

**A Study on the Oligomerization of Olefins by
Nickel Complexes. VI.¹⁾
A Kinetic Study of Propylene Dimerization Catalyzed by
Bis(acetylacetonato)nickel(II)-Triethyldialuminium
Trichloride-Triphenylphosphine**

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The kinetics of homogeneous propylene dimerization catalyzed by bis(acetylacetonato)nickel(II)-triethyldialuminium trichloride-triphenylphosphine in toluene was investigated at low temperatures, -50 – -20°C and high propylene concentrations, 0.44 – 2.25 mol l^{-1} (propylene/nickel molar ratio of 240 – 2400). The rate of dimer formation can be represented by the form:

$$\frac{d[\text{C}_3\text{H}_6]}{dt} = k[\text{Ni}][\text{C}_3\text{H}_6]$$
$$k = 10^{10.1} \exp(-13000/RT) \text{ mol}^{-1} \text{ l s}^{-1}$$

where $[\text{Ni}]$ and $[\text{C}_3\text{H}_6]$ are the nickel and propylene concentrations, respectively. The reaction mechanism is discussed in the light of the kinetic results and useful information.

KEY WORDS: Catalyst activity / Dimerization rate / Kinetic parameter / Mechanism /

INTRODUCTION

Previously, the authors investigated the dimerization of propylene with bis(acetylacetonato)nickel(II)-triethyldialuminium trichloride-triphenylphosphine as homogeneous catalyst.^{2,3)} In this paper, a kinetic study was made for the dimerization of propylene in order to obtain some insight into the mechanism of this interesting catalytic reaction.

A few kinetic studies⁴⁾ have been made of the dimerization of propylene with homogeneous nickel catalysts. Hojabri⁵⁾ investigated the kinetics using the above catalyst at a temperature range of 25 – 50°C and has pointed out that the dimerization rate was second order in both nickel and propylene. In this investigation, special attention was paid to the reproducibility of the catalyst activity because the catalyst is unstable, and the measurements of initial rate were made at low temperatures. The kinetic results were different from those reported by Hojabri.

EXPERIMENTAL

Reagents. Toluene was purified and dried by the ordinary method. Com-

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mercial propylene (98.5 vol% pure) was well dried with molecular sieves. Bis(acetylacetonato)nickel, triethyldialuminium trichloride (Ethyl Corp.), and triphenylphosphine were obtained from commercial sources.

Catalyst Preparation. A standard procedure is exemplified. In a 300-ml flask equipped with a three-way stop cock and a thermometer were placed 360 mg (1.40 mmol) of bis(acetylacetonato)nickel and 1.47 g (5.60 mmol) of triphenylphosphine, and the flask was pumped for 1 h, followed by the addition of 210 ml of toluene. After cooling to -40°C in a Dry Ice-ethanol bath, the solution was degassed by evacuation and purged three times with nitrogen. At the temperature 3.47 g (14.0 mmol) of triethyldialuminium trichloride was slowly injected into the solution with stirring under nitrogen atmosphere. The solution, containing each component in a ratio of $\text{Ni} : \text{Al}_2 : \text{P} = 1 : 10 : 4$, was then slowly warmed to 0°C and stored in a refrigerator (at about 5°C). Aliquots (mainly 30 ml) of this solution were used as the catalyst for each kinetic run.

Dimerization and Its Kinetic Measurement. A typical example is as follows. A 200-ml three-necked flask equipped with a thermometer, a gas inlet, and a three-way stop cock was charged with 70 ml of toluene and cooled to -40°C . The air in the flask was replaced with nitrogen, and then 10 g of propylene was dissolved in the toluene. The dimerization reaction was started by injecting 30 ml of the catalyst solution into the propylene solution at $-40 \pm 0.5^{\circ}\text{C}$ with stirring and allowed to continue at the temperature. Samples (*ca.* 2 ml) were withdrawn *via* the three-way stop cock using a well precooled syringe from time to time for analysis, and methanol-hydrochloric acid (2 : 3) was added to stop the reaction. The toluene layer was separated, washed with water, and dried over anhydrous calcium chloride. The dimerization products²⁾ were quantitatively analyzed by gas chromatography using a sebaconitrile column (10 m $\times$ 3 mm) at 50°C with helium as a carrier gas. Heptane was used as an internal standard. The maximum initial rate of the dimer formation was calculated from the curve of dimer yield against time.

RESULTS AND DISCUSSION

Catalyst Activity and Its Reproducibility. In a previous paper⁶⁾ the authors have pointed a notable fact that $\text{Ni}(\text{acac})_2-(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3-\text{P}(\text{C}_6\text{H}_5)_3$ catalyst showed a higher activity at 10°C than at 26°C in the isomerization reaction of 2-methyl-1-pentene. This suggests that the catalytic species is thermally unstable even at 26°C . Thus, in this study, low temperatures of -50 — -20°C were employed in order to prevent the deactivation of the catalyst, and the dimerization reaction was carried out in a static system containing propylene of comparatively high concentrations.

