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Hydrogenation by Cyanocobaltate. II.[1] Mechanisms of the Hydrogenations of 1,3-Butadiene and Isoprene Catalyzed by Pentacyanocobaltate(II) in Aqueous Solution

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Hydrogenations of 1,3-Butadiene and isoprene catalyzed by pentacyanocobaltate(II) have been studied by the measurements of infrared and nuclear magnetic resonance spectra on the reaction solutions and by following the time-courses of the reactions. Infrared spectroscopy has revealed: (1) The aging reaction is promoted by CN^- ion and it hardly occurs at a low CN/Co ratio. (2) In the hydrogenation of butadiene the formation of a σ-but-2-enyl complex at a high CN/Co ratio is very rapid, but that of a *syn*-π-(1-methylallyl) complex at a low CN/Co ratio is generally slow. The rate of the formation of these complexes is affected by the relative concentration of butadiene to $Co(CN)_5H^{3-}$. (3) In the hydrogenation of isoprene a σ-3-methylbut-2-enyl complex is formed regardless of the CN/Co ratio. Nuclear magnetic resonance spectroscopy has confirmed the structures of these complexes and it also showed that the σ-but-2-enyl complex consists of simliar amounts of the *cis*- and *trans*-isomers. The reactions are explained by the mechanisms, in which intermediate complexes in the formation of alk-1-enes and alk-2-enes are the *cis*- and *trans* σ-but-2-enyl and the *syn*-π-(1-methylallyl) complexes in the case of butadiene, and the σ-2- and -3-methylbut-2-enyl and the π-(1,2-dimethylallyl) complexes in the case of isoprene. It is described that the reactivity and the selectivity in the hydrogenation of conjugated dienes are strongly controlled by the steric factor in the transition state.

Pentacyanocobaltate(II) is one of the typical transition metal complexes which hydrogenate conjugated dienes selectively to simple-olefins, and has been studied by many authors.[2] Two mechanisms have been proposed for the selective hydrogenation; the one involves organocobalt complexes as intermediates, and the other free radicals. In the former case it has been found that the selectivity depends on the CN/Co ratio. The hydrogenation of butadiene has been studied in most detail, because the effect of the CN/Co ratio is most remarkable,[3] and the reaction has been interpreted in terms of the following scheme.

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[1] Part I. T. Funabiki and K. Tarama, This Bulletin, **44**, 945 (1971).

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

[3] (a) M. S. Spencer and D. A. Dowden, U. S., 3009969 (1961). (b) J. Kwiatek, I. L. Mador, and J. K. Seyler, *Advan. Chem. Ser.*, **37**, 201 (1963). (c) J. Kwiatek and J. K. Seyler, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, 1964 (V. Gutmann, ed.) Springer, Vienna (1968), p. 308. (d) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965). (e) T. Suzuki and T. Kwan, *Nippon Kagaku Zasshi*, **86**, 713 (1965).

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

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

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

Kwiatek and Seyler[3c,3d] have proposed a mechanism in which σ-but-2-enyl pentacyanocobaltate [I] and π-methylallyltetracyanocobaltate [II] are the intermediates in the formations of 1- and *trans*-2-butenes, respectively. They isolated the complex [I] in an impure solid state and studied its reactivity with $Co(CN)_5H^{3-}$. Although the NMR spectrum observed at 60 MHz was not analyzed completely, [I] was assumed on the analogy with σ-but-2-enyl-π-cyclopentadienyldicarbonyliron. The equilibrium between the complexes [I] and [II] was assumed on the analogy with the equilibrium between σ- and π-allyl complexes which was demonstrated by NMR. This mechanism has been generally accepted, but the lack of any kinetical study would be its greatest defect. Afterwards, Burnett *et al.*,[4] tried kinetical treatments and proposed a mechanism in which the direct intermediate in the formation of 1-butene is not [I] but σ-1-methylprop-2-enyl pentacyanocobaltate [III] on the basis of the hypothesis that the additions of $Co(CN)_5H^{3-}$ to butadiene and intermediate complexes may proceed through a 1,2-addition mechanism. In spite of the detailed discussion, the proposed mechanism was not convincing because the variation of the amount of the intermediate complexes was not followed.

The hydrogenation of isoprene, on the other hand, has not been studied in detail and some complicating results have been reported: The selectivity depends not only on the CN/Co ratio but on the ratio of the concentration of isoprene to cobalt and on the presence of hydrogen.[2,5] No mechanism to explain satisfactorily these results has been proposed.

Recently the present authors have found a novel solvent effect on the selectivity in the hydrogenation of butadiene.[1,6] The formation of *cis*-2-butene, which is hardly observed in aqueous solution, is greatly promoted in the glycerol-methanol or ethylene glycol-water solvent in the presence of excess cyanide ion. In consideration of the solvent effect, it seemed essential to clarify the mechanism in aqueous solution. For this purpose, it is important to discuss on the hydrogenations of butadiene and isoprene at the same time, because the former can give one terminal and two internal olefins, while the latter gives two terminal and one internal olefins. In this paper, mechanisms of these reactions are proposed from the time-courses of the formations of the products and of the complexes including the intermediate complexes, and from the confirmation of the structures of the intermediate complexes. These were performed by the gaschromatographic analysis of gas samples and by the measurements of IR and NMR spectra on the reaction solution without isolating the unstable species.

