

Oligomerization of Butadiene with Bis(π -cycloocta-1,5-diene)Nickel in Alcohols

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ABSTRACT: Butadiene was found to oligomerize readily with bis(π -cycloocta-1,5-diene)nickel in alcohols, yielding linear conjugated and unconjugated dimers, trimers, and tetramers. The oligomers and their yields were affected by the solvents used. When primary alcohols, such as methyl, ethyl, and *n*-butyl, were used as the solvent, only small amounts of hydrooligomers were formed. On the other hand, in *tert*-butyl and isopropyl alcohols *n*-octa-1,6- and -2,6-diene and *n*-octa-1,3,6-triene were catalytically obtained, accompanied by small quantities of cyclododeca-1,5,9-triene, *n*-dodeca-1,6,10-triene, and *n*-hexadeca-2,6,10,14-tetraene. Addition of amines had little effect, except that diethylamine deactivated the catalysts. From the results of spectrometric analyses and pyrolysis of the nickel complex formed in the reaction of bis(π -cycloocta-1,5-diene)-nickel with butadiene in isopropyl alcohol, it has been deduced that the linear butadiene oligomers are formed through a complex composed of monomeric butadiene, butadiene oligomer, isopropoxy group, and nickel atom.

KEY WORDS Oligomerization / Butadiene / Bis(π -cycloocta-1,5-diene)Nickel / Oligomers / Hydrooligomers / Isopropyl Alcohol / *tert*-Butyl Alcohol / Spectrometric Analyses / Pyrolysis / Complex /

It has been known for some time that many transition-metal complexes catalyzed the oligomerization of butadiene.¹ Wilke and his coworkers have reported that bis(π -cycloocta-1,5-diene)nickel reacts with butadiene at lower temperatures to give dodeca-2,6,10-triene-1,12-diylnickel and at higher temperatures causes the catalytic trimerization of butadiene to cyclododeca-1,5,9-triene.² During studies on the electrolytic reduction of transition-metal compounds in the presence of butadiene in polar solvents, we found that linear oligomers were obtained in alcohols.³ The catalyst was assumed to be a nickel complex of zero valence with π -allylic ligands, of which the precise structure was obscure. In order to clarify the mechanism of the reaction and the structure of the complex, we attempted to compare its catalytic activity with that of a complex of similar structure. We have found that bis(π -cycloocta-1,5-diene)nickel, like the nickel complexes produced in the electrolysis, oligomer-

ized butadiene in alcohols, yielding linear conjugated and unconjugated dimers, trimers, and tetramers.

This paper deals with the results of the linear oligomerization of butadiene with bis(π -cycloocta-1,5-diene)nickel in alcohols, where the identification of the oligomers, the effects of alcohols and amines on the oligomerization, and a proposed mechanism for the oligomerization are described.

EXPERIMENTAL

Materials

Methyl, ethyl, *n*-butyl, isopropyl, and *tert*-butyl alcohols were dried with magnesium or sodium alkoxides and then purified by distillation under nitrogen. Pyridine, piperidine, ethylenediamine, triethylamine, and *n*-butylamine were distilled over NaOH.

Bis(π -cycloocta-1,5-diene)nickel was prepared by the modified method,⁴ as follows. A mixture of 89.2 g of tetrakis(pyridine)nickel(II) chloride

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(200 mmol) and 64.8 g of *cis*, *cis*-cycloocta-1,5-diene (600 mmol) in 120 ml of tetrahydrofuran was treated with 9.2 g of sodium metal (400 mmol) at room temperature for 4 hr. The resulting dark-brown solution was concentrated by evaporation of the volatile compounds under reduced pressure. On addition of methyl alcohol to the concentrated solution, a yellow crystal of bis(π -cycloocta-1,5-diene)nickel deposited. The crystal was washed with methyl alcohol ten times and dried under reduced pressure (yield, 31 g).

