Hydrogenation by Cyanocobaltate. Part III. Kinetic and Deuterium Tracer Studies of the Mechanism of the Hydrogenation of *trans*-1-Phenylbuta-1,3-diene catalysed by Pentacyanocobaltate(II)

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Hydrogenation of *trans*-1-phenylbuta-1,3-diene by pentacyanocobaltate has been studied in water, glycerol–methanol, and ethylene glycol–water. Kinetic and deuterium tracer studies have confirmed that the hydrogenation proceeds by a mechanism involving organocobalt intermediates. It has been concluded that the hydrogenation by pentacyanocobaltate involves intermediates whose structure depends on the solvent as well as the olefin substrate.

THE hydrogenations of many conjugated olefins by pentacyanocobaltate(II) have been reported, and two types of mechanism have been suggested, one involving organocobalt intermediates (mechanism 1) and the other involving free-radical intermediates (mechanism 2).[2] Co, CoH, and S denote $Co(CN)_5^{3-}$, $Co(CN)_5H^{3-}$, and a conjugated olefin, respectively. Mechanism 1 was initially suggested for the hydrogenation of butadiene[3] and may be applicable to its alkyl-substituted derivatives.[4] Recently we have obtained data which confirm mechanism 1 in the hydrogenation of butadiene and isoprene.[1] On the other hand, mechanism 2 has been suggested for the hydrogenation of activated olefins such

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[1] Part II, T. Funabiki, M. Matsumoto, and K. Tarama, *Bull. Chem. Soc. Japan*, 1972, **45**, 2723.

[2] J. Kwiatek, ' Transition Metals in Homogeneous Catalysis,' ed. G. Schrauzer, Marcel Dekker, New York, 1971, p. 13.

[3] J. Kwiatek and J. K. Seyler, Proc. Eighth Int. Conf. Coord. Chem., Vienna, 1964, p. 308.

[4] J. Kwiatek, *Catalysis Rev.*, 1967, **1**, 37.

as styrene[5] and cinnamate.[6] In mechanism 2, the reverse reaction of (4) was added, on the basis of the

$$\begin{aligned} 2\mathrm{Co} + \mathrm{H_2} &\rightleftharpoons 2\mathrm{CoH} && (1)\\ \mathrm{CoH} + \mathrm{S} &\rightleftharpoons \mathrm{CoSH} && (2)\\ \mathrm{CoSH} + \mathrm{CoH} &\longrightarrow 2\mathrm{Co} + \mathrm{SH_2} && (3) \end{aligned}$$

MECHANISM 1

$$\begin{aligned} 2\mathrm{Co} + \mathrm{H_2} &\rightleftharpoons 2\mathrm{CoH} && (1)\\ \mathrm{CoH} + \mathrm{S} &\rightleftharpoons \mathrm{Co} + \cdot\mathrm{SH} && (4)\\ \mathrm{CoH} + \cdot\mathrm{SH} &\longrightarrow \mathrm{Co} + \mathrm{SH_2} && (5)\\ \mathrm{Co} + \cdot\mathrm{SH} &\rightleftharpoons \mathrm{CoSH} && (6) \end{aligned}$$

MECHANISM 2

deuterium tracer study,[4] to the original mechanism which was suggested on the kinetic study of the hydrogenation of cinnamate.[6] In mechanism 2 it has been thought that an organocobalt complex CoSH is not directly involved in the catalytic cycle.[2] Support for the radical mechanism has been found in kinetic studies,[6,7] radical trapping experiments,[8] and the non-stereoselectivity of hydrogen addition.[9] But the relation between structures of olefins and mechanisms has not been clarified.

We have studied the solvent effect for the hydrogenation of conjugated dienes by pentacyanocobaltate(II). Alcoholic solvents such as methanol, ethylene glycol, and glycerol strongly affect the selectivity of the hydrogenation of butadiene.[10] A free-radical mechanism has been suggested to explain the remarkable formation of *cis*-but-2-ene in the presence of excess of CN^- in glycerol–methanol,[11] but a kinetic study to confirm the mechanism was difficult on account of the high vapour pressure of butadiene.[10] The aim of the present paper is to establish that the change of solvent results in the change of the reaction mechanism, which brings about the change of selectivity. Kinetic and deuterium tracer studies were performed in water and in alcoholic solvents.

