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The Oligomerization of Butadiene with Iron Complex Catalysts. II. The Effects of Additives

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In the oligomerization of butadiene with the catalyst composed of iron(III) acetylacetonate and triethylaluminum, the degree of digomerization and the structures of the oligomers were strongly affected by the addition of an electron donor as a catalyst component. When triphenylphosphine was added, linear dimers composed of 3-methylhepta-1, 4, 6-triene and *n*-octa-1, 3, 6-triene were formed, while the addition of 2, 2'-dipyridyl produced cyclic dimers composed of cycloocta-1, 5-diene and 4-vinylcyclohex-1-ene. Besides the above donors, triphenylphosphite, tri(*o*-tolyl)-phosphite, tri(*p*-tolyl)phosphite, phosphorus trichloride, triethylamine and pyridine as monodentate, and *o*-phenanthroline, 2(2'-pyridyl)imidazoline and oxine as bidentate ligands, were tried, and the effects of those donors upon the reaction were studied. The transition states in these catalyst systems were also considered by means of studies of the effects of the molar ratio of catalyst components and by the measurements of infrared, ESR and visible light absorption spectra or magnetic susceptibilities of the reaction solutions.

Introduction

In a previous report[1] the authors mentioned that butadiene trimerized to *n*-dodeca-1, 3, 6, 10-tetraene with the catalyst prepared from the reaction of iron(III) acetylacetonate and triethylaluminum in the presence of butadiene. The formation of the *n*-dodecatetraene was considered to proceed through an intermediate complex in which three molecules of butadiene are coordinated to a low valent iron atom. It may, then, be expected that if a proper electron donor is added to the system, the donor will occupy one or more coordination sites around the low valent iron atom corresponding to the available coordinating sites of the electron donor and its amount, and that, hence, the degree of oligomerization and the structure of the oligomers will be changed. During the course of our study, it was found that butadiene dimerizes selectively to 3-methylhepta-1, 4, 6-triene with a catalyst combining iron(III) acetylacetonate, triethylaluminum and triphenylphosphine; on the other hand, butadiene dimerized selectively to cycloocta-1, 5-diene and 4-vinylcyclohex-1-ene with the catalyst prepared from the reaction of iron(III) acetylacetonate, triethylaluminum and 2, 2'-dipyridyl. In this report, besides the above donors, phosphorus trichloride, triphenylphosphite, tri(*o*-tolyl)phosphite, tri(*p*-tolyl)phosphite, triethylamine and pyridine as monodentate and *o*-phenanthroline, 2(2'-pyridyl)-imidazoline and oxine as bidentate ligands were used, and the effects of these donors upon the products were studied. The nature of the catalyst systems was also discussed by measuring the infrared spectra, the visible light absorption spectra, the ESR spectra and the magnetic susceptibilities of the reaction solutions.

Experimental

Reagents.—The methods of preparing or purifying butadiene, benzene, triethylaluminum and iron(III) acetylacetonate were the same as those mentioned in the previous paper.[1] The electron donors, such as triethylamine, phosphorus trichloride, triphenylphosphine, 2, 2'-dipyridyl, *o*-phenanthroline and oxine, were those of commercial reagents. Triphenylphosphite, tri(*o*-tolyl)phosphite, tri(*p*-tolyl)phosphite and 2(2'-pyridyl)imidazoline were prepared by usual methods.

Procedure.—The reaction was usually carried out with a 30-ml.glass tube. In a typical reaction, benzene (9.2 g.), butadiene (3.0 g.), and triethylaluminum (0.1 g.) were added in this order to the tube which had been charged with iron(III) acetylacetonate (0.10 g.) and a calculated amount of an electron donor. Butadiene, benzene and triethylaluminum were added in a dry nitrogen atomosphere. The tube was cooled during the operations to prevent the evaporation of butadiene. The tube was then closed by fusing and kept at 50°C during the reaction. The reaction products were then analyzed by gas chromatography. The columns and the conditions employed were the same as those described in the previous paper.[1]

For the isolation and confirmation of the reaction products, the reaction was carried out in a 200-ml. glass autoclave. The reaction solution was first washed with dilute hydrochloric acid and then with water. After the solution had been dried with anhydrous sodium sulfate, it was distilled under a nitrogen atmosphere. Products of a high purity were obtained

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[1] M. Hidai, Y. Uchida and A. Misono, This Bulletin, **38**, 1243 (1965).

