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Hydrooligomerization of Butadiene with Nickel Complex Catalyst

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SUMMARY

Oligomerization of butadiene with the catalyst system of nickel(II)chloride, electron donor, and lithium aluminum hydride or sodium borohydride has been studied. Most oligomers obtained with this catalyst were linear, and dihydrogenated dimers, trimers, and tetramers. They were *n*-octa-1,6-diene, *n*-octa-1,7-diene, *n*-dodeca-1,6,10-triene, and *n*-hexadeca-1,6,10,14-tetraene, which were identified by means of infrared, nuclear magnetic resonance, and mass spectrometry. Yields of each oligomer were strongly affected by the nature of the electron donors used. The hydrogen required for the formation of the hydrooligomers was assumed to originate from the lithium aluminum hydride or sodium borohydride used as a reducing agent. A proposed mechanism for the hydrooligomerization is that butadiene is oligomerized on the nickel atom, and the produced oligoolefins, bonded to the nickel by two terminal π -allylic bonds, are dihydrogenated to linear hydrooligomers.

INTRODUCTION

Many complex catalyst systems of transition metals for oligomerization of butadiene have been reported, most of which are obtained from the first-row transition metal compounds and organometallic compounds. In

particular, the catalysts containing zero-valent nickel have been known to yield cyclic oligomers from butadiene in aprotic solvents [1]

In a previous paper [2], however, we reported briefly that a dihydrogenated linear tetramer of butadiene was recovered from an oligoolefin-nickel complex produced by electrolytic reduction of tetrakis(pyridine)nickel(II) chloride in the presence of butadiene. In the course of investigations on the formation mechanism of the linear oligoolefin-nickel complexes by means of electrolysis, we found that the same hydrooligomers of butadiene were also obtained with reducing agents including active hydrogen, such as lithium aluminum hydride and sodium borohydride.

This paper deals with results of the hydrooligomerization of butadiene and attempts to elucidate the mechanism of the reaction.

EXPERIMENTAL

Materials

1,2-Dimethoxyethane, produced by the Ansul Company, and ethyl ether were dried with lithium aluminum hydride and metal sodium, respectively, and distilled under nitrogen. Ethyl alcohol was purified and dried with a Grignard's reagent according to the method described by Lund and Bjerrum [3].

Butadiene was dried with lithium aluminum hydride and freshly distilled before use. Triphenylphosphine was recrystallized from ethyl alcohol solution. Pyridine and piperidine were distilled over NaOH under nitrogen. Nickel(II)chloride was prepared by dehydrating hexa-aqua-nickel(II)chloride with thionylchloride [4]. Lithium aluminum hydride and sodium borohydride were used without further purification.

Oligomerization Reactions

Reactions were carried out under nitrogen in a 500-ml, four-necked flask fitted with a reflux condenser cooled with dry ice and methyl alcohol, a dropping funnel, a nitrogen inlet, and a thermometer. In a typical experiment, after being filled with nitrogen, the flask was charged with 25 mmoles of nickel(II)chloride, 50 ml of 1,2-dimethoxyethane, and a chemical equivalent amount of an electron donor such as pyridine or triphenylphosphine. Freshly distilled butadiene (0.5 mole) was trapped in the flask, which was cooled in a Dry Ice and methyl alcohol bath and then warmed to room temperature in a water bath. A solution

of 4 g (0.1 mole) of lithium aluminum hydride in 100 ml of 1,2-dimethoxyethane was gradually added dropwise from the dropping funnel into the flask with magnetic stirring. After all the solution of lithium aluminum hydride in dimethoxyethane was added, the reaction mixture, which became dark brown, was stirred for 1 hr. The reaction mixture was then treated with 2 N HCl in order to destroy the produced oligoolefin-nickel complexes and the unreacted lithium aluminum hydride. A mixture of butadiene oligomers was extracted with diethyl ether; the extract was washed with water several times, dried over Na_2SO_4 , and recovered by removal of diethyl ether under reduced pressure.