Experimental

Infrared Spectral Measurements. IR spectra of the reaction solutions were recorded on a JASCO DS-403G spectrophotometer in the 2000—2200 cm^{-1}. To enable the quick and repeated samplings and measurements of the complexes sensitive to air and heat of an infrared ray, a polyethylene cell placed between two plates of rock salt was used. Frequency was accurate to within ±1 cm^{-1}.[7]

Nuclear Magnetic Resonance Spectral Measurements. NMR spectra of the reaction solutions were recorded in most cases at 100 MHz with a Varian HR-100D spectrometer, but JEOL C-60HL and Varian HR-220 were also used. D_2O was usually used as a solvent, but H_2O was also used to confirm the proportion of the intensity of the bands corresponding to CH_2 and CH_3 groups. Measurements were performed either at room temperature or at 5°C.

Hydrogenation Procedure. The hydrogenation was carried out in a 100 m*l* flask containing a 25 or 50 m*l* solution with a cobalt concentration of 0.2 M. Gases in the reaction vessel were circulated through the solution at a flow rate of about 500 m*l* per minute.[1] Gas and aqueous samples picked out by injection syringes were analyzed by glc and IR, respectively. In the case of butadiene, reactions were carried out under three different conditions: (A) In the absence of hydrogen, the reaction of $Co(CN)_5^{3-}$ was started under an atmosphere of butadiene, (B) The reaction of $Co(CN)_5H^{3-}$, which was previously prepared, was started under an atmosphere of butadiene and a small amount of hydrogen, (C) The reaction of $Co(CN)_5^{3-}$ was started under an atmosphere of hydrogen and butadiene. In the case of isoprene, reactions were carried out under the conditions similar to (A) and (B). For the NMR measurements reactions were carried out in 2 m*l* solutions at 0°C.

Results and Discussion

Reactions of Pentacyanocobaltate(II) with Water and Hydrogen. It has been well known that pentacyanocobaltate(II) reacts with water to form hydridopentacyanocobaltate (aging reaction), and the reaction has been explained in terms of the Eq. (1)[8] or (2).[2]

$$2Co(CN)_5^{3-} + H_2O \longrightarrow Co(CN)_5H^{3-} + Co(CN)_5OH^{3-} \quad (1)$$

$$2Co(CN)_5^{3-} + 2H_2O \longrightarrow Co(CN)_5H^{3-} + Co(CN)_5OH_2^{2-} + OH^- \quad (2)$$

As seen in Fig. 1a, the IR spectra of the pentacyanocobaltate(II) solution under an atmosphere of nitrogen at 0°C in the presence of excess cyanide ion (CN/

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[4] M. G. Burnett, P. J. Connoly, and C. Kemball, *J. Chem. Soc., A*, **1968**, 991.

[5] (a) T. Suzuki and T. Kwan, *Nippon Kagaku Zasshi*, **86**, 1341 (1965). (b) J. Kwiatek and J. K. Seyler, *Advan. Chem. Ser.*, **70**, 207 (1968).

[6] (a) K. Tarama and T. Funabiki, This Bulletin, **41**, 1744 (1968). (b) T. Funabiki and K. Tarama, *Tetrahedron Lett.*, **1971**, 1111.

[7] T. Funabiki and K. Tarama, This Bulletin, **45**, 2945 (1972)

[8] (a) N. K. King and M. E. Winfield, *J. Amer. Chem. Soc.*, **83**, 3366 (1961). (b) B. DeVries, *J. Catal.*, **1**, 489 (1962). (c) O. Piringer and A. Farcus, *Z. Phys. Chem. N. F.*, **46**, 190 (1965). (d) M. G. Burnett, P. J. Connoly, and C. Kemball, *J. Chem. Soc., A*, **1967**, 800.

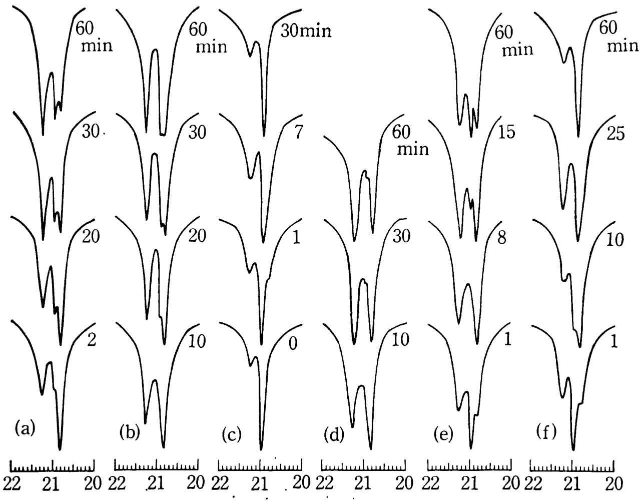

Fig. 1. IR spectra of the reaction solution in H_2O at 0°C in the hydrogenation of butadiene.
(a) Aging reaction at CN/Co=6.0, (b) Under condition (A) at CN/Co=6.0, (c) Under condition (B) at CN/Co=6.0, (d) Under condition (A) at CN/Co=4.5 (e) Under condition (B) at CN/Co=4.5, (f) Under condition (B) at CN/Co=5.0

Co=6.0) showed a gradual decay of the 2082 cm^{-1} band of $Co(CN)_5{}^{3-}$ in accompany with growths of the 2097 cm^{-1} band of $Co(CN)_5H^{3-}$ and of the band near at 2127 cm^{-1}. In the absence of excess cyanide ion (CN/Co=5.0), however, the reaction was so slow that only a weak shoulder band of $Co(CN)_5H^{3-}$ was observed even after one hour. In the presence of deficient cyanide ion (CN/Co=4.5), the formation of $Co(CN)_5H^{3-}$ was much slower. Although it has been reported that the aging reaction is promoted by alkali metal ions,[8c,9] the addition of KCl to the solution at CN/Co=5.0 had no effect. These results suggest that the cyanide ion rather than the potassium ion is responsible for the promotion of the aging reaction, and that the following reactions take place rather rapidly even at low temperatures in the presence of excess cyanide ion.

