}_2)$. The kinetic data are consistent with a mechanism in which the terminating hydrogenolysis step of the nickel-alkyl complex is the rate-determining step of the catalytic cycle with all preceding steps at equilibrium. The first-order dependence on the substrate is confirmed by the results with other substrates, as the hydrogenation rate strongly depends on the nature of the substrate. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nickel; Phosphane ligands; Homogeneous hydrogenation; Kinetics; Reaction mechanism

1. Introduction

Recently, it was reported that selected nickel(II) diphosphane complexes are able to hydrogenate homogeneously 1-octene to *n*-octane [1]. In subsequent studies the influence of solvent and anion on the hydrogenation activity was studied, and based on the observations a mechanism was proposed [2].¹ It has been long recognized that the study of the overall kinetics is an important tool in the elucidation

of the mechanism of a homogeneously catalyzed reaction, for example, homogeneous hydrogenation [3]. To get more insight into the mechanism of the nickel-catalyzed hydrogenation, the overall kinetics of the hydrogenation of 1-octene have been studied. It was found that nickel complexes containing the ligand 1,2-bis(di(*o*-methoxyphenyl)phosphanyl)ethane (*o*-MeO-dppe) are involved in a disproportionation equilibrium under catalytic reaction conditions [4], leading to a more complex catalytic system. Therefore, a catalyst containing the ligand 1,3-bis(di(*o*-methoxyphenyl)phosphanyl)propane (*o*-MeO-dppp) was selected to study the kinetics of the hydrogenation of 1-octene. From NMR studies it appeared that complexes containing this ligand are not involved in a disproportionation equilibrium [5].

Herein, the results of the kinetic study using nickel(II) acetate in combination with the ligand *o*-MeO-dppp as the catalyst precursor are presented.

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¹ The presence of a protic solvent was found to be essential in order to observe catalytic activity. When decreasing the polarity of solvent mixtures the hydrogenation activity increases. However, after a maximum in hydrogenation activity (at 50/50, v/v MeOH/CH₂Cl₂), the hydrogenation activity drops significantly when more apolar solvent is added.

A mechanism for the catalytic hydrogenation is derived from the obtained data. The effects of temperature and dihydrogen pressure on the hydrogenation of 1-octene were studied as well as the influence of nickel and substrate concentrations.

2. Experimental

2.1. General

All chemicals were reagent grade and were used as received or synthesized as described below. Reactions were carried out under an atmosphere of dry argon or dry dinitrogen, unless stated otherwise, using standard Schlenk techniques. Solvents were degassed prior to use. The ligand *o*-MeO-dppp was synthesized according to a literature procedure [6]. To remove peroxides from 1-octene, it was led through a column containing alumina.

Hydrogenation reactions were carried out in a 100 ml Parr stainless steel autoclave equipped with a glass inner beaker, and a motor driven stirrer. The temperature of the autoclave was controlled by an electronic heating mantle, using a thermocouple in the reaction mixture. The autoclave was connected to a recorder to register the pressure during the reaction. GC analyses were performed on a Chrompack 437A chromatograph fitted with a flame ionization detector and a 50 m cp sil 5 cb column.

2.2. Kinetic experiments

In a typical experiment nickel acetate and *o*-MeO-dppp were placed in round bottom flask in an argon atmosphere. After the addition of 10 ml dichloromethane and 10 ml methanol a clear orange solution was obtained. Then the substrate was added and the solution was transferred, under dioxygen-free conditions, into the autoclave. After flushing with dihydrogen to remove argon, the reactor was charged to the desired pressure, and the reaction was started by activation of the stirrer. For the reactions at elevated temperatures the catalyst precursor was prepared in 5 ml of the dichloromethane/methanol (1:1, v/v) mixture and placed in a Hoke tube, which was attached on top of the autoclave. The bulk of the reaction mixture (solvents and substrate) was heated to the

desired temperature under a dihydrogen pressure of 40 bar. After 30 min the catalyst solution was added and a dihydrogen pressure of 50 bar was applied. After 60 min the reaction was stopped and the excess pressure was released. In the reactions in which the 1-octene concentration was varied, hexane was added to the reaction mixture, so that the total amount of 1-octene and hexane was 31.2 ml.