Analysis

All yields were based on weights of distilled products and were determined by gas chromatographic analysis of known weights of mixtures of isomeric dimers, trimers, and tetramers of butadiene obtained by the reactions described herein. Yield of each oligomer was calculated from relative signal intensity in the gas chromatogram. The components of oligomer mixtures were isolated by preparative gas chromatography on silicon grease, and their respective structures were verified by infrared, ultraviolet, nuclear magnetic resonance, mass spectrometric, and/or elemental analysis.

A gas chromatograph (Ökura-Rikagaku) fitted with a copper tube (4 mm X 4 m) packed with Apiazon L on Diasolid was employed, and hydrogen was used as a carrier gas. The gas chromatograph was operated under the following conditions: For the analysis of dimers of butadiene, the temperatures of the column and the injection part were 120 and 200°C, respectively, and the hydrogen flow rate was 60 ml/min. For trimers and tetramers, the temperatures of the column and the injection part were 180 and 250°C, respectively, and the hydrogen flow rate was 120 ml/min.

Infrared spectra were recorded on a Jasco double-beam infrared spectrophotometer, Model IR-G, as a liquid film, as ultraviolet and visible spectra on a Shimadzu Model SV-50A spectrophotometer, as nuclear magnetic resonance spectra at 60 Mc on a JEOL Model C-60 in carbon tetrachloride solution with tetramethylsilane as internal standard, and as mass spectra on a Hitachi Model RMU-5B.

Identification of Oligomers

The results of infrared, nuclear magnetic resonance, and mass spectrometric analysis of each oligomer of butadiene are shown in Table 1.

Table 1. Spectrometric Analysis of Oligomers

Components	Molecular weight ^a	IR			NMR	
		Frequency, cm ⁻¹	Vibration mode	τ value, ^b ppm	Intensity ratio	Assignment
A _C	108	1650(s)	Conjugated	3.4-4.7	1	=CH-
		1605(s)	ν C=C			
		1410(s)	ν CH ₂ (CH=CH ₂)			
		1000(s)	δ CH ₂ (CH=CH ₂)			
		965(s)	δ CH(transCH=CH ₂)			
		913(s)	δ CH ₂ (CH=CH ₂)			
B	110	1640(s)	Unconjugated	3.8-4.9	3	=CH-
		1410(s)	ν C=C			
		1380(s)	ν CH ₂ (CH=CH ₂)			
		995(s)	δ CH ₃			
		965(s)	δ CH ₂ (CH=CH ₂)			
		913(s)	δ CH(transCH=CH ₂)			
				8.83	2	-CH ₂ -
				8.49	3	=C-CH ₃
				8.0	4	=C-CH ₂ -
				4.9-5.45	2	=CH ₂

C	110	1640(s)	Unconjugated	3.9-4.86	1	=CH-
		1410(s)	ν C=C			
		990(vs)	ν CH ₂ (CH=CH ₂)	4.86-5.40	2	=CH ₂
		910(vs)	δ CH ₂ (CH=CH ₂)	7.9	2	=C-CH ₂ -
			δ CH ₂ (CH=CH ₂)	8.63	2	-CH ₂ -
D	164	1640(s)	Unconjugated	3.90-4.86	1	=CH-
		1410(s)	ν C=C			
		1380(s)	ν CH ₂ (CH=CH ₂)	4.86-5.50	2	=CH ₂
		990(s)	δ CH ₃	8.0	8	=C-CH ₂ -
		965(s)	δ CH ₂ (CH=CH ₂)	8.48	3	=C-CH ₃
		910(s)	δ CH(transCH=CH ₂)			
			δ CH ₂ (CH=CH ₂)	8.73	2	-CH ₂ -

^aDetermined by mass spectrometry (parent peak m/e).

^bAll chemical shifts are reported in parts per million downfield from tetramethylsilane.

^cThe ultraviolet spectrum of A showed an absorption due to the conjugated double bond at 226.5 m μ . Analysis: Calculated for C₈H₁₂: C, 88.82; H, 11.18. Found: C, 88.49; H, 11.18.