First, attempts were made to select the conditions of the development of the catalytic species, because reproducible rates were difficult to obtain even with immediate use of the catalyst prepared at a low temperature of -40°C . Figure 1 shows the variation of the rate (r) of dimer formation with the time during which the catalyst was stored at about 5°C prior to its use. In order to check the reproducibility of the data, four series of rate measurements were made using four catalyst solutions prepared separately. The initial deactivation was pronounced uniformly in each of the four series, though

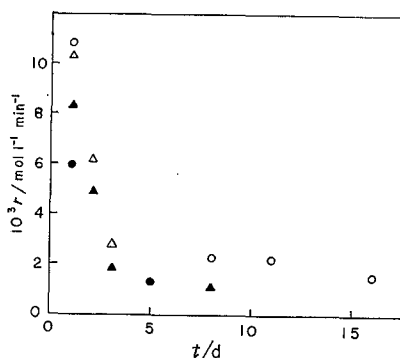


Fig. 1. Variation of the dimerization rate with storage time. The initial rates at -40°C were measured; the same mark means a series of measurements made using the catalyst solution prepared in one run.

the cause is unclear, but after several days the activity was roughly the same. In the following experiments, therefore, every catalyst solution prepared was stored in a refrigerator for several days and used for a series of kinetic measurements.

Rate Law. Dependence on Propylene Concentration: Initial rates were measured with varying the propylene concentration from 0.44 to 2.25 mol l^{-1} at a nickel concentration of 1.82 mmol l^{-1} and -40°C . A plot of $\log r$ vs. $\log [\text{C}_3\text{H}_6]$, though the points somewhat scatter along a straight line, indicates that the rate under such conditions is first order with respect to the propylene concentration (Fig. 2).

Dependence on Catalyst Concentration: The effect of the catalyst concentration was examined by varying the nickel concentration from 0.91 to 3.64 mmol l^{-1} at a propylene concentration of 2.18 mol l^{-1} and -40°C . A plot of $\log r$ vs. $\log [\text{Ni}]$ indicates that the rate is first order with respect to the nickel concentration (Fig. 3).

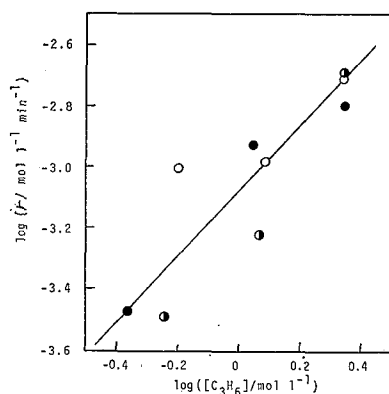


Fig. 2.

Fig. 2. Plot of $\log r$ vs. $\log [\text{C}_3\text{H}_6]$.

Three series of measurements, $\circ$, $\bullet$, and $\circ$, were made at Ni : 1.82 mmol l^{-1} and -40°C .

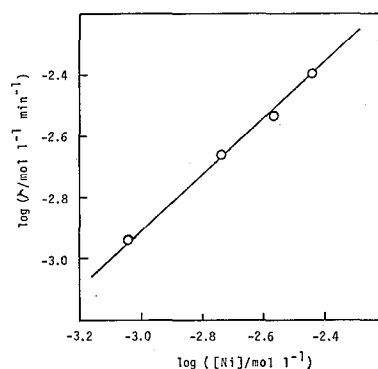


Fig. 3.

Fig. 3. Plot of $\log r$ vs. $\log [\text{Ni}]$.

Propylene: 2.18 mol l^{-1} , Temp: -40°C .

Kinetic Study of Propylene Dimerization

Table I. Dependence of Rate Constant on Temperature

$\frac{T}{K}$	$\frac{10^2 k}{\text{mol}^{-1} \text{ l s}^{-1}}$
253	6.75
243	2.58
	2.31
233	0.798
223	0.205
	0.228

Propylene: 2.18 mol l⁻¹, Ni: 1.82 mmol l⁻¹.

