The Oligomerization of Butadiene with an Iron Complex Catalyst

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Several complex catalyst systems for the selective dimerization and trimerization of butadiene have been reported,[1] most of them are composed of first-row transition metal complexes and organometallic compounds. Attempts have also been made to elucidate the relationship between the sorts of transition metals and electron-donating additives as catalyst components, on the one hand, and the structure of the oligomers formed therewith on the other.

In a previous paper[2] the authors reported that butadiene dimerizes selectively to 3-methylhepta-1, 4, 6-triene with the catalyst prepared by the reaction of cobalt(III) acetylacetonate and triethylaluminum in the presence of butadiene. It has now been found that *n*-dodeca-1, 3, 6, 10-tetraene is formed selectively with the catalyst prepared by the reaction of iron(III) acetylacetonate instead of the cobalt complex.

This paper will be concerned, in particular, with the structural determination of the trimers and of the factors affecting the reaction. Measurements of the visible light absorption spectra and of the magnetic susceptibility of the reaction solution for the elucidation of the transition complex of the oligomerization will also be described.

Experimental

Reagents.—Benzene was purified by washing it with concentrated sulfuric acid and then distilling it over metallic sodium under nitrogen.

Triethylaluminum (Ethyl Corporation, U. S. A.) was used without further purification.

Butadiene (Nihon Petrochemical Company) was dried by passing it through columns of calcium chloride and silica gel.

Iron(III) acetylacetonate was prepared according to the method described by Steinbach et al.[3]

Procedure.—A 30 ml. Schlenk tube or a 200 ml. glass autoclave was used as a reactor. Calculated amounts of iron(III) acetylacetonate, benzene, butadiene and triethylaluminum were introduced in that order into the reactor, which had previously been swept with nitrogen. During the procedure, the reactor was cooled below −10°C to prevent the evaporation of butadiene. Then the reactor was sealed or stoppered and kept at 50°C during the reaction. Products were analyzed by gas chromatography immediately or after hydrogenation with palladium black.

Analysis.—*Gas Chromatography.*—For the analysis of the dimers, a copper tube (4 mm. in diameter and 2.5 m. long) packed with tricresylphosphate on Simalite (Shimadzu Seisakusho Ltd.) was used. The temperatures of the thermostat and the inlet were 90°C and 140°C respectively; the helium gas speed was 30 ml./min. For the trimers, a copper tube (4 mm. in diameter and 7 m. long) packed with polydiethylene glycol-succinate on Diasolid (Shimadzu Seisakusho Ltd.) was used. The temperatures of the thermostat and the inlet were 130°C and 220°C respectively, and the helium gas speed was 22 ml./min. For the determination of the molecular distribution of the products, hydrogenated products were used. Hydrogenation was carried out with 5% of palladium black under atmospheric pressure at room temperature. C_{16}- and C_{20}-products were determined by gas chromatography with a copper tube (4 mm. in diameter and 7 m. long) packed with polydiethylene glycol-succinate on Diasolid. The conditions were as follows; temperature of thermostat, 190°C: that of inlet, 270°C, and helium gas speed, 22 ml./min.

Distillation.—For the determination of the molecular weight distribution of the reaction products, hydrogenated products were fractionated by vacuum distillation and molecular distillation (10^{-3} mmHg) into 7 parts. The average molecular weight of each fraction was determined by vapor pressure osmometry.

Infrared Spectra. — The spectra of the samples were taken with a Nihon-bunko double-beam spectrometer model 401 G.

NMR Spectra.—The spectra were recorded on a Nihon-Denshi model 3H-60.

Ultraviolet and Visible Light Spectra.—The spectra were recorded on a Hitachi model EPS spectrometer, using a 10 mm.-path-length quartz cell for the ultraviolet measurements and a 0.1 mm.-path-length quartz cell for the visible light spectra measurements. Magnetic susceptibilities were measured with a Gouy balance in the field of 10000 gauss at room temperature.

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[1] Studiengesellschaft Kohl, *Austrian.*, 219580 (1962); G. Wilke, *Angew. Chem.*, **75**, 10 (1963); S. Ohtsuka, T. Taketomi and T. Kikuchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 1094 (1963); *J. Am. Chem. Soc.*, **85**, 3709 (1963); H. Takahashi, *J. Org. Chem.*, **28**, 1409 (1963); S. Tanaka, K. Mabuchi and N. Shimazaki, ibid., **29**, 1636 (1964).

[2] T. Saito, T. Ohno, Y. Uchida and A. Misono, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 1099 (1963).

[3] J. F. Steinbach and J. H. Burns, *J. Am. Chem. Soc.*, **80**, 1839 (1958).

Results and Discussion

The Identification Oligomers. — Liquid polymer, trimers and dimers were obtained by the reaction. The conversion of butadiene versus the reaction time is shown in Fig. 1, while the yields of each oligomer is given in Fig. 2. The yield of the dimers was only a small percentage of the products. The dimers were identified as 3-methylhepta-1, 4, 6-triene, *n*-octa-1, 3, 6-triene, 4-vinylcyclohexene and cycloocta-1, 5-diene by gas chromatography. Trimers consisted of two kinds of isomers. One of the main products was separated and purified with preparative gas chromatography, and then the structure was determined. The results of elemental analysis (C, 87.5%; H, 11.2%) and molecular weight determination (M. W. = 162) indicate that this compound is a trimer of butadiene. From the iodine value and the infrared spectra, it was confirmed that the trimer has two isolated double bonds and a pair of conjugated double bonds in its structure. In the infrared spectra (shown in Fig. 4) the absorption of the C=C conjugated stretching vibration (1650, 1600 cm^{-1}), the C-H out of plane deformation vibration of the conjugated vinyl group (895, 1000 cm^{-1}), that of the trans double bond (970 cm^{-1}), that of the conjugated trans double bond (955 cm^{-1}), and that of the cis double bond (700 cm^{-1}) were observed. In the ultraviolet spectra, the absorption of the conjugated double bond was observed at 228 mμ, the molecular absorption coefficient being 3×10^4. In the NMR spectra (shown in Fig. 5) the absorption of the protons of the methylene group between two double bonds, those of the methylene group adjacent to a double bond and those of the methyl group adjacent to a double bond were found at 7.1, 7.8 and 8.3 τ respectively. The ratio of the peak areas was 2 : 4 : 3. Moreover, the hydrogenated product of this trimer was identified as *n*-dodecane by gas chromatography. Judging from these results the structure of the trimer is *n*-dodeca-1, 3, 6, 10-tetraene.

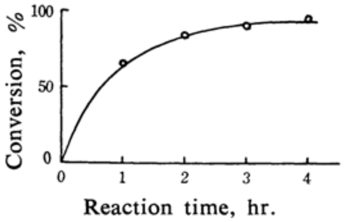

Fig. 1. Conversion of butadiene.

Benzene : 7.4 g. Butadiene : 3.7 g.
Fe(acac)$_3$/BD : 4×10^{-3} AlEt$_3$/Fe(acac)$_3$: 3
Reaction temp. : 50°C

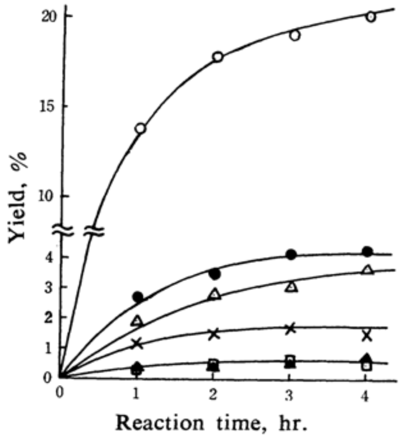

Fig. 2. Relation between reaction time and yields of products.