$$Co(CN)_5OH^{3-} + CN^- \longrightarrow Co(CN)_6{}^{3-} + OH^- \quad (3)$$

$$Co(CN)_5OH_2{}^{2-} + CN^- \longrightarrow Co(CN)_6{}^{3-} + H_2O \quad (4)$$

It has been supposed that these reactions are very slow at low temperatures,[2,8a] and the band near at 2127 cm^{-1} can not be corresponded exclusively to $Co(CN)_6{}^{3-}$ because $Co(CN)_5OH_2{}^{2-}$ shows a similar band, but the above proposals seem to be supported by the following results. (1) From the linear relationship between CN stretching frequencies and the Taft's σ_I function,[7] it is expected that $Co(CN)_5OH^{3-}$ shows the band near at 2110 cm^{-1}. (2) It has been reported that in the visible and ultraviolet spectroscopic study of the aging reaction, the formation of $Co(CN)_6{}^{3-}$ instead of $Co(CN)_5OH^{3-}$ was observed and it exceeded that of $Co(CN)_5OH_2{}^{2-}$ except in the initial stage.[8d]

When hydrogen was absorbed by pentacyanocobaltate(II) at 0°C, a strong $Co(CN)_5H^{3-}$ band together with a weak broad band near at 2125 cm^{-1} were observed regardless of the CN/Co ratio (*cf.* Fig. 1c). At 20°C, the $Co(CN)_5{}^{3-}$ band did not disappear completely, demonstrating that the reaction is reversible and the equilibrium constant depends on the reaction temperature.

Hydrogenation of Butadiene. (i) In the Presence of Excess Cyanide Ion (CN/Co=6.0) at 0°C. Under condition (A), a slow growth of a new band of the complex [I] at 2091 cm^{-1} was observed accompanied by a slow decay of the $Co(CN)_5{}^{3-}$ band (Fig. 1b). The formation of 1-butene as a main product was very slow but was continuous, reflecting that the aging reaction proceeds under this condition.

Under condition (B), the IR spectral changes as shown in Fig. 1c were observed. In the initial stage of the reaction, the $Co(CN)_5{}^{3-}$ band appeared in accompany with a decay of the $Co(CN)_5H^{3-}$ band, but both were rapidly replaced by the band of the complex [I]. The formation of butenes (1-(90%), *trans*-2-(8%), *cis*-2-(2%)) was remarkable in the initial stage, but it did not proceed any more after about 15 minutes when the formation of [I] was accomplished.[10]

Under condition (C), the accomplishment of the formation of [I] took place after 45 minutes when the ratio of butadiene to hydrogen was 1/1 (vol). Under this condition, the formation of 1-butene was remarkable: 1-(98%), *trans*-2-(1%), *cis*-2-(1%). It appeared that the lower ratio of butadiene to hydrogen was advantageous for the product formation while the higher one was so for the formation of the complex [I]. The $Co(CN)_5H^{3-}$ band was not observed in the course of reaction.

(ii) In the Presence of Deficient Cyanide Ion (CN/Co=4.5) at 0°C. Under condition (A), a weak 2098 cm^{-1} band of the complex [II] barely appeared after 30 minutes, but its growth and a decay of the $Co(CN)_5{}^{3-}$ band were very slow (Fig. 1d). The yield of butenes (the main product was *trans*-2-butene) was much lower than that in (i), reflecting that the aging reaction hardly proceeds under this condition.

Under condition (B), a rapid decay of the $Co(CN)_5H^{3-}$ band and a growth of the $Co(CN)_5{}^{3-}$ band were observed in accompany with an initial rapid formation of *trans*-2-butene (1-(14%), *trans*-2-(82%), *cis*-2-(4%)).[10] Different from the mode in (i), the band of [II] appeared after the complete disappearance of the $Co(CN)_5H^{3-}$ band and grew gradually, whereas the $Co(CN)_5{}^{3-}$ band decayed (Fig. 1e).

Under condition (C), the formation of [II] was greatly affected by the ratio of butadiene to hydrogen and was remarkable at a high ratio. When the ratio was 6/1, a steady growth of the band of [II] and a decay of the $Co(CN)_5{}^{3-}$ band took place immediately. When the ratio was 1/1, a weak shoulder band of [II] which appeared in the initial stage did not grow, and the strong $Co(CN)_5{}^{3-}$ band hardly changed. On the other hand, the formation of butenes was more

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[9] N. K. King and M. E. Winfield, *J. Amer. Chem. Soc.*, **80**, 2060 (1958).

[10] The mode of the time courses of the formation of butenes were similar to those at 20°C, which were reported in the previous paper (Ref. 1).

remarkable in the latter than in the former. The composition of butenes (1-, *trans*-2-, *cis*-2-) was: 15%, 84%, 1% in the former and 10%, 89%, 1% in the latter. (In the experiments (i) and (ii), the composition of butenes was nearly constant in the course of reaction.)

(iii) In the Presence of the Stoichiometric Amount of Cyanide Ion (CN/Co=5.0) at 0°C. The relation between the variation of the complexes and the composition of butenes was rather complicated. As seen in Fig. 1f, the IR spectral change under condition (B) was similar to that in Fig. 1c showing the formation of the complex [I], except an initial great growth of the $Co(CN)_5^{3-}$ band. *trans*-2-Butene was the main product as reported[1,3] (1-(12%), *trans*-2-(81%), *cis*-2-(7%) after 10 min.), but a slight increase of 1-butene was observed with the elapse of time (1-(18%), *trans*-2-(76%), *cis*-2-(6%) after 60 min).

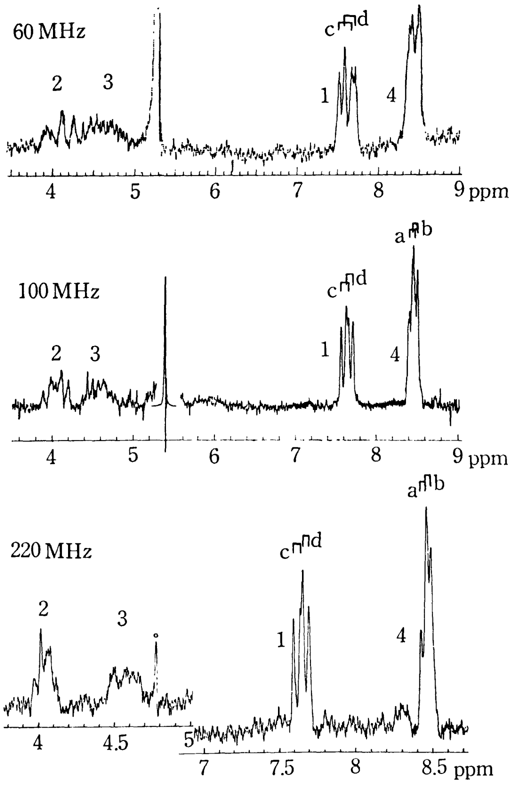
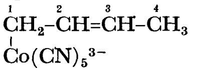


Fig. 2. NMR spectra of the reaction solution at CN/Co=6.0 and D_2O in the hydrogenation of butadiene. Observed at 60, 100, and 220 MHz and at room temperature.
○, Side band of H_2O.



$$\overset{1}{C}H_2\text{-}\overset{2}{C}H\text{=}\overset{3}{C}H\text{-}\overset{4}{C}H_3$$
$$\underset{\qquad}{Co(CN)_5^{3-}}$$

Confirmation of the Structures of the Intermediate Complexes in the Hydrogenation of Butadiene. Although Kwiatek and Seyler could not analyze the NMR spectra of the σ-butenyl complex observed at 60 MHz,[3d] the comparison of the NMR spectra measured directly on the reaction solution at 60, 100, and 220 MHz made it possible to reveal that the solution contained two complexes with very similar configurations (Fig. 2). They were assigned to the *cis*- and *trans*-isomers of [I].[11] Although it could not been determined clearly which signal corresponded to each isomer, slightly stronger bands (b and d) may correspond to the *trans*-isomer, because the *trans*-isomer may be more stable than the *cis*-isomer and because $J_{3,4}$ of the *trans*-isomer of the analogous compounds is in most cases smaller than that of the *cis*-isomer. It was also demonstrated that the proportion of the isomers did not depend on the CN/Co ratio so long as an excess cyanide ion was present. It is noteworthy that the proportion of the deuterium atom incorporated into the terminal methyl groups of the complexes prepared in D_2O under an atmosphere of hydrogen varied with the reaction condition. When the enough butadiene was added to the solution of the hydridocomplex under condition (B), one deuterium atom per mole of the complex was incorporated, but when the complex was prepared under condition (C), the proportion decreased greatly. It has been reported that the rate of the H–D exchange between $Co(CN)_5H^{3-}$ and D_2O is certainly very much faster than the addition reaction.[8d,12] A study on this problem is in progress.

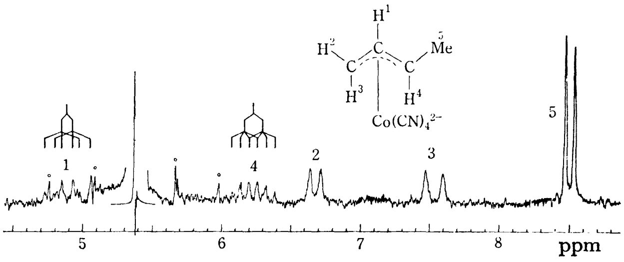


Fig. 3. NMR spectrum of the reaction solution at CN/Co=4.5 in D_2O in the hydrogenation of butadiene. Observed at 100 MHz and at 5°C.
○, Side band of H_2O.

It has been considered that the complex [II] is too unstable to be observed,[3d] but the IR spectra showed the formation of an intermediate complex in the presence of deficient cyanide ion and made it possible to find an appropriate condition for its formation. The NMR spectrum observed after the separations of the residual $Co(CN)_5^{3-}$ by an addition of $BrCCl_3$ and of precipitates by filteration, revealed that the solution contained only a *syn*-π-(1-methylallyl) complex (Fig. 3).[11] It is noteworthy that an *anti*-complex was not contained. Deuterium atom was not incorporated into the complex in spite of the reaction in the D_2O solvent. It was also demonstrated by IR and NMR that [II] was converted to [I] and *vice versa* by the addition of either the KCN or $CoCl_2$ solution to the solution containing each complex. Chemical shifts and coupling constants are summarized in Table 1.

Hydrogenation of Isoprene. Figure 4 shows the typical results under condition (A) at 30°C with a cobalt concentration of 0.2M ($CoCl_2$=10 mmol) and with 10 mmol of isoprene. It shows clearly the dependence of product compositions on the reaction time and the CN/Co ratio. The results can be considered from

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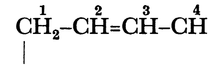
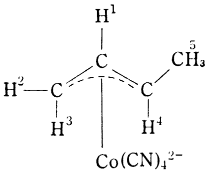
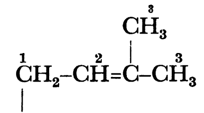
[11] T. Funabiki and K. Tarama, *Chem. Commun.*, **1971**, 1177.

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

TABLE 1. CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR THE INTERMEDIATE COMPLEXES

Complexes	Chemical shift τ (ppm)	Coupling constant J (Hz)
 $\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_3$ with $Co(CN)_5^{3-}$ on C-1	H^4 (b) 8.46(d)	$J_{3,4}$ (b) 6.5
	(a) 8.43(d)	(a) 7.0
	H^3 4.30(m)	
	H^2 4.01(m)	
	H^1 (d) 7.67(d)	$J_{1,2}$ (d) 8.6
	(c) 7.61(d)	(c) 9.4
	H^5 8.50(d)	$J_{4,5}$ 6.2
	H^4 6.23(dq)	$J_{1,4}$ 12.3
	H^3 7.53(d)	$J_{1,3}$ 12.3
	H^2 6.68(d)	$J_{1,2}$ 7.8
	H^1 4.89(dt)	
 $\overset{1}{C}H_2-\overset{2}{C}H=C(\overset{3}{C}H_3)-\overset{3}{C}H_3$ with $Co(CN)_5^{3-}$ on C-1	H^3 8.42(s)	
	H^2 4.30(t)	$J_{1,2}$ 9.5
	H^1 7.63(d)	

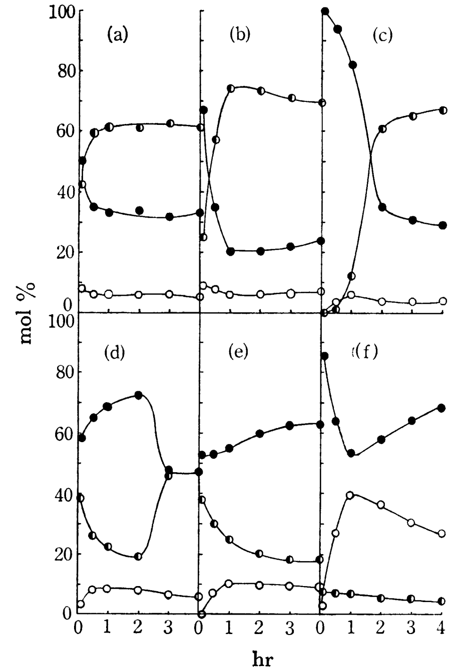


Fig. 4. Time-courses of the composition of products in the hydrogenation of isoprene in H_2O, at 30°C, and under condition (A).
●: 2-methyl-1-butene, ○: 3-methyl-1-butene,
◐: 2-methyl-2-butene
At CN/Co=(a) 5.0, (b) 5.2, (c) 5.4, (d) 5.6, (e) 5.8, (f) 6.0

the two different relations; (i) between 2-methyl-1- and 2-methyl-2-butenes, (ii) between 2-methyl-1- and 3-methyl-1-butenes.

(i) Figure 4 shows that 2-methyl-2-butene is produced even in the presence of excess cyanide ion and that the proportion of 2-methyl-1- and -2-butenes is abruptly replaced in the course of reaction. This change took place when green precipitates appeared in the solution and was caused by the abrupt formation of 2-methyl-2-butene in accompany with the stop of the formation of 2-methyl-1-butene (Fig. 5). The time when the change took place depended on the cyanide ion concentration and on the reaction temperature; the lower the concentration and the higher the temperature, the earlier the change took place. These results may be most reasonably explained by the following. The cyanide ion concentration decreases in the course of reaction owing to the aging reactions (1)—(4) or to the hydrolysis of the cyanide ion, and 2-methyl-2-butene is formed when the cyanide ion becomes deficient.

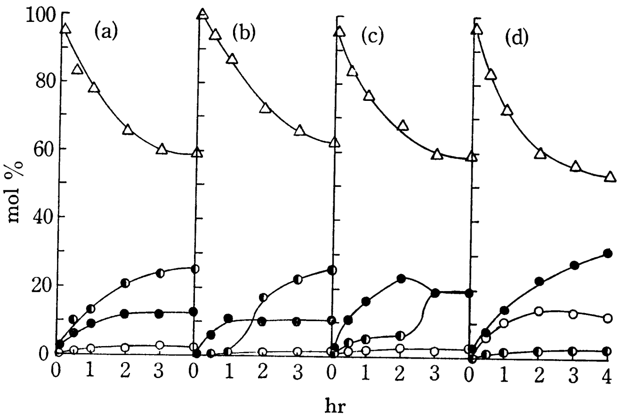


Fig. 5. Time-courses of the composition of products and isoprene in the hydrogenation of isoprene in H_2O, at 30°C, and under contition (A).
●: 2-methyl-1-butene, ○: 3-methyl-1-butene,
◐: 2-methyl-2-butene △: isoprene
At CN/Co=(a)5.0, (b) 5.4, (c) 5.6, (d) 6.0

(ii) The mode of the formation of the two terminal olefins was remarkably different. The formation of 2-methyl-1-butene was always greater than that of 3-methyl-1-butene in an initial stage of the reaction. Although the formation of 3-methyl-1-butene was generally small, it became remarkable in the presence of a large excess cyanide ion. As the aging reaction was promoted by the excess cyanide ion, it was supposed that the increase in the relative concentration of Co-$(CN)_5H^{3-}$ to isoprene might promote the formation of 3-methyl-1-butene. This was demonstrated by the result in Fig. 6, in which the effect of the relative concentration of isoprene to cobalt was examined.

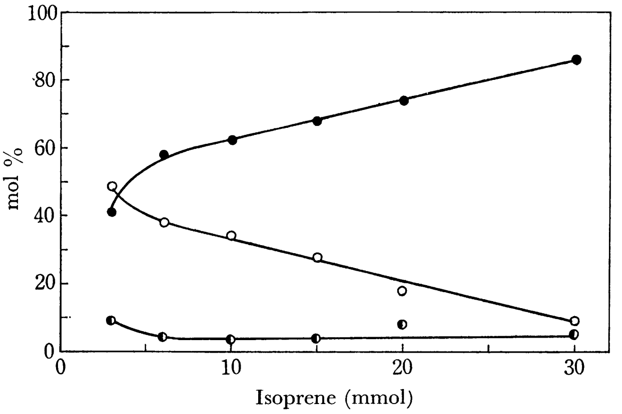


Fig. 6. Effect of the relative concentration of isoprene to $Co(CN)_5^{3-}$ in the hydrogenation of isoprene (Compositions after 3 hr) in H_2O, at 30°C, under condition (A), and with $CoCl_2$=10 mmol.
●: 2-methyl-1-butene, ○: 3-methyl-1-butene,
◐: 2-methyl-2-butene

Under condition (B), the formations of 3-methyl-1-butene at CN/Co=6.0 and of 2-methyl-2-butene at CN/Co=5.0, were greatly promoted. At CN/Co=6.0, the composition of the products (2-methyl-1-, 3-methyl-1-, 2-methyl-2-butenes) was 51%, 33%, 16% after 5 min and it became 2%, 70%, 9% after 20 min, which was maintained subsequently. It is noteworthy that the composition of 3-methyl-1-butene is greater than that of 2-methyl-1-butene. At CN/Co=5.0, the composition (8%, 9%, 83%) was nearly constant throughout the course of reaction.

The IR spectra of the reaction solutions in the presence of excess cyanide ion showed similar changes to the case of butadiene, showing the band of the intermediate complex at 2090 cm^{-1}. At CN/Co=4.5, however, the same band at 2090 cm^{-1} together with the shoulder band of $Co(CN)_5{}^{3-}$ was observed, contrary to the expectation that a new band may be observed at higher frequencies than 2090 cm^{-1}.

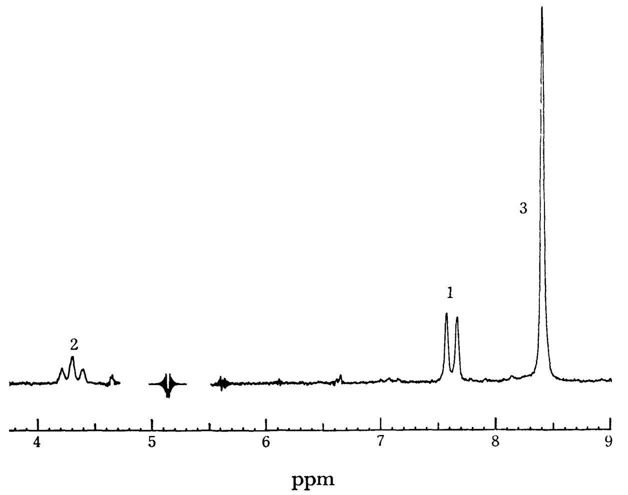
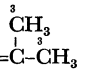


Fig. 7. NMR spectrum of the reaction solution at CN/Co=6.0 in D_2O in the hydrogenation of isoprene. Observed at 100 MHz and 5°C.



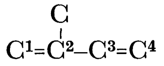
$$\underset{\substack{|\\ Co(CN)_5{}^{3-}}}{\overset{1}{CH_2}}-\overset{2}{CH}=\overset{\substack{\overset{3}{CH_3}\\|}}{C}-\overset{3}{CH_3}$$

The NMR spectrum observed in the D_2O solution under condition (B) (Fig. 7) demonstrated that the solution at CN/Co=6.0 contained only a σ-3-methyl-but-2-enyl complex [VII],[13] and that the complex at CN/Co=4.5 was not a π-allylic complex but the σ-complex [VII].

Mechanisms of the Hydrogenations of Butadiene and Isoprene in Aqueous Solution. (i) Mechanism of the Initial Interaction of $Co(CN)_5H^{3-}$ with Substrates to form the Intermediate Complexes. In the hydrogenation by other transition metal complexes, the coordination of the substrate at a vacant site on the metal is mostly required, but in the case of pentacyanocobaltate(II) it has been proposed that the hydrogen of the hydridocomplex approaches the positive β-carbon of an activated double bond to form the four-center transition state [A][2,4] or the radical transition state [B].[13,14]

[A] [B]

[A] has been proposed on the analogy with the transition state in the formation of $Co(CN)_5H^{3-}$ from $Co(CN)_5{}^{3-}$ and hydrogen,[4] but the kinetic trends in the addition of $Co(CN)_5H^{3-}$ to α,β-unsaturated compounds indicated that [B] best describes the initial interaction of $Co(CN)_5H^{3-}$ with most activated olefins.[13] The result that substituents on the β-carbon, regardless of their electron-donating (*e.g.* CH_3, $CO_2{}^-$)[12,13] or -attracting (*e.g.* C_6H_5)[15] properties, interfere with the reaction of $Co(CN)_5H^{3-}$ with substrates, and that the kinetic trends fail to parallel the stability of $CoC(CH_3)X$ adducts,[13] indicate that steric rather than electronic factors control the initial step and the C···H bonding rather than the C···Co is important in the transition state. Thus, [B] is preferable to [A].