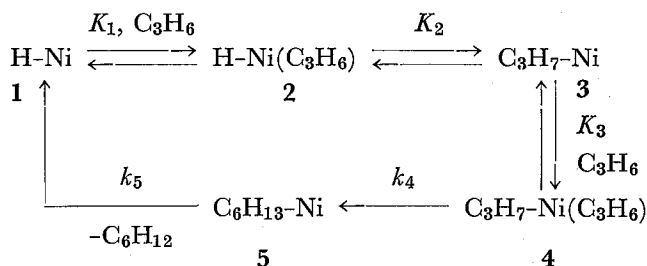
From the above results, the experimental rate law is:

$$r = k[\text{Ni}][\text{C}_3\text{H}_6] \quad (1)$$

where [Ni] and [C₃H₆] are the concentrations of bis(acetylacetonato)nickel and propylene used, respectively. The rate law is different from that at a high temperature of 30°C presented by Hojabri.⁵⁾ Here, it must be kept in mind that he measured the rate by an integral method without paying special attention to the deactivation of the catalyst.

Kinetic Parameters. The effect of temperature on the rate was examined at temperatures ranging from -50 to -20°C in order to obtain kinetic parameters. The rate constants, shown in Table I, give a linear Arrhenius plot and is summarized by the equation: $k = 10^{10.1} \exp(-13000/RT) \text{ mol}^{-1} \text{ l s}^{-1}$. From a value of E_a of 13.0 kcal mol⁻¹ and the specific rate constant at -40°C of $7.98 \times 10^{-3} \text{ mol}^{-1} \text{ l s}^{-1}$, the following activation parameters at -40°C were calculated: $\Delta H^\ddagger = 12.5 \text{ kcal mol}^{-1}$, $\Delta F^\ddagger = 15.8 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -13.8 \text{ cal mol}^{-1} \text{ K}^{-1}$. It is interesting to compare these values with those found by Hojabri:⁵⁾ $\Delta H^\ddagger = 8.95 \text{ kcal mol}^{-1}$, $\Delta F^\ddagger = 8.95 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 0 \text{ cal mol}^{-1} \text{ K}^{-1}$ (calculated for $r = -d[\text{C}_3\text{H}_6]/dt$).

Mechanistic Implications. The catalytically active species for the dimerization reaction is considered to be a square-planar nickel hydride^{4,7)} which is formed as a result of β -elimination of ethylene from an intermediate ethylnickel.^{8,9)} The kinetic results observed can be explained in terms of a mechanism shown in Scheme 1. The mechanism is essentially the same with that proposed in previous papers.^{2,3)} The first, second, and third steps are reversible. The fourth step is irreversible. The fifth



Scheme 1. Mechanism of the dimerization

step gives the dimer and a nickel hydride, the latter of which continues the kinetic chain. At the fifth step the reversible reaction may be neglected because the dimer concentration is low in an early stage and the coordination ability of the dimer to the nickel hydride is weak compared with that of propylene.

The above kinetic results do not give any information concerning the rate-determining step in the mechanism; the observed rate law (Eq. (1)) can be derived on certain assumptions even though any step in Scheme 1 is the rate-determining step. The fourth step, however, seems to be the rate-determining step in view of the observation by Cramer¹⁰ that the insertion of ethylene into an ethylrhodium complex is the rate-determining step of rhodium catalyzed ethylene dimerization. Thus, it is assumed that the preequilibria prior to the fourth step are set up quickly and the C_6H_{12} -Ni intermediate (5) is sufficiently reactive and scarce for steady-state treatment to be applied. From the above assumption

$$[Ni^*] = f[Ni] = [1] + [2] + [3] + [4] \quad (2)$$

if the total concentration of the catalytically active nickel species, $[Ni^*]$, is directly proportional to $[Ni]$. The rate of dimer formation can be presented by the following equation:

$$r = \frac{d[C_6H_{12}]}{dt} = \frac{fK_1K_2K_3k_4[Ni][C_3H_6]^2}{1 + K_1(1 + K_2)[C_3H_6] + K_1K_2K_3[C_3H_6]^2} \quad (3)$$

where K_1 , K_2 , and K_3 are the equilibrium constants for the first, second, and third steps respectively. Now, if $K_1(1 + K_2)[C_3H_6] \gg 1 + K_1K_2K_3[C_3H_6]^2$ in the denominator of Eq. (3), i.e. $[2] + [3] \gg [1] + [4]$ in the steady state, Eq. (3) is reduced to

$$r = \frac{fK_2K_3k_4}{1 + K_2} [Ni][C_3H_6] \quad (4)$$

which rate equation is in agreement with the observed rate law (Eq. (1)). That is to say, $k = fK_2K_3k_4/(1 + K_2) = 10^{10.1} \exp(-13000/RT) \text{ mol}^{-1} \text{ l s}^{-1}$. Conversely, this agreement appears to suggest that in the catalytic cycle 2 and/or 3 of the preequilibrium intermediates, 1-4, exist in high concentrations under our conditions: low temperatures, -50 — -20°C and high propylene concentrations, 0.44 – 2.25 mol l^{-1} ($[C_3H_6]/[Ni]$ ratio = 240 – 2400).

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