○ *n*-Dodeca-1, 3, 6, 10-tetraene
● A trimer
△ Cycloocta-1, 5-diene
× 3-Methylhepta-1, 4, 6-triene
■ *n*-Octa-1, 3, 6-triene
▲ 4-Vinylcyclohexene

$$\begin{gathered}CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH{=}\\CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_3\end{gathered}$$

Another trimer, which was formed in an amount about one-fourth of *n*-dodecatetraene, was a branched-chain isomer, judging from infrared and NMR observations.

Molecular Weight Distribution of the Product. —To solve the question of whether these trimers are the lower parts of liquid polybutadiene or those formed by a process different from polymerization, the molecular weight distribution was determined with the hydrogenated products. The hydrogenated products were fractionated into 7 fractions by vacuum distillation (trimers) followed by molecular distillation (5 fractions and the residue). The amounts and the average molecular weight of the fractions are given in Table I. For the fraction with the average polymerization degree of 4.5, the C_{12}, C_{16} and C_{20} contents were measured by gas chromatography. From these results and from the amount and average polymerization degree of the fraction, the C_{24} content was calculated. In the same way, for the fraction with the average polymerization degree of 5.5, the C_{12} (which could not be found), C_{16} and C_{20} contents were determined by gas chromatography. Then the C_{24} and C_{28} contents were calculated on the assumption that the fraction with an average polymerization degree between n and $n+1$, obtained by molecular distillation, consists of $C_{4(n-1)}$, C_{4n}, $C_{4(n+1)}$ and $C_{4(n+2)}$. From the results concerning both fractions, the mole ratio of components was

TABLE I. $\overline{P}$ OF FRACTIONATED PRODUCT

Fraction	B. p. °C/mmHg	$\overline{P}$	Weight, g.*
1		2	0.6
2	90/8	3	3.3
3	90—100/10^{-3}	4.5	1.1
4	100—120/10^{-3}	5.5	1.4
5	120—130/10^{-3}	6.5	1.2
6	130—160/10^{-3}	7.5	1.6
7	160—210/10^{-3}	8.5	2.4
8	Dist. residue	9.5	1.1

* The amount of dimers were determined by gas chromatography.

estimated to be nearly $C_{4(n-1)}:C_{4n}:C_{4(n+1)}:C_{4(n+2)}=1:3:3:1$. On the assumption that the fractions with an average polymerization degree larger than 5.5 consisted of components in the same 1 : 3 : 3 : 1 ratio, the amounts of all the component in the fractions were estimated. By obtaining the sum of the components of each fraction, the molecular weight distribution of products was estimated (Fig. 3). The result shows that the products evidently consist of two parts, one of which is dimers and trimers and the other is liquid polybutadiene, with an average polymerization degree of seven. It was, therefore, concluded that trimers were formed by a mechanism different from that of polymerization.

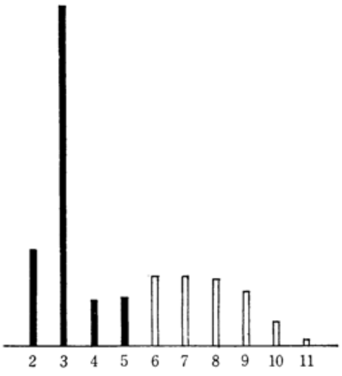

Fig. 3. Molecular weight distribution of products.

▬ : The molecular weight distribution of these components was also determined by gas chromatography.

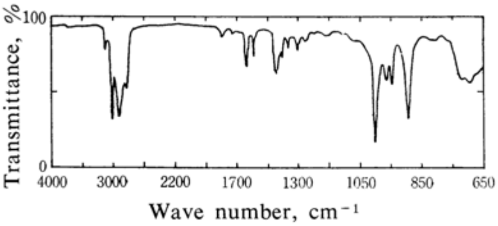

Fig. 4. Infrared spectra of *n*-dodeca-1, 3, 6, 10-tetraene.

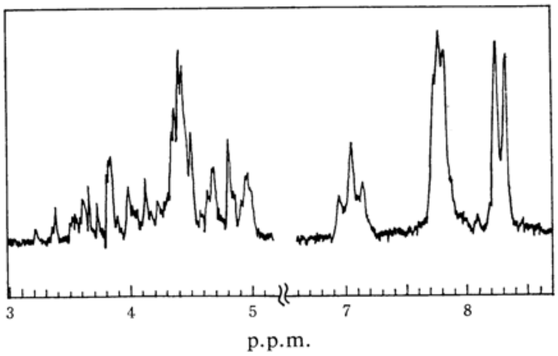

Fig. 5. NMR spectrum of *n*-dodeca-1, 3, 6, 10-tetraene.

The Effect of the Ratio of $AlEt_3$ to Fe(acac)$_3$. —Figure 6 shows the relation between the selectivity of linear trimer formation and the mole ratio of catalyst components. When more than 3 times the amount of the iron(III) acetylacetonate of triethylaluminum was used, the selectivity of the formation of trimers was lowered and polymer formation became predominant. However, the *n*-dodecatetraene ratio in linear trimers was not affected. Figure 7 gives the effect of the ratio of catalyst components on the apparent reaction rates of the formation of the linear trimers and liquid polybutadiene. It indicates that the rate of the formation of liquid polybutadiene is nearly proportional to the ratio of triethylaluminum to the iron(III) acetylacetonate used. When

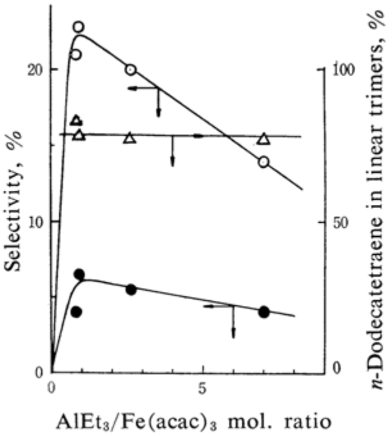

Fig. 6. Relation between selectivity of linear trimers and $AlEt_3$/Fe(acac)$_3$ mol. ratio.

○ *n*-Dodeca-1, 3, 6, 10-tetraene
● A branched trimer
△ *n*-Dodecatetraene in linear trimers
Benzene : 7.3 g. Butadiene : 2.1 g.
Fe(acac)$_3$/BD : 5×10^{-3} Reaction temp.: 50°C

TABLE II. MIXING ORDER OF CATALYST COMPONENTS

Mixing order	Conversion of BD, %	Composition of product, %		
		Dimer	Linear trimer	Poly-BD
Fe+Bz+BD+Al	82	6	31	62
Fe+Bz+Al+BD	40	5	27	68

$Fe(acac)_3$: 0.100 g. Benzene: 8.1 g. Butadiene: 3.8 g.
Al/Fe mol. ratio: 3 Reaction temp.: 46°C Reaction time: 3 hr.

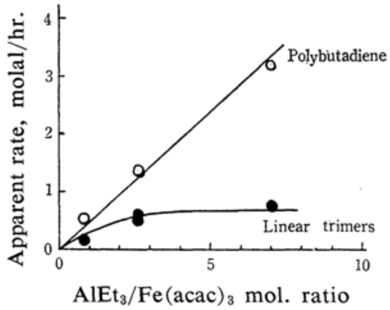

Fig. 7. Effect of $AlEt_3/Fe(acac)_3$ mol. ratio on apparent rate.

only triethylaluminum was applied as a catalyst, butadiene did not react. This phenomenon suggests that both iron and aluminum compounds take part in the formation of the active transition state of the catalyst for polymerization, while only the iron reduced, perhaps to the zero-valent state, by a definite amount of triethylaluminum is involved in the trimerization of butadiene.

