Transition Metal Complex Catalysts for the Oligomerization of Butadiene. III. The Behavior of Evolved Ethylene from Triethylaluminum in the Catalyst-forming Reaction

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The reaction of the ethyl radical formed by the decomposition of such organoaluminum compounds as triethylaluminum and diethylaluminum chloride in the polymerization of butadiene with cobalt complex catalysts has aroused much interest and discussion in connection with the polymerization mechanism.[1-3]

In the course of our studies of the reaction of triethylaluminum and cobalt(III) acetylacetonate, which are used for the linear dimerization of butadiene,[4,5] we found that the gas evolution in the reaction was much less than the theoretical value (about 60% of the calculated volume) and that it was composed mostly of ethane.[6] However, when butadiene was present in the system, a product other than butadiene dimers was detected by gas chromatography. We supposed that this is a C_6 hydrocarbon formed by the reaction of butadiene and ethylene from triethylaluminum. In order to prove this hypothesis, we carried out the reaction of butadiene and ethylene with the same catalyst system, thus obtaining a product. On the basis of chemical analysis, infrared and NMR spectra, this product was determined to be *n*-hexa-1, 3-diene.

$$CH_3CH_2CH{=}CHCH{=}CH_2$$

The gas chromatographic retention time of the unknown product described above exactly coincided with that of *n*-hexa-1, 3-diene, and the amount of it nearly corresponded to the amount calculated for ethylene.

These findings can be explained by assuming that, in the reaction, the ethylation of the reduced cobalt takes place as the first step, followed by the rapid disproportionation of the ethyl radical to give equimolecular ethane and ethylene, while the ethylene remains complexed with the cobalt. The ethylene does not come out of the system because of the complexing, but it is active enough to react with butadiene to form *n*-hexa-1, 3-diene, which is also obtained in a large quantity by the reaction of ethylene and butadiene with the same catalyst as is used for methyl-heptatriene synthesis. At the present time, however, we do not know whether or not ethylene interacts with cobalt as a π-bonding ligand. If it did, it would prevent cobalt from coagulation even when butadiene is absent in the system. This is not the case, however, and so we tentatively propose that ethylene combines with cobalt as a ligand with a weak π-bonding nature.

Experimental

1) 1×10^{-3} mol. of cobalt(III) acetylacetonate, and 3.5×10^{-3} mol. of butadiene were dissolved in

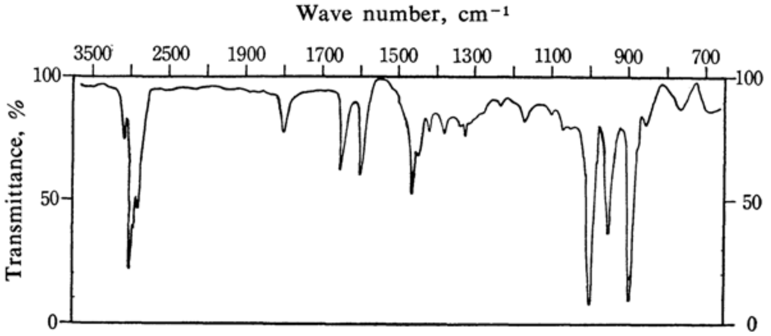

Fig. 1

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1) C. W. Childers, *J. Am. Chem. Soc.*, **85**, 229 (1963).

2) W. Cooper, D. E. Evans and G. Vaughan, *Makromol. Chem.*, **67**, 229 (1963).

3) G. Natta, L. Porri, A. Carbonaro and A. Greco, ibid., **71**, 207 (1964).

4) T. Saito, T. Ohno, Y. Uchida and A. Misono, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 1094 (1963).

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

6) K. Tamai, T. Saito, Y. Uchida and A. Misono, ibid., to be published.

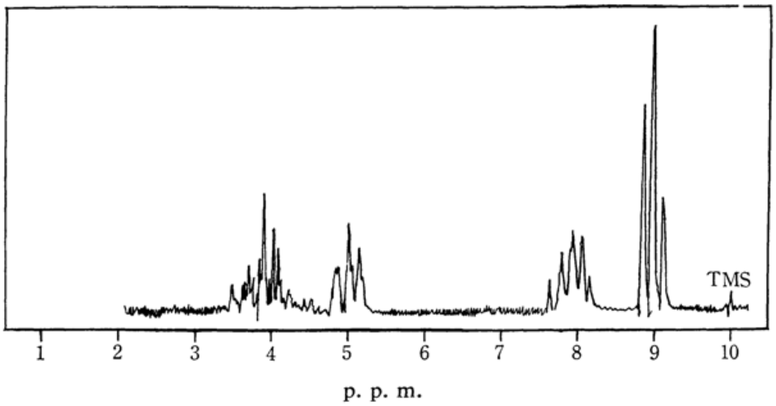

Fig. 2

10 g. of benzene, and then 1×10^{-3} mol. of triethylaluminum was added to the solution under nitrogen. The reaction was carried out at 20°C, and the products were identified and quantitatively analyzed by a gas chromatograph. *n*-Hexa-1, 3-diene was formed in about 70% of the calculated value (1.5×10^{-3} mol., if the ethylene reacted completely with butadiene), in 100 hr.

2) 0.37 g. of cobalt(III) acetylacetonate and 10 g. of butadiene were dissolved in 50 ml. of toluene, and then 2 ml. of triethylaluminum in toluene (14.5 wt.% solution) was added to the solution at a low temperature under nitrogen. The whole solution was then transferred to a 300-ml. stainless autoclave and 6 g. of ethylene was pressured in. The reaction was carried out at 30°C overnight. (The initial pressure was ca. 8 atm.) The reaction mixture was washed with dilute hydrochloric acid and distilled. The yields of *n*-hexa-1, 3-diene and butadiene dimers were 10 mol.% and 25 mol.% respectively, based on the charged butadiene, and the rest were unreacted monomers and low molecular-weight polymers. The hexadiene part was further purified by a preparative gas chromatograph. The elemental analysis, the molecular weight measurement, and the infrared (Fig. 1) and NMR (Fig. 2) spectra indicated that it was *n*-hexa-1, 3-diene.

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