A Cobalt Complex Catalyst for the Linear Dimerization of Butadiene

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We have found that the selective dimerization of 1, 3-butadiene to 3-methyl-hepta-1, 4, 6-triene is carried out by a complex catalyst composed of triethylaluminum and cobalt complexes such as cobalt(III) acetylacetonate, cobalt salicyl aldehyde, a cobalt chloride pyridine complex, and cobalt chloride. Some of the results using cobalt(III) acetylacetonate have been previously reported.[1] The order of mixing cobalt acetylacetonate, butadiene and triethylaluminum had a great effect on the rate of formation of the butadiene dimer; the best results were obtained when cobalt acetylacetonate, butadiene and triethylaluminum were mixed in that order. These results suggest that the coordination of butadiene to cobalt is affected by the mixing order of the monomer and catalyst components and has an important influence on the dimerization of butadiene.

In this paper, an explanation for the formation of an active complex will be attempted by means of the results from infrared spectra, magnetic susceptibility and electron spin resonance spectra.

Experimental

Reagents. — Benzene was purified by washing it with concentrated sulfuric acid and then distilling it with metallic sodium in an atmosphere of nitrogen gas.

Triethylaluminum (made by the Ethyl Corp., U. S. A.) was used in the experiments without further purification.

Cobalt acetylacetonate was synthesized according to the method described in "Inorganic Syntheses."[2]

Infrared Analysis. — The infrared spectra of the samples were found by means of a Nihon-Bunko double-beam spectrometer model 401 G for the sodium chloride region and model 201 for the potassium bromide region.

Known amounts of cobalt acetylacetonate, butadiene (benzene solution) and triethylaluminum (benzene solution) were introduced into a glass tube in an atmosphere of nitrogen gas, and a part of the solution was transfused into a 0.1 mm.-path. length sodium chloride cell with a glass syringe.

TABLE I. THE PREPARATION METHOD OF THE SAMPLES EMPLOYED

1) Infrared analysis

Fig. No.	No.	Molar ratio				Mixing order
		Benzene	C_4H_6	Co(acac)$_3$	AlEt$_3$	
1	1	177	9.5	1	4.2	Bz+Co+BD+Al
	2	183	9.6	1	4.1	Bz+BD+Al+Co
	3	182	9.6	1	4.0	Bz+Co+Al+BD
2	4	75	0	1	0	Bz+Co
	5	65	5.0	0	0	Bz+BD
	6	71	4.8	1	2.5	Bz+Co+BD+Al
	7	69	5.3	1	2.1	Bz+Co+Al+BD

2) Magnetic susceptibility

No.	Weight fraction				Mixing order	χ_g for complex $\times 10^6$	χ_M for cobalt $\times 10^6$	μ_{eff}	n
	Benzene	C_4H_6	Co(acac)$_3$	AlEt$_3$					
8	0.949	0.0300	0.0100	0.0111	Bz+Co+Al+BD	9.74	7320	3.95	3.18
9	0.908	0.0565	0.0185	0.0170	Bz+Co+BD+Al	1.23	867	1.41	0.72

3) Electron spin resonance

Fig. No.	No.	Molar fraction				Mixing order
		Benzene	C_4H_6	Co(acac)$_3$	AlEt$_3$	
3	10	181	6	1	2.4	Bz+Co+Al+BD
	11	181	6	1	2.4	Bz+Co+BD+Al

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

[2] J. C. Bailar, Jr., "Inorganic Syntheses," Vol. 5, 188 (1953).

Magnetic Susceptibility. — The Gouy method was adopted for observing the magnetic susceptibility of the compounds placed between the poles of an electric magnet with a value of 25000 gauss; a quartz sample tube was also employed. The measurement were carried out at 10°C. The samples were prepared in the way described in the above section.

Electron Spin Resonance Spectra. — The spectra were recorded in the X-band (9400 Mc.) with 100 kc. modulation by means of a Nihon-Denshi Model JES-3B ESR spectrometer. The method of sample preparation was the same as that described above; the conditions of sample preparation for each experiment are shown in Table I.

Results and Discussion

When triethylaluminum reacts with cobalt acetylacetonate in the presence of butadiene, the resultant solution shows a marked catalytic activity in the linear dimerization of butadiene, whereas the solution prepared by the reaction of cobalt acetylacetonate and triethylaluminum without butadiene is considerably inactive. Thus, the order of mixing the catalyst and butadiene components is very important in obtaining the active catalyst.[1]

Infrared spectra were recorded for each solution of a different mixing order of the components. In the infrared spectrum in the sodium chloride region, the decrease in the absorptions of the CH- and CH_2-wagging vibrations of butadiene, at 1008 and 908 cm^{-1} respectively, was very marked in the sample prepared by adding triethylaluminum last (Fig. 1-1). This result indicates that butadiene molecules are strongly bound in that case. Triethylaluminum is assumed to play the role of reducing cobalt to the state in which butadiene molecules readily coordinate to cobalt. On the other hand, when triethylaluminum is added before butadiene (Fig. 1-3), a complex is formed to which butadiene molecules hardly coordinate at all. Figure 1-2 displays the intermediate state.

Infrared spectra in the potassium bromide region were recorded to elucidate the bond structure between the transition metal and the oxygen atoms of acetylacetone ligands. Nakamoto[3] has reported on the infrared spectra in the potassium bromide region of acetylacetonates of trivalent metals. He assigned the 466 and 490 cm^{-1} bands to Co–O and Al–O stretching vibrations respectively. In the present investigation, the reaction mixtures of cobalt acetylacetonate, butadiene and triethylaluminum in both orders of mixing (Figs. 2-6 and 2-7) showed the Al–O band at 490 cm^{-1} instead of the Co–O band at 466 cm^{-1}, indicating that the acetylacetone ligands of cobalt acetylacetonate come to be coordinated to aluminum as the result of the ligand exchange reaction effected by triethylaluminum.

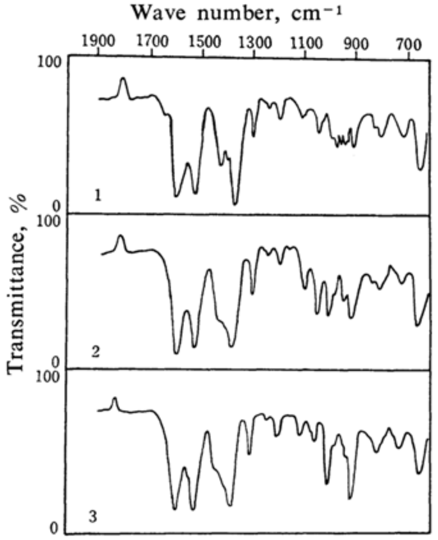

Fig. 1. IR spectra of the solutions prepared by different orders of mixing.

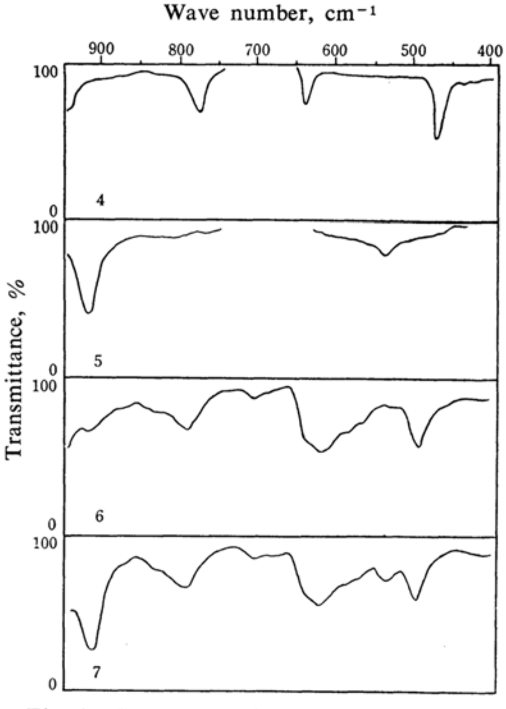

Fig. 2. IR spectra of the solutions prepared by different orders of mixing.

