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The Oligomerization of Butadiene with Nickel Complexes Produced by Means of the Electrolysis of Nickel(II) Chloride

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The oligomerization of butadiene has been found during the electrolysis of solutions containing nickel(II) chloride and electron donors. The oligomerization was affected by the nature of the electron donors used. When the ethanolic solutions of tetrakis(pyridine)nickel(II) chloride or nickel(II) chloride and pyridine with tetra-*n*-butyl ammonium perchlorate or methanolic solutions without the perchlorate were electrolyzed in the presence of butadiene, a number of linear and dihydrogenated oligomers, with small amounts of branched oligomers, were obtained. The main oligomers were identified as *n*-octadiene, *n*-dodecatriene, and *n*-hexadecatetraene. By adding triphenylphosphine to the reaction system in place of pyridine, *n*-octatriene and alkoxyoctadiene were catalytically produced instead of hydrooligomers, accompanied by tetrakis(triphenylphosphine)nickel(0). A mechanism involving π-allyl intermediates was proposed for the oligomerization.

It has been known that butadiene is oligomerized selectively to cyclic dimers and trimers with various catalyst systems containing lower-valency transition-metal compounds. Recently, several reports on the linear dimerization of butadiene by cobalt,[1] iron,[2] rhodium,[3] palladium,[4] and nickel[5] catalysts have been

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[1] E. W. Duck, D. K. Jenkins, J. M. Locke, and S. R. Wallis, *J. Chem. Soc., C*, **1969**, 227; S. Otsuka, T. Taketomi, and T. Kikuchi, *Kogyo Kagaku Zasshi*, **66**, 1094 (1963); T. Saito, T. Ono, Y. Uchida, and A. Misono, *ibid.*, **66**, 1099 (1963); D. H. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963); S. Tanaka, K. Mabuchi, and N. Shimazaki, *J. Org. Chem.*, **29**, 1626 (1964); M. Iwamoto, K. Tani, H. Igaki, and S. Yuguchi, *ibid.*, **32**, 4148 (1967).

[2] H. Takahashi, S. Tai, and M. Yamaguchi, *J. Org. Chem.*, **30**, 1661 (1965); M. Hidai, Y. Uchida, and A. Misono, This Bulletin, **38**, 1243 (1965); A. Carbonaro, A. Greco, and G. Dall, Asta, *Tetrahedron Lett.*, **1967**, 2037.

[3] T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **87**, 5638 (1965).

[4] a) S. Takahashi, T. Shibano, and N. Hagihara, *Tetrahedron Lett.*, **1967**, 2451; S. Takahashi, T. Shibano, and N. Hagihara, This Bulletin, **41**, 454 (1968); b) E. J. Smutny, *J. Amer. Chem. Soc.*, **89**, 6793 (1967).

[5] H. Muller, D. Wittenberg, H. Seibt, and E. Scharf, *Angew. Chem.*, (*Intern. Ed.*), **4**, 327 (1965); H. Seibt and N. V. Kutepow, *Belg. Pat.* 635483 (1964), *Chem. Abstr.*, **61**, 11891 (1964).

presented.

In a previous paper,[6] we reported that dihydrogenated linear dimers, trimers, and tetramers of butadiene were obtained with catalysts composed of nickel (II) chloride, electron donors, and lithium aluminum hydride or sodium borohydride. In the course of our studies of the synthesis of oligoolefin-metal complexes by means of the electrolytic reduction of metal salts, a novel tetramer of butadiene has been found.[7] We have also studied the oligomerization of butadiene in detail. This paper will deal with the results of butadiene oligomerizations by means of the electrolysis of alcoholic solutions containing nickel(II) chloride and electron donors, and with the identification of the oligomers obtained.

Experimental

Materials. Methyl and ethyl alcohols were purified and dried with the corresponding magnesium alkoxides according to the method by Lund and Bjerrum.[8] Ethyl ether was dried over Na and then with $LiAlH_4$, and distilled under a nitrogen stream. Butadiene was dried with $LiAlH_4$ and freshly distilled before use. Triphenylphosphine was recrystallized from ethyl alcohol. Pyridine, piperidine, and triethylamine were distilled over sodium hydroxide under nitrogen. Nickel(II) chloride, tetrakis(pyridine)nickel(II) chloride, and tetra-*n*-butylammonium perchlorate were prepared according to the known procedures and were purified by the usual methods.[9]

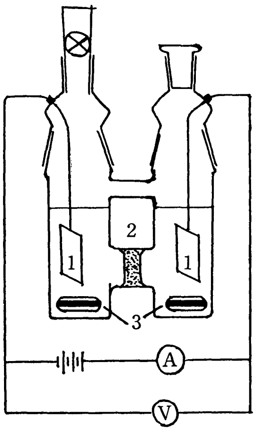

Fig. 1. Electrolysis cell.