Oligomerization

Oligomerization was performed in a 100-ml glass ampoule. In a typical experiment, 20 mmol of bis(π -cycloocta-1,5-diene)nickel, 80 mmol of pyridine, and 50 ml of ethyl alcohol were placed under nitrogen stream in an ampoule which

had previously been charged with dry nitrogen. The mixture in the ampoule was degassed at liquid-nitrogen temperature by use of a conventional vacuum line. Under vacuum 200 mmol of butadiene was trapped in the ampoule, which was cooled in a Dry Ice—methanol bath. The ampoule was sealed off and set in a water bath controlled at 50°C. After 24 hr the reaction mixture was poured into a large excess of methyl alcohol containing small amounts of hydrochloric acid. Butadiene oligomers produced were extracted with ether, washed with water, and dried over anhydrous Na₂SO₄. The extract was concentrated under reduced pressure and yields of each oligomer were determined by gas chromatography (GC).

Table I. IR, NMR elemental analyses, and molecular-weight measurements of butadiene oligomers

Fraction no.	Empirical formula	Elemental analysis ^a	Molecular weight ^a	IR		NMR		Assignment	
				Frequency, cm ⁻¹	Vibration mode	τ value ^b	Intensity ratio		
PO-165-1	C ₁₆ H ₂₆	C, 87.49 (88.00)	—	1643	unconjugated	4.30—4.75(m)	4	=CH—	
		H, 12.51 (12.00)		1380	ν C=C	7.70—8.20(m)	6	=C—CH ₂ —	
		965		δ CH ₃	8.20—8.56(m)	3	=C—CH ₃		
				965	δ CH ₂ (<i>trans</i> CH=CH)				
PO-165-2	C ₁₆ H ₂₆	C, 87.75 (88.00)	—	1643	unconjugated	4.30—4.75(m)	7	=CH—	
		H, 12.25 (12.00)		1380	ν C=C	4.75—4.90(m)	2	=CH ₂	
		995		δ CH ₂ (CH=CH ₂)	4.90—5.27(m)	1	=C—CH—		
		965		δ CH(<i>trans</i> CH=CH)	7.70—8.20(m)	9	=C—CH ₂ —		
		910		δ CH ₂ (CH=CH ₂)	8.20—8.45(m)	6	=C—CH ₃		
				910	δ CH ₂ (CH=CH ₂)	8.75—8.96(m)	2	=C—CH ₂ —C—	
PO-194	C ₈ H ₁₄	C, 87.12 (87.74)	110 ^c (110.2)	1650	unconjugated	4.50—4.85(m)	2	=CH—	
		H, 12.88 (12.26)		1380	ν C=C	7.85—8.20(m)	2	=C—CH ₂ —	
		965		δ CH ₃	8.20—8.55(m)	3	=C—CH ₃		
				965	δ CH(<i>trans</i> CH=CH)				
PO-195-2	C ₈ H ₁₂	C, 88.30 (88.82)	108 ^c (108.18)	1650	unconjugated	3.30—5.30(m)	7	=CH—	
		H, 11.70 (11.18)		1605	conjugated			=CH ₂	
					1380	ν C=C	7.00—7.95(m)	2	=C—CH ₂ —C=
					1005	δ CH ₂ (CH=CH ₂)	8.20—8.55(m)	3	=C—CH ₃
					970	δ CH(<i>trans</i> CH=CH)			
					900	δ CH ₂ (CH=CH ₂)			

^a A value in parentheses shows a calculated value for the respective compound.

^b The symbol m in parentheses shows multiplet.

^c Determined by mass spectrometry (parent peak *m/e*).

Analyses

Amounts of the oligomers obtained were calculated from the calibration curve for cyclododeca-1,5,9-triene, and each oligomer was isolated by preparative gas chromatography, as described in a previous paper.³ The structures of the isolated oligomers were verified by IR, NMR, and mass spectrometries, and by elemental analyses.

A gas chromatograph (Shimadzu Seisakusho Ltd., GC-4APT) was used to detect dimeric, trimeric, and tetrameric butadiene isomers. The gas chromatograph was operated under the same conditions as described previously.³ Butene isomers were detected by using a gas chromatograph (Ohkura-Rikagaku) fitted with a copper tube (4 mm × 1 m) packed with ODPN on alumina, with hydrogen as the carrier gas. The gas chromatograph was operated under the following conditions: the temperatures of the column and the injection port were 30°C and the hydrogen flow rate was 30 ml/min. IR, NMR, mass, and electronic spectrometries were conducted under the same conditions as described in a previous paper.³

Identification of Oligomers

Table I shows results of IR and NMR spectroscopic and elemental analyses and molecular-weight measurement of the oligomers of butadiene obtained.

