Reaction of Butadiene in the Presence of a Three-component Catalyst Consisting of Iron(III)acetylacetonate, a Phosphorus Compound, and Bis(diethylaluminum)sulfate

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It has been reported that a catalyst composed of iron(III)acetylacetonate and triethylaluminum is active in the reaction of butadiene with ethylene, yielding 1,4-hexadiene,[1] and also in the trimerization of butadiene, yielding *n*-dodeca 1,3,6,10-tetraene.[2] Hidai and his co-workers[3] studied the effect of adding triphenylphosphine as an electron donor to the catalyst system in the reaction of butadiene ; they found that the selectivity of the reaction was altered with an increase in the molar ratio of triphenylphosphine to iron(III)acetylacetonate. They obtained liquid polybutadiene as a by-product when the molar ratio was larger than five. On the other hand, we obtained a solid polymer composed of 1,2-addition sequences when three or four moles of triphenylphosphine per mole of iron(III)acetylacetonate were added to the catalyst system.[4]

In this note, the author will describe the characteristics of a three-component catalyst containing bis(diethylaluminum)sulfate as an organoaluminum compound. In a previous paper,[5] we reported on

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[1] G. Hata, *J. Am. Chem. Soc.*, **86**, 3903 (1964).

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

[3] M. Hidai, K. Tamai, Y. Uchida and A. Misono, *ibid.*, **39**, 1357 (1966).

[4] M. Iwamoto, Unpublished work.

TABLE 1. REACTIONS OF BUTADIENE IN THE PRESENCE OF $\mathrm{Fe(acac)_3\text{-}P(C_4H_9)_3\text{-}[(C_2H_5)_2Al]_2SO_4}$ CATALYST

Benzene m*l*	$\mathrm{Fe(acac)_3}$ mmol	$\mathrm{P(C_4H_9)_3}$ mmol	$\mathrm{[(C_2H_5)_2Al]_2SO_4}$ mmol	Butadiene g	React. temp.[a] °C	React time hr	Products (g)		
							MHT	OT	Residue
20	1	0	4.1	40	55—60	18.5	0.8	—	4.9
20	1	1	4.1	40	55—60	2	16.9	5.3	9.5
20	1	2	4.1	40	55—60	2	19.2	3.8	10.9
20	1	4	4.1	40	55—60	2	12.7	1.6	14.3
20	1	4	6.0	40	30—32	2	24.6	6.0	10.5
40	0.25	1	3.0	33.5	40	2	21.0	4.5	3.2
40	0.25	1	3.0	20	r.t.[b]	1	8.0	3.5	7.6
40	0.25	1	3.0	20	r.t.	2	8.7	4.0	7.8
40	0.25	1	3.0	20	r.t.	4	10.3	4.7	6.1

a) bath temperature   b) r.t.=room temperature

the vinyl-polymerization of butadiene and isoprene in the presence of a catalyst composed of the cobalt thiocyanate - triphenylphosphine complex and bis(diethylaluminum) sulfate. Bis(diethylaluminum)-sulfate has been found to act somewhat differently from triethylaluminum.

A mixture of butadiene linear dimers composed of 9.5 g of 3-methyl-1,4,6-heptatriene (MHT) and 12.7 g of 1,3,6-octatriene (OT) was obtained, along with 4 g of a by-product, in a reaction of butadine carried out at 50—60°C for 5 hr in the presence of a catalyst consisting of 0.5 mmol of iron(III)acetylacetonate, 2 mmol of triphenylphosphine, and 3.6 mmol of bis(diethylaluminum)sulfate. In this case, there was a selective formation of the linear dimers, and more 1,4-addition product, OT, than 1,2-addition product, MHT, was formed. The results obtained in the reaction of butadiene with a catalyst, using tributylphosphine as an electron donor, are summarized in Table 1. It was found that the amount of MHT in the dimer mixture was affected by the P/Fe molar ratio, and that the residue in the atmospheric distillation of the reaction mixture increased with an increase in the P/Fe molar ratio. As compared with the catalyst containing triphenylphosphine, the catalyst containing tributylphosphine tends to form more of the 1,2-addition product than of the 1,4-addition product, just as cobalt catalysts do.[6]

When diphenylphosphine was added to the catalyst system as an electron donor, a rubber-like polymer was obtained as the main product, together with a small amount of linear dimers. The infrared spectrum of the polymer shows strong absorption peaks at 910 and 955 cm^{-1}, suggesting a high content of the 1,2-addition sequence in the polymer chain. Triethylphosphite also promoted the polymerization of butadiene, yielding a colorless polymer mainly composed of the 1,2-addition sequence. When tributylphosphite or phosphorus oxychloride was added, the reaction proceeded less selectively to yield both the dimers and a polymeric substance.

It is considered that the catalytic formation of the oligomers is closely related to the vinyl-polymerization of butadiene, and these facts in turn suggest a similarity in the catalytically-active complex for both the reactions. The variation in the properties of the catalytic system is considered to depend on the physical and chemical characteristics of the electron donor added and may be explained in a way similar to that presented in a previous report.[3] Moreover, it has been found that the organoaluminum compound also affects the properties and the activity of the catalyst system.

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5) M. Iwamoto and S. Yaguchi, *Polymer Letters*, **5**, 1007 (1967).

6) T. Saito, T. Ohno, Y. Uchida and A. Misono, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **66**, 1099 (1963); This Bulletin, **37**, 105 (1964).