A, ammeter; V, voltameter; 1, electrode; 2, sintered glass disk; 3, magnetic stirring bar

Electrolyses. The electrolyses were carried out in the modified H-type glass cell shown in Fig. 1. In a typical experiment, a cell equipped with a stopcock and containing 25 mmol of tetrakis(pyridine)nickel(II) chloride and magnetic stirring bars was dried under a vacuum. The atmospheric pressure was then restored using purified nitrogen. Under a blanket of nitrogen, 180 m*l* of methyl alcohol was transferred to the cell, which was then cooled in a dry ice-methyl alcohol bath and degassed on a vacuum system. Under a vacuum, butadiene was introduced *via* the trap-to-trap method. The stopcock connecting the cell to the vacuum line was then closed, and the electrolyte was warmed to the room temperature. The electrolysis was performed at ambient temperature, with the terminal voltage maintained at about 50 V for 20—40 hr; during this time, an amount of electricity of 2 Faradays per mol of nickel(II) chloride, as calculated from the current and time, was passed through the solution. The current was almost constant throughout the electrolysis, being 30 mA in ethyl alcohol and about 70 mA in methyl alcohol.

After electrolysis, the catholyte was treated with dilute hydrochloric acid in order to destroy the produced nickel complexes, which consisted of an oligoolefin, pyridine, and nickel. A mixture of the butadiene oligomers formed was extracted with diethyl ether, followed by washing with water and drying over anhydrous sodium sulfate, and concentrated under reduced pressure. Then the oligomers were fractionated by distillation.

Analyses. The amounts of all the oligomers obtained herein were calculated from the calibration curve for cyclododeca-1,5,9-triene, assuming that the molar responses of the dimers, trimers, and tetramers of butadiene to cyclododeca-1,5,9-triene are 1.25, 1, and 0.8 respectively, (It has been observed that the molar responses of 1-octene and hexadeca-1,6,10,14-tetraene to cyclododeca-1,5,9-triene are 1.25 and 0.8 respectively). The yields of the oligomers were based on the amounts of butadiene introduced. Each oligomer was isolated by fractional distillation and or by preparative gas chromatography, and their structures were verified by IR, NMR, and mass spectrometries and by elemental analyses.

A gas chromatograph (Shimadzu Seisakusho Ltd., GC-4APT) fitted with a copper tube (3 mm × 3 m) packed with Apiezon grease-L on Diasolid was employed to detect and determine dimeric, trimeric, and tetrameric isomers. The gas chromatograph was operated under the following conditions: for the analyses of the 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 m*l*/min. For trimers and tetramers, the temperatures of the column and the injection part were 180 and 200°C respectively, and the hydrogen flow rate was 120 m*l*/min. In order to isolate the respective oligomers, a gas chromatograph (Ohkura-Rikagaku) fitted with a copper tube (4 mm × 2 m) packed with Apiezon grease-L or polydiethylene glycol succinate on Diasolid was used under the same conditions as those presented above.

The infrared spectra were recorded on a Jasco IR spectrophotometer, Model IR-G, as a liquid film, the UV and visible spectra, on a Shimadzu Model SV-50A spectrophotometer, the NMR spectra, at 60 MHz on a JEOL Model C-60 in a carbon tetrachloride solution, with tetramethylsilane as the internal standard, and the mass spectra, on a Hitachi Model RMU-5B.

Identification of Oligomers. The results of the IR and NMR spectra, the elemental analyses, and the molecular-weight measurements of each oligomer of butadiene are shown in Table 1. On the basis of these results, the four oligomer fractions, 3-MOD, 1-MOD, 3-EOD, and 1-EOD, were confirmed to be 3-methoxyocta-1,7-diene, 1-methoxyocta-2,7-diene, 3-ethoxyocta-1,7-diene, and 1-ethoxyocta-2,7-diene respectively. On the contrary, to the other oligomer fractions, P-6, P-7, P-9, P-10, and P-11, many isomeric structures

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6) N. Yamazaki and T. Ohta, *J. Macromol. Sci.*, **A3**, 1571 (1969).

7) N. Yamazaki and S. Murai, *Chem. Commun.*, **1968**, 147.

8) H. Lund and J. Bjerrum, "Technique of Organic Chemistry. VII." Organic Solvents, Arnold Weissberger, Interscience Publisher, New York (1955), p. 334.

9) A. R. Pray, "Inorganic Synthesis. V," J. C. Bailar, Jr., Mcgrow-Hill Book Company, New York (1953), p. 153.

which give essentially identical IR and NMR spectra can be derived from the results of their spectrometric analyses. However, in view of the formation mechanism of the oligomers described in a following section, the structures of P-6, P-7, P-9, P-10, and P-11 of the oligomer fractions may be assumed to be 5-vinyldeca-2,8-diene, 3-methylundeca-1,5,10-triene, 1-methoxydodeca-2,6,11-triene, 5-vinyltetradeca-1,8,13-triene, and *n*-hexadeca-1,6,10,15-tetraene respectively (Table 2).