On the basis of these results, oligomer fractions PO-194 and PO-195-2 are identified as *n*-octa-2,6-diene and *n*-octa-1,3,6-triene respectively. Other oligomer fractions PO-165-1 and PO-165-2 are assumed to be *n*-hexadeca-2,6,10,14-tetraene and 5-vinyltetradeca-2,8,12-triene respectively.

Other oligomers such as *n*-octa-1,3,7-triene and 3-methylhepta-1,4,6-triene were identified by comparing retention times with those of authentic samples, which were either commercially available or were prepared by known methods.

RESULTS AND DISCUSSION

Effect of Alcohols on the Oligomerization

Though bis(π -cycloocta-1,5-diene)nickel was sparingly soluble in alcohols, it dissolved easily in the presence of butadiene to yield a dark-reddish solution, even at -30°C; probably it formed complexes with the butadiene. During the oligomerization for 24 hr the dark-reddish-brown reaction mixture was homogeneous and the color remained unchanged. The mixture of butadiene oligomers produced was analysed by GC. The results are shown in Table II.

The catalyst specificity and yields of oligomers were remarkably affected by the kind of alcohols used. In primary alcohols, such as methyl, ethyl, and *n*-butyl, small amounts of linear hydrooligomers were produced. On the other hand,

Table II. Oligomerization of butadiene with bis(π -cycloocta-1,5-diene) nickel in protic solvents^a

Expt no.	Ni(COD) ₂ , mmol	Solvent, 50 ml	Amine	Yield, ^b %	Produced oligomer, mmol ^c		
					<i>n</i> -C ₈	<i>n</i> -C ₁₂	<i>n</i> -C ₁₆
172	24.1	MeOH	—	37.1	4.78	1.95	0.77
173	20.2	EtOH	—	44.1	5.33	1.74	1.76
174	24.1	<i>n</i> -BuOH	—	36.8	4.08	2.23	1.04
194	15.6	<i>i</i> -PrOH	—	530	75.5	4.96	1.44
195	21.1	<i>t</i> -BuOH	—	195	37.6	0.44	4.04
163	20.2	EtOH	Pyridine	58.7	7.75	2.00	1.94
168	21.5	EtOH	EDA ^d	0			
167	20.8	EtOH	TEA ^d	27.4	4.54	2.18	1.01
169	20.2	EtOH	BA ^d	37.8	4.78	1.19	1.60
166	21.2	EtOH	Piperidine	60.3	6.38	2.71	3.57

^a Oligomerization conditions: molar ratio C₄H₆/Ni(COD)₂, *ca.* 15; amine/Ni(COD)₂, *ca.* 4; reaction temp, 50°C; reaction time, 24 hr.

^b Based on mol of bis(π -cycloocta-1,5-diene)nickel Ni(COD)₂.

^c *n*-C₈, chain butadiene dimers; *n*-C₁₂, chain trimers; *n*-C₁₆, chain tetramers.

^d EDA, ethylenediamine; TEA, triethylamine; BA, *n*-butylamine.

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use of *tert*-butyl and isopropyl alcohols led to the catalytic formation of linear conjugated and unconjugated dimers of butadiene. In addition, small quantities of cyclododeca-1,5,9-triene and chain trimers and tetramers were formed.

In isopropyl alcohol, the dimers were predominantly *n*-octa-2,6-diene, and the trimers and tetramers were *n*-dodeca-1,6,10-triene, *n*-hexadeca-2,6,10,14-tetraene, and their isomers.

tert-Butyl alcohol changed the catalyst specificity to produce almost equal amounts of *n*-octa-1,3,6-triene and *n*-octa-1,6-diene. *n*-Hexadeca-2,6,10,14-tetraene and cyclododeca-1,5,9-triene were also formed in slightly increased amounts compared with the oligomerization in isopropyl alcohol.