Table 2. Hydrooligomerization of Butadiene with Nickel(II) Compounds and Sodium Borohydride in Ethyl Alcohol

Expt. no.	Ni(II) compounds, mmoles	Butadiene $\frac{\text{Ni(II)}}{\text{Ni(II)'}}$, mole ratio	NaBH ₄ $\frac{\text{Ni(II)'}}, mole ratio$	Conversion, ^a %	Products ^b (mmoles) ^c			
					OD	OT	DT	HDT
I-011	NiCl ₂ ·2PPh ₃ 10	40	4	60	79	39	Trace	0
I-013d	NiCl ₂ ·2PPh ₃ 10	40	4	58	68	28	Trace	0
035	NiCl ₂ ·4Pyridine 100	12	2	7.7	38	0	32	22

^aBased on the amount of butadiene added.

^bSmall amounts of isomers have been identified. OD: n-octa-1,6- and -1,7-diene; OT: n-octa-1,3,7-triene; DT: n-dodeca-1,6,10-triene; HDT: n-hexadeca-1,6,10,14-tetraene.

^cDetermined by gas chromatography.

^dHydrogen gas was bubbled through the reaction mixture during the addition of a solution of sodium borohydride in ethyl alcohol.

Components A, B, and C were confirmed to be *n*-octa-1,3,7-triene, *n*-octa-1,6-diene, and *n*-octa-1,7-diene, respectively. The spectrometric analysis of D indicates that it should be *n*-dodeca-1,6,10-triene or *n*-dodeca-1,5,10-triene, both of which had essentially identical infrared and nuclear magnetic resonance spectra. However, on considering the formation mechanism described in a following section, the structure of D may be assumed to be *n*-dodeca-1,6,10-triene.

Other components of butadiene oligomers obtained herein, such as 4-vinyl-cyclohexene, cycloocta-1,5-diene, cyclododeca-1,5,9-triene, and *n*-hexadeca-1,6,10,14-tetraene, were identified by gas chromatography. The identification by gas chromatography was conducted by comparing retention times with those of authentic samples, which were either available commercially or were prepared by known methods.

RESULTS AND DISCUSSION

Oligomerization of Butadiene with Nickel(II) Compounds-Sodium Borohydride

A mixture of nickel(II) compounds and sodium borohydride in the presence of butadiene in ethyl alcohol at room temperature and atmospheric pressure gave a dark-brown solution. The solution was treated with 2 N HCl and extracted with diethyl ether. A mixture of butadiene oligomers was recovered from the extracts, and most of the oligomers were found to be linear and dihydrogenated. The results of these experiments are indicated in Table 2.

When bis(triphenylphosphine)nickel(II)chloride was used with sodium borohydride, resultant complexes catalyzed hydrooligomerization of butadiene to *n*-octa-1,6- and -1,7-diene, accompanied by dimerization to *n*-octa-1,3,7-triene. With tetrakis(pyridine)nickel(II)chloride instead of the phosphine compound, only hydrooligomers, *n*-octa-1,6- and -1,7-diene, *n*-dodeca-1,6,10-triene, and *n*-hexadeca-1,6,10,14-tetraene were obtained, exclusive of *n*-octa-1,3,7-triene. The formation of the hydrooligomers appears to be affected by the rate of addition of ethanolic sodium borohydride solution; generally, a slower rate increases the formation of the hydrooligomers.