The other oligomers, *n*-octa-1,6- and -1,7-diene, *n*-octa-1,3,7-triene, and *n*-dodeca-1,6,10-triene, were identified by vpc. The identification by vpc was conducted by comparing the retention times with those of authentic samples, which were prepared by the previously-described reactions.[6]

TABLE 1. ELEMENTAL ANALYSIS AND SPECTROMETRIC, AND MOLECULAR WEIGHT MEASUREMENTS OF THE OLIGOMERS

Fraction number	Empirical formula	Elemental[a] analysis %	Molecular[a] weight	IR		NMR		
				Frequency cm^{-1}	Vibration mode	τ value[b]	Intensity ratio	Assignment
3-MOD,	$C_9H_{16}O$	C, 77.13 (77.09) H, 12.05 (11.50)	140[c] (140.2)	1643	unconjugated	3.90—4.75(m)	2	$=CH-$
					ν C=C	4.75—5.35(m)	4	$=CH_2$
				1380	δ CH_3	6.45—6.80(m)	2	$-C-\underset{\overset{\mid}{O}}{CH}-C-$
				1101	ν C–O(OCH_3)			
				990	δ $CH_2(-CH=CH_2)$	6.85 (s)	3	$-OCH_3$
				925		7.70—8.30(m)	2	$=C-CH_2-C-$
				910		8.30—8.80(m)	4	$-C-CH_2-C-$
1-MOD,	$C_9H_{16}O$	C, 77.12 (77.09) H, 11·80 (11.50)	140[c] (140.2)	1670	unconjugated	4.00—4.75(m)	3	$=CH-$
					ν C=C(internal)	4.75—5.40(m)	2	$=CH_2$
				1638	ν C=C(terminal)	6.30 (d)	2	$-O-CH_2-C=$
				1360	δ CH_3	6.85 (s)	3	$-OCH_3$
				1115	ν C–O($-OCH_3$)	7.70—8.30(m)	4	$=C-CH_2-$
				991	δ $CH_2(-CH=CH_2)$	8.30—8.70(m)	2	$-C-CH_2-C-$
				970	δ CH(*trans*-CH=CH–)			
				910	δ $CH_2(-CH=CH_2)$			
3-EOD,	$C_{10}H_{18}O$	C, 78.00 (77.90) H, 11.35 (11.75)	154[c] (154.3)	1643	unconjugated	3.80—4.75(m)	2	$=CH-$
					ν C=C	4.75—5.35(m)	4	$=CH_2$
				1373	δ CH_3	6.20—7.15(m)	3	$-O-CH_2-CH_3$
				1095	ν C–O($-OCH_3$)			$-C-\underset{\overset{\mid}{O}}{CH}-C-$
				1000	δ $CH_2(-CH=CH_2)$			
				925		7.65—8.20(m)	2	$=C-CH_2-C-$
				915		8.40—8.75(m)	4	$-C-CH_2-C-$
						8.85 (t)	3	$-CH_2-CH_3$
1-EOD,	$C_{10}H_{18}O$	C, 77.88 (77.90) H, 11.62 (11.75)	154[c] (154.3)	1670	unconjugated	3.80—4.70(m)	3	$=CH-$
					ν C=C(internal)	4.70—5.80(m)	2	$=CH_2$
				1638	ν C=C(terminal)	6.25 (d)	2	$-O-CH_2-CH=$
				1375	δ CH_3	6.65 (q)	2	$-O-CH_2-CH_3$
				1105	ν C–O($-OC_2H_5$)	7.70—8.30(m)	4	$=C-CH_2-C-$
				990	δ $CH_2(-CH=CH_2)$	8.30—8.75(m)	2	$-C-CH_2-C-$
				970	δ CH(*trans*-CH=CH–)			
				910	δ $CH_2(-CH=CH_2)$	8.87 (t)	3	$-CH_2-CH_3$
P-6,	$C_{12}H_{20}$	C, 87.30 (87.75) H, 12.55 (12.25)	—	1643	unconjugated	3.80—4.85(m)	5	$=CH-$
					ν C=C	4.85—5.40(m)	2	$=CH_2$
				1380	δ CH_3	7.65—8.28(m)	5	$=C-CH_2-$ $=C-\underset{\mid}{CH}-$
				996	δ $CH_2(-CH=CH_2)$			
				970	δ CH(*trans*-CH=CH–)			
				910	δ $CH_2(-CH=CH_2)$	8.28—8.53(m)	6	$=C-CH_3$
						8.53—8.90(m)	2	$-C-CH_2-C-$
P-7,	$C_{12}H_{20}$	C, 87.27 (87.75) H, 12.41 (12.25)	168[d] (164.3)	1643	unconjugated	4.00—4.85(m)	4	$=CH-$
					ν C=C	4.85—5.35(m)	4	$=CH_2$
				1375	δ CH_3	7.65—8.30(m)	7	$=CH-CH_2-$ $=C-\underset{\mid}{CH}-$
				995	δ $CH_2(-CH=CH_2)$			
				970	δ CH(*trans*-CH=CH–)			
				910	δ $CH_2(-CH=CH_2)$	8.53—8.90(m)	2	$-C-CH_2-C-$
						9.02 (d)	3	$-CH-CH_3$