by preparative gas chromatography. The infrared spectra, visible light absorption spectra, ESR spectra and magnetic susceptibilities of the reaction solutions were measured in order to study the reaction intermediates in these catalyst systems. These measurements were carried out in the same way as has been described in the previous paper.[1]

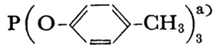
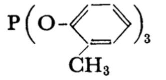
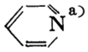
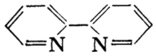
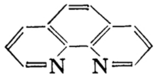
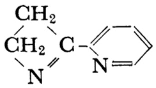
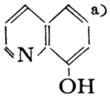
Results

In order to examine the effects of electron donors on the reaction, a series of reactions with various catalyst systems were carried out. The main products formed by the catalysts with various electron donors are listed in Table I.

The Addition of Monodentate Ligands.—*The Addition of Triethylamine.*—The addition of triethylamine did not affect the composition of the products. The conversion of butadiene was slightly decreased by the addition of triethylamine, but the selectivity of the formation of *n*-dodecatetraene was the same as in the case of an iron(III) acetylacetonate and triethylaluminum system.

The Addition of Triphenylphosphine.—When more than one mole of triphenylphosphine was added to one mole of iron(III) acetylacetonate, butadiene dimerized selectively. The dimers were identified as 3-methylhepta-1, 4, 6-triene and *n*-octa-1, 3, 6-triene by the measurements of the retention times by means of gas chromatography and a study of the infrared spectra. The relationship between the conversion of butadiene or the yield of the dimers and the molar ratio of triphenylphosphine to iron(III) acetylacetonate is shown in Fig. 1. When one mole of triphenylphosphine was added to one mole of iron(III) acetylacetonate (the molar ratio of triethylaluminum to iron(III) acetylacetonate was 3 to 1), the products lower than the trimer were methylheptatriene and *n*-octatriene, and no linear trimers formed by the catalyst without triphenylphosphine could be observed. The conversion of butadiene and the dimer formation increased until the molar ratio of the donor to iron(III) acetylacetonate reached 4—5, although the selectivity of dimer formation decreased slightly. When more than 5 times as much triphenylphosphine as iron(III) acetylacetonate was added, the formation of

TABLE I. EFFECT OF ELECTRON DONORS

Donor	D/Fe	Reaction temp., °C	Reaction time, hr.	Conv. %	Yield, %				
					MHT	NOT	VCH	COD	NDTe & a trimer
None	0	46	3	90	t	t	t	t	16
NEt_3	1—20	46	3	80	t			t	16
PPh_3	5.4	50	6	60	37	7			
$P(OPh)_3$	1	50	3	100	t				Polybutadiene
 a)	3	50	5	25	t				
	1	50	3	100					High polybutadiene
PCl_3	1	50	25	5					
 a)	7.3	50	3.5	20					
	1	50	4	73			12	33	
 ·H_2O	1	50	4	100			3	13	Polybutadiene
	1	50	4	100					Polybutadiene
 a)	1	50	7	100	t			t	14

Unless noted, 3.0 g. of butadiene was reacted with the catalyst composed of 0.100 g. of $Fe(acac)_3$, 0.100 g. of $AlEt_3$, and calculated amout of a donor in 9.2 g. of benzene.

a) In these cases 2.4 g. of butadiene was reacted with the catalyst composed of 0.100 g. of $Fe(acac)_3$, 0.100 g. of $AlEt_3$, and calculated amount of a donor in 14 g. of benzene.

b) Abbreviation
MHT: 3-methylhepta-1,4,6-triene, VCH: 4-vinylcyclohex-1-ene, NOT: *n*-octa-1,3,6-triene
COD: cycloocta-1,5-diene, NDTe: *n*-dodeca-1,3,6,10-tetraene, t: yield below 5%
D/Fe: mol. ratio of a donor to iron(III) acetylacetonate