EXPERIMENTAL

Materials.—*trans*-1-Phenylbuta-1,3-diene was synthesized from cinnamaldehyde and phenylmagnesium bromide.[12] Purity was 99·8%. Deuterium gas was prepared from D_2O by the reaction with calcium metal. D_2O was obtained from E. Merck Co. (purity: 99·75%). Methanol, ethylene glycol, and glycerol were guaranteed grade reagents and were used after distillation. KCN and anhydrous $CoCl_2$ were dried before use.

Hydrogenation Procedure.—Hydrogenation was followed by measuring hydrogen absorption at 20 °C and atmospheric pressure in apparatus similar to that described previously.[10] Reaction was carried out in a vessel (100 ml) containing 50 ml of solution. Hydrogen gas was circulated through the solution which was stirred vigorously. The solution of pentacyanocobaltate(II) was prepared by an addition of $CoCl_2$ solution (10 ml) to KCN solution (40 ml) under hydrogen. After the preliminary hydrogen absorption by pentacyanocobaltate to form hydridopentacyanocobaltate, phenylbutadiene in 5 ml of toluene was added. Initial rates of the hydrogenation were evaluated from the hydrogen absorption curves. The hydrogenation was followed also by the gas-chromatographic analysis of substrates, and by i.r. spectroscopic analysis of complexes in solution. Thus liquid samples were withdrawn by an injection syringe through a rubber serum cap. They were extracted with toluene and the extracts were analysed by g.l.c. Products were confirmed by comparison of retention time with those of authentic samples. A 3 m column of 4% Ucon-oil on Chromosorb W was used. I.r. spectra of liquid samples were observed in the 2000—2200 cm^{-1} region as described.[13]

Deuterium Tracer Study.—The solution (10 ml) of the complex was prepared in a 20 ml reaction vessel in a deuterium atmosphere by the addition of solvents to the solid mixture of KCN and $CoCl_2$. After the preliminary deuterium absorption, phenylbutadiene in benzene (1 ml) was added to the solution. After the scheduled reaction time, gas samples were collected and liquid samples were extracted with benzene. Gas samples were subjected to mass spectrometry (JEOL, 01SG). Extracts of the liquid samples were concentrated and subjected to g.l.c.–m.s. (Hitachi, RMS-4).

RESULTS

Hydrogenation in Water.—In the presence of excess of CN^- (CN : Co = 6·0), the hydrogenation of phenylbutadiene was much slower than the preliminary hydrogen absorption (Table 4). The hydrogenation was of the first order with respect to the total concentration of phenylbutadiene ([S]) (Figure 1, plot A), and of the second order with respect to the total concentration of the cobalt complexes ($[\mathrm{Co}]_0$) at its lower concentration (Figure 2, plot A), but the latter deviated to the lower order at the higher cobalt concentration. The value of the apparent activation energy was estimated to be 4·07 kcal mol^{-1} at temperatures of 10—30 °C.

The colour of the solution (greenish yellow) changed little when phenylbutadiene was added to the solution of $Co(CN)_5H^{3-}$. The i.r. spectra of the reaction solution indicated that a peak of $Co(CN)_5H^{3-}$ hardly changed throughout the course of the reaction.

As seen in Table 1, the main product was *trans*-1-phenylbut-1-ene and small amounts of *cis*- and *trans*-1-phenylbut-2-enes were formed. The compositions were constant throughout the reaction. The amount of products estimated from the g.l.c. analysis coincided with that estimated from the hydrogen absorption.

At CN : Co = 5·0, the greenish yellow solution became brown when phenylbutadiene was introduced. The composition of products changed with the reaction time. In the initial stage, it was close to that at CN : Co = 6·0, but gradually changed to that at CN : Co = 4·0.

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[5] W. Strohmeier and N. Iglauer, *Z. phys. Chem.* (*Leipzig*), 1966, **51**, 50.

[6] L. Simandi and F. Nagy, *Acta Chim. Acad. Sci. Hung.*, 1965, **46**, 137.

[7] J. Halpern and L. Wong, *J. Amer. Chem. Soc.*, 1968, **96**, 6665.