TABLE 1. Continued

P-9,	$C_{13}H_{22}O$	—	—	1643	unconjugated	4.00—4.85(m)	5	$=CH-$
					ν C=C	4.85—5.50(m)	3	$=CH_2$
				1375	δ CH_3	6.25 (d)	2	$-O-CH_2CH=$
				1110	ν C-O($-OCH_3$)	6.80 (s)	3	$-OCH_3$
				990	δ $CH_2(-CH=CH_2)$	7.70—8.30(m)	8	$=C-CH_2-$
				965	δ CH(*trans*-CH=CH-)	8.30—8.90(m)	2	$-C-CH_2-C-$
				910	δ $CH_2(-CH=CH-)$			
P-10,	$C_{16}H_{26}$	C, 87.71 (88.00) H, 12.29 (12.00)	225$^{d)}$ (218.4)	1640	unconujgated	3.85—4.85(m)	5	$=CH-$
					ν C=C	4.85—5.35(m)	6	$=CH_2$
				990	δ $CH_2(-CH=CH_2)$	7.70—8.30(m)	9	$=C-CH_2-$
				970	δ CH(*trans*-CH=CH-)			$=C-CH-$
				910	δ $CH_2(-CH=CH_2)$	8.30—8.90(m)	6	$-C-CH_2-C-$
P-11,	$C_{16}H_{26}$	C, 87.99 (88.00) H, 12.01 (12.00)	228$^{d)}$ (218.4)	1640	unconjugated	3.90—4.80(m)	6	$=CH-$
					ν C=C	4.80—5.35(m)	4	$=CH_2$
				990	δ $CH_2(-CH=CH_2)$	7.70—8.30(m)	12	$=C-CH_2-$
				965	δ CH(*trans*-CH=CH-)	8.40—8.80(m)	4	$-C-CH_2-$
				908	δ $CH_2(-CH=CH_2)$			

a) A value in parentheses shows a calculated value for the respective compound.
b) Symbols in parentheses show: m, multiplet; d, doublet; s, singlet; q, quintet.
c) Determined by mass spectrometry (parent peak m/e).
d) Determined by cryoscopic method in benzene.

TABLE 2. CHEMICAL STRUCTURES OF OLIGOMERS

Fraction number	Compound	Constitutional formula
3-MOD	3-methoxyocta-1,7-diene	$CH_2=CHCH(OCH_3)CH_2CH_2CH_2CH=CH_2$
1-MOD	1-methoxyocta-2,7-diene	$CH_3OCH_2CH=CHCH_2CH_2CH_2CH=CH_2$
3-EOD	3-ethoxyocta-1,7-diene	$CH_2=CHCH(OC_2H_5)CH_2CH_2CH_2CH=CH_2$
1-EOD	1-ethoxyocta-2,7-diene	$C_2H_5OCH_2CH=CHCH_2CH_2CH_2CH=CH_2$
P-6 (5-VDD)	5-vinyldeca-2,8-diene	$CH_3CH=CHCH_2CH_2CH(CH=CH_2)CH_2CH=CHCH_3$
P-7 (3-MUDT)	3-methylundeca-1,5,10-triene	$CH_2=CHCH(CH_3)CH_2CH=CHCH_2CH_2CH_2CH=CH_2$
P-9 (1-MODT)	1-methoxydodeca-2,6,11-triene	$CH_3OCH_2CH=CHCH_2CH_2CH=CHCH_2CH_2CH_2CH=CH_2$
P-10 (5-VTDT)	5-vinyltetradeca-1,8,13-triene	$CH_2=CHCH_2CH_2CH(CH=CH_2)CH_2CH_2CH=CHCH_2CH_2CH_2CH=CH_2$
P-11 (NHDT)	hexadeca-1,6,10,15-tetraene	$CH_2=CHCH_2CH_2(CH_2CH=CHCH_2)_2CH_2CH_2CH=CH_2$

Results and Discussion

On the electrolysis of the alcoholic solutions containing nickel(II) chloride and electron donors in the presence of butadiene, the initial blue or yellow color of nickel(II) ion in the solution changed to a dark brown-red, which color disappeared in air. Using pyridine as an electron donor, a number of linear and dihydrogenated oligomers were obtained, plus small amounts of branched oligomers. By adding triphenylphosphine to the reaction system in place of pyridine, *n*-octatriene and alkoxyoctadiene were catalytically produced instead of hydrooligomers, accompanied by tetrakis(triphenylphosphine)nickel(0). In neither case were cyclic oligomers produced. The yields and selectivities of the oligomers were affected by the nature of the electron donors and solvents used (Tables 3 and 4). The current efficiency of the nickel(0) complex was about 75%, based on the 2e process.