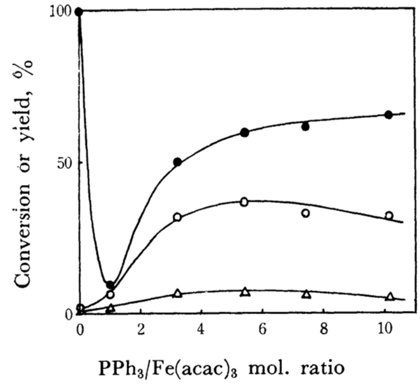


Fig. 1. Effect of molar ratio of triphenylphosphine to iron(III) acetylacetonate.
Reaction temp.: 50°C, Reaction time: 6 hr.
AlEt$_3$/Fe(acac)$_3$ mol. ratio: 3.1
●: Conversion of butadiene, %
○: Yield of 3-methylhepta-1,4,6-triene, %
△: Yield of *n*-octa-1,3,6-triene, %

dimers was rather depressed, although the conversion of butadiene was increased. In this case liquid polybutadiene was formed as a by-product. On the other hand, both the conversion of butadiene and the dimer formation were also affected by the amount of triethylaluminum added, as is shown in Fig. 2. In the case of the catalyst composition in which 3 times as much triphenylphosphine as iron(III) acetylacetonate was added, both the conversion of butadiene and the yield of dimers reached maxima at the point in which the ratio of triethylaluminum to iron(III) acetylacetonate was three. When more than 3 times as much triethylaluminum as iron(III) acetylacetonate was used, the conversion of butadiene and the dimer formation were rather depressed. It is remarkable that in the catalyst system in which more than 3 times as much triphenylphosphine as iron(III) acetylacetonate was added, the effect of triethylaluminum in depressing the methylheptatriene formation became smaller as the amount of triphenylphosphine added was increased.

The Addition of Phosphites.—By the addition of triphenylphosphite, tri(*o*-tolyl)phosphite, and tri(*p*-tolyl)phosphite, polybutadiene was formed as a main product. In the case of tri(*o*-tolyl)phosphite, the reaction was vigorous as compared with other phosphites, and the polybutadiene formed was solid, although in the case of triphenylphosphite and tri(*p*-tolyl)phosphite the polybutadiene formed was liquid.

Addition of Other Donors.—When one mole of phosphorus trichloride was added to one mole of iron(III) acetylacetonate, the reaction was strongly inhibited. The addition of pyridine also stopped the reaction.

The Addition of Bidentate Ligands. — *The Addition of 2, 2'-Dipyridyl.*—When more than one mole of 2, 2'-dipyridyl was added to one mole of iron(III) acetylacetonate, butadiene dimerized selectively. The dimers were identified as cycloocta-1, 5-diene and 4-vinylcyclohex-1-ene (in the ratio 3 : 1) by the measurements of the retention times by means of gas chromatography and a study of the infrared spectra. The relationship between the conversion of butadiene or the yields of the dimers and the molar ratio of 2, 2'-dipyridyl to iron(III) acetylacetonate is given in Fig. 3. When the molar ratio of 2, 2'-dipyridyl to iron(III) acetylacetonate was 1, for example, after 4-hrs.' reaction at 50°C, 73% of the butadiene reacted, of which 45% was changed to cycloocta-1, 5-diene and 15% to 4-vinylcyclohex-1-ene. All the products except the dimers were polybutadiene, and no *n*-dodecatetraene formed by the catalyst without

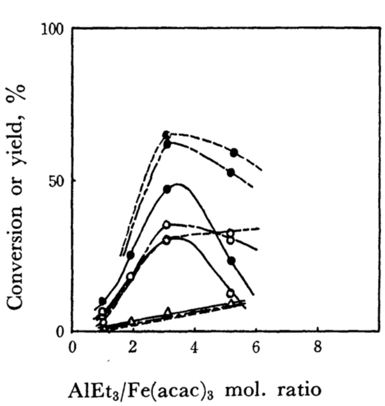


Fig. 2. Effect of composition of catalyst components.
——: PPh$_3$/Fe(acac)$_3$ mol. ratio: 3.0
– – –: PPh$_3$/Fe(acac)$_3$ mol. ratio: 7.0
----: PPh$_3$/Fe(acac)$_3$ mol. ratio: 10.0

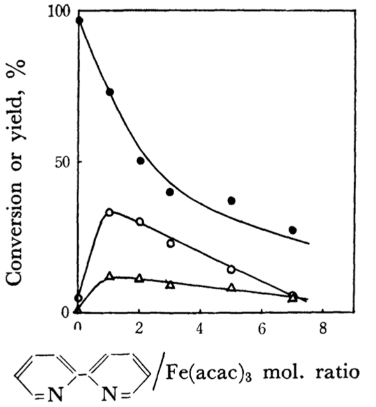


Fig. 3. Effect of molar ratio of 2,2'-dipyridyl to iron(III) acetylacetonate.
Reaction temp.: 50°C, Reaction time: 4 hr.
AlEt$_3$/Fe(acac)$_3$ mol. ratio: 3
●: Conversion of butadiene, %
○: Yield of cycloocta-1,5-diene, %
△: Yield of 4-vinylcyclohex-1-ene, %