The Effect of Catalyst Concentration.—The effect of the catalyst concentration on the apparent reaction rate is shown in Fig. 8. The apparent rates of the formation of both trimers and liquid polybutadiene were nearly proportional to the catalyst concentration.

The Effect of the Mixing Order of the Catalyst Components.—As has been mentioned in previous papers,[2,4] in the linear dimerization of butadiene with a catalyst composed of cobalt(III) acetylacetonate and triethylaluminum, the order of mixing the catalyst components and butadiene has a great effect on the rate of the formation of the dimer. The same phenomenon was expected in the present reaction. The effect of the order of mixing the catalyst components and butadiene is given in Table II. The apparent rate of the oligomerization of butadiene was greater when iron(III) acetylacetonate, butadiene and triethylaluminum were mixed in that order than when triethylaluminum was allowed to react with iron(III) acetylacetonate in the absence of butadiene. These results suggest that the coordination of butadiene to reduced iron prevents the coagulation of reduced iron and plays an important role in the formation of the oligomers.

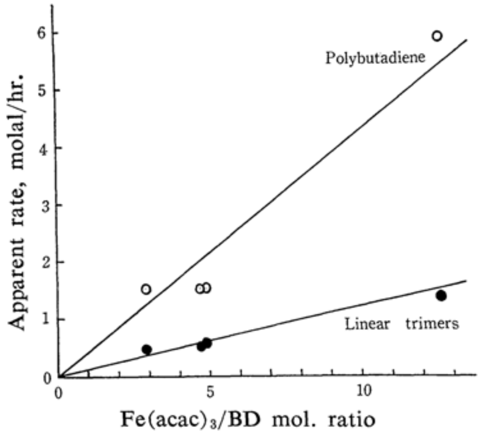

Fig. 8. Effect of concentration of catalyst.

Benzene: 7.3 g. Butadiene: 2.1 g.
$AlEt_3/Fe(acac)_3$: 2.5 Reaction temp.: 50°C

The Observation of the Reaction Solution.—When triethylaluminum was added to a benzene solution of iron(III) acetylacetonate (Fe^{3+} was reduced to Fe^{2+} and then to the zero-valent state.), the solution became unstable and immediately gave rise to a black precipitate. The system showed a ferromagnetism probably caused by the coagulated reduced iron. In the presence of butadiene, the solution became reddish brown and showed paramagnetism, while a shoulder absorption was found at about 400—420 mμ in the visible light absorption spectrum. This absorption has also been observed in π-[BD $Co(CO)_2]_2$ and π-BD $Fe(CO)_3$.[5] On the basis of these results and on the assumption that the active complex for polymerization is diamagnetic,[6] *n*-dodecatetraene is considered to be formed through a paramagnetic intermediate complex in which three molecules of butadiene coordinate to a zero-valent iron atom.

Summary

The oligomerization of butadiene with the catalyst system of iron(III) acetylacetonate and triethylaluminum has been studied. The

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[4] T. Saito, Y. Uchida and A. Misono, This Bulletin, **37**, 105 (1964).

[5] S. Ohtsuka, *Kagaku-Zokan*, No. 13, 87, (1964).

[6] K. Tamai, M. Hidai, Y. Uchida and A. Misono, This Bulletin, to be published.

products obtained by the use of this catalyst consist of two types, one of which is dimers and trimers, and the other is polybutadiene, with an average polymerization degree of seven. The dimers are 3-methylhepta-1, 4, 6-triene and cycloocta-1, 5-diene. The trimers have been confirmed to be *n*-dodeca-1, 3, 6, 10-tetraene and a branched isomer.

The effects of the ratio of the catalyst components to the concentration of the catalyst have been also studied.

From these results, it has been concluded that oligomerization proceeds by a mechanism different from that of polymerization.

To elucidate a transition state for oligomerization, the visible light spectra and the magnetic susceptibility of the reaction solution have been measured and a complex in which butadiene coordinates to reduced iron atom has been assumed as the transition state.

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