Effects of Electron Donors on the Oligomerization of Butadiene. (I) Effects of Pyridine: When pyridine was used as the electron donor, an air-sensitive and dark brown-red solution containing oligoolefin-nickel (0) complexes was produced. The properties and structures of the complexes will be reported in a following paper. Most of the oligomers obtained by decomposing the complexes with dilute hydrochloric acid were found to be linear and dihydrogenated dimers, trimers, and tetramers. No oligomers higher than tetramers could be detected by gas chromatography or gel-permeation chromatography. A programmed-temperature gas chromatogram of a mixture of the oligomers is indicated in Fig. 2. Oligomers at the peak numbers of 6, 7, 8, 9, 10, and 11 were isolated by means of preparative gas chromatography with Apiezon grease-L and polydiethyleneglycol succinate; they were spectrometrically analyzed (Table 1). Their structures may be characterized as in Table 2. Although dimeric butadiene isomers at the peak numbers of 2 and 3 could not be separated with any of the columns employed (Apiezon grease-L, polydiethyleneglycol succinate, dioctylsebacate, and squalene), they were identified as octa-1,6- and -1,7-diene respectively by comparing the retention times with those of authentic samples. In the same way, oligomers corresponding to the peak numbers of 4 and 5 have also been found to be 3-methoxyocta-1,7-diene and 1-methoxyocta-2,7-diene respectively.

A gas chromatogram of a mixture of those oligomers

TABLE 3. OLIGOMERIZATION OF BUTADIENE WITH NICKEL COMPLEXES PRODUCED BY MEANS OF ELECTROLYSIS OF NICKEL(II) CHLORIDE AND ELECTRON DONOR IN PROTIC SOLVENTS

Expt. No.	$NiCl_2$ mmol	Butadiene mmol	Electron donor (mmol)	Solvent[a]	Amount of current × 10^2 F	Yield[c] %	Produced oligomers, %		
							Dimers	Trimers	Tetramers
014	23	400	—	EtOH	5	0			
E-029	20	220	—	MeOH	5	1.4	53	7	40
104	20	250	Pyridine (80)	MeOH	4	25.6	60	27	13
103	10	250	HMPA[b] (80)	MeOH	4	7.45	95	5	0
083	10	300	Triphenylphosphine (20)	MeOH and Benzene	2	45.6	>95		
012	25	300	Triphenylphosphine (50)	EtOH	5	47.3	>95		
100	20	250	Acetonitrine (80)	MeOH	4	0			
101	20	250	Piperidine (80)	MeOH	4	0			
112	20	250	Triethylamine (80)	MeOH	4	0			

a) 90 m*l* of the solvent (containing 1.7 g of Bu_4NClO_4 in the case of ethyl alcohol) in each compartment of the electrolysis cell.
b) Hexamethylphosphoramide.
c) Based on the mole of butadiene introduced.

TABLE 4. DIMERS OF BUTADIENE FORMED WITH ELECTROLYSIS OF NICKEL (II) CHLORIDE IN THE PRESENCE OF TRIPHENYL PHOSPHINE IN METHYL ALCOHOL AND ETHYL ALCOHOL

Expt. No.	Yield,[c] %	Components dimer mixture, %				
		NOT[d]	3-MOD	1-MOD	3-EOD	1-EOD
083[a]	45.6	27.4	28.8	43.8	—	—
082[b]	28.1	33.3	22.2	44.5	—	—
012[a]	47.3	83.7	—	—	2.80	9.50
011[b]	47.2	71.6	—	—	2.50	10.0

a) $PPh_3/Ni(II)$, 2; b) $PPh_3/Ni(II)$, 4.
c) Based on the mole of butadiene introduced.
d) Octa-1,3,7-triene.