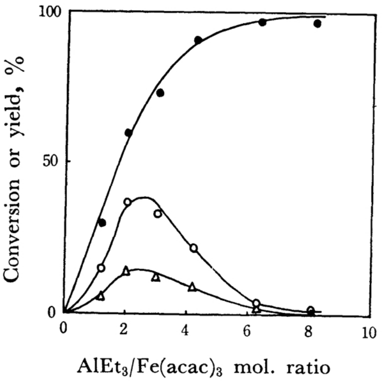
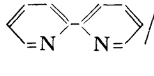


Fig. 4. Effect of molar ratio of triethylaluminum to iron(III) acetylacetonate.
Reaction temp.: 50°C, Reaction time: 4 hr.



/Fe(acac)$_3$ mol. ratio: 1

2, 2′-dipyridyl was observed. When the molar ratio of 2, 2′-dipyridyl to iron(III) acetylacetonate became more than 1, both the conversion of butadiene and the yield of the dimers were decreased. In Fig. 4 is shown the effect of triethylaluminum added. When more than 3 times as much triethylaluminum as iron(III) acetylacetonate was added, the conversion of butadiene increased, but the polymerization became dominant and the yield of dimers was decreased. The same phenomenon had been observed in the case of the linear trimerization of butadiene with a catalyst composed of triethylaluminum and iron(III) acetylacetonate.

The Addition of o-Phenanthroline. — The addition of *o*-phenanthroline also gave the cyclic dimers as in the case of 2, 2′-dipyridyl, but the selectivity of dimer formation was lower than in the case of the catalyst system with 2, 2′-dipyridyl.

The Addition of 2(2′-Pyridyl)imidazoline or Oxine.— Upon the addition of 2(2′-pyridyl)imidazoline, only polymerization took place. On the other hand, when oxine was added as a catalyst component, the reaction almost the same as in the system without oxine.

Discussion

In the series of reactions described above, not only the dimerization or trimerization of butadiene took place; polymerization also occurred as a result of the change of catalyst components. As was reported in a previous paper,[2] the essential reaction of catalyst components to form active species is the reduction of iron(III) acetylacetonate with triethylaluminum to a low valent state, estimated as zero valent. We consider that the coordination of a donor as a catalyst component to the reduced iron atom changes the active complex form. If some kinds of complex formation are realized among butadiene, an electron donor, and iron atom, then the magnetic properties of the resultant system must differ from those of the system without the electron donor. With this in mind, the magnetic susceptibilities of the reaction solutions were measured. The results are listed in Table II. As was mentioned in the previous papers,[1,2] when triethylaluminum was added to a benzene solution of iron(III) acetylacetonate, Fe^{3+} was reduced to Fe^{2+} and then to a zero valent state. The resultant solution was unstable, and immediately a black precipitate appeared. The system showed the ferromagnetism of an effective magnetic moment of 11—18 B. M., probably caused by the metallic iron. In the presence of butadiene, the solution became reddish brown and showed the paramagnetism of an effective magnetic moment of 4—5 B. M. A shoulder absorption was found at about 400—450 mμ in the visible light absorption spectrum; this absorption has been observed in bisbutadiene dicobalt tetracarbonyl and butadiene iron tricarbonyl.[3] From these results, a paramagnetic intermediate complex in which butadiene is coordinate to the zero valent iron atom may be expected.

A Reaction Solution with a Catalyst Composed of Iron(III) Acetylacetonate, Triethylaluminum and Triphenylphosphine.—In this case, when triphenylphosphine was added, even if in the absence of butadiene, the value of the magnetic susceptibility of the solution decreased, as is shown in Table II-3. When butadiene was present before the addition of triethylaluminum, the reaction solution was bright brown and showed an effective magnetic moment of about 1 B. M.; this finding supported the coordination of both butadiene and triphenylphosphine to the reduced iron atom. In this case a shoulder absorption at 400—420 mμ was also observed. From the observation of the infrared spectra in the potassium bromide region of the reaction solution with various contents of triphenylphosphine, it was observed that, when the ratio of triphenylphosphine to iron(III) acetylacetonate was equal to 0.6 and 1, the absorption at near 500 cm^{-1} characteristic of triphenylphosphine did not appear and that, when the ratio was larger than 1, this absorption appeared and increased with an increase in the ratio of triphenylphosphine to iron(III) acetylacetonate (shown in Figs. 5-1 and 5-2). On the other hand, when the ratio was 0.6, new absorptions at 512 and 538 cm^{-1} appeared. These absorptions became strong when the ratio approached 1. However, the absorptions almost did not change at all when the ratio increased above 1. These new absorptions at 512 and 538 cm^{-1} were also observed in a triphenylphosphine iron complex

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[2] K. Tamai, T. Saito, Y. Uchida and A. Misono, This Bulletin, **38**, 1575 (1965).

Table II-1. Effective magnetic moment of $Fe(acac)_3$-$AlEt_3$ system

Al/Fe	Weight fraction			$\chi_g \times 10^6$ for solution	$\chi_m \times 10^6$	μ_{eff}(B.M.)
	C_6H_6	$Fe(acac)_3$	$AlEt_3$			
1.3	0.980	0.0147	0.0061	+4.55	126000	16.7
2.4	0.972	0.0155	0.0122	+5.07	131000	17.6
4.8	0.962	0.0149	0.0228	+1.932	62500	10.9

χ_g : gram susceptibility of sample solution
χ_m : molar susceptibility based on iron atom
μ_{eff} : effective magetic moment

Table II-2. Effective magnetic moment of $Fe(acac)_3$-C_4H_6-$AlEt_3$ system

Al/Fe	Weight fraction				$\chi_g \times 10^6$ for solution	$\chi_m \times 10^6$	μ_{eff}(B.M.)
	C_6H_6	D_4H_6	$Fe(acac)_3$	$AlEt_3$			
2.2	0.915	0.0562	0.0171	0.0121	−0.318	7660	4.2
2.8	0.908	0.0529	0.0207	0.0188	+0.065	12840	5.4
5.1	0.907	0.0512	0.0157	0.0258	−0.222	10600	4.9

Table II-3. Effective magnetic moment of $Fe(acac)_3$-PPh_3-AlEt system

Al/Fe	P/Fe	Weight fraction				$\chi_g \times 10^6$ for solution	$\chi_m \times 10^6$	μ_{eff}(B.M.)
		C_6H_6	PPh_3	$Fe(acac)_3$	$AlEt_3$			
2.1	2.0	0.969	0.0144	0.0098	0.0066	+1.935	95500	15.1
2.2	6.1	0.933	0.0490	0.0108	0.0073	+0.945	53700	11.1
4.8	6.2	0.902	0.0630	0.0138	0.0213	−0.389	7950	4.3

Table II-4. Effective magnetic moment of $Fe(acac)_3$-C_4H_6-PPh_3-$AlEt_3$ system

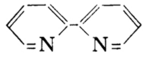
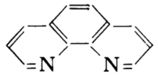
Al/Fe	P/Fe	Weight fraction					$\chi_g \times 10^6$ for solution	$\chi_m \times 10^6$	μ_{eff}(B.M.)
		C_6H_6	PPh_3	C_4H_6	$Fe(acac)_3$	$AlEt_3$			
2.0	4.0	0.893	0.0325	0.0564	0.0109	0.0071	−0.695	diamag	
2.1	4.0	0.875	0.0456	0.0542	0.0154	0.0103	−0.671	482	1.1
2.1	4.0	0.889	0.0354	0.0599	0.0120	0.0080	−0.642	1450	1.8
5.2	1.0	0.887	0.0113	0.0510	0.0152	0.0255	−0.568	2920	2.6
5.1	3.9	0.869	0.0424	0.0495	0.0148	0.0244	−0.650	1050	1.5
4.3	6.1	0.850	0.0638	0.0524	0.0142	0.0196	−0.664	745	1.3

Table II-5. Effective magnetic moment of $Fe(acac)_3$-C_4H_6-Donor-$AlEt_3$ system