Urry and his coworkers⁵ have investigated the chain addition of a free radical from alcohols to olefins induced with peroxides. The order of increasing ease of addition was methyl alcohol < other primary alcohols < secondary alcohols, which was in agreement with the order of increasing resonance stabilization of the respective α -hydroxyalkyl radicals resulting from hydrogen abstraction. In addition, it was shown that the rate of isopropyl alcohol on the copper catalysts was about five times the rates of the primary alcohols.⁶ Therefore, the ease of dehydrogenation of the isopropyl and *tert*-butyl alcohols appears to affect the formation of the hydro-oligomers.

The difference between the distribution of the dimers obtained in *tert*-butyl and in isopropyl alcohol is shown in Table III. That higher

It is to be noticed that acetone, as well as *n*-octa-2,6-diene, was catalytically formed in isopropyl alcohol. This suggests that hydrogen originated from the isopropyl alcohol employed as a solvent. It has been reported that small quantities of *n*-octa-2,6-diene and acetone were brought about in the dimerization of butadiene with $\text{Ni}(\text{CO})_2(\text{PR}_3)_2$ to *n*-octatriene in isopropyl alcohol. They are apparently formed by the homogeneous hydrogenation of *n*-octa-1,3,6-triene.⁷

Effect of Reaction Time

Molar ratios of the oligomers yields/bis(π -cycloocta-1,5-diene)nickel vs. reaction time for the oligomerization of butadiene in isopropyl alcohol are shown in Figure 1. Figure 1 shows the oligomerization in which the hydrodimer was gradually formed with time.

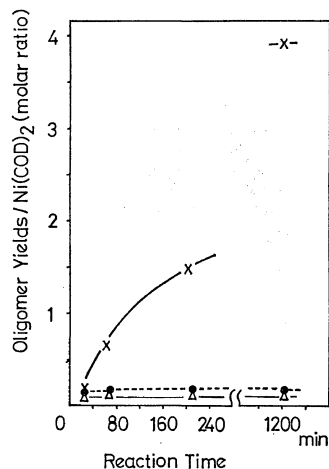


Figure 1. Oligomer yields vs. reaction time: molar ratio $\text{C}_4\text{H}_6/\text{Ni}(\text{COD})_2$, ca. 40; solvent, 50 ml of isopropyl alcohol; reaction temperature, 50°C; —x—, chain dimers of butadiene; —●—, chain trimers of butadiene; —▲—, chain tetramers of butadiene.

On the other hand, the hydro-trimers and -tetramers were formed initially in the oligomerization and their amounts soon leveled off. A reaction of long duration resulted in the deposition of a bluish-violet compound from the oligomerization system.

Effect of Reaction Temperature

The effects of reaction temperature on the

Table III. Distribution of butadiene dimers

Expt no.	Solvent	Dimer, ^a %		
		OD(1,6)	OD(2,6)	OT(1,3,6)
194	Isopropyl alcohol	15.9	75.5	8.6
195	<i>tert</i> -Butyl alcohol	50.5	trace	49.5

^a OD(1,6), *n*-octa-1,6-diene; OD(2,6), *n*-octa-2,6-diene; OT(1,3,6), *n*-octa-1,3,6-triene.

quantities of *n*-octa-1,3,6-triene were formed in *tert*-butyl alcohol than in isopropyl alcohol reflects the ease of dehydrogenation from isopropyl alcohol as compared with *tert*-butyl alcohol.

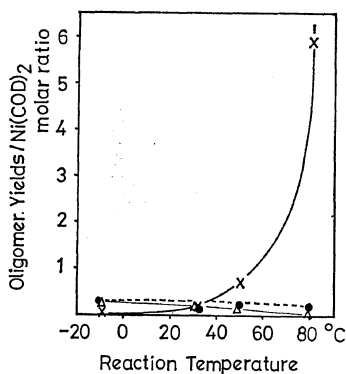


Figure 2. Yields of oligomers vs. reaction temperature: molar ratio $C_4H_6/Ni(COD)_2$, ca. 40; solvent, 50 ml of isopropyl alcohol; reaction time, 60 min; —x—, chain dimers of butadiene; —●—, chain trimers of butadiene; —▲—, chain tetramers of butadiene.

oligomerization in isopropyl alcohol are shown in Figure 2. The apparent rate of formation of *n*-octa-2,6-diene increased beyond 50°C. Between 50 and 80°C, the apparent rate of formation of *n*-octadiene was enhanced by about 10 times and the overall activation energy was calculated to be about 37 kcal/mol. In contrast, yields of the higher oligomers, such as *n*-dodecatriene and *n*-hexadecatetraene, were little affected by the reaction temperatures below 50°C, and then decreased with temperature.