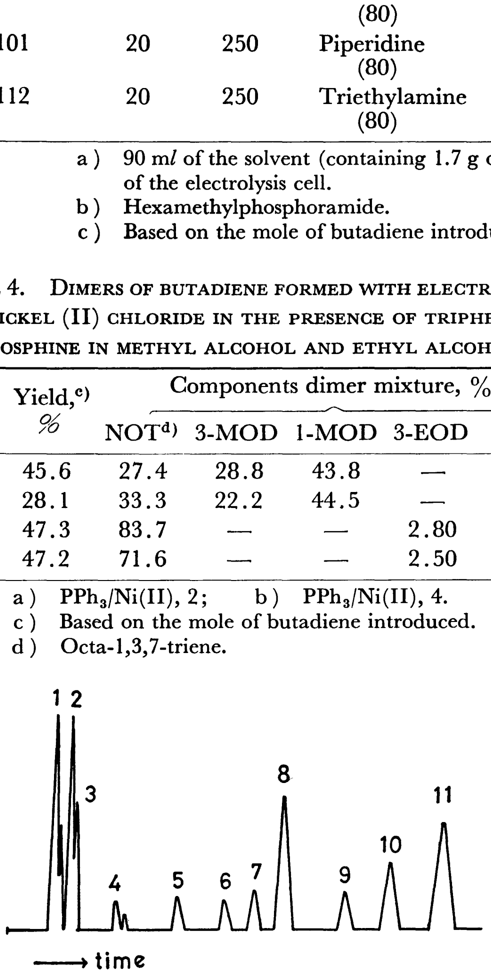

Fig. 2. A programmed temperature gas chromatogram of a mixure of oligomers obtained by means of electrolysis of $NiCl_2 4NC_5H_5$.
Oligomers corresponding to peak numbers: 2, octa-1,6-diene; 3, octa-1,7-diene; 4, 3-methoxyocta-1,7-diene; 5, 1-methoxyocta-2,7-diene; 6, 5-vinyldeca-2,8-diene; 7, 3-methylundeca-1,5,10-triene; 8, dodeca-1,6,10-triene; 9, 1-methoxydodeca-2,6,11-triene; 10, 5-vinyltetradeca-1,8,13-triene; 11, hexadeca-1,6,10,15-tetraene.
Conditions: initial temperature, 80°C; final temperature, 180°C; rate of temperature increase, 2°C/min; column, Apiezon grease-L (3 mm × 3 m); hydrogen flow rate, 120 m*l*/min.

was very close to that of the oligomers obtained by reducing tetrakis(pyridine)nickel(II) chloride with lithium aluminum hydride or sodium borohydride in the presence of butadiene.[6] This finding might suggest a similarity in mechanisms for the oligomerization in these reaction systems. For the oligomerization by the catalysts participated with the chemical reducing agents, we previously proposed a mechanism involving bis-π–allylic $C_8H_{12}Ni$ and $C_{12}H_{18}Ni$ complexes as intermediates.[6]

The yields of the oligomers were affected by the molar ratios of pyridine to nickel(II) chloride, but not by the amounts of the electric current when it was passed over two Faradays to mol of nickel(II) chloride. The maximum yield was obtained at the molar ratio two of pyridine to nickel(II) chloride.[10]

(II) Effects of triphenylphosphine: On the electrolyses of ethanolic solutions containing nickel(II) chloride, a fourfold excess of triphenylphosphine in place of pyridine, and the supporting electrolyte, the initial yellow color of the catholyte changed to a dark brown-red, and at the end of the electrolysis a brown solid precipitated. The dark brown-red color of the cathodic solution faded when it was exposed to the air.

From the cathodic solution, octa-1,3,7-triene was obtained catalytically, plus small amounts of 3-ethoxyocta-1,7-diene and 1-ethoxyocta-2,7-diene. From the anolyte were obtained small amounts of the oligomers. Probably, the oligomers formed in the catholyte were transferred through the glass filter of the cell to the anodic compartment. When methyl alcohol containing a small amount of benzene to dissolve triphenylphosphine was substituted for ethyl alcohol as a reaction medium, approximately equimolar amounts of octa-1,3,7-triene, 3-methoxyocta-1,7-diene, and 1-methoxyocta-2,7-diene were obtained (Table 4).

The brown precipitate described above was filtered, washed with ethyl alcohol, and dried under a vacuum

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[10] T. Ohta, K. Ebina, and N. Yamazaki, unpublished data.

TABLE 5. DIMERIZATION OF BUTADIENE WITH TETRAKIS(TRIPHENYLPHOSPHINE)-NICKEL (0) IN METHYL ALCOHOL AND ETHYL ALCOHOL[a]

Expt. No.	$Ni(PPh_3)_4$, mmol	Butadiene, mmol	Solvent, (ml)	Yield,[b] %	Component of dimer mixture, %				
					NOT[c]	3-MOD,	1-MOD,	3-EOD,	1-EOD
102	1.35	100	MeOH (20) and Benzene (10)	16.5	28.2	32.3	39.5	—	—
113	1.40	180	EtOH (30)	100	83.0	—	—	3.5	8.7

a) Dimerization of butadiene was carried out in a 100-m*l* glass tube at 20—30°C for 48 hr

b) Based on the mole of butadiene introduced.

c) Octa-1,3,7-triene.