Donor	Al/Fe	D/Fe	Weight fraction					$\chi_g \times 10^6$ for solution	$\chi_m \times 10^6$	μ_{eff}(B.M.)
			C_6H_6	Donor	C_4H_6	$Fe(acac)_3$	$AlEt_3$			
a	3.1	1.1	0.963	0.0070		0.0149	0.0149	+0.490	28000	8.0
a	3.2	1.0	0.904	0.0068	0.0579	0.0151	0.0158	−0.555	3060	2.6
a	4.7	6.8	0.869	0.0422	0.0531	0.0140	0.0212	−0.648	908	1.4
b	2.9	6.6	0.872	0.0362	0.0546	0.0192	0.0179	−0.246	8230	4.3
c	3.0	3.2	0.851	0.0594	0.0531	0.0185	0.0180	−0.622	1220	1.7
d	2.8	3.3	0.857	0.0536	0.0540	0.0186	0.0167	−0.626	1081	1.6

a: 2, 2′-Dipyridyl b: Triethylamine c: Tri(*o*-tolyl)phosphite d: Triphenylphosphite

Table III. Valency orbitals of some ligands stabilizing low oxidation states of transition metals

Ligand	Donor orbital	Acceptor orbital	Effectiveness as a σ donor	Effectiveness as a π acceptor
PCl_3	sp^3 on P	$d\pi$ on P	poor	good
$P(OPh)_3$	sp^3 on P	$d\pi$ on P	poor	good
PPh_3	sp^3 on P	$d\pi$ on P	moderate	moderate
	sp^2 on N	$p\pi$ delocalized	good	moderate
	sp^2 on N	$p\pi$ delocalized	good	moderate

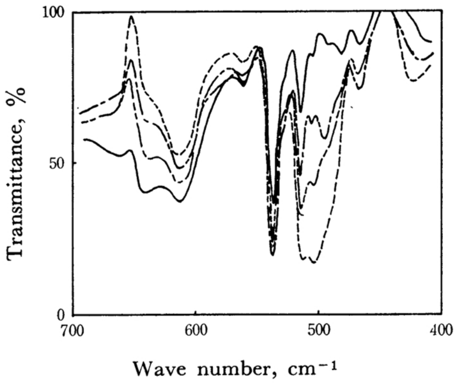


Fig. 5-1. Infrared spectra of reaction solution in KBr region.

——: $PPh_3/Fe(acac)_3=0.6$
–––: $PPh_3/Fe(acac)_3=1.0$
—-—: $PPh_3/Fe(acac)_3=3.2$
----: $PPh_3/Fe(acac)_3=7.0$
$Fe(acac)_3 : C_4H_6 : AlEt_3 : C_6H_6=1.0 : 4.5 : 3.1 : 56$ (mol. ratio)

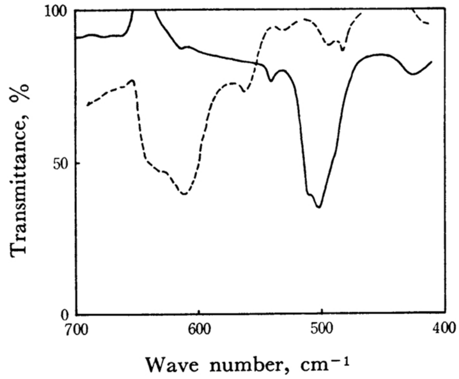


Fig. 5-2. Infrared spectra of reaction solution in KBr region.

——: $PPh_3 : C_6H_6=1 : 24$
----: $Fe(acac)_3 : C_4H_6 : AlEt_3 : C_6H_6=1.0 : 4.5 : 3.1 : 56$ (mol. ratio)

isolated from the solution containing diethylmonoethoxyaluminum, iron(III) acetylacetonate and triphenylphosphine. Therefore, these absorptions were supposed to be characteristic of triphenylphosphine coordinated to an iron atom. From these results it was considered that one molecule of triphenylphosphine is coordinate to the reduced iron atom in the reaction solution, even if an excess of triphenylphosphine is present in the solution.

The effect of amounts of triphenylphosphine on the reaction can be explained by the following consideration. In the reaction system composed of iron(III) acetylacetonate, triethylaluminum and triphenylphosphine, the iron atom coordinated by triphenylphosphine and butadiene is solvated by a solvent or by an aluminum compound such as diethylaluminum acetylacetonate and stabilized as a homogeneous solution. When more than one mole of triphenylphosphine to one mole of iron(III) acetylacetonate is present in the solution, the excess of triphenylphosphine which is not coordinate to the iron atom interacts with the aluminum compound surrounding the iron-butadiene-triphenylphosphine intermediate. This causes a change in solvation and a resultant change in the oligomerization reaction. The phenomena that an excess of triethylaluminum depresses the reaction may also be explained as the solvation of the aluminum compound to the reaction intermediate complex. In the case of a large excess of triphenylphosphine in the solution, the excess of triethylaluminum does not affect the reaction course. It may be supposed that the excess triphenylphosphine reacts with triethylaluminum and that the resultant compound is probably not so active as to affect the solvation conditions surrounding the intermediate. Therefore, the reaction was almost the same as the one catalyzed by the system which did not contain an excess of triethylaluminum.