[8] (*a*) J. Kwiatek and J. K. Seyler, *Adv. Chem. Ser.*, 1968, **70**, 207; (*b*) K. Tarama and T. Funabiki, *Nippon Kagaku Zasshi*, 1968, **89**, 88; (*c*) M. G. Swanwick and W. A. Waters, *J. Chem. Soc.* (*B*), 1971, 1059.

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

[10] K. Tarama and T. Funabiki, *Bull. Chem. Soc. Japan*, 1968, **41**, 1744; T. Funabiki and K. Tarama, *ibid.*, 1970, **43**, 3965; *Tetrahedron Letters*, 1971, 1111; *Bull. Chem. Soc. Japan*, 1971, **44**, 945.

[11] K. Tarama, T. Funabiki, and M. Mohri, *Shokubai*, 1969, **11**, 35.

[12] *Org. Synth., Coll. Vol.*, 1963, **4**, 771.

[13] T. Funabiki and K. Tarama, *Bull. Chem. Soc. Japan*, 1972, **45**, 2945.

At CN : Co = 4·0, the colour change was similar to that at CN : Co = 5·0, but the solution contained much precipitate. The composition of products was independent of the reaction time. The proportion of 1-phenylbut-1-ene to but-2-enes, and of *trans*- to *cis*-isomer of the latter, increased with the decreasing cyanide concentration.

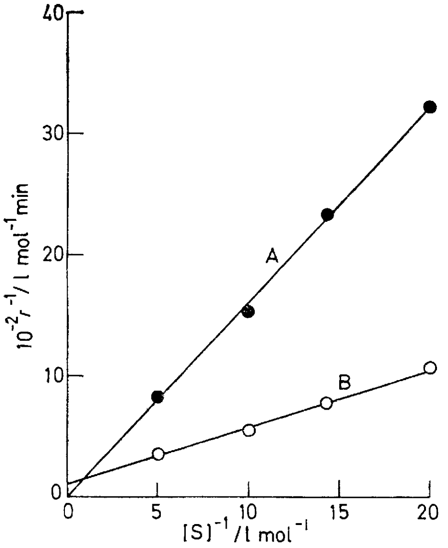

FIGURE 1 Hydrogenation of phenylbutadiene; A, in water; B, in water–ethylene glycol (30 ml: 20ml)

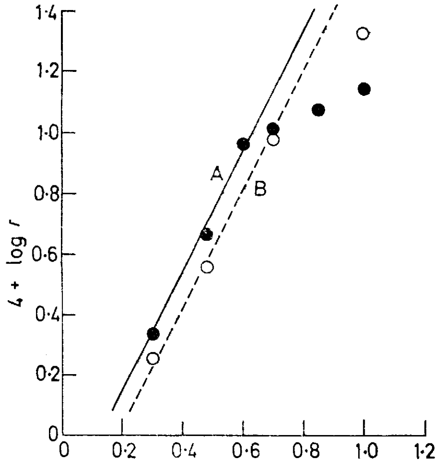

FIGURE 2 Hydrogenation of phenylbutadiene; A, in water; B, in water–ethylene glycol (30 ml: 20 ml)

As the results in the deuterium tracer study were very similar both at CN : Co = 5·0 and 6·0, only the latter are given here. Table 2 gives the isotopic distributions of reactant and products together with those of gaseous samples, and Table 3 gives those of demethylated fragments of products. In H_2O the yield of deuteriated products was very low. Phenylbutadiene was not deuteriated, whereas the yield of H_2 and HD was remarkable. In D_2O, D_2 components of the products were produced in a high yield. Phenylbutadiene contained D_1 components.

Hydrogenation in Glycerol–Methanol.—As described,[10] the preliminary hydrogen absorption by pentacyanocobaltate was very slow in comparison with that in water. When phenylbutadiene was added to the yellow solution after the preliminary hydrogen absorption at CN : Co = 6·0, the solution rapidly became dark green. The i.r. spectra of the reaction solution demonstrated that after addition of phenylbutadiene the peak of $Co(CN)_5H^{3-}$ disappeared and the peak of $Co(CN)_5{}^{3-}$ reappeared. The formation of products estimated from the g.l.c. analysis of the liquid sample was greater than that estimated from the hydrogen absorption. The composition of the products was given in Table 1, and was independent of the CN : Co ratio. The formation of 1-phenylbut-1-ene was highly selective. The colour change at low CN : Co ratio was similar to that reported.[10]

The results of the deuterium tracer study are given in Tables 2 and 3. Despite the solvents containing a hydroxyl group, deuteriation was more remarkable than in water. D_0—D_4 components were found in the reduction products and the proportion of deuteriated phenylbutadiene to non-deuteriated ones was greater than that in D_2O. The deuteriation was more remarkable with the greater conversion. The compositions of H_2 and HD in the gaseous sample changed little after the hydrogenation.

Hydrogenation of Ethylene Glycol–Water.—In ethylene glycol (40 ml)–water (10 ml), which exhibited the same effect on the selectivity as glycerol–methanol in the hydrogenation of butadiene,[10] the rates were independent of the concentration of phenylbutadiene at CN : Co = 6·0. The colour of the solution changed rapidly from greenish yellow to dark green after the addition of phenylbutadiene, which correlated with the change of the main complex in solution from $Co(CN)_5H^{3-}$ to $Co(CN)_5{}^{3-}$. The composition of products was similar to those in glycerol–methanol, and it was clearly demonstrated that the proportion of 1-phenylbut-1-ene to but-2-enes was less in an initial stage. When the hydrogenation was started without the preliminary hydrogen absorption, the composition was constant throughout the course of the reaction (92 : 6 : 2). The results in the deuterium tracer study were very similar to those in glycerol–methanol in spite of the presence of water (Tables 2 and 3). At CN : Co $\leqslant$ 5·0, a heterogeneous blue-green solution was obtained by the preliminary hydrogen absorption, and it changed to green on addition of phenylbutadiene and afterwards to brown. The composition of products was same as those at CN : Co = 6·0.

To examine the effect of ethylene glycol on the reaction rate, reaction was carried out in the solvents of various compositions of ethylene glycol and water. As shown in Table 4, the rate and amount of hydrogen absorption by pentacyanocobaltate decreased with the increasing content of ethylene glycol, while the rate of the hydrogenation increased so long as the rate of the former reaction was much greater than that of the latter.* In the solvent of greater ethylene glycol content, the rate of hydrogenation must exceed that of formation of $Co(CN)_5H^{3-}$. In ethylene glycol (20 ml)–water (30 ml), the colour of the solution was similar to that in water except for a slight increase in green colour accompanying the introduction of phenylbutadiene. The rate was of less than the first order in substrate [S] (Figure 1, plot B), but was of the second order with respect to the cobalt concentration at its lower concentration

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* The hydrogen absorption by $Co(CN)_5{}^{3-}$ in water was so rapid that the rate was liable to be affected by the stirring of solution, but the rate of hydrogenation was slow enough to be followed in the steady condition.

TABLE 1

Selectivity in the hydrogenation of *trans*-1-phenylbuta-1,3-diene [a]

		Products (mol %)				
Solvent (ml)	CN : Co	*trans*- Ph–C=C–C–C	*trans*- Ph–C–C=C–C	*cis*- Ph–C–C=C–C	*cis* : *trans* (Ph–C–C=C–C)	Reaction time/min
H_2O (50)	4·0	85	13	2	0·14	120
	5·0	78	17	5	0·31	15
		81	15	4	0·26	60
		83	14	3	0·23	120
	6·0	73	20	7	0·42	120
Glycerol (35)	4·0	94	4	2	0·35	120
Methanol (15)	5·0	95	4	1	0·35	120
	6·0	94	4	2	0·36	120
Ethylene glycol (40)	4·0	94	4	2	0·35	120
H_2O (10)	4·8	93	5	2	0·37	120
	5·0	93	5	2	0·39	15
		93	5	2	0·36	120
	6·0	85	11	4	0·37	15
		92	6	2	0·39	60
Ethylene glycol (20)	4·0	88	10	2	0·25	120
H_2O (30)	5·0	88	9	3	0·29	120
	6·0	85	11	4	0·40	120

[a] [Co] = 0·2M, [S] = 0·2M.