at room temperature. The compound was assumed to be a tetrakis(triphenylphosphine)nickel(0) complex from elemental analysis (Calcd for $C_{72}H_{60}P_4Ni$: C, 78.06; H, 5.45; Ni, 5.30. Found: C, 76.35; H, 5.05; Ni, 5.25); the yield was 87% based on nickel(II) chloride. When this complex was used separately as a catalyst for the dimerization of butadiene in ethyl or methyl alcohol containing benzene, octa-1,3,7-triene 3-alkoxyocta-1,7-diene, and 1-alkoxyocta-2,7-diene were formed; their proportions were similar to those of the oligomers produced by electrolysis in each case (Table 5). These results led us to assume that nickel (II) chloride, in the presence of triphenylphosphine, was electrochemically reduced to the tetrakis(triphenylphosphine)nickel(0), and that the resulting complex in alcohol reacted with butadiene to give, catalytically, octa-1,3,7-triene and alkoxyoctadiene. It is noteworthy that tetrakis(triphenylphosphine)nickel(0) was prepared by means of the electrolytic reduction of nickel(II) chloride in the presence of triphenylphosphine in ethyl alcohol.

Octa-1,3,7-triene and alkoxyoctadienes have also been obtained with palladium-complex catalysts or other metal complexes of the VIII group (*e.g.*, Ru and Pt).[4b] These oligomers may be produced through a π-allyl intermediate analogous to that proposed by Wilke.[11]

(III) Effects of Other Electron Donors: Differently from the cases of pyridine and triphenylphosphine, the addition of acetonitrile, piperidine, or triethylamine to the electrolysis system resulted in a change in the color of neither the catholyte nor oligomers, but a large amount of metallic nickel was deposited on the cathodic electrode, as in the absence of electron donors. The absence of a color change in the catholyte on electrolysis indicates that no nickel complexes were produced. The use of hexamethylphosphoramide as an electron donor gave a small amount of the oligomers, composed predominantly of the dimers.

Pyridine and triphenylphosphine have both σ-donor and π-acceptor properties and can stabilize lower-valency transition-metal complexes by a combination of the two properties. On the other hand, acetonitrile, piperidine, and triethylamine, which lack suitable low-lying empty orbitals, act only as donors and formed less robust metal complexes than pyridine and triphenylphosphine. The above facts suggest that nickel(II) chloride, in the presence of pyridine and triphenylphosphine, is electrochemically reduced to yield lower-valency nickel-electron donor complexes and that the butadiene oligomers are produced on the complexes.

Electrochemical Reduction Process of Nickel(II) Chloride In the present electrolysis systems, three components, Ni^{2+} salt, the electron donor, and butadiene, can be reduced, and three probable modes of reduction can be visualized: (1) a direct electron transfer from the cathode to the nickel ion; (2) the reduction of the nickel(II) ion with the anion radicals (or dianions) formed by the reduction of the electron donors,[12,13] and (3) the reaction of the nickel(II) ion with the anionic species produced by direct-electron transfer from the cathode to butadiene.

It was previously reported that the electron was preferably transferred from the cathode to butadiene, followed by the initiation of anionic polymerization in the n-Bu_4NClO_4-dimethoxyethane system.[14] However, in protic solvents, neither polymers nor oligomers could be obtained. The addition of nickel(II) chloride and electron donors to the electrolysis system gave a variety of linear oligomers of butadiene. Probably, the anionic species produced by path (3) would react with the solvent prior to reacting with nickel(II) chloride.[15] These results may exclude path (3). In the absence of electron donors, small amounts of oligomers were obtained, plus a large amount of metallic nickel. This indicates that nickel(II) chloride was electrochemically reduced through path (1). A half-wave potential of Ni(pyridine)$_4^{2+}$, -0.78 V *vs.* SCE (1 M KCl, 0.5 M pyridine)[16] is less negative than those of butadiene ($E_{1/2} = -3.27$ V *vs.* SCE in dimethoxyethane).[14] pyridine ($E_{1/2} = -2.48$ V or less in pyridine),[12] and triphenylphosphine ($E_{1/2} = -2.70$ V in dimethylformamide);[13] this finding also supports path (1).

On the basis of these results, we assume that path (1) is predominant for the primary electrode process, although path (2) cannot be ruled out.

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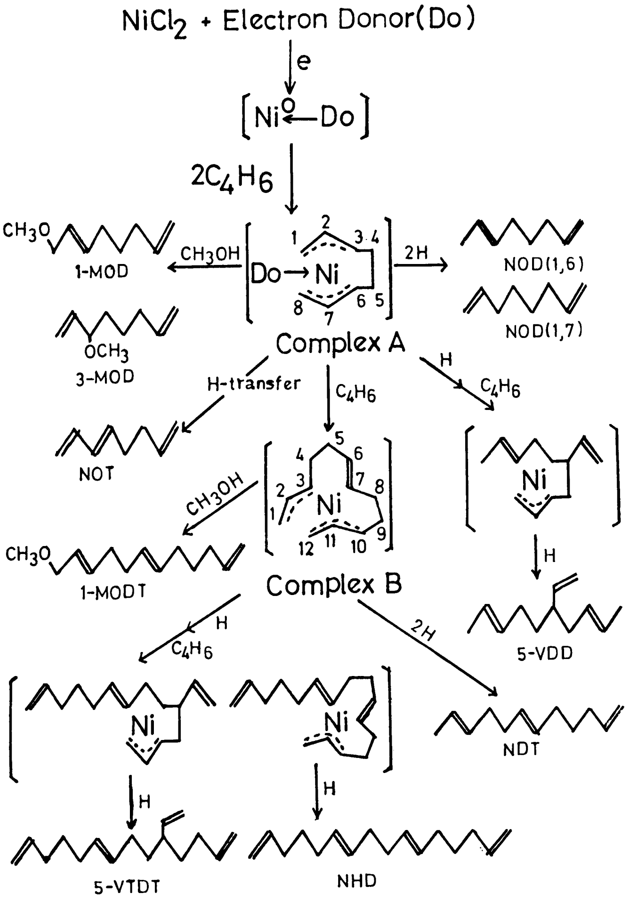

Fig. 3. A scheme for the oligomerization.

Mechanism of Oligomerization. The dark brown-red solution produced on the electrolysis of tetrakis-(pyridine)nickel(II) chloride in the presence of butadiene was concentrated by evaporating methyl alcohol, unreacted butadiene, and free pyridine. The resulting dark brown-red compound was soluble in benzene and methyl alcohol to give brown-red solutions which were air-sensitive and which gradually decomposed to nickel metal and the corresponding oligomers at room temperature. The UV and visible spectra of the compound in *n*-hexane showed the maximum absorptions at 290—295 mμ ($\varepsilon \sim 3.2 \times 10^3$) and 422 m$\mu$ ($\varepsilon \sim 5.9 \times 10^2$); these absorptions disappeared in air. In its infrared spectrum, absorptions at 1000, 910, and 965 cm^{-1} due to terminal and trans-internal double bonds were observed. A far-infrared spectrum of the compound gave two air-sensitive absorptions at 530 and 305 cm^{-1} and showed two air-sensitive absorptions at 630 and 430 cm^{-1} due to pyridine coordinated to nickel. These results led us to assume that nickel complexes bonded with π-allylic structure of oligoolefins, such as octa-2,6-diene-1,8-diyl(pyridine)nickel(0), complex A, and dodeca-2,6,10-triene-1,12-diylnickel(0), complex B, shown in Fig. 3, were produced in the catholyte. When triphenylphosphine was used instead of pyridine, the resulting complex, tetrakis(triphenylphosphine)nickel (0), has been found to catalyze the dimerization of butadiene to *n*-octatriene and alkoxyoctadiene (Table 4).

On the basis of these findings, a mechanism for the oligomerization of butadiene by means of the electrolysis of alcoholic solutions containing nickel(II) chloride, electron donors, and butadiene may be proposed to be as follows. Nickel(II) chloride is electrochemically reduced to give electron donor-nickel(0) complexes, and butadiene is reacted with the complexes to yield complexes A and B (Fig. 3); then the 1,6- or 3,6-carbon of C_8H_{12} in complex A and the 1,10-carbon of $C_{12}H_{18}$ in complex B are hydrogenated or alkoxylated to octa-1,6- and -1,7-diene, and dodeca-1,6,10-triene or 1-alkoxyocta-2,7-diene, 3-alkoxyocta-1,7-diene, and 1-alkoxydodeca-2,6,11-diene respectively. In the formation of a linear tetramer and a branched trimer and tetramer, one hydrogen atom attacks the 1-carbon of a π-allylic group of complex A and the 3-carbon of a π-allylic group of complex B to destroy a rare gas structure of nickel atom and activate the other π-allylic groups of complexes A and B. Then one molecule of butadiene is inserted in the bond between the nickel atom and the 6-carbon of complex A or the 10- or 12-carbon of complex B, and the $C_{12}H_{19}$ or $C_{16}H_{25}$ produced on the nickel atom is hydrogenated to 5-vinyldeca-2,8-diene, and 5-vinyltetradeca-1,8,13-triene or hexadeca-1,6,10,15-tetraene.

It has been reported that cyclic dimers were formed *via* $C_8H_{12}NiPR_3$, similar to complex A in the reaction of butadiene with $Ni(CO)_2(PR_3)_2$ in benzene,[11] whereas octa-1,3,7-triene, accompanied by small amounts of octa-2,6-diene and acetone, were formed in isopropyl alcohol and monodeutrated octa-1,3,7-triene in C_6H_5OD.[17] In the IR spectra of a mixture of dimers obtained by means of electrolysis, an absorption at 1740 cm^{-1} due to the aldehyde group was observed. These facts suggest that the octa-1,3,7-triene obtained herein may be produced by the hydrogen transfer of C_8H_{12} in a complex with alcohol, and that hydrogen required for the hydrooligomerizations may originate from the alcohol used as a solvent.

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