The Hydrogenation of Butadiene Catalyzed by Pentacyanocobaltate(II) in Aqueous and Non-aqueous Solvents

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The hydrogenation of butadiene catalyzed by pentacyanocobaltate(II) was studied in water and in glycerol-methanol-water and ethylene glycol-methanol solutions. The amount of hydrogen absorbed, and the rate of hydrogen absorption, in the water solvent were much greater than in the other solvents. The composition of the butenes produced by the hydrogenation in the water solution was *trans*-2-$\gg$1-$>$*cis*-2-butene at CN/Co$<$5.1, and 1-$\gg$*trans*-2-$>$*cis*-2-butene at CN/Co$>$5.1; this composition was affected by the concentration of the complex. The composition of the butenes produced in the glycerol-methanol solution was *trans*-2-$\gg$1-$>$*cis*-2-butene at CN/Co$<$5.4 and 1-$>$*cis*-2-$\gg$*trans*-2-butene at CN/Co$>$5.4; a concentration effect similar to that in the water solution was observed. The composition of butenes in the glycerol-methanol-water solution at CN/Co=6.0 was remarkably affected by the composition of the solvent. In the ethylene glycol-methanol solution, *cis*-2-butene was much more producible than in the glycerol-methanol solution. The mechanism of the hydrogenation of butadiene by pentacyanocobaltate(II) was discussed on the basis of these solvent effects on the composition of products, and on the basis of the kinetical behavior of this hydrogenation reaction.

Pentacyanocobaltate(II) is a typical and interesting complex in the areas of both coordination chemistry and catalysis,[1] and its typical nature has been made clear in recent years as part of development of the chemistry of homogeneous catalysis, but our understanding of this complex can still be said to be inadequate. Recently, the present authors investigated this complex with two objects; one was to find organic solvents to increase the reactivity of this complex, and the other was to make sure of the radical mechanism proposed for the reaction of this complex. We found that pentacyanocobaltate(II) easily initiates the halomethylation of olefin in the glycerol-methanol solvent.[2] In a study related to this interesting solvent effect, we have found that the hydrogenation of butadiene catalyzed by pentacyanocobaltate(II) in the glycerol-methanol solvent gives very different results from those in water, as has already reported briefly.[3] It has been also found that butadiene is hydrogenated in the absence of hydrogen in these solvents,[3] but the results are somewhat different from those in the presence of hydrogen. In this paper, we will report more detailed results of the hydrogenation of butadiene in these solvents in the presence of hydrogen.

Experimental

Reagents. The glycerol and ethylene glycol (Nakarai Chemicals, LTD., Guaranteed Pure Grade) were distilled *in vacuo*. The methanol (Nakarai Chemicals, LTD., Guaranteed Pure Grade) was dried by the use of magnesium methoxide. The KCN (Nakarai Chemicals, LTD., Guaranteed Pure Grade) was dried in a vacuum desicator containing P_2O_5. Anhydrous $CoCl_2$ (Nakarai Chemical, Extra Pure Grade), butadiene (Takachiho Chemicals, containing 0.5—0.7% 1-butene), and hydrogen and nitrogen gases (Teikoku-Sanso) in commercial cylinders were all used without further purification.

Apparatus. The reaction vessel was 100-m*l*, three-necked flask equipped with a 50-m*l* dropping funnel; it was connected to two gas burets for hydrogen and butadiene, a mercury manometer, a gas-flow meter, and a stroke pump (Rigo-sha), which was used to circulate the gases in the reaction vessel through the solution at a flow rate of about 500 m*l* per minute. The solution was stirred magnetically and maintained at 20°C by means of a thermostat.

Procedure. The procedure consisted of two steps: the first step was hydrogen absorption by pentacyanocobaltate(II), and the second step was butadiene hydrogenation by the solution obtained in the first step.

(a) Hydrogen Absorption: In a hydrogen atmosphere, 10 m*l* of the $CoCl_2$ solution in the dropping funnel was added to 40 m*l* of the KCN solution in the reaction vessel while the solution was stirred vigorously and the gas was circulated, the volume of hydrogen absorbed at a constant atmospheric pressure was recorded as a function of the time for 1 hr in the case of the water solution and for 2 hr in the case of the glycerol-methanol solution. (When a mixture of 35 m*l* of glycerol and 15 m*l* of methanol was used as the solvent, the $CoCl_2$ was dissolved in 10 m*l* of methanol.) 10 mmol of $CoCl_2$ was used, except in examining the effect of the concentration of the complex.

(b) Hydrogenation of Butadiene: After the hydrogen-absorption procedure (a), about 130 m*l* of butadiene was introduced into the reaction vessel in such a way as replacing the hydrogen in the gas phase by butadiene as completely as possible. Stirring and circulation were started again after the above procedure. (This is the start of the hydrogenation.) While butadiene was supplied to maintain a constant atmospheric pressure, 2-m*l* gas samples were picked out by an injection-syringe at 10- or 20-min intervals for 4 hr; these samples were analyzed by means of a gas chromatograph (Shimadzu, Type GC-2B), using a 3.5-m column of DMS at room temperature. The moles of each butene produced were calculated, assuming that the sums of the relative amounts of butene and butadiene on the gas chromatograph correspond to the total moles of butadiene introduced into the reaction vessel until the sampling time.

Results

Hydrogen Absorption. Figure 1 shows typical examples of the hydrogen absorption by pentacyano-

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[1] See the recent review by J. Kwiatek, "Catalysis Reviews" Vol. 1, ed. by H. Heinemann, Marcel Dekker, New York (1968), p. 37.

[2] K. Tarama and T. Funabiki, *Nippon Kagaku Zasshi*, **89**, 88 (1968).

[3] K. Tarama and T. Funabiki, This Bulletin, **41**, 1744 (1968).

cobaltate(II) in water and the glycerol-methanol solution respectively. In the water, an initial rapid absorption of hydrogen was observed and the amount of hydrogen absorbed was nearly equal to the expected value (from the concentration of the complex), but in the glycerol-methanol solution, the rate of absorption was much slower and the amount of it was much less. (In the latter case, an initial increase in the gas volume was observed during the addition of the $CoCl_2$ solution to the KCN solution.) The amount of hydrogen absorbed tended to decrease with an increase in the CN/Co ratio; this tendency was more remarkable in the glycerol-methanol solution than in the water.

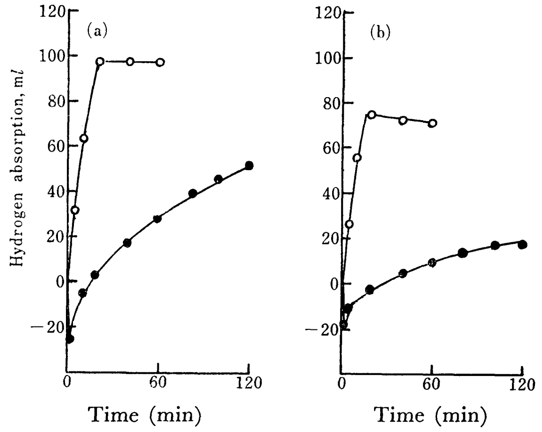

Fig. 1. Hydrogen absorption by pentacyanocobaltate(II).
(a) CN/Co=5.0 (b) 6.0
○ in water (50 m*l*)
● in glycerol (35 m*l*)+methanol(15 *ml*)
$CoCl_2$=10 mmol, 20°C

Hydrogenation of Butadiene in Water Solution. *The Effect of the CN/Co Ratio*: As is shown in Fig. 2,[4] a result similar to those obtained by other authors[5,6] was obtained: *trans*-2-butene is selectively produced in the low CN/Co region, and 1-butene in the high CN/Co region, while *cis*-2-butene is always negligible. The variation in the total yield of butenes was not remarkable. Figure 3 shows the time courses of the formation of each butene at several CN/Co ratios; it is known that the hydrogenation almost stops within 1 hr.

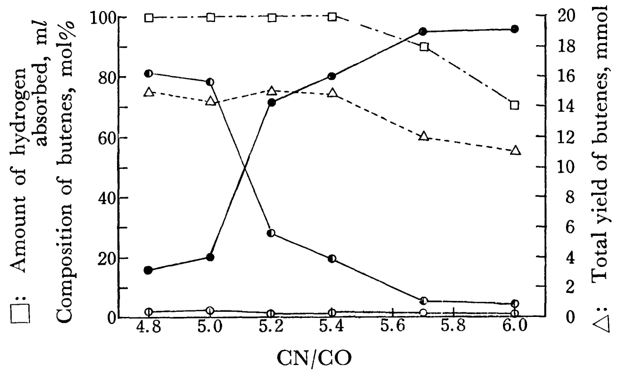

Fig. 2. Effect of CN/Co ratio in water.
● 1-butene, ◐ *trans*-2-butene, ○ *cis*-2-butene
Solvent: water 50 m*l*, $CoCl_2$=10 mmol, 20°C

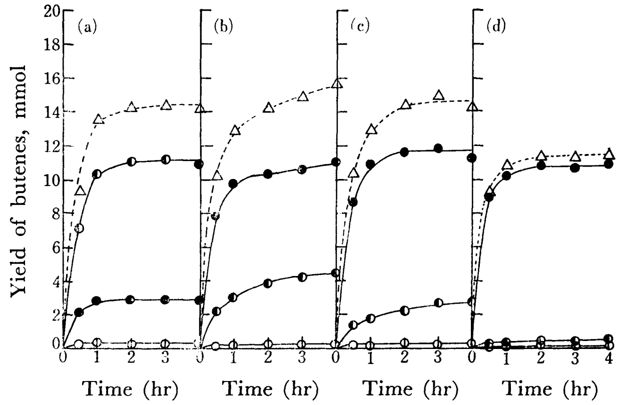

Fig. 3. Butene formation at different CN/Co ratio in water.
(a) CN/Co=5.0 (b) 5.2 (c) 5.4 (d) 6.0
● 1-butene, ◐ *trans*-2-butene, ○ *cis*-2-butene,
△ Total yield of butenes
Solvent: water 50 m*l*, $CoCl_2$=10 mmol, 20°C