Effect of Amines

When pyridine, piperidine, *n*-butylamine, and triethylamine were added to the reaction system consisting of bis(π -cycloocta-1,5-diene)nickel, butadiene, and ethyl alcohol, the resulting reaction mixtures were dark-reddish-brown solutions, as in the absence of the amines (Table II). The addition of the amines resulted in neither a remarkable increase of the yield nor in selectivity of the oligomers. Pyridine and piperidine somewhat increased the yields of the oligomers.

In the case of diethylamine, a transparent blue solution which showed absorption bands at 334 and 540 $m\mu$ was brought about. However, no oligomers were obtained from the solution.

Identification of a Bluish-Violet Compound

When the oligomerization was continued at 50°C for as long as 24 hr, bluish-violet compounds were precipitated from the brown solu-

tion in isopropyl as well as *tert*-butyl alcohol. These compounds were hygroscopic and only slightly soluble in hydrocarbon. Results of elemental analyses of the compounds after purification were Ni 32.10% (Calcd for $C_8H_{14}O_2Ni$, 33.2%) in isopropyl alcohol and 29.00% (Calcd for $C_8H_{18}O_2Ni$, 29.87%) in *tert*-butyl alcohol.

IR spectra of the compounds were similar to those of isopropyl and *tert*-butyl alcohol and their far-infrared spectra exhibited absorption bands at 625 and 400 cm^{-1} , and 625 and 475 cm^{-1} respectively, which may be assigned to the Ni—O stretching vibration.^{8,9} When the compounds were decomposed with dilute hydrochloric acid, the respective alcohols which were detected by GC, were formed. From these results the bluish-violet compound may be identified as nickel(II) isopropoxide and *tert*-butoxide. The yields of these compounds were almost quantitative.

Detection of Acetone in the Reaction Mixture

In the previously described filtrate from the reaction mixture a large amount of acetone was found indicating that the hydrogen required for the formation of the hydrooligomers originated from the isopropyl alcohol used as a solvent.

IR and Far-Infrared Spectra of Nickel Complex Formed in the Reaction of Bis(π -cycloocta-1,5-diene)Nickel with Butadiene in Isopropyl Alcohol

The reaction of bis(π -cycloocta-1,5-diene)nickel with butadiene in isopropyl alcohol, which was performed at about 15°C for 1 hr, yielded the dark-reddish-brown solution. When the solution was evaporated *in vacuo*, there remained a dark-red, syrupy substance which was stable at room temperature under nitrogen, but decomposed on exposure to air.

The IR spectrum of the syrupy substance is indicated in Figure 3. The spectrum showed a number of absorption bands at 1370, 1355, 1140, 965, 620, and 510 cm^{-1} . The sharp absorption bands at 1370 and 1355 cm^{-1} may be assigned to the double bond coordinated to the nickel atom,⁹ the band at 965 cm^{-1} to the CH_2 deformation mode of *trans* double bond, and the band at 620 cm^{-1} to the Ni—O stretching vibration.⁹ However, no vibrations assigned to the stretching mode of the uncoordinated and conjugated double bonds have been observed in the region of 1600 cm^{-1} . Moreover, the IR spectrum lacked

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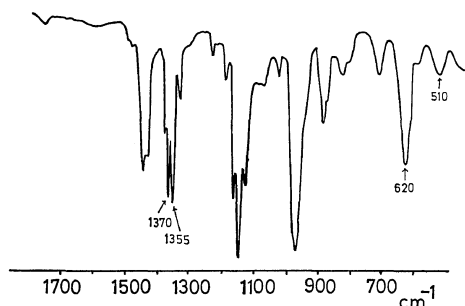


Figure 3. IR spectrum of the nickel complex ($\text{Ni}(\text{COD})_2/\text{Butadiene}/i\text{-PrOH}$).

the bands characteristic of π -allyl nickel complexes and corresponding to vinyl groups.