By evaporating the solvent and low-boiling materials from the reaction solution of cobalt acetylacetonate, butadiene and triethylaluminum in benzene, a catalytically-active solid

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[3] K. Nakamoto, *J. Am. Chem. Soc.*, **83**, 1066 (1961).

was obtained. By sublimation of the solid, it was confirmed that one sublimate was aluminum acetylacetonate. The sublimation residue was cobalt metal. These results support the theory that the reduction of the cobalt and ligand exchange reaction between cobalt and aluminum take place.

The magnetic susceptibilities of these reaction solutions were measured to determine the number of unpaired electrons of cobalt. Calculations based on the assumption that the sum of $w_i\chi_{gi}$ equals the χ_g value of the solution, where w_i is a weight fraction and χ_{gi} is a gram susceptibility of a component, indicated that the reaction product of cobalt acetylacetonate, butadiene and triethylaluminum mixed in that order is slightly paramagnetic, while, on the other hand, the product prepared by mixing cobalt acetylacetonate, triethylaluminum and butadiene in that order is strongly paramagnetic. Although the calculations are not decisive enough, because of the obscurity of the structure of the complex formed, to determine unequivocally the exact number of unpaired electrons of cobalt the reaction product of cobalt acetylaluminum with triethylaluminum in the presence of butadiene is probably diamagnetic. (The paramagnetism is due to the partial reaction of cobalt acetylacetonate and triethylaluminum without butadiene.) It is considered to be a diamagnetic complex formed by the removal of the acetylacetone ligands of cobalt acetylacetonate by triethylaluminum, with the simultaneous π-bonding of butadienes to cobalt.

The electron spin resonance spectra support the noticeable relation between the paramagnetism and the mixing order of the catalyst and butadiene components. The strong paramagnetism of the sample agrees very well with the results of the magnetic susceptibility measurement.

It may be suggested on the basis of these experimental results that the active catalyst complex for the dimerization is probably a π-complex of cobalt. Triethylaluminum deprives cobalt acetylacetonate of acetylacetone ligands, and simultaneously butadiene molecules coordinate to cobalt to form the active catalyst complex for the dimerization. Butadiene molecules coordinated to cobalt are considered to form a dimer, and the coordination force of the dimer is so much weaker than that of butadiene that the formed dimer is removed from the cobalt by ligand exchange with the butadiene in the solution. Dimerization will proceed until butadiene is consumed by repeated coordination, dimerization and detachment by ligand exchange processes.

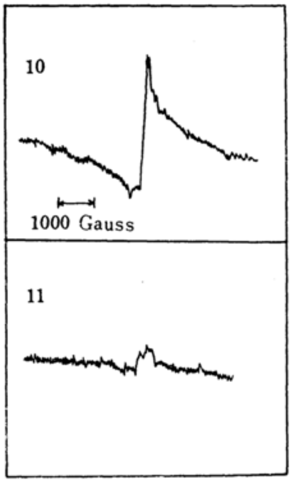

Fig. 3. ESR spectra of the solutions prepared by different orders of mixing.

Summary

In the linear dimerization of butadiene, the mixing order of butadiene and catalyst components, cobalt acetylacetonate and triethylaluminum affects the activity of the catalyst. When cobalt acetylacetonate and triethylaluminum react in the presence of butadiene, the solution possesses marked catalytic activity. In the infrared spectrum of this system, the intensity of the absorption peaks of the CH- (1008 cm^{-1}) and CH_2- (908 cm^{-1}) wagging vibrations of butadiene decrease significantly as compared with the case when butadiene is added last. In both cases, the absorption of Co–O (466 cm^{-1}) disappered and that of Al–O (490 cm^{-1}) was found. These results indicate that triethylaluminum reduces cobalt acetylacetonate and coordinates butadiene to cobalt. When butadiene is absent, triethylaluminum and cobalt acetylacetonate react to form a complex to which butadiene coordinate scarcely at all afterwards. The former solution shows a weak paramagnetism ($\mu_{eff}=1.4$), while the latter shows a strong paramagnetism ($\mu_{eff}=4.0$). From these results, the catalyst of the reaction is considered to be a diamagnetic complex of cobalt coordinated by butadiene.

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