Linear dimerizations of butadiene have been carried out with complex catalysts containing cobalt [5], iron [6], nickel [7], palladium [8], or rhodium [9], to form methylheptatriene and/or *n*-octatriene. A linear

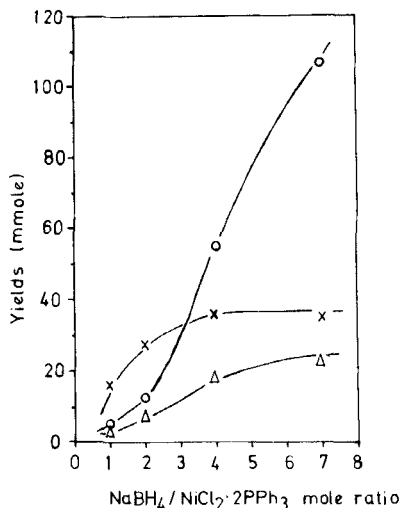


Fig. 1. Yields of each oligomer vs. mole ratio $\text{NaBH}_4/\text{NiCl}_2 \cdot 2\text{PPh}_3$. $\text{NiCl}_2 \cdot 2\text{PPh}_3$, 10 mmole; butadiene, 400 mmole; reaction temperature, 15–25°C; reaction time, 3 hr. ○, n-octa-1,6-diene; △, n-octa-1,7-diene; ×, n-octa-1,3,7-triene.

trimer, n-dodecatetraene, was obtained with the catalyst containing iron [6] or palladium [8]. We reported that a linear tetramer, n-hexadecatetraene, was obtained with electrolytic reduction of nickel compounds in the presence of butadiene.

Figure 1 shows that yields of each oligomer obtained by reducing $\text{NiCl}_2 \cdot 2\text{PPh}_3$ with NaBH_4 in the presence of butadiene depend on the mole ratio $\text{NaBH}_4/\text{NiCl}_2 \cdot 2\text{PPh}_3$. As the mole ratio increases, the yield of n-octa-1,6-diene increases remarkably, whereas that of n-octa-1,3,7-triene is gradually increased and reaches constant value. This fact suggests that the hydrogen of NaBH_4 contributes to the formation of the hydro-oligomers.

A profile of yields of oligomers vs. reaction time for the oligomerization of butadiene with the combined catalyst of $\text{NiCl}_2 \cdot 2\text{PPh}_3$ and NaBH_4 in ethyl alcohol is shown in Fig. 2, where the same amounts of butadiene and sodium borohydride as in the first addition were added after 120 min (↑ in figure). Figure 2 features the oligomerization where hydro-oligomers, n-octa-1,6- and -1,7-diene, are produced only during the addition of the solution of NaBH_4 in ethyl alcohol at both first and second addition of

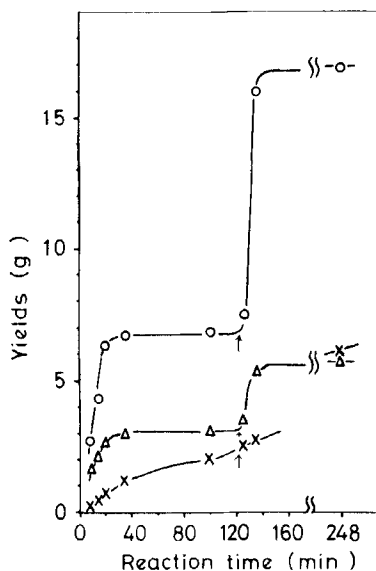


Fig. 2. Yields of oligomers vs. reaction time. First feed: $\text{NiCl}_2 \cdot 2\text{PPh}_3$, 10 mmoles; butadiene, 400 mmoles; NaBH_4 , 40 mmoles. Second feed (\uparrow): butadiene, 400 mmoles; NaBH_4 , 40 mmoles. \circ , n-octa-1,6-diene; Δ , n-octa-1,7-diene; \times , n-octa-1,3,7-triene.

NaBH_4 and butadiene. In contrast, n-octa-1,3,7-triene is gradually formed, independent of the addition of NaBH_4 . From the results, it is suggested that hydrogen required for the formation of the hydrooligomers originates from the sodium borohydride used as a reducing agent. The active complexes for the oligomerization are immediately formed at the addition of NaBH_4 , and they are stable enough to reveal their activity at the second addition of butadiene and sodium borohydride. The apparent rate of formation of n-octa-1,3,7-triene decreases during the addition of sodium borohydride. Therefore, n-octa-1,6- and -1,7-diene may not be produced by dihydrogenation of n-octa-1,3,7-triene but by another process.