When the compound was exposed to air for one day all the six absorption bands described above diminished or disappeared and new bands appeared at 1640 and 910 cm^{-1} , which are attributed to the uncoordinated double bond and vinyl group respectively. The band ascribed to methyl group at 1380 cm^{-1} remained unchanged.

Decomposition Products of the Nickel complex

Pyrolysis of the dark-red, syrupy compound obtained from isopropyl alcohol *in vacuo* resulted in the formation of metallic nickel, butadiene oligomers, and *n*-butene isomers. Distributions of the oligomers and *n*-butene isomers in the decomposition products are summarized in Table IV.

Cycloocta-1,5-diene, which was found in the volatiles from the reaction mixture under reduced pressure, was in a quantity corresponding to that

of the original bis(π -cycloocta-1,5-diene)nickel used. The linear dimers of butadiene, however, could scarcely be detected.

When the syrupy compound was dissolved in ether and subjected to decomposition with dilute hydrochloric acid, a mixture of *n*-butene isomers, *n*-butene, linear hydrodimers, and isopropyl alcohol was recovered. However, neither butadiene nor conjugated butadiene dimers, such as *n*-octa-1,3,6-triene, could be found and the result differed from the pyrolysis.

A Proposed Structure of the Nickel Complex

On the basis of these results, we assert that the dark-reddish-brown complex is composed of monomeric butadiene, butadiene oligomer, isopropoxide, and nickel atom, where all double bonds of monomeric butadiene and butadiene

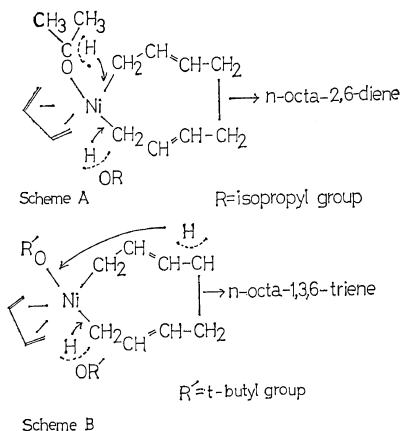


Figure 4. Dimerization of butadiene.

Table IV. Distribution of compounds produced by pyrolysis of the nickel complex^a

Sample	C ₄ Compound, ^a %				C ₈ Compound, ^a %			
	BD	Bu-1	<i>t</i> -Bu-2	<i>c</i> -Bu-2	OD(1,6)	OD(2,6)	OT(1,3,6)	COD
Decomposition products ^b	21.2	18.2	47.4	13.2	20.8	57.0	22.0	trace
Evaporated compounds ^c	—	4.4	28.4	67.2	0	0	0	100

^a Prepared by evaporating the volatiles under reduced pressure from the solution produced in the reaction of 4.82 mmol of bis(π -cycloocta-1,5-diene)nickel, 130 mmol of butadiene, and 30 ml of isopropyl alcohol at 150°C for 1 hr. Description of notations: Bu-1, butene-1; *t*-Bu-2, *trans*-butene-2; *c*-Bu-2, *cis*-butene-2; BD, butadiene; OD(1,6), *n*-octa-1,6-diene; OD(2,6), *n*-octa-2,6-diene; OT(1,3,6), *n*-octa-1,3,6-triene; COD, cycloocta-1,5-diene.

^b The pyrolysis was performed at 100°C *in vacuo*.

^c Evaporated from the reaction solution (a).

^d Calculated from the ratio of peak areas in gas chromatograms.

oligomer share the nickel through δ - or π -bonding, and that the butadiene oligomers on the nickel atom are converted to *n*-octa-1,6- and 2,6-diene by the hydrogenation with the solvent (Figure 4, Scheme A) or to a conjugated dimer *n*-octa-1,3,6-triene by the hydrogen transfer, as suggested by J. Feldman, *et al.*⁷ (Figure 4, Scheme B).

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