Effect of the Concentration of the Complex: Figure 4 shows the results of the experiments in which the concentration of the complex was varied between 0.05 M and 0.25 M at CN/Co=5.0 (Fig. 4-a), and between 0.10 M and 0.20 M at CN/Co=6.0 (Fig. 4-b). At CN/Co=5.0, the mole fraction of *trans*-2-butene in the product decreased, while those of 1- and *cis*-2-butene increased with a decrease in the cobalt concentration[7]: at CN/Co=6.0, that of 1-butene decreased with the cobalt concentration. The total yield of butenes decreased linearly with the cobalt concentration.

Hydrogenation of Butadiene in the Glycerol-Methanol Solution. *The Effect of the CN/Co Ratio*: The

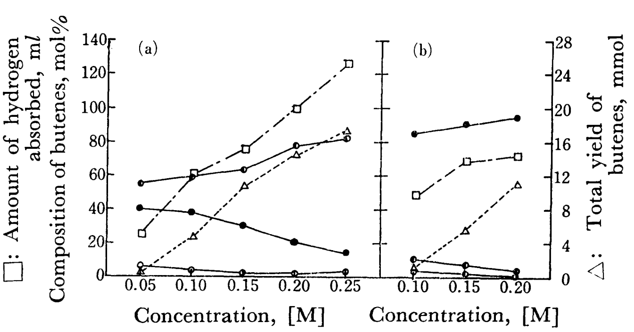

Fig. 4. Effect of concentration of the complex in water.
(a) CN/Co=5.0 (b) 6.0
● 1-butene, ◐ *trans*-2-butene, ○ *cis*-2-butene,
Solvent: water 50 m*l*, 20°C

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[4] The data for the composition and yield of each butene in Figures 2, 4, 5, 7, 8, and 10 are those obtained 3 hr after the start of the hydrogenation of butadiene. The data for the amount of hydrogen absorbed are those obtained by the procedure (a).

[5] M. S. Spencer and D. A. Dowden (Imperial Chemical Industries Ltd.), U. S. 3009969 (1061).

[6] J. Kwiatek, I. L. Mador, and J. K. Seyler, *Advan. Chem. Ser.*, **37**, 201 (1963).

[7] This result at CN/Co=5.0 is not consistent with that obtained by Piringer *et al.*, in which the main product was 1-butene at a high cobalt concentration. *cf.* A. Farcus, U. Luca, and O. Piringer, "Progress in Coordination Chemistry" (Proceedings of the 11th International Conference on Coordination Chemistry Haifa and Jersulem, September, 1968), ed. by M. Cais, Elsevier Publishing Company, Amsterdam (1968), p. 29.

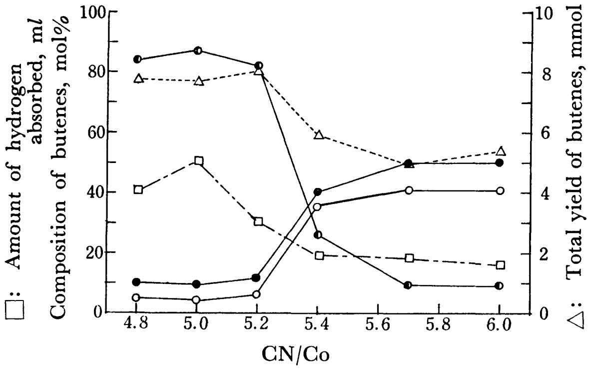


Fig. 5. Effect of CN/Co ratio in glycerol-methanol.
● 1-butene, ◐ *trans*-2-butene, ○ *cis*-2-butene,
Solvent: glycerol (35 m*l*)+methanol (15 m*l*),
$CoCl_2$=10 mmol, 20°C

results of the hydrogenation in the glycerol (35 m*l*)-methanol (15 m*l*) solution were remarkably different from those in the water, as is shown in Fig. 5 (*cf.* Fig. 2). *trans*-2-Butene was exclusively produced in the low CN/Co region, as in the water, while *cis*-2-butene was produced as much as 1-butene in the high CN/Co region. That is to say, the composition of the products was *trans*-2-$\gg$1->*cis*-2-butene at CN/Co<5.4, and 1->*cis*-2-$\gg$*trans*-2-butene at CN/Co>5.4. The total yield of butenes and the amount of hydrogen absorbed decreased with an increase in the CN/Co ratio. The results in water and in glycerol-methanol are compared in Table 1.

Table 1. Effect of CN/Co ratio in the butadiene hyerogenation in water and in glycerol-methanol[a)]

CN/Co	Composition of butenes (mol%)[b)]					
	in water			in glycerol-methanol		
	1-	*trans*-2-	*cis*-2-	1-	*trans*-2-	*cis*-2-
4.8	16	81	2	10	84	5
5.0	20	78	2	9	87	4
5.2	71	28	1	12	82	6
5.4	80	19	1	40	26	35
5.7	94	5	1	50	9	41
6.0	95	4	1	50	9	41

a) Water (50 m*l*), Glycerol (35 m*l*)+Methanol(15 m*l*), $CoCl_2$=10 mmol, 20°C
b) Composition after 3 hr from the start of the hydrogenation

Figure 6 shows the time courses of the formation of butenes at several CN/Co ratios in the glycerol-methanol solvent. Although almost all the *trans*-2-butene was formed within the initial hour at a rapid rate, *cis*-2-butene and 1-butene were formed gradually at rather slow rates. In comparison with the formation of *cis*-2-butene, an initial rapid formation was observed in the case of 1-butene.

Effect of the Concentration of the Complex. Figure 7 shows the results when the concentration of the complex was varied between 0.05 M and 0.20 M at CN/Co=5.0 and 6.0 in the glycerol (35 m*l*)-methanol (15 m*l*) solution. At CN/Co=5.0, the mole fraction of *trans*-2-butene in the products decreased, and those of 1- and *cis*-2-butene increased, with a decrease in the cobalt concentration (Fig. 7-a). At CN/Co=6.0, the mole fraction of 1-butene decreased and that of *cis*-2-butene increased with a decrease in the cobalt concentration (Fig. 7-b). The total yield of butenes decreased linearly with the cobalt concentration, but this tendency was greater at CN/Co=5.0 than at CN/Co=6.0.

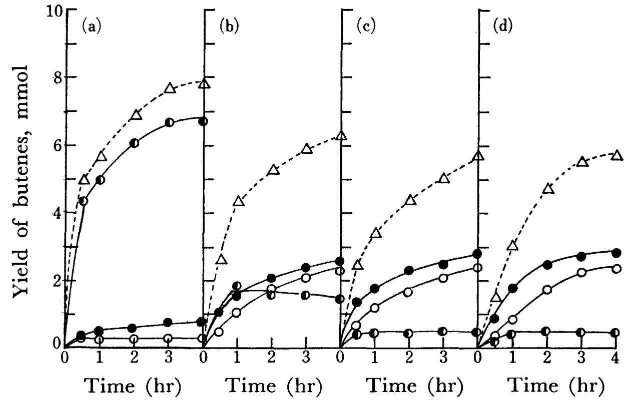


Fig. 6. Butene formation at different CN/Co ratio in glycerol-methanol.
(a) CN/Co=5.0 (b) 5.4 (c) 5.7 (d) 6.0
● 1-butene, ◐ *trans*-2-butene, ○ *cis*-2-butene,
△ Total yield of butenes
Solvent: glycerol (35 m*l*)+methanol (15 m*l*), $CoCl_2$=10 mmol 20°C

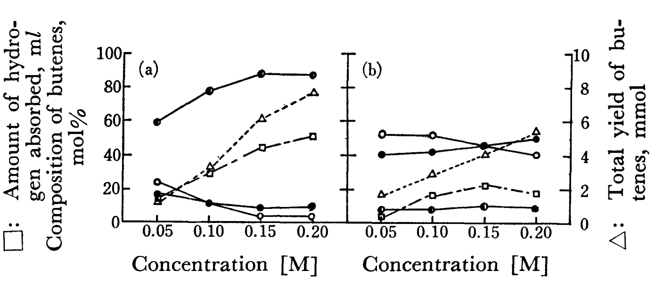


Fig. 7. Effect of concentration of the complex in glycerol-methanol.
(a) CN/Co=5.0 (b) 6.0
● 1-butene, ◐ *trans*-2-butene, ○ *cis*-2-butene,
Solvent: glycerol(35 m*l*)+methanol(15 m*l*), 20°C

Effect of Solvent Composition in the Glycerol-Methanol-water Solutions: Figure 8 shows the results at CN/Co=6.0 in the solvents with a total volume of 50 m*l*, containing glycerol (35 m*l*), methanol (15→0 m*l*), and water (0→15 m*l*). The increase in the water content (which involves, at the same time, the decrease in the methanol content) resulted in a great increase in the mole fraction of 1-butene and a decrease in that of *cis*-2-butene. The amount of hydrogen absorbed and the total yield of the butenes showed little change. Figure 9 shows the time courses of the formation of butenes in these solvents; it indicates that, although the initial rate of the formation of 1-butene changes little, that of *cis*-2-butene greatly decreases as the content of water increases.

Figure 10 shows the results at CN/Co=6.0 in the solvents containing glycerol (35 m*l*), methanol (15 m*l*),

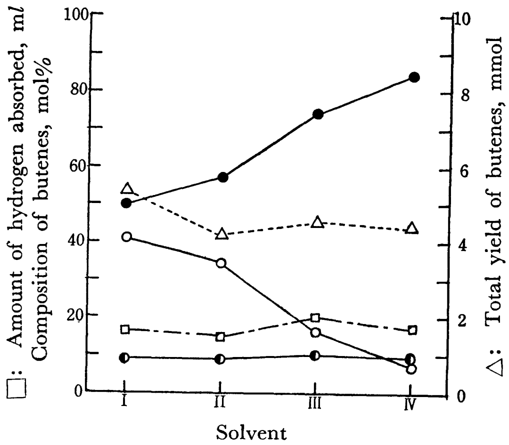


Fig. 8. Effect of composition of solvent in glycerol-methanol-water at CN/Co=6.0 (1).

● 1-butene, ◐ *trans*-2-butene, ○ *cis*-2-butene

	Glycerol	MeOH	H_2O
I	35 m*l*	15 m*l*	0 m*l*
II	35 m*l*	10 m*l*	5 m*l*
III	35 m*l*	5 m*l*	10 m*l*
IV	35 m*l*	0 m*l*	15 m*l*

$CoCl_2$=10 mmol, 20°C

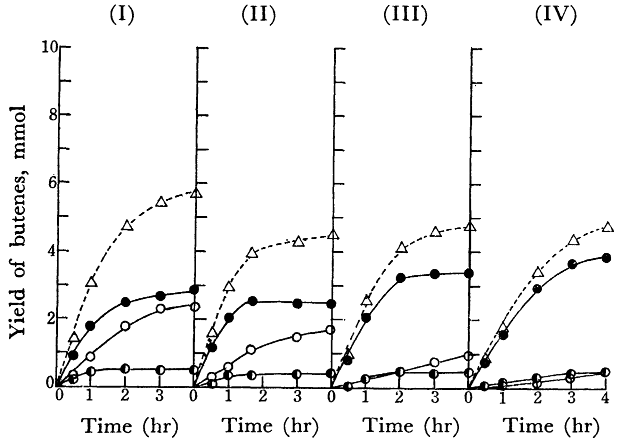


Fig. 9. Effect of composition of solvent in glycerol-methanol-water at CN/Co=6.0 (1).

● 1-butene, ◐ *trans*-2-butene, ○ *cis*-2-butene

△ Total yield of butenes

Solvents in I-IV corresponds to those in Fig. 8

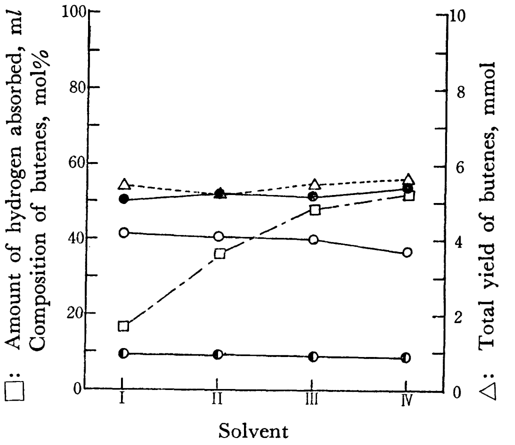


Fig. 10. Effect of composition of solvent in glycerol-methanol-water at CN/Co=6.0 (2).

● 1-butene, ◐ *trans*-2-butene, ○ *cis*-2-butene

	Glycerol	MeOH	H_2O
I	35 m*l*	15 m*l*	0 m*l*
II	35 m*l*	15 m*l*	5 m*l*
III	35 m*l*	15 m*l*	10 m*l*
IV	35 m*l*	15 m*l*	15 m*l*

$CoCl_2$=10 mmol, 20°C

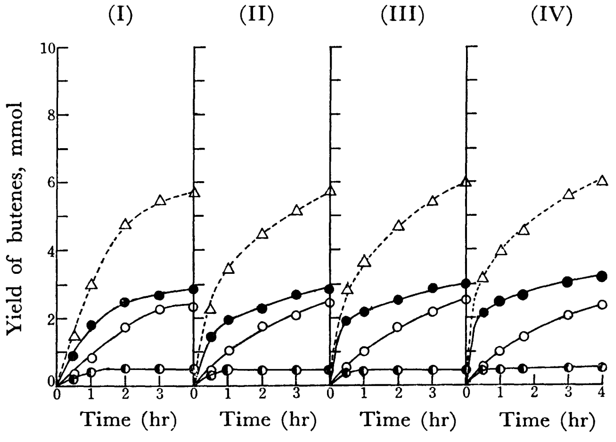


Fig. 11. Effect of composition of solvent in glycerol-methanol-water at CN/Co=6.0 (2).

● 1-butene, ◐ *trans*-2-butene, ○ *cis*-2-butene

△ Total yield of butenes

Solvents in I-IV corresponds to those in Fig. 10.

and water (0→15 m*l*). Remarkably different from the results shown in Fig. 8, the composition and the total yield of butenes did not vary in spite of the increase in the water content, although the amount of hydrogen absorbed increased with the water content. Figure 11 shows the time courses of the formation of butenes in these solvents; it indicates that, although the initial rate of the formation of 1-butene increases with the water content, that of *cis*-2-butene is little affected.

Color of the Solution: The aqueous solution of pentacyanocobaltate(II) was dark green and clear just after its preparation so long as CN/Co>4.8 ([Co]=0.2 M). After the hydrogen absorption, the color of the solution changed from dark green to a greenish yellow. Upon the introduction of butadiene to the solution, the solution became dark green within about 5 min, but it turned yellow green or yellow as the reaction proceeded. During the hydrogen absorption and the hydrogenation processes, a precipitate was formed at CN/Co<5.0. In the case of the glycerol (35 m*l*)-methanol (15 m*l*) solvent ([Co]=0.2 M), the solution was always clear, even in the low CN/Co region. At CN/Co<5.2, the dark green which was found just after the preparation of the complex soon turned dark brown and changed to red brown in the process of the hydrogen absorption. When butadiene was introduced, the red brown rapidly changed to dark brown, but it became red brown again during the process of the hydrogenation. At CN/Co>5.7, a color change similar to that in the water solution was observed, except that the yellow color was generally deeper in this solvent. In the region of CN/Co=5.2—5.7, a color change intermediate between the above two typical cases was observed.

Hydrogenation of Butadiene in the Ethylene Glycol-Methanol Solution. The preliminary experiment of the hydrogenation of butadiene in the ethylene glycol (35 m*l*)-methanol (15 m*l*) solution showed rather different features from that in the glycerol-methanol solution. At CN/Co=6.0, the solution of the complex, just after having been prepared in a hydrogen atmosphere, was dark green and contained a precipitate, although the KCN and $CoCl_2$ solutions were both clear before mixing. After the hydrogen absorption (47 m*l* of hydrogen was absorbed), the solution remained dark green and contained a precipitate. When butadiene was introduced, a rapid absorption of butadiene was observed for the initial 10 min; the solution immediately became clear and yellow in its color within 5 min. The composition of butenes was *cis*-2->1-≫*trans*-2-butene even in the initial stage; after 3 hr, it was *cis*-2-(50%)>1-(45%)≫*trans*-2-butene (5%).

At CN/Co=5.0, the solution after the hydrogen absorption (41 m*l* of hydrogen was absorbed) was also dark green and contained many precipitates. When hydrogenation was started, a rapid absorption of butadiene was observed, but the change in color (to orange) and disappearance of the precipitate was slow. The composition of butenes was *trans*-2->*cis*-2->1-butene in the initial stage, but it became *cis*-2-(44%)>1-(36%)>*trans*-2-butene(20%) after 3 hr. The time courses of the formation of butenes at CN/Co=5.0 and 6.0 are shown in Fig. 12.

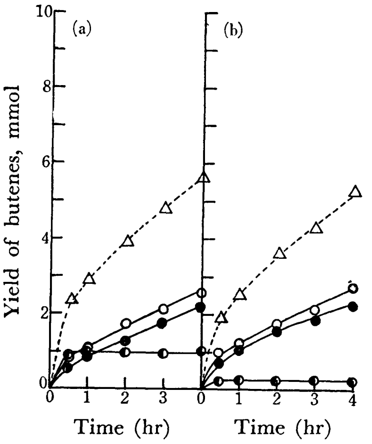


Fig. 12. Butene formation in ethylene glycol-methanol.
(a) CN/Co=5.0, (b) 6.0
● 1-butene, ◐ *trans*-2-butene, ○ *cis*-2-butene
△ total yield of butenes
Solvents: ethylene glycol (35 m*l*)+methanol (15 m*l*)
$CoCl_2$=10 mmol, 20°C

Discussion

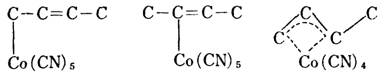
The hydrogenation of butadiene by pentacyanocobaltate(II) was first reported by Spencer and Dowden,[5] who described that 1-butene was produced at a high CN/Co ratio and *trans*-2-butene, at a low ratio. Kwiatek *et al.*[6] studied this reaction in detail, varying the CN/Co ratio, changing the order of the introduction of hydrogen and butadiene into the complex solution, and using deuterium instead of hydrogen; they reported that the composition of butenes varies at CN/Co=5.5—6.0,[8] that the active species of the reaction is the hydrido-complex $HCo(CN)_5^{3-}$, and that the reaction intermediates are fairly stable organocyanocobaltates(III). They have proposed the following mechanism (Eqs. (1)—(3)), in which the rate-determining step is (3):

$$2\,Co(CN)_5^{3-} + H_2 \rightleftarrows 2\,Co(CN)_5H^{3-} \quad (1)$$

$$Co(CN)_5H^{3-} + C_4H_6 \rightleftarrows Co(CN)_5(C_4H_7)^{3-} \quad (2)$$

$$Co(CN)_5H^{3-} + Co(CN)_5(C_4H_7)^{3-} \rightarrow 2\,Co(CN)_5^{3-} + C_4H_8 \quad (3)$$

As the structure of the intermediate complex, $Co(CN)_5(C_4H_7)^{3-}$, the following three types have been proposed:[9,10] two σ-type complexes (σ_1 and σ_2) and one π-allyl-type complex (π), and it has been considered that the composition of butenes depends on the concentration of each intermediate. Kwiatek and Seyler considered that, in the high CN/Co region, (σ_1) is the most stable and 1-butene is produced exclusively from it, while in the low CN/Co region, (π) is the most stable and 2-butene (*trans*≫*cis*) is produced exclusively from it. On the other hand, Burnett *et al.*,[11] who studied this butadiene hydrogenation kinetically, proposed a mechanism in which 1-butene is produced from (σ_2); *trans*- and *cis*-2-butene, from (σ_1), and *trans*-2- and 1-butene, from (π). The basic difference between the two mechanisms is in the way of the attack of the hydrido-complex $HCo(CN)_5^{3-}$ on butadiene and on the intermediate complexes; in the former mechanism, it is a 1,4-addition and γ-attack, while in the latter, it is a 1,2-addition and α-attack. Although Jackman *et al.*[12] reported that the reaction of conjugated olefin with hydridopentacyanocobaltate occurs in the *cis*-1,2-addition, the present authors consider that the hydrogenation of a conjugated diene such as butadiene must be a special case.



(σ_1) (σ_2) (π)

In discussing the mechanism of the hydrogenation of butadiene by pentacyanocobaltate(II), it should be noticed that the results which have been obtained by other authors were obtained in water and so the proportion of *cis*-2-butene to *trans*-2- and 1-butene was always negligible. The most characteristic result which was obtained in the glycerol-methanol solution was that *cis*-2-butene is produced in the high CN/Co region, and the time course of its formation is very different from that of *trans*-2-butene; in the case of *trans*-2-butene, a rapid initial formation, followed by

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8) Suzuki reported later that the composition varies very sharply at CN/Co=5.1—5.2 (*cf.* T. Suzuki and T. Kwan, *Nippon Kagaku Zasshi*, **86**, 713 (1965)).

9) J. Kwiatek and J. K. Seyler, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, 1964 (V. Gutmann, ed.), Springer, Vienna (1964), p. 308.

10) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965).

11) M. G. Burnett, P. J. Connoly, and C. Kemball, *J. Chem. Soc.*, *A*, **1968**, 991.

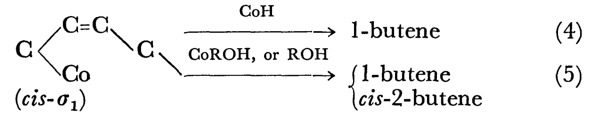
12) L. M. Jackman, J. A. Hamilton, and J. M. Lawlor, *J. Amer. Chem. Soc.*, **90**, 1914 (1968).

a slow formation or none at all, is observed, while *cis*-2-butene is produced gradually and successively. Therefore it is reasonable to assume that the structure of the intermediate for the *cis*-2-butene formation resembles that for 1-butene rather than that for *trans*-2-butene. If it is supposed that such organocyano-complexes as (σ_1), (σ_2), and (π) are the intermediates for the butadiene hydrogenation by pentacyanocobaltate(II),[13] and that σ complex is stable in the high CN/Co region, it is natural to consider that the (σ_1) of the *cis* configuration (*cis*-σ_1) is probably an intermediate for the *cis*-2-butene formation, because with other σ complexes such as the (σ_1) with a *trans* configuration and the (σ_2), there is the great probability of the formation of *trans*-2-butene besides *cis*-2-butene.

As an intermediate for 1-butene formation, two complexes (σ_1 and σ_2), should be considered, because either complex may produce 1-butene, by the γ- or the α-attack of the hydrido-complex. Although it is difficult to decide which is the proper intermediate, at this stage we prefer *cis*-σ_1, because it seems to be more appropriate to consider a common intermediate for the two butenes (1- and *cis*-2-butene) rather than different intermediates. Hence, in the mechanism here proposed, butadiene and the hydro-complex react in the 1,4-addition to form a *cis*-butenyl complex at first.

The present authors observed a difference in the time courses of the formation of 1- and *cis*-2-butene in the glycerol-methanol and the glycerol-methanol-water solutions. The rate of the formation of 1-butene in the initial stage is greater than that of *cis*-2-butene; this difference becomes more obvious with an increase in the water content in the solvent. This result may be explained in terms of the difference in the reactivity of the two active reducing species, provided that there exists another reactive reducing species besides the hydrido-complex: The reaction of the hydrido-complex with *cis*-σ_1 is rapid and produces exclusively 1-butene in the initial stage (the quantity of 1-butene produced by this reaction may be rather small, because the amount of hydrogen absorbed in this solvent is generally small), but another reactive reducing species, which may be a solvent molecule or a cyanocobalt-complex coordinated by the solvent, reacts to produce nearly equal amounts of 1- and *cis*-2-butene at a relatively slower rate than the hydrido-complex. This may be written schematically as in Scheme 1, where CoH, CoROH and ROH denote the hydrido-complex, the cyanocobalt complex coordinated by an alcoholic solvent, and the alcoholic solvent respectively. If there is enough CoH for the second step in Scheme 1, an initial rapid formation of 1-butene will be observed, and *vice versa*. This proposal may well be supported by the following facts: 1) In the water solution, 1-butene is selectively formed in the high CN/Co region; this can be ascribed to the selective performance of reaction (4). 2) In the glycerol-methanol solution in the high CN/Co region in the absence of hydrogen, the composition of butenes is *cis*-2->1-≫*trans*-2-butene;[3] this can be ascribed to the absence of the hydrido-complex. 3) In the ethylene glycol-methanol solution at CN/Co=6.0, the composition of butenes is also *cis*-2->1-≫*trans*-2-butene, even in the initial stage; this can be ascribed to the rapid reaction of butadiene with hydrido-complex to produce the intermediate complex (*cis*-σ_1) without saving the hydrido-complex for the second step. (This may be connected with the rate of the dissolution of butadiene into the solvent or with the precipitate formation.)

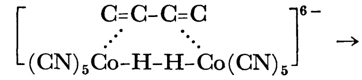
$$(CoH,\ CoROH) + C{=}C{-}C{=}C \rightarrow$$



Scheme 1

The probable intermediate for the *trans*-2-butene formation may well be a π-methallyl-complex (π), as was proposed by Kwiatek,[9] but it seems to be rather difficult to explain the initial rapid formation of *trans*-2-butene from the (π) complex, for the rate of isomerization between σ-allyl and π-allyl complexes presumed from the NMR spectra with an allyl-pentacyanocobaltate(III)[10] is not very great. We wish here to propose another route for the formation of *trans*-2-butene, in which *trans*-2-butene is produced in one step via a butadiene-bridged transition state which is produced by one molecule of butadiene and a dimeric-type hydrido-complex, such as proposed by Piringer and Farcas;[14] the mechanism may be shematically written as in Scheme 2:

$$(CN)_5Co{-}H{-}H{-}Co(CN)_5^{6-} + C{=}C{-}C{=}C \rightarrow$$



trans-2-butene (+*cis*-2-butene)

Scheme 2

In these mechanisms, the selectivity of the hydrogenation of butadiene by pentacyanocobaltate(II) largely depends on the type of hydrido-complexes which are in equilibrium in the solution and whose equilibrium constant is affected by the CN/Co ratio and the concentration of the complex. It is supposed that the monomeric form exists selectively in the high CN/Co region, and that the monomeric form increases with the a decrease in the concentration in the low CN/Co region (*cf.* Figs. 4 and 7).

The color change of the solution suggests a variation of the structure of the complexes in solution, but we should be careful in discussing these data. At this stage, it cannot be decided whether or not the brown color observed in the glycerol-methanol solution in the low CN/Co region is connected with the structure of the complex which produces *trans*-2-butene.

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[13] Although the present authors have proposed another possible mechanism of the formation of 1- and *cis*-2-butene in the high CN/Co region, supposing that the *cis*-2-buteneyl radical is the intermediate, this radical mechanism will not be discussed further in this paper (*cf.* K. Tarama, T. Funabiki, and M. Mohri, *Shokubai*, **11**, 35 (1969)).

[14] O. Piringer and A. Farcas, *Z. Phys. Chem. N.F.*, **46**, 190 (1965).

The solvent effect on the hydrogenation by pentacyanocobaltate(II) is rather complicated. The presence of water is surely important in 1-butene formation (Fig. 8), but it is not decisive (Fig. 9). The presence of methanol seems to be important for the *cis*-2-butene formation, but the role of methanol cannot be discussed in detail before the effect of glycerol becomes clear. At this stage, the results in the solvent containing glycerol-methanol-water (Figs. 8—11) may be explained as follows, on the basis of the proposed mechanism: the constancy of the initial rate of the formation of 1-butene in the solvents of Figs. 8 and 9 may be ascribed to the constancy of the concentration of the hydridocomplex (the amount of hydrogen absorbed in each solvent was nearly constant), and the great decrease in the rate of formation of *cis*-2-butene may be ascribed to the decrease in the methanol content. The increase in the initial rate of formation of 1-butene with the increase in the water content in the solvents of Figs. 10 and 11 may be ascribed to the increase in the concentration of the hydrido-complex (the amount of hydrogen absorbed increases with an increase in the water content), and the constancy of the rate of the formation of *cis*-2-butene may be ascribed to the nearly constant content of methanol. The present authors consider that the difference in the reactivity of pentacyanocobaltate(II) between that in water and that in these alcoholic solvents is due partly to the difference in the structures of the reactive species, to for example, the difference between the free ion in water and the ion-pair in alcoholic solvents, and partly to the difference of the solvating ability of the solvents.