It has been reported that cycloocta-1,5-diene and 4-vinylcyclohexene were formed via $\text{C}_8\text{H}_{12}\text{Ni}\cdot\text{PR}_3$ complex in the reaction of butadiene with $\text{Ni}(\text{CO})_2(\text{PR}_3)_2$ in benzene [10], whereas n-octa-1,3,7-triene, accompanied with small amounts of n-octa-2,6-diene, and acetone were formed in isopropyl alcohol and in $\text{C}_6\text{H}_5\text{OD}$ monodeuterated n-octa-1,3,7-triene. These findings lead us to assume that n-octa-1,3,7-triene and n-octa-2,6-diene are produced by hydrogen transfer and by hydrogenation of C_8H_{12} in the

Table 3. Oligomerization of Butadiene with Nickel(II)chloride-Electron Donor-Lithium Aluminum Hydride in 1,2-Dimethoxyethane

Expt. no.	NiCl ₂ , mmoles	Butadiene Ni(II) mole ratio	LiAlH ₄ Ni(II) mole ratio	Electron donors ^a	Conversion, ^b %	Products ^c (mmoles) ^d		
						OD	DT	HDT
050	50	12	2	—	20	13	27	Trace
053	25	39	4	Triphenyl- phosphine (2)	46	156	Small	0
054 ^e	25	35	4	Triphenyl- phosphine (2)	30	100	Small	0
025	25	17	2	Pyridine (8)	43	27	8	Small
049 ^e	50	13	2	Pyridine (4)	14	40	4	0
043	50	15	2	Piperidine (4)	26	16	28	12
037	50	20	2	ttt-Cyclo- dodecatriene (1)	45	30	71	Trace

^aA value in parentheses shows the mole ratio of electron donor/NiCl₂.

^bBased on the mole of butadiene introduced.

^cSmall amounts of cyclic and linear dimers and trimers have been identified. OD: n-octa-1,6- and -1,7-diene; DT: n-dodeca-1,6,10-triene; HDT: n-hexadeca-1,6,10,14-tetraene.

^dDetermined by gas chromatography.

^eHydrogen gas was bubbled through the reaction mixture during the addition of a solution of lithium aluminum hydride in 1,2-dimethoxyethane.

complex $C_8H_{12}Ni \cdot PPh_3$ with alcohol, respectively. On the basis of the facts, the hydrodimers *n*-octa-1,6- and -1,7-diene obtained with the catalyst composed of $NiCl_2 \cdot 2PPh_3$ and $NaBH_4$ appear to result from the hydrogenation of oligoolefin C_8H_{12} produced on the nickel atom with the hydrogen of $NaBH_4$ and/or ethyl alcohol.

The participation of transition metal hydrides in the hydrogenation of olefins with the homogeneous catalyst has been proposed by a number of workers [12]. Sloan and co-workers found a catalyst derived from bis(tri-*n*-butylphosphine)nickel(II)chloride and triisobutylaluminum to be an effective olefin hydrogenation catalyst [13]. In the absence of hydrogen gas, the same system catalyzed the codimerization of ethylene and butadiene [14]. A number of hydrooligomers of butadiene were produced with combined catalysts based on nickel compounds and sodium borohydride in the absence of hydrogen gas. However, in the presence of hydrogen gas, the same catalyst system sparingly decreased the amounts of hydrooligomers formed. From these results, it is assumed that nickel hydrides are not formed by reducing nickel(II) compounds with $NaBH_4$ in the presence of butadiene, and that sodium borohydride directly attacks the oligoolefin produced on the nickel atom to yield the hydrooligomers.

