Butadiene Hydrogenation by Pentacyanocobaltate(II) in Glycerin Solvent

Kimio TARAMA and Takuzo FUNABIKI

Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

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Pentacyanocobaltate (II) has catalytic activity for the hydrogenation of conjugated dienes such as butadiene[1,2]. In the study of this complex, water has been used as a solvent exclusively. In the present communication, we report that the butadiene hydrogenation by pentacyanocobaltate in glycerin-methanol (MeOH) has very different characteristics from that in water, and that butadiene is hydrogenated without H_2 even in alcoholic solvent.

The reaction was carried out in closed system at 20°C. The reaction gas was circulated vigorously through the magnetically stirred solution of cyanocobaltate, which was prepared by mixing the glycerin-MeOH solution of KCN with the MeOH solution of $CoCl_2$ in N_2 atmosphere (Fig. 1) or in H_2 atmosphere (Fig. 2). Butadiene was supplied continuously to maintain atmospheric pressure, and the gas sample was analyzed by gaschromatography every 10 or 20 min. The reaction medium was always homogeneous.

As shown in Fig. 1, composition of the isomeric butenes produced in glycerin-MeOH solvent without H_2 changes very sharply with the ratio of CN/Co (=R). In the region of $R<5.2$, butenes are produced in the order of *trans*-2-$>>$1-$>$*cis*-2-butene as in water, but the order in the region of $R>5.2$ is *cis*-2$>$1-$>>$*trans*-2-butene and this order markedly differs from that in water (1-$>>$*trans*-2-$>$*cis*-2-butene). When H_2 was absorbed (*cf.* Fig. 2) similar result was observed except 1-$>$*cis*-2-$>>$*trans*-2-butene at $R>5.2$.

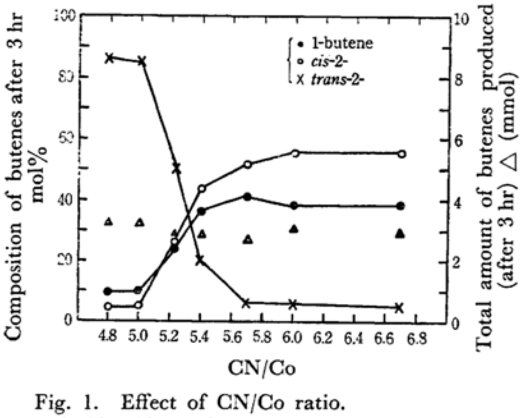

Fig. 1. Effect of CN/Co ratio.
$CoCl_2$ = 10 mmol
Solvent: glycerin 35 ml + MeOH 15 m*l*
without H_2 at 20°C

Because this hydrogenation was performed without H_2 in this solvent, hydrogen source should be alcoholic solvent.

Figure 2 shows the effect of some additives at R=5.7. When water was added in this solvent system, the formation of *cis*-2-butene was greatly suppressed and approached to the result in water. Addition of ethylenediamine increased the formation of *cis*-2-butene.

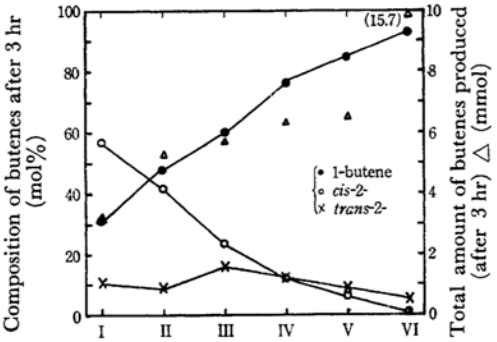

Fig. 2. Effect of additives.
$CoCl_2$ = 10 mmol
H_2 was absorbed for 2 hr before butadiene was added at 20°C.

I	Glycerin 35 m*l* + MeOH 10 m*l* + En	5 m*l*
II	Glycerin 35 m*l* + MeOH 15 m*l*	
III	Glycerin 35 m*l* + MeOH 10 m*l* + H_2O	5 m*l*
IV	Glycerin 35 m*l* + MeOH 5 m*l* + H_2O	10 m*l*
V	Glycerin 35 m*l* + MeOH 0 m*l* + H_2O	15 m*l*
VI	H_2O 50 m*l*	

(En = ethylenediamine)

It is noteworthy that *cis*-2-butene is very much producible at $R>5.2$ in glycerin-MeOH solvent. This result can not be explained by the π-allyl complex mechanism[1,2] acceptable in the case of water solvent. Detailed discussion of the mechanism of this reaction will be given in the forthcoming paper.

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[1] J. Kwiatek, K. L. Mador, and J. K. Seyler, *Adv. Chem. Ser.*, **37**, 201 (1963).

[2] T. Suzuki and T. Kwan., *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 715 (1965).