Although it had been supposed that the hydridocomplex adds to activated olefins as though it were polarized Co^+–H^-,[2] it is well assumed from the infrared spectroscopic study that the polarization must be in a slight degree.[7] The view that the atomic hydrogen rather than the anionic hydrogen of $Co(CN)_5H^{3-}$ approaches the β-carbon, is supported by the result that the formation of 3-methyl-1-butene exceeds that of 2-methyl-1-butene in the presence of excess $Co(CN)_5H^{3-}$ in the hydrogenation of isoprene, because radicals approach more readily C^1 than C^4 in  $C^1{=}\overset{\substack{C\\|}}{C^2}{-}C^3{=}C^4$ and *vice versa* in the case of anions.[16]

The previous authors have proposed that the 1,2-adduct $CoC(CH_3)X$ is first formed inevitably *via* the transition state [A] or [B] and it isomerizes readily to the more stable 1,4-adduct in the hydrogenation of conjugated dienes,[4,13,14] but the result of the hydrogenation of isoprene suggests that this may not necessarily be the case. Mechanism 1 shows the probable courses for the formation of the intermediate complexes and the products in the hydrogenation of isoprene. It is well assumed that the rate of the reaction (6) is greater than that of (5), because the formation of 3-methyl-1-butene is greater than that of 2-methyl-1-butene in the presence of excess $Co(CN)_5H^{3-}$, under which condition intermediates are more completely converted to products. Even if the hydrogen atom of $Co(CN)_5H^{3-}$ approaches C^1 more readily than C^4, the mechanism, in which the 1,2-adducts [IV] and [VI] should be first formed, seems to be unfavorable to explain the rate difference, because the tertiary alkyl complex [VI] must be extremely less stable than [IV]. On the base that the thermodynamic stability

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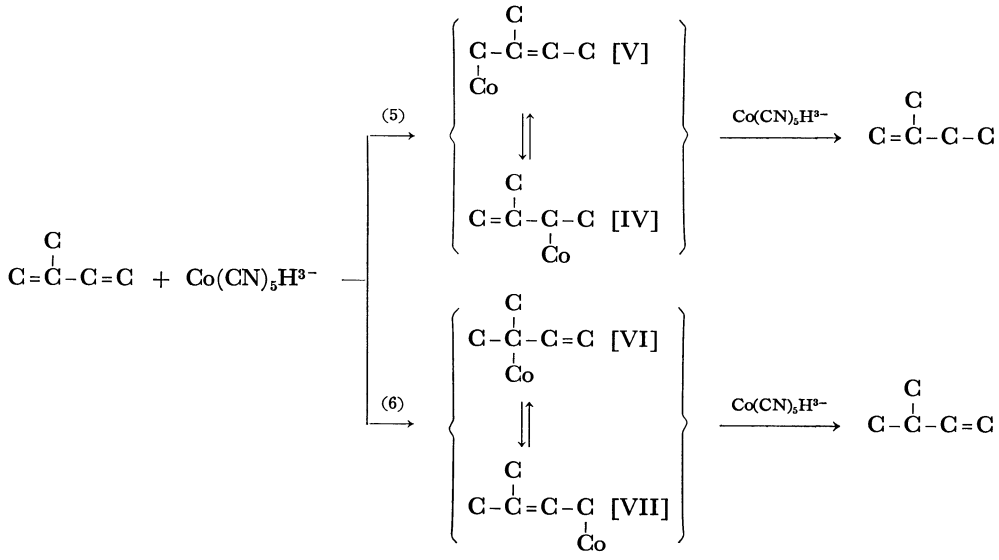
[13] J. Halpern and L. Y. Wong, *J. Amer. Chem. Soc.*, **90**, 6665 (1968).

[14] J. Kwiatek, "Transition Metals in Homogeneous Catalysis", ed. by G. N. Schrauzer, Marcel Dekker, Inc., N. Y. (1971), p. 13.

[15] T. Funabiki, unpublished results.

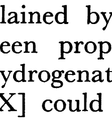
[16] K. Hayashi, T. Yonezawa, C. Nagata, S. Okamura, K, Fukui, *J. Polym. Sci.*, **20** 537 (1956); T. Yonezawa T. Higashimura. K. Katagiri, K. Hayashi, S. Okamura, and K. Fukui, *ibid.*, **26,** 311 (1957).

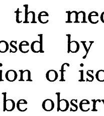


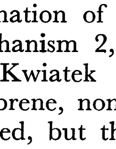
Mechanism 1.

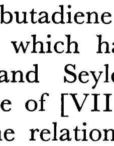
may be in order of [VII]≥[V]>[IV]>[VI] and that the reactions (5) and (6) are reversible, the 1,4-addition mechanism may be probable so long as it is supposed that the C···Co bonding in the transition state is not important. This is supported by the following. From the point of view that the process consists of the radical addition to the radicals, $[\mathrm{C^1{=}\overset{C}{\overset{|}{C^2}}{=}C^3{-}C^4H_3}]$ and $[\mathrm{H_3C^1{-}\overset{C}{\overset{|}{C^2}}{=}C^3{=}C^4}]$, about the same probability is expected for the addition of Co to C^1 and to C^3 in the reaction (5), but the addition to C^4 must be greater than to C^2 in the reaction (6).[16] Similarly, in the hydrogenation of butadiene, the 1,2- and 1,4-additions seem to have the same probability, but the latter may be predominant on account of the greater stability of the 1,4-adducts.

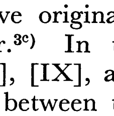
(ii) Mechanisms of the Conversion of σ-Complexes to π-Allylic Complexes. The complexes [II], [II′], [VIII], [IX], and [X] are the possible π-allylic complexes in the hydrogenations of butadiene and isoprene.


[II]

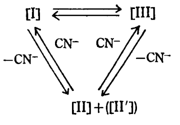

[II′]


[VIII]

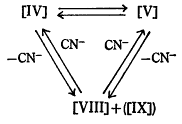

[IX]


[X]

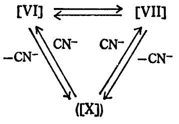
The present results that have demonstrated the formation of [II] and the equilibrium between [I] and [II] in the hydrogenation of butadiene are well explained by the mechanism 2, which have originally been proposed by Kwiatek and Seyler.[3c] In the hydrogenation of isoprene, none of [VIII], [IX], and [X] could be observed, but the relation between the 2-methyl-1- and -2-butenes in Fig. 4 indicates that the equilibrium in the mechanism 3 is taking place. [VIII] must be too unstable to have been observed on account of an additional methyl group to [II]. It is well assumed that the formations of [IX] and [X] may be negligible, because they must be less stable than [II′]. The observation of the σ-complex [VII] in the deficient cyanide concentration indicates that the equilibrium in the mechanism 4 hardly takes place.



Mechanism 2



Mechanism 3



Mechanism 4

The isomerisation between [I] and [III] or [IV] and [V] may occur *via* the transition states which do not require ligand dissociation.[3c] The equilibrium [I]⇄[III] can explain the formation of similar amounts of the *cis*- and *trans*-isomers of [I] and the independence of the proportion on the CN/Co ratio. It is supposed that *cis*-[I] is slightly less stable than *trans*-[I] and it may be the origin of the selective formation of *cis*-2-butene in the presence of excess cyanide ion in the alcoholic solvents.[1,6]

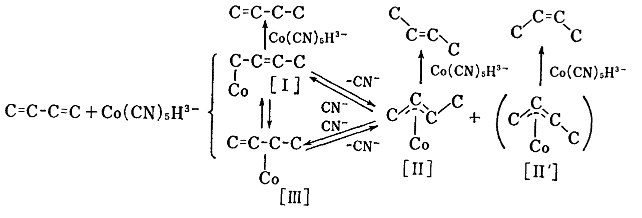
(iii) Mechanisms of the Product Formation. The result that the formation of 2-methyl-1-butene is always greater than that of 3-methyl-1-butene in the initial stage of the hydrogenation of isoprene may arise from that the intermediate for the latter is more stable than that for the former. Although the mechanism in which the 1,2-adducts [IV], [VI] are the direct intermediates for these alk-1-enes may not be excluded only for the reason that [VI] is less stable than [IV], the mechanism seems implausible because the principle proposed in the mechanism[4] can not be applied in general, especially to the radical mechanism. Alternatively, the results are clearly explained by the mechanism in which the 1,4-adducts are the direct intermediates. As described previously, the thermodynamic stability of [V] and [VII] seems similar ([VII] may be slightly more stable than [V] because a methyl group is located at the β-position in [V] and at the γ-position in [VII]). When the hydrogen atom of $\mathrm{Co(CN)_5H^{3-}}$ approaches the γ-carbon in [V] or [VII], the steric factor, which controls the initiation step, should control the reactivity. Two methyl groups on the γ-carbon in [VII] must

hinder more strongly the approach of the hydrogen atom of $Co(CN)_5H^{3-}$ than the single methyl group in [V], resulting in the greater kinetic stability of [VII] than [V]. Similarly, [I] should be the direct intermediate for the formation of 1-butene in the hydrogenation of butadiene. The dependence of the rate of the formation of [I] and 1-butene on the ratio of butadiene and hydrogen under condition (C) supports this mechanism. The steric factor can also explain that [VII] is kinetically more stable than [I] despite the thermodynamic stability seems reverse.

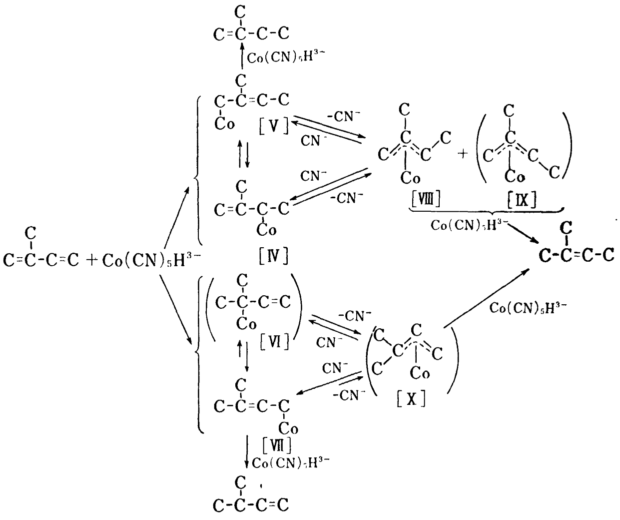
It is evident that the π-allylic complexes [II] and [VIII] are the direct intermediates for *trans*-2-butene and 2-methyl-2-butene, respectively. This is strongly supported by the result that the formations of [II] and of *trans*-2-butene depend greatly on the relative concentration of butadiene and hydrogen under condition (C). The difficulty of the formation of [II] compared with [I] may be attributable to the lower kinetic stability of [II] than [I], because their thermodynamic stability may be similar or reverse. The result at CN/Co=5.0 in the hydrogenation of butadiene is readily understood by this difference of the kinetic stability between these two complexes which must be formed in similar amounts. The difference of the kinetic stability is interpreted in terms of the steric factor. The hydrogen atom of $Co(CN)_5H^{3-}$ can approach more readily [II] than [I] because [II] has an unsubstituted carbon atom. This steric factor explains also that 1-butene is not formed from [II], because the hydrogen of $Co(CN)_5H^{3-}$ can approach the unsubstituted carbon more readily than the carbon substituted by a methyl group.

The explanation by the steric factor can be applied in general to the hydrogenation by pentacyanocobaltate(II) and excludes the mechanism in which the Co···Co bonding is included in the transition state.[4,5b)]

In conclusion, the hydrogenations of butadiene and isoprene in aqueous solution are interpreted satisfactorily in terms of the mechanisms 5 and 6, respectively.



Mechanism 5



Mechanism 6