Oligomerization of Butadiene with Nickel(II)chloride-Lithium Aluminum Hydride

Nickel(II)chloride was reduced with lithium aluminum hydride in the presence of butadiene and an electron donor in 1,2-dimethoxyethane; it gave a dark-brown solution, which discolored in air. The oligomers obtained herein were mostly linear and dihydrogenated, as in the case of sodium borohydride (Table 3). The catalyst specificity and conversion of butadiene to oligomers were affected by the nature of electron donors used. When triphenylphosphine was used as an electron donor, linear hydrodimers such as *n*-octa-1,6- and -1,7-diene and small amounts of cycloocta-1,5-diene and 4-vinylcyclohexene were catalytically formed. *n*-Octa-1,3,7-triene could not be detected by gas chromatography. When pyridine or piperidine was used instead of triphenylphosphine, *n*-dodeca-1,6,10-triene and *n*-hexadeca-1,6,10,14-tetraene, as well as *n*-octadienes, were produced as in the case of sodium borohydride. In these experiments cyclic dimers and trimers were also formed as minor products. Amounts of oligomers were affected by the rate of addition of lithium aluminum hydride. A slower rate increased the amounts of linear oligomers, whereas the amounts of cyclic oligomers decreased. In the

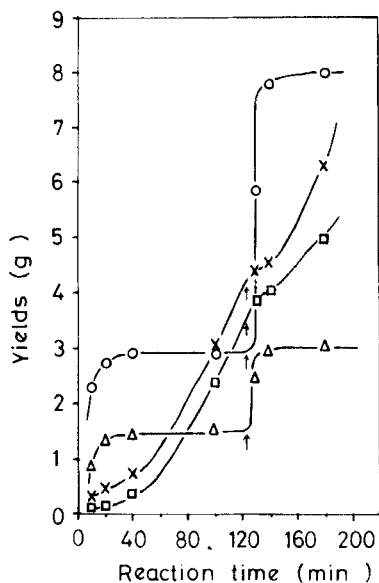


Fig. 3. Yields of oligomers vs. reaction time. First feed: NiCl_2 , 25 mmoles; PPh_3 , 50 mmoles; butadiene, 500 mmoles; LiAlH_4 , 50 mmoles. Second feed (\uparrow): Butadiene, 500 mmoles; LiAlH_4 , 50 mmoles. \circ , n-octa-1,6-diene; Δ , n-octa-1,7-diene; \times , 4-vinylcyclohexene; \square , cycloocta-1,5-diene.

presence of ttt-cyclododeca-1,5,9-triene, a main product was n-dodeca-1,6,10-triene.

The catalysts containing zero-valent nickel have yielded mostly cyclic oligomers from butadiene in aprotic solvents [10], and linear oligomers in protonic solvents [11]. In experiments carried out in an aprotic solvent such as 1,2-dimethoxyethane, linear hydrooligomers were obtained with the nickel catalysts using lithium aluminum hydride as a reducing agent. These facts suggest that hydrogen participates in the formation of the linear hydrooligomers. The hydrogen required for the formation of the hydro oligomers might originate from the lithium aluminum hydride, since the linear hydrooligomers n-octa-1,6- and -1,7-diene are formed only during the addition of the solution of lithium aluminum hydride (Fig. 3). Although Fig. 3 reveals features identical with those in the case of sodium borohydride, 4-vinylcyclohexene and cycloocta-1,5-diene are formed in place of n-octa-1,3,7-triene. The formation of the two cyclic dimers is slightly

Table 4. Visible Spectra Measurements

Samples	Solvent	λ max, $m\mu$	Ref.
NiCl ₂ ·butadiene-LiAlH ₄	DME ^d	425	
Ni·CDT ^a	DME	400	
Ni·CDT-butadiene ^b	DME	425	
C ₁₂ H ₁₉ ·NiCl ^c	n-Heptane	425	[15]

^attt-Cyclododeca-1,5,9-triene nickel (O) complex.

^bA solution after reaction of ttt-cyclododeca-1,5,9-triene nickel (O) complex with butadiene in 1,2-dimethoxyethane at 0°C for 3 hr.

^cDodeca-2,6,10-triene-1,12-diylnickel(I)chloride.