These solvation effects will also affect the magnetic properties of the solution. However, the

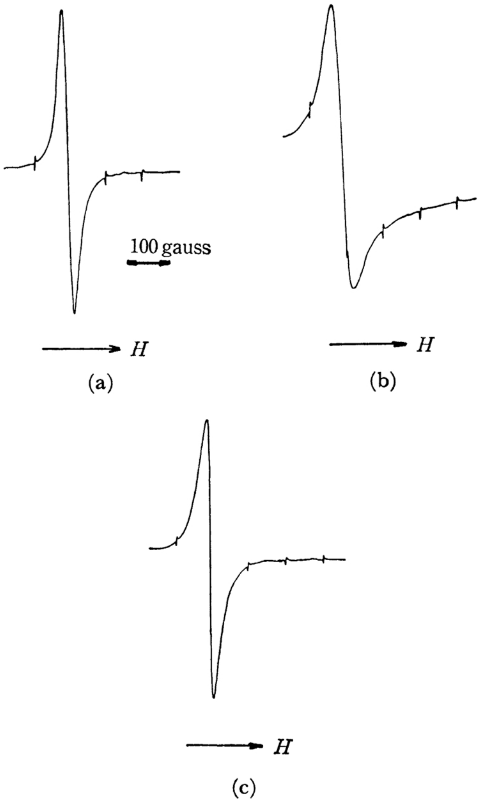


Fig. 6. ESR spectra of reaction solution.

	$Fe(acac)_3$	$AlEt_3$	PPh_3	C_4H_6	C_6H_6
(a)	1.0	3.3	4.0	10	145
(b)	1.0	7.9	3.9	10	137
(c)	1.0	7.9	9.5	10	137

(mol. ratio)

accuracy of the measurement of the magnetic susceptibility does not allow any further discussion. The ESR observation of the reaction solution with various ratios of catalyst components is shown in Fig. 6. When triphenylphosphine : iron(III) acetylacetonate : triethylaluminum was 1 : 1 : 3, a broad signal due to the iron atom was observed at the *g*-value of 2.08. This signal was sharpened by the further addition of triphenylphosphine. When the amount of triethylaluminum increased, the absorption became broad again, and upon the further addition of excess triphenylphosphine, the absorption became sharp again. These phenomena may be supposed to be due to the change in coordination or solvation conditions around the iron atom and to be consistent with the above explanation.

The Reaction Solutions with Other Monodentate Ligands.—The addition of triethylamine did not affect the reaction. The effective magnetic moment of the solution was about 4, which is almost the same as that of the reaction solution containing iron(III) acetylacetonate, butadiene and triethylaluminum. From this result, it may be supposed that triethylamine does not coordinate to a low valent iron atom in the system.

When phosphite compounds were added to the catalyst system, the main product was a polymer. In these cases, the reaction solutions were almost diamagnetic and the coordination of phosphites to iron atom may be supposed.

The Reaction Solution with 2, 2′-Dipyridyl.—The magnetic susceptibility of the reaction solution became smaller than the case without a donor, and the difference was greater as the amount of 2, 2′-dipyridyl increased. This suggests that 2, 2′-dipyridyl coordinates to the iron atom in the reaction system. Actually, in the reaction between iron(III) acetylacetonate, 2, 2′-dipyridyl and diethylmonoethoxyaluminum in ether, the diethyl bis-2, 2′-dipyridyl iron complex was isolated. This complex showed catalytic activity in the cyclic dimerization of butadiene.⁴⁾ When butadiene was reacted with the complex, 2, 2′-dipyridyl was isolated from the reaction solution. On the other hand, the best ratio of 2, 2′-dipyridyl to iron(III) acetylacetonate was 1 for the cyclooctadiene formation. From these results, a paramagnetic complex in which butadiene and one molecule of 2, 2′-dipyridyl coordinated to the iron atom may be supposed to be an intermediate of this reaction.