TABLE 2

Deuteriation of *trans*-1-phenylbuta-1,3-diene [a]

Solvent	Conversion (%)	*trans*-Ph–C–C=C–C (%)					*trans*-Ph–C=C–C–C (%)					*trans*- Ph–C=C–C=C (%)			Gas composition (%)		
		D_0	D_1	D_2	D_3	D_4	D_0	D_1	D_2	D_3	D_4	D_0	D_1	D_2	H_2	HD	D_2
H_2O	64	88·7	11·3				90·2	9·8				100			29·2	10·2	60·6 [b]
D_2O	57	0	7·6	73·5	17·6	1·3	0	5·2	73·8	18·8	2·2	88·7	11·3		0·7	2·8	96·5 [b]
Glycerol Methanol	67	48·8	29·1	14·7	7·5		42·4	31·2	18·3	6·7	1·4	31·8	47·8	20·4	0·8	3·9	95·3 [c]
Glycerol Methanol	100	19·6	18·0	21·3	22·2	12·7 [e]	21·0	23·5	24·5	21·6	9·5				1·0	4·2	94·8 [c]
Ethylene glycol H_2O	78	37·6	33·5	21·0	6·2	1·7	36·2	36·9	19·0	7·5	0·4	51·8	37·0	11·2	2·9	13·7	83·5 [d]
Ethylene glycol D_2O	62	39·7	39·9	16·4	3·5	0·6	33·9	42·1	18·8	4·5	0·7	72·6	22·5	4·9	0·9	9·1	90·0 [d]

[a] CN : Co = 6·0, [Co] = 0·2, [S] = 0·2M. Compositions of deuterium gas used were: [b] (H_2 : HD : D_2) = (0·2 : 3·3 : 96·4); [c] (2·1 : 4·0 : 93·9); [d] (0·0 : 7·1 : 92·9); [e] 6·2% D_5.

TABLE 3

Isotopic distributions of fragments

Parents	*trans*-Ph–C–C=C–C				*trans*-Ph–C=C–C–C		
Fragments	Ph–C⋯C⋯C$^+$ (%)				Ph–C⋯C⋯C$^+$ (%)		
Solvent	D_0	D_1	D_2	D_3	D_0	D_1	D_2
H_2O	93·8	6·2			94·1	5·9	
D_2O	4·8	88·9	6·3		5·3	91·1	3·6
Glycerol Methanol [a]	80·1	17·7	2·0		53·2	35·8	11·0
Glycerol Methanol [b]	64·9	26·6	5·5	2·9	61·0	35·3	3·7
Ethylene glycol H_2O	65·4	31·4	3·3		65·3	31·9	2·8
Ethylene glycol D_2O	64·0	34·4	1·5		60·5	36·5	3·1

[a] Conversion; 67%. [b] Conversion; 100%.

(Figure 2, plot B). The apparent activation energy was estimated to be 6·71 kcal mol^{-1} at 10—30 °C. The composition of products was dependent on the CN : Co ratio, but was intermediate between that in water and ethylene glycol (40 ml)–water (10 ml) at each CN : Co ratio (Table 1).

TABLE 4

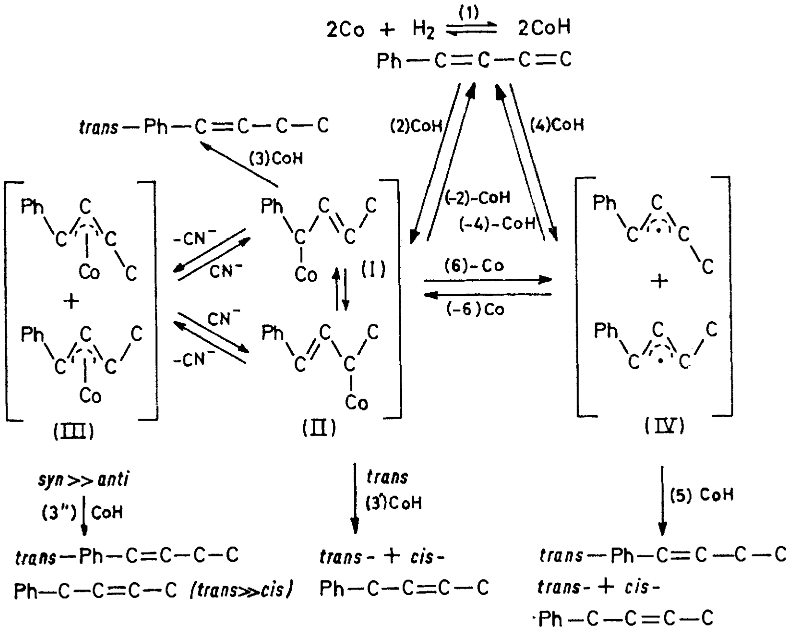
Rates of the hydrogen absorption in ethylene glycol–water [a]

Solvent/ml		H_2 absorbed [b]	Formation of $Co(CN)_5H^{3-}$	Hydrogenation of phenylbutadiene
Ethylene glycol	Water	ml	$10^3 r$/mol l^{-1} min^{-1}	$10^3 r$/mol l^{-1} min^{-1}
0	50	95	9·91	1·19
10	40	92	9·74	1·71
20	30	89	7·64	2·90
30	20	83	4·44	2·52
40	10	74	2·06	1·64

[a] CN : Co = 6·0, [Co] = 0·2M, [S] = 0·2M. [b] In the preliminary step to form $Co(CN)_5H^{3-}$.

DISCUSSION

According to the general scheme which was originally suggested by Kwiatek,[4] mechanism 3 may be probable in the case of phenylbutadiene. Other forms of products and intermediates are sterically unfavourable. In mechanism 1 the steps (4, —4) and (6, —6), and in mechanism 2 the steps (2, —2) and (3, 3′, 3″) are regarded as unimportant. The probability of the steps (4, —4), (6, —6), and (5) in the case of conjugated dienes has not been reported.



MECHANISM 3

Mechanism of the Hydrogenation of Phenylbutadiene in Water.—The dependence of the isomer distribution of the products on the CN : Co ratio strongly suggests mechanism 1. The proportion of 1-phenylbut-1-ene to but-2-enes at CN : Co = 6·0 must reflect the relative stability of intermediate (I) towards (II) and the difference of steric effect in the step (3) and (3′). Increased proportions of 1-phenylbut-1-ene to but-2-enes and of *trans*-1-phenylbut-2-ene to *cis*-isomer at CN : Co ⩽ 5 suggest the intermediate (III).[1,14]

The kinetic evidence presented above is consistent with mechanism 1. Reaction (2) is not favoured in water although (2) and (—2) must both occur in order to explain the exchange results. The rate-determining step for hydrogenation must be reaction (3), and the rate equation is (7), which gives a first-order dependence on substrate concentration if K_2 is small.

$$r = \frac{k_3K_2[S][Co]_0^2}{\{1 + K_2[S] + (1/K_1[H_2])^{1/2}\}^2} \qquad (7)$$

The evidence of the colour changes during hydrogenation suggests that the condition is satisfied. The deviation from the second-order dependence on cobalt concentration at its higher concentration may be due to the decrease in the effectiveness of catalyst concentration on the reacting surface in the heterogeneous solvent system.

The rapid exchange [15] between the deuterium ligand and the solvent protons explains the slight deuteriation occurring in water. The very substantial exchange in both products and reactants in D_2O suggests that reaction (2) and (—2) both occur in the system at a rate

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

[15] (*a*) G. A. Mills, S. Weller, and A. Wheeler, *J. Phys. Chem.*, 1959, **63**, 403; (*b*) J. Kwiatek, I. L. Mador, and J. K. Seyler, *Adv. Chem. Ser.*, 1963, **37**, 201; (*c*) A. F. Mabrouk, E. Selke, W. K. Rohwedder, and H. J. Dutton, *J. Amer. Oil Chemists' Soc.*, 1965, **42**, 432; (*d*) G. G. Strathdee and M. J. Quinn, *Canad. J. Chem.*, 1972, **50**, 3144.

comparable with that of hydrogenation suggesting that mechanism 1 is applicable. A comparison of the isotopic distributions in the $PhC\overline{\cdots}C\overline{\cdots}C^{+}$ fragments (Table 3) with those in the parent compounds (Table 2) suggests that the hydrogen atoms are more rapidly exchanged in the δ position than elsewhere in the butadiene chain, but that the second atom of hydrogen giving products enters at the α, β, or γ position. A similar result was obtained earlier for methyl sorbate.[15c]

Mechanism of the Hydrogenation of Phenylbutadiene in Glycerol–Methanol and Ethylene Glycol–Water.—The kinetic data in ethylene glycol (20 ml)–water (30 ml) are consistent with the equation (7) provided the value of K_2 is large enough to make K_2[S] a significant term in the denominator. Equation (7) may be rearranged into the form of equation (8) for the purpose of testing the rate data. The results of this test are shown in Figure 3.

$$1 + K_2[\mathrm{S}] + (1/K_1[\mathrm{H_2}])^{1/2} = \sqrt{\{k_3K_2[\mathrm{Co}]_0{}^2([\mathrm{S}]/r)\}} \quad (8)$$

Increase in the rate with alcohol content at the higher cobalt concentration may be due to the increase in the effectiveness of catalyst. Dependence of the composition of products on the CN : Co ratio suggests that the products are formed mainly in mechanism 1, but a slight deviation from that in water suggests that the composition is affected by the solvent composition.

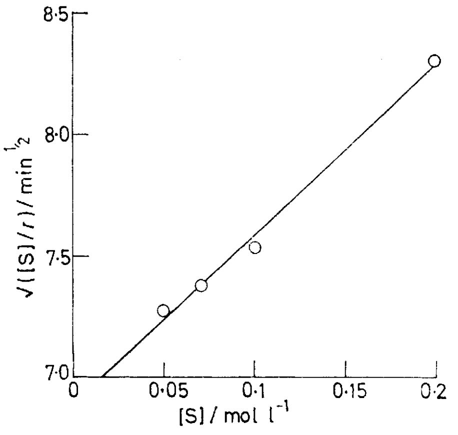

FIGURE 3

The absence of a cyanide-ion effect on the isomer distribution of the products in glycerol–methanol and in ethylene glycol (40 ml)–water (10 ml) suggests that the products are formed from the radical intermediates (IV) in these solvents. The highly selective formation of 1-phenylbut-1-ene is consistent with this intermediate. As indicated by the colour change and the i.r. spectra of the solution accompanying the introduction of phenylbutadiene, the characteristic of the reaction in these solvents is that reaction (1) is the slowest step and the concentration of $Co(CN)_5H^{3-}$ is very low. This may enable the rate of step (6) to exceed that of step (3). This is very probable because the composition of products comes close to that in water when the concentration of $Co(CN)_5H^{3-}$ is high as shown in the initial stage of reaction (Table 1). This result suggests also that the radical intermediate (IV) may not directly be formed by the step (4), but stepwisely from the organocobalt intermediates.

The increase in the value of K_2 with alcohol content, and the rapid colour change accompanying the introduction of phenylbutadiene, suggest the increased k_2 value. Step (6) may be the slowest step in the absence of excess of $Co(CN)_5H^{3-}$, apart from step (1). These are consistent with the increased proportion of deuteriated products and reactant. The increased value of k_2 and the low concentration of $Co(CN)_5H^{3-}$ probably explains the absence of hydrogen or HD in the gas phase after reaction even though a considerable proportion of the products contained only hydrogen. It is apparent that $Co(CN)_5D^{3-}$ exchanges with alcohols at a rate approaching its exchange rate with water. The interpretation previously offered for the exchange reactions in water is also substantially similar to that applicable in this case.

The mechanism suggested for the hydrogenation of phenylbutadiene can explain the results in the hydrogenation of butadiene,[10] provided that the *cis*-butenyl radical is selectively formed in the presence of excess of cyanide ion in glycerol–methanol or in ethylene glycol–water. This is probable because the σ-but-2-enylcobaltate may be less stable than the *trans*-isomer. Initial rapid formation of but-1-ene in these solvents is very similar to that in the case of phenylbutadiene, in the respect that the presence of excess of $Co(CN)_5H^{3-}$ brings about the results close to that in water.

As seen from the above results, solvent may affect the rate and equilibrium constants in each step of the reaction, but the effect on step (6) seems to be most remarkable. It has been observed that the selectivity in water is independent of the $Co(CN)_5H^{3-}$ concentration, and that the σ-but-2-enyl complex gradually decomposes in glycerol–methanol to form *cis*- and 1-butenes in the absence of hydrogen while hardly in water.[16] These indicate that the values of k_6 and/or K_6 are dependent on solvent as well as the olefin substrate. Increase in the values of k_6 and/or K_6 with the alcohol content may be related to the ion-pair formation of intermediate complexes, but the details are now under investigation.

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[16] T. Funabiki, unpublished result.