In all cases, the reaction was followed by measuring the dihydrogen pressure as a function of time. Then the $\Delta p(\text{H}_2)$ values, which are proportional to the amount of *n*-octane produced, were calculated and these values were plotted as a function of time. It appeared that in most of the experiments an induction period was observed during which the actual catalyst is formed. This was indicated by a non-linear drop in the $\Delta p(\text{H}_2)$ versus time plot in the first 10 min and therefore, the initial rate was determined from the slope between 15 and 25 min. It appeared that in the case of the reactions at elevated temperatures the induction period was somewhat longer, due to the fact that the catalyst solution is injected. The hydrogenation reaction started immediately after the injection, but the concentration of active species appeared to be stabilized only after 20 min. In these cases, the initial rate was determined from the slope of the $\Delta p(\text{H}_2)$ versus time plot between 25 and 35 min.

All straight lines were fitted by the use of conventional linear regression software.

3. Results

3.1. General considerations

The hydrogenation of 1-octene to *n*-octane was carried out using an in situ formed catalyst by mixing nickel acetate with *o*-MeO-dppp in a dichloromethane/methanol (1:1, v/v) solution. In all cases, a small excess (10%) of ligand was used. It is assumed that the concentration of dihydrogen in the solution is, in all cases, proportional to the dihydrogen pressure, and that the dissolution of dihydrogen is fast enough to exclude mass transport limitations. This fast dissolution of dihydrogen is confirmed by the fact that the hydrogenation rate is not altered with increasing stirring rate. The kinetics of the hydrogenation reaction were studied by following the

Table 1

Kinetic data for the hydrogenation of 1-octene with in situ formed [Ni(*o*-MeO-dppp)(OAc)₂] as the catalyst precursor

Entry	10 ³ [Ni] ^a (M)	[1-Octene] (M)	<i>p</i> (H ₂) (bar)	<i>T</i> (°C)	10 ³ <i>r</i> _i (bar s ⁻¹)	<i>k</i> _{cat} (mol ⁻² l ² s ⁻¹) ^b
1	0.35	2.81	50	24	0.64 ^c	0.013
2	0.70	2.81	50	24	0.95 ^c	0.010
3	1.40	2.81	50	24	1.83 ^c	0.009
4	2.81	2.81	50	24	3.61 ^c	0.009
5	0.98	0.98 ^d	50	52	1.58 ^e	0.033
6	0.98	2.93 ^d	50	52	5.16 ^e	0.036
7	0.98	3.91 ^d	50	52	7.13 ^e	0.037
8	1.40	2.81	30	24	1.14 ^c	0.010
9	1.40	2.81	40	24	1.68 ^c	0.011
10	1.40	2.81	50	24	1.83 ^c	0.009
11	1.40	2.81	60	24	2.37 ^c	0.010
12	1.40	2.81	50	24	1.83 ^c	0.009
13	1.40	2.81	50	34	2.66 ^e	0.014
14	1.40	2.81	50	41	3.20 ^e	0.016
15	1.40	2.81	50	52	6.41 ^e	0.033
16	1.40	2.81	50	62	10.38 ^e	0.053

^a The ligand-to-nickel ratio was in all cases 1:1.^b *k*_{cat} was calculated with Eq. (1) (see text).^c The *r*_i was determined using the dihydrogen pressure drop between 15 and 25 min.^d *n*-Hexane was added to the reaction mixture to keep the nickel concentration and the polarity of the solution constant (see text).^e The *r*_i was determined using the dihydrogen pressure drop between 25 and 35 min.

dihydrogen pressure decrease in time at different catalyst and substrate concentrations, and at different temperatures and dihydrogen pressures. It appeared that in most of the experiments an induction period was needed in which the actual catalyst is formed. In all cases, the conversion of 1-octene was low enough in the studied period of time, so that the initial rate method can be applied. Values for initial rates under different reaction conditions are collected in Table 1.

3.2. Nickel concentration

The concentration of the catalyst precursor was varied in the 0.35–2.81 mM range (Table 1, entries 1–4), while the 1-octene concentration (2.81 M), dihydrogen pressure (50 bar) and the temperature (24°C) were kept constant. The initial rate (*r*_i) shows a direct dependence with respect to the catalyst concentration (see Fig. 1). A plot of $-\ln r_i$ versus $-\ln[\text{Ni}]$ (Fig. 1(a)) yields a straight line ($-\ln r_i = -0.9605 \ln[\text{Ni}] - 0.0153$; $R^2 = 0.999$), which is in agreement with a first-order rate dependence. Due to the small amount of nickel(II) acetate and, consequently the relatively large experimental error, entry

1 was not included in the linear fit. The first-order rate dependence is also suggested from Fig. 1(b). The intercept on the rate axis is zero, which is expected for a catalytic reaction. Furthermore, the first-order rate dependence confirms the homogeneity of the hydrogenation reaction, as does the satisfactory reproducibility of the kinetic measurements.

3.3. Substrate concentration

The effect of 1-octene concentration was studied in the 0.98–3.91 M range (Table 1, entries 5–7). In kinetic experiments it is essential that if one parameter is varied all other parameters are kept constant. It was shown that the polarity of the solvent has an influence on the activity of the hydrogenation catalysts containing the ligand *o*-MeO-dppp [2]. By changing the amount of substrate from 50 mmol (7.8 ml) to 200 mmol (31.2 ml) the polarity of the reaction mixture and the nickel concentration would be altered considerably. In order to keep the nickel concentration and the polarity of the solution constant in these experiments, *n*-hexane was added so that the total volume of 1-octene and *n*-hexane was 31.2 ml. The difference

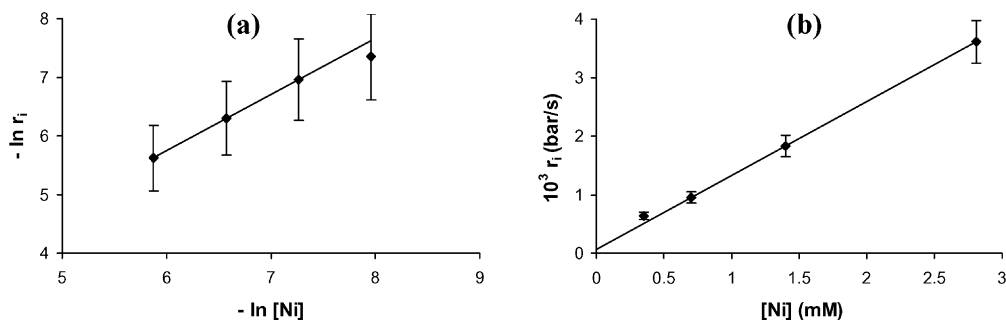


Fig. 1. Hydrogenation of 1-octene: rate dependence on nickel concentration. Conditions as given in Table 1. (a) $-\ln r_i$ vs. $-\ln[\text{Ni}]$; (b) r_i vs. $[\text{Ni}]$.

in the polarity of 1-octene and *n*-hexane is negligible with respect to that of methanol and the polarity of the reaction mixture is thus constant for all reactions. As the hydrogenation activity of the catalyst decreases because of the lower polarity of the reaction mixture [2], the experiments were performed at a higher temperature (52°C). It appeared that the addition of *n*-hexane has a negative influence on the reproducibility of the experiments. In the case of 1.95 M 1-octene no reproducible values could be obtained. So far, it is not clear what causes this effect on the reproducibility.

The initial rates (r_i) show a direct dependence on the 1-octene concentrations (see Fig. 2). The results suggest a first-order dependency of the hydrogenation rate on the 1-octene concentration ($-\ln r_i = -1.0867 \ln[1\text{-octene}] + 6.4295$, $R^2 = 1$) (Fig. 2(a)). As expected the r_i versus $[1\text{-octene}]$ plot goes through the intercept of the axes (Fig. 2(b)).

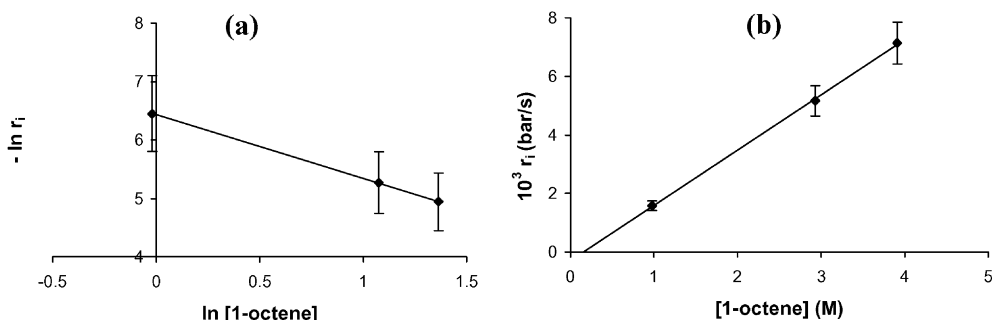


Fig. 2. Hydrogenation of 1-octene: rate dependence on 1-octene concentration. Conditions as given in Table 1. (a) $-\ln r_i$ vs. $\ln[1\text{-octene}]$; (b) r_i vs. $[1\text{-octene}]$.

It is expected that the addition of *n*-hexane only influences the rate of the hydrogenation reaction, but has no influence on the mechanism of that reaction. Therefore, it is assumed that the hydrogenation reaction is first-order in 1-octene, also when no *n*-hexane is added to the reaction mixture.

3.4. Dihydrogen pressure

Fig. 3 shows the dependence of the initial rate at 24°C on the dihydrogen pressure, varied in the 30–60 bar range (Table 1, entries 8–11), at 1-octene and catalyst concentrations of 2.81 M and 1.40 mM, respectively. Fig. 3(a) shows that the reaction is first-order in dihydrogen pressure ($-\ln r_i = -0.9951 \ln p(\text{H}_2) + 10.134$, $R^2 = 0.962$). As expected, the r_i versus $p(\text{H}_2)$ plot goes through the origin of the axes (Fig. 3(b)).

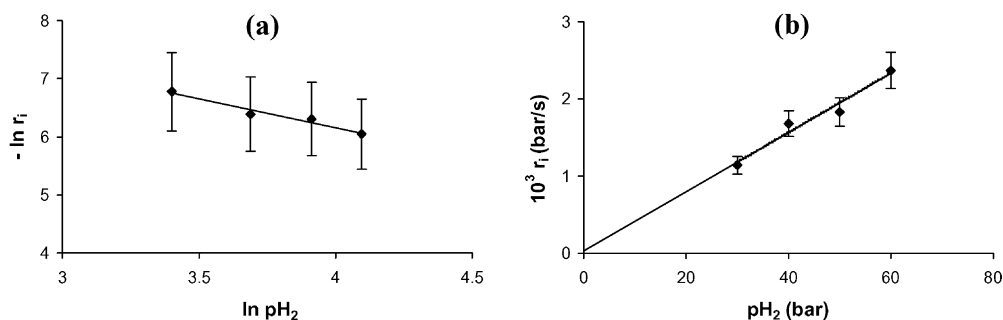


Fig. 3. Hydrogenation of 1-octene: rate dependence on dihydrogen pressure. Conditions as given in Table 1. (a) $-\ln r_1$ vs. $\ln p(H_2)$; (b) r_1 vs. $p(H_2)$.

3.5. Derivation of the experimental rate law

The results discussed above suggest that the nickel-catalyzed hydrogenation of 1-octene proceeds according to the experimental rate law

$$r = k_{\text{cat}}[\text{Ni}][1\text{-octene}]p(\text{H}_2) \quad (1)$$

The hydrogenation reaction is first-order in nickel, 1-octene and dihydrogen concentration. In the next section a theoretical rate law, based on a proposed mechanism, is derived. The value for the catalytic rate constant at 297 K was calculated from Eq. (1) resulting in: $k_{\text{cat}} = 0.009 \text{ mol}^{-2} \text{ l}^2 \text{ s}^{-1}$. To study the effect of the temperature on the rate constant the hydrogenation of 1-octene was performed at different temperatures.

3.6. Temperature

The effect of the temperature on the hydrogenation rate was studied in the 24–62°C range at a 1-octene concentration of 2.81 M, a nickel concentration of 1.40 mM and a dihydrogen pressure of 50 bar (Table 1, entries 12–16). It is assumed that the solubility of dihydrogen is not rate-limiting in the temperature range that was studied. The plot of $-\ln k_{\text{cat}}$ versus $1/T$, depicted in Fig. 4, yields a straight line ($-\ln k_{\text{cat}} = -4673.4/T - 10.936$, $R^2 = 0.976$), as expected from the Arrhenius equation (Eq. (2)).

$$k_{\text{cat}} = A \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

The activation energy of the hydrogenation reaction, E_a , can be calculated from the slope of the graph

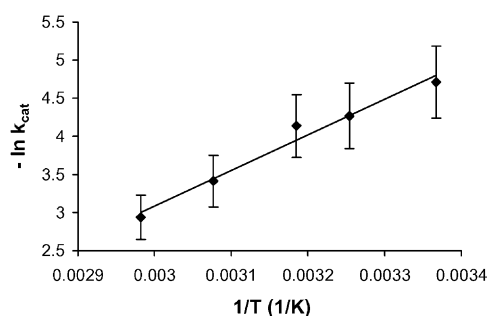


Fig. 4. Hydrogenation of 1-octene: rate dependence on temperature. Conditions as given in Table 1.

depicted in Fig. 4, the frequency factor A can be calculated from the intercept with the y-axis. Furthermore, the extrapolated value of the rate constant at 298 K and the values of enthalpy, entropy and free energy of activation can be calculated (from the equations $\Delta H^\ddagger = E_a - RT$, $\Delta S^\ddagger = R \ln(hA/e^2 K_B T)$, and $\Delta G^\ddagger = \Delta H - T\Delta S$, respectively). The calculated values are listed in Table 2.

Table 2
Activation parameters for the hydrogenation of 1-octene catalyzed by $[\text{Ni}(o\text{-MeO-dppp})(\text{OAc})_2]$

Parameter	Value
E_a	38.9 (kJ mol ⁻¹)
A	5.6×10^4 (mol ⁻² l ² s ⁻¹)
k_{cat} (298 K)	8.7×10^{-3} (mol ⁻² l ² s ⁻¹)
ΔH^\ddagger	36.4 (kJ mol ⁻¹)
ΔS^\ddagger	-170.6 (J K ⁻¹ mol ⁻¹)
ΔG^\ddagger	87.2 (kJ mol ⁻¹)

The values in Table 2 are similar to the values obtained [7] for the homogeneous hydrogenation of cyclohexene with $[\text{RuH}(\text{CO})(\text{NCMe})_2(\text{PPh}_3)_2](\text{BF}_4)_2$. The relatively small activation energy for the nickel-catalyzed hydrogenation of 1-octene indicates that the nickel–phosphane complex is a fairly efficient catalyst precursor for this reaction.

It appears that the addition of *n*-hexane does not significantly influence the catalytic rate constant of the hydrogenation reaction at room temperature, $k_{\text{cat}} = 0.036$ (entry 6, Table 1) compared to $k_{\text{cat}} = 0.033$ (entry 15, see Table 1).

3.7. Other substrates

The catalyst containing the ligand *o*-MeO-dppp was tested in the hydrogenation of a number of substrates. The results are presented in Table 3.

It appeared that the hydrogenation rate of an internal alkene (cyclooctene) is much lower compared to that of a terminal alkene (1-octene). The catalyst thus shows the same behavior towards different substrates as does the Wilkinson's catalyst [8]. However, the hydrogenation of ethene was found to be very fast compared to that of 1-octene. This fast hydrogenation rate is remarkable, as ethene is not hydrogenated by the otherwise very active Wilkinson's catalyst. It was found that ethene forms a very stable complex once it is coordinated to the rhodium ion [8]. The fast hydrogenation of ethene indicates that the intermediate nickel ethene complex formed with our catalyst is relatively unstable, which goes along with the

fact that a nickel complex is used for the oligomerization of ethene (SHOP process) [9]. These observations are in agreement with the substrate appearing in the rate-determining step of the hydrogenation, as the hydrogenation rate is highly dependent on the substrate that is used.

When 1,7-octadiene is used as the substrate the hydrogenation activity was observed in first 10 min of the reaction. In the remaining 50 min no hydrogenation activity can be observed. It is assumed that the diene is not only hydrogenated, but also isomerized to conjugated dienes. These conjugated dienes may result in the formation of stable allyl complexes with nickel, leading to catalyst deactivation. It is likely that these inactive allyl complexes are also formed when styrene is used as the substrate. Finally, it appears that the nickel catalyst is not able to hydrogenate alkynes.

4. Discussion

The kinetic analysis presented above allows proposing a catalytic cycle for the hydrogenation of 1-octene. The proposed catalytic cycle depicted in Scheme 1 largely resembles the catalytic cycle which was proposed after an investigation of the influence of solvents and anions on the nickel-catalyzed hydrogenation of 1-octene [2]. As the selectivity of the hydrogenation is in all cases well above 90%, the isomerization of 1-octene to internal octenes is not taken into account. First, the coordinating acetate anions are (partly) replaced by solvent molecules and cationic species are formed. Subsequently, dihydrogen is activated via heterolytic cleavage. It has been reported that this heterolytic cleavage of dihydrogen is greatly enhanced in the presence of a base [10]. In the present case the acetate anions can serve as a base and stabilize the proton which is released in the heterolytic cleavage of dihydrogen as the nickel hydride species $[\text{NiH}(\textit{o}\text{-MeO-dppp})\text{S}]^+$ (B) is formed. Compound (B) is the active intermediate entering the catalytic cycle, which can then be constructed through three simple consecutive steps. Complex (B) reacts with 1-octene to form compound (C) through an equilibrium K_1 . In a consecutive equilibrium K_2 complex (C) converts to the nickel–alkyl derivative (D). Finally, species (D) undergoes reaction with dihydrogen to yield *n*-octane, thus regenerating compound (B) for the next cycle.

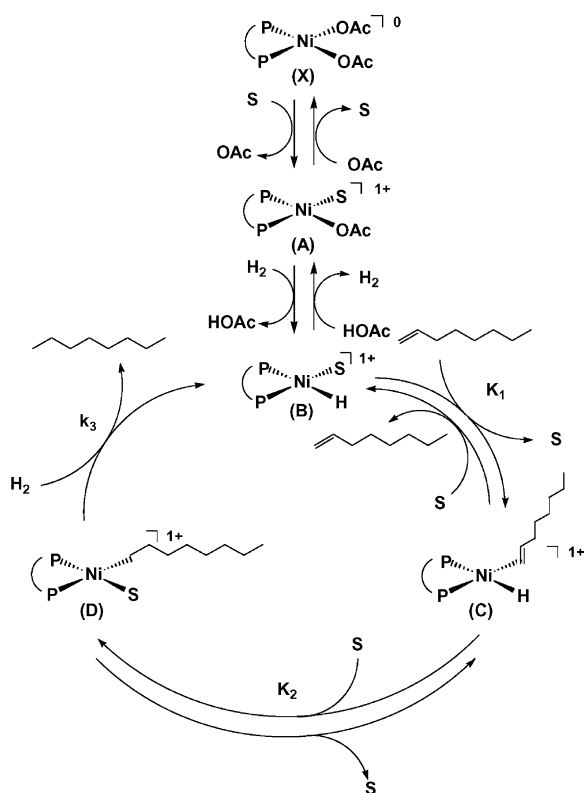
Table 3
Different substrates in the nickel-catalyzed hydrogenation^a

Entry	Substrate	TOF ^b	Substrate/ nickel	Main product
1	1-Octene	1480	2000	<i>n</i> -Octane
2	Ethene ^c	9000	2000	Ethane
4	Cyclooctene	30	400	Cyclooctane
5	1,7-Octadiene	30	1000	1-Octene
6	Styrene	0	200	
7	1-Octyne	0	250	

^a Reactions conditions: $[\text{Ni}] = 2.5 \text{ mM}$ (before substrate is added), $t = 1 \text{ h}$, $p(\text{H}_2) = 50 \text{ bar}$, $T = 50^\circ\text{C}$, in 20 ml dichloromethane/methanol (1:1, v/v).

^b Turnover frequency is mol converted substrate per mol nickel in 1 h.

^c $T = 40^\circ\text{C}$ and $t = 10 \text{ min}$.



Scheme 1.