The Elucidation of the Transition State and the Effect of Electron Donors.—From the above-mentioned experimental results and discussions, it was concluded that, by the addition of an adequate electron donor as a catalyst component, the oligomerization of butadiene with an iron complex catalyst was strongly affected. It was also found that, for the formation of the linear dimers, the addition of a monodentate ligand such as triphenylphosphine was effective, while for the formation of the cyclic dimers, such bidentate ligands as 2, 2′-dipyridyl or *o*-phenanthroline were effective.

During the course of his study of the oligomerization of butadiene, Dr. Wilke⁵⁾ isolated a complex, $NiC_{12}H_{18}$, in which three molecules of butadiene were changed to a C_{12} chain by the formation of one trans double bond and two terminal π-allyl groups. He also isolated a complex, $Ni(PR_3)C_8H_{12}$, in which two molecules of butadiene were changed to a C_8 chain by the formation of two terminal π-allyl groups. It was suggested that the former complex was the intermediate complex for the all-trans-cyclododecatriene formation in the reaction of butadiene with the catalyst composed of nickel acetylacetonate and triethylaluminum, while the latter complex was the intermediate complex for the cyclic dimerization of butadiene with the catalyst composed of nickel acetylacetonate, triphenylphosphine and triethylaluminum. According to his view, three molecules of butadiene approach the nickel atom to form the cyclic trimer through the $NiC_{12}H_{18}$ complex. In the case of the catalyst composed of nickel acetylacetonate, triphenylphosphine and triethylaluminum, one of the coordination sites of nickel is occupied by triphenylphosphine; therefore, only two molecules of butadiene can approach the reaction field, so the dimers are formed through the $Ni(PPh_3)C_8H_{12}$ complex. The degree of the oligomerization of products by the iron complex catalyst can be similarly explained. The formation of the cyclic dimers with the combined catalyst of iron(III) acetylacetonate, 2, 2′-dipyridyl and triethylaluminum can be explained by considering that the donor occupies two coordination sites of the low valent iron atom and that two molecules of butadiene approach the iron atom to form the cyclic dimers through a $Fe(dipy)C_8H_{12}$ complex. The formation of methylheptatriene can also be explained in the same way. Two molecules of butadiene approach the iron atom to which one molecule of triphenylphosphine is coordinated.

Besides the above-mentioned discussions about the number of coordination sites of metal, the sort or the nature of donor must be considered. The polymerization proceeds by some electron donors, while by the other donors the reaction was inhibited or specific oligomerization occurred. These are considered to be due to the difference in the strength of the coordination of a donor to metal and the resultant change in bond strength between the butadiene and the metal. The ligands which are

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3) S. Ohtsuka, Kagaku-Zokan, No. 13, 87 (1964).

4) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida and A. Misono, *J. Am. Chem. Soc.*, **87**, 4652 (1965).

5) G. Wilke, *Angew. Chem.*, **73**, 755 (1961); G. Wilke, ibid., **75**, 10 (1963).

found experimentally to stabilize the lower valency states of the transition metals are collected in Table III.[6] It will be noted that each of these ligands has available acceptor orbitals for π electrons and that other ligands, which do not have these acceptor orbitals, are much less effective stabilizers of low valencies, though they have similar properties in every other way. Thus, it may readily be understood that the reaction of butadiene by the combined catalyst of iron(III) acetylacetonate and triethylaluminum was not affected by the addition of triethylamine, which does not have available acceptor orbitals for π electrons, but it was affected by the addition of an electron donor, such as 2, 2′-dipyridyl, triphenylphosphine, phosphorus trichloride, or triphenylphosphite, which has acceptor orbitals. Moreover, it will be noted that such ligands as 2, 2′-dipyridyl or triphenylphosphine, by the addition of which an active complex for dimerization is formed, are moderate as acceptors for π electrons, while triphenylphosphite, by which an active complex for polymerization is formed, is strong as an acceptor, and phosphorus trichloride, by the addition of which the reaction of butadiene is stopped, is a very strong acceptor for π electrons. Thus, a ligand which is coordinated to the low valent iron atom and forms an active complex for the dimerization of butadiene, must have available acceptor orbitals for π electrons of adequate energy levels.

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[6] L. E. Orgel, "An Introduction to Transition-Metal Chemistry," Methuen, London (1961).