^d1,2-Dimethoxyethane.

depressed during addition of lithium aluminum hydride. This indicates that 4-vinylcyclohexene and cycloocta-1,5-diene are formed on the same active species as those for n-octa-1,6- and -1,7-diene.

As in the case of sodium borohydride, hydrogen gas bubbled through the reaction mixture during the addition of lithium aluminum hydride rather decreased the amounts of hydroooligomers. The hydroooligomers, therefore, appear to be produced by the direct attack of lithium aluminum hydride on oligoolefin nickel complexes such as C₈H₁₂Ni·PR₃, which is assumed to be an active species for the formation of cycloocta-1,5-diene and 4-vinylcyclohexene [10].

Mechanism for Hydroooligomerization

We have obtained a number of butadiene oligomers with combined catalysts composed of nickel(II)chloride, electron donor, and lithium aluminum hydride or sodium borohydride, almost all of the oligomers being linear and dihydrogenated. It has been proposed that the hydroooligomers are produced by the hydrogen attack on the oligoolefin nickel complexes, and that the hydrogen arises from lithium aluminum hydride or sodium borohydride used as a reducing agent.

In order to study the coordination structure of the oligoolefin to nickel atom, two experiments were carried out. One used visible spectra measurements. As shown in Table 4, the reaction mixture produced by reducing nickel(II)chloride with lithium aluminum hydride in the presence of

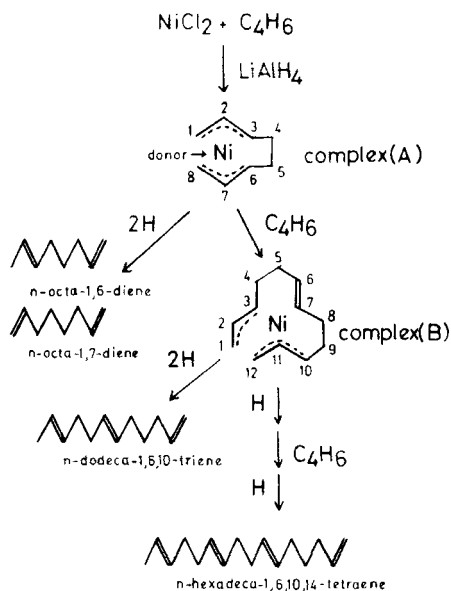


Fig. 4. Scheme for a mechanism of hydroooligomerization.

butadiene in 1,2-dimethoxyethane gave an absorption at $425 \text{ m}\mu$, compared with a solution of nickel (O)-cyclododecatriene complex in 1,2-dimethoxyethane, which exhibited a strong absorption at $400 \text{ m}\mu$. When the solution was treated with butadiene for 3 hr at 0°C , the absorption band shifted to $425 \text{ m}\mu$, which may be due to the coordination of π -allylic group to nickel atom (d-d transition) [10, 15]. These results led us to assume that π -allylic complexes such as octa-2,6-diene-1,8-diyl(donor) nickel (complex A) and dodeca-2,6,10-triene-1,12-diylnickel (complex B), shown in Fig. 4, are produced in this experiment.

The other experiment was an attempt to confirm the structure of the π -allylic complexes. After treating butadiene with the combined catalyst of nickel(II)chloride and lithium aluminum hydride in 1,2-dimethoxyethane, unreacted butadiene was removed from the reaction mixture under reduced pressure. The residual solution was divided equally into two parts. One was treated with 2 N HCl (HCl-treatment) and the other was treated with 2 N HCl after adding triphenylphosphine (PPh_3 -HCl treatment). The butadiene oligomers were extracted with diethyl ether. The HCl treatment yielded linear dimers and trimers as main products, whereas the PPh_3 -HCl

Table 5. Yields of Each Oligomer by Two Different Treatments

(A) NiCl ₂ -butadiene-LiAlH ₄ -DME system (NiCl ₂ , 50 mmoles; LiAlH ₄ /Ni(II), 2; butadiene/Ni(II), 12; reaction temperature, 15-25°C; reaction time, 3 hr)					
Treatments	Oligomer yield, g				
	Dimers ^a			Trimers ^b	
	n-OD	VCH	COD	n-DT	CDT
2 N HCl	0.71	0.10	0	2.20	0.25
PPh ₃ -2 N HCl	0.36	0.10	0.06	0.55	1.29

(B) NiCl ₂ -butadiene-PPh ₃ -LiAlH ₄ -DME system (NiCl ₂ , 25 mmoles; LiAlH ₄ /Ni(II), 4; butadiene/Ni(II), 39; reaction temperature, 15-25°C; reaction time, 3 hr)					
Treatments	Oligomer yield, g				
	Dimers			Trimers	
	n-OD	VCH	COD	n-DT	CDT
2 N HCl	8.50	1.10	0.60	0.50	0.40
PPh ₃ -2 N HCl	8.40	1.20	0.60	0.50	0.40

^an-OD: n-octadiene; VCH: vinylcyclohexene; COD: cyclooctadiene.

^bn-DT: n-dodecatriene; CDT: cyclododecatriene.

treatment gave cyclic dimers, cycloocta-1,5-diene and 4-vinylcyclohexene, and increased the amount of cyclododeca-1,5,9-triene [Table 5 (A)]. These results agree with the fact that complexes A and B reacted with triphenylphosphine to give respective cyclic oligomers, and with Al(C₂H₅)₂H and water to yield respective linear oligomers [10]. From the agreement, one would assume that complexes A and B might form in the reaction mixture. This is also supported by the results shown in Table 5 (B). Since bis π -allyl-type ligands of the complexes might be cyclized in the presence of triphenylphosphine before the treatments, two different treatments gave almost the same results. Complexes A and B have been assumed to be intermediates in the cyclic dimerization and trimerization of butadiene, respectively [11]. It is noteworthy that small amounts of the cyclic dimers and trimers of butadiene were formed in the reaction

of nickel(II) compound with lithium aluminum hydride in the presence of butadiene.

On the basis of these results, a mechanism for the formation of the hydrodimers and hydrotrimers with the combined catalyst of nickel(II)chloride, electron donor, and lithium aluminum hydride may be proposed as follows: Nickel(II)chloride is reduced to nickel atom by lithium aluminum hydride, and butadiene is oligomerized on the nickel atom to yield complexes A and B; then 1,6- or 3,6-carbons of C_8H_{12} in complex A and 1,10-carbons of $C_{12}H_{18}$ in complex B are directly dihydrogenated with lithium aluminum hydride to n-octa-1,6- or -1,7-diene, and n-dodeca-1,6,10-triene, respectively (Fig. 4).

The selective hydrogenation of the 1,6- or 3,6-carbons of C_8H_{12} in complex A can be explained by considering that 4-vinylcyclohexene and divinylcyclobutane were formed by coupling of the 1,6- and 3,6-carbons of C_8H_{12} in complex A [16].

When trialkylaluminum having no active hydrogen was used as a reducing agent in place of lithium aluminum hydride, cyclododeca-1,5,9-triene was catalytically formed, but n-hexadecatetraene was not formed. We may suppose that in the system containing lithium aluminum hydride, hydrogen rather than butadiene might attack $C_{12}H_{18}$ in complex B.

Therefore, in the case of the formation of n-hexadeca-1,6,10,14-tetraene as a hydrotetramer, one hydrogen atom attacks a π -allylic group of $C_{12}H_{18}$ in complex B to destroy a rare gas structure of nickel atom and to activate the other π -allylic group at the end of $C_{12}H_{18}$. Then one molecule of butadiene is inserted in the bonding between the π -allylic group and nickel atom, and the $C_{16}H_{26}$ produced on the nickel atom is directly hydrogenated to n-hexadeca-1,6,10,14-tetraene (Fig. 4).

The hydrooligomers obtained with the combined catalyst including sodium borohydride may be formed in the same way as in the case of lithium aluminum hydride.

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