This final reaction with dihydrogen could be through oxidative addition followed by rapid reductive elimination, as is suggested for some Ru(II) catalysts [7,11]. In the present case, however, this is not so likely, because oxidative addition of dihydrogen involves the formation of a nickel(IV) species, which is rather unstable [12]. Therefore, another heterolytic cleavage (hydrogenolysis) is considered to be most likely at this moment.

If we assume that the rate-determining step of the catalytic cycle is the reaction of (D) with dihydrogen, then the overall hydrogenation rate will be given by Eq. (3).

$$r = k_3[D][H_2] \quad (3)$$

Considering the equilibria K_1 and K_2 and the mass balance for the amount of nickel involved in the catalytic cycle ($[Ni]_{cat} = [B] + [C] + [D]$), $[D]$ can be solved. After substitution in Eq. (3), the rate

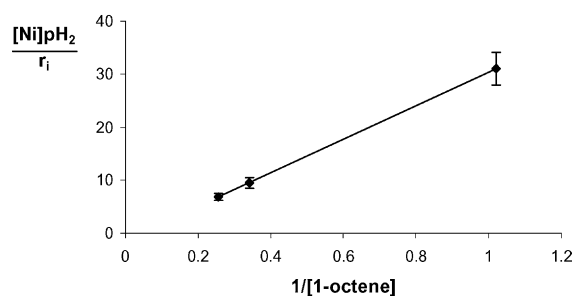


Fig. 5. Hydrogenation of 1-octene: correlation derived from rate expression (Eq. (4)) based on data from Table 1.

expression can be rewritten as

$$r = \frac{k_3 K_1 K_2 [Ni]_{cat} [1\text{-octene}] [H_2] [S]}{[S] + (K_1 [1\text{-octene}]) (1 + K_2 [S])} \quad (4)$$

Eq. (4) can be reorganized as

$$\frac{[Ni]_{cat} [H_2]}{r} = \frac{1}{k_3 K_1 K_2 [1\text{-octene}]} + \frac{1 + K_2 [S]}{k_3 K_2 [S]} \quad (5)$$

In the mass balance for the total amount of nickel species (X) and (A) are also taken into account

$$[Ni]_{tot} = [Ni]_{cat} + [X] + [A] \quad (6)$$

It is assumed that the concentrations of (X) and (A) are negligible after the induction period in which species (B), which enters the catalytic cycle, is formed. This is confirmed by the zero intercept of the r_i versus $[Ni]$ plot (see Fig. 1) with the y-axis and the first-order dependency of the hydrogenation rate of the nickel concentration. The amount of nickel in the catalytic cycle is thus equal to the total amount of nickel in the reaction mixture.

A plot of $[Ni]p(H_2)/r_i$ versus the reciprocal of 1-octene concentration gives a straight line ($[Ni]p(H_2)/r_i = 31.614/[1\text{-octene}] - 1.2508$, $R^2 = 1$) in agreement with derived rate law given in Eq. (5) (Fig. 5).

5. Conclusion

The rate expression for the homogeneous hydrogenation of 1-octene (Eq. (4)) derived from the proposed mechanism (Scheme 1) is in complete accordance with the surprisingly simple experimental

rate law (Eq. (1)). The first-order dependence in the nickel concentration suggests that no dinuclear nickel complexes with two bridging hydrides are formed and that only mononuclear nickel complexes are present. This absence of such dinuclear species is remarkable as these dinuclear complexes $[\text{Ni}(\text{L})(\mu\text{-H})_2]$, have been described for a number of didentate phosphane ligands, namely 1,2-bis(dicyclohexylphosphanyl)-ethane or -propane [13], 1,2-bis(diisopropylphosphanyl)-ethane [14] or -propane [15] and 1,2-bis(di-*tert*-butylphosphanyl)-ethane [16]. The molecular structure of $[\text{Ni}(\text{dcp})(\mu\text{-H})_2]$ determined by X-ray crystallography has been reported [17].

The proposed mechanism is in accordance with earlier reported observations [2]. Species S (coordinated solvent or anion) appears in the derived rate expression (Eq. (4)) and thus plays an important role in the hydrogenation. The dependence of the hydrogenation activity on the substrate provides evidence for the requirement that both the substrate and dihydrogen have to be activated by coordination to the transition metal before reaction can take place.

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