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A NOVEL SOLVENT EFFECT ON THE SELECTIVITY OF THE HYDROGENATION OF BUTADIENE CATALYZED BY PENTACYANOCOBALTATE(II)

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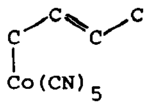
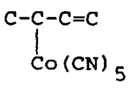
Nature of pentacyanocobaltate(II) has been studied extensively by many workers(1). On the other hand, the importance of the solvent in the homogeneous catalysis has been recently noticed. We have reported that the selectivity of the hydrogenation of butadiene by pentacyanocobaltate(II) is very much affected by solvent(2): Cis-2-butene is greatly produced in glycerol-methanol in the high region of R(R=CN/Co>5.2), although it had been reported that 1-butene is produced selectively in the high region of R, trans-2-butene in the low region of R, and cis-2-butene always negligibly in water(3),(4), and that this solvent effect should be available to rescrutinize the mechanism of the hydrogenation of butadiene which has been generally accepted. To clarify the role of water and alcohol in this reaction, the hydrogenation in the mixtures of water and various alcohols was studied, and we wish to report in this paper that special alcohols promote greatly the formation of cis-2-butene in the high region of R and to propose the mechanism of 1- and cis-2-butene formation.

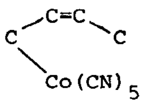
The reaction was carried out in the same way as previously reported(2). The reaction conditions were written under the tables. Reaction gases were circulated through the solution, and gas sample was picked out by an injection syringe from time to time, which was analyzed by VPC. The results in the tables are those of after 3 hours from the start of the hydrogenation.

The results in Table 1 are those in the solvents composed of water and various alcohols in the absence of hydrogen. In this case, the source of hydrogen should be solvent molecules. The results in Table 2 are those in the ethylene glycol-water solvents in the presence of hydrogen: Hydrogen was absorbed by pentacyanocobaltate(II) to produce the hydrido-complex prior to the introduction of butadiene. The results are summarized as follows: (1)Water promotes selectively the formation of 1-butene, but its presence in the alcoholic solvents does not completely inhibit the formation of cis-2-butene. (2)The formation of cis-2-butene is promoted greatly by methanol and ethylene glycol, slightly by glycerol and not by ethanol and propanols. (3)The mole fraction of cis-2-butene increases with the increase of the methanol or ethylene glycol content, but not with the ethanol content. (4)The red-violet precipitate, which may be $K_6[Co_2(CN)_{10}]$, is formed when the content of methanol and ethanol increases, but it is always homogeneous in the ethylene glycol-water or glycerol-water solutions. (5)Hydrido-complex previously prepared by the absorption of hydrogen generally promotes the formation of 1-butene, especially in the water rich solvents. (6)The relative yield does not greatly vary in the absence of hydrogen, but it greatly decreases with the increase of the ethylene glycol content in the presence of hydrogen.

Although two complexes [I](5) and [II](6) have been proposed as the intermediate for the 1-butene formation, we propose [III] as a most probable intermediate complex for the cis-2-butene formation, and we suppose, at present, that [III] is common to the formation of both 1- and cis-2-butenes. Because it is well assumed from the results above described, that the effect of solvent on the selectivity can be explained by the specific solvation and that alcohol also plays a role as a hydrogen source as well as water, we propose the mechanism (1) for the formation of 1- and cis-2-butene in the high region of R, in which CoH, CoROH and ROH denote $Co(CN)_5H^{3-}$, $Co(CN)_5ROH^{3-}$ and alcohol, respectively. Thus, in


[I]


[II]


[III]

$$\begin{tikzcd}[column sep=small] (\mathrm{CoH, or\ CoROH}) + \mathrm{C{=}C{-}C{=}C} \arrow[r] & {[III]} \arrow[r, "\mathrm{CoH}"] \arrow[dr, "\mathrm{CoROH\ or\ ROH}"'] & \text{1-butene} \\ & & \text{1- and cis-2-butene} \end{tikzcd} \qquad (1)$$

Table 1. Effect of Alcohols on the Selectivity of the Hydrogenation of Butadiene by Pentacyanocobaltate(II)[a]

No.	Alcohol	(ml)	H_2O (ml)	Butenes (mol %)[b] 1-	trans-2-	cis-2-	Yield[c] (mmole)
1		0	50	89	5	6	1.19
2	MtOH	5	45	84	6	10	0.99
3	"	10	40	80	6	14	1.18
4	"	15	35	69	7	24	1.14
5	"	20	30	56	5	39	0.47[d]
6	EtOH	5	45	90	6	4	0.93
7	"	10	40	88	6	6	1.06
8	"	15	35	85	7	8	0.39[d]
9	PrOH(n-)	10	40	91	5	4	1.11
10	PrOH(iso-)	10	40	91	5	4	1.12
11	Ethylene Glycol	10	40	77	6	18	1.28
12	"	15	35	71	7	22	0.95
13	"	20	30	60	7	33	0.95
14	"	30	20	45	6	49	1.22
15	"	40	10	39	5	56	1.55
16	Glycerol	10	40	85	5	10	1.78
17	"	20	30	82	5	13	2.55
18	"	30	20	79	6	15	2.91
19	"	40	10	85	8	7	2.73

a) CN/Co=6.0, 20°C, $CoCl_2$=10 mmol, In the absence of hydrogen

b) Composition of after 3 hours from the start of the hydrogenation

c) Relative yield of after 3 hours from the start of the hydrogenation

d) Precipitate was formed.

the water rich solutions, hydrido-complex prepared by the reaction of water or hydrogen with pentacyanocobaltate(II) contributes mainly to the formation of

1-butene, but in the alcohol rich solutions, solvated alcohol or free alcohol contributes to the formation of cis-2-butene and 1-butene, in the rate determining step. In the latter case, only special alcohols are available.

Table 2. Effect of Ethylene Glycol on the Selectivity of the Hydrogenation of Butadiene by Pentacyanocobaltate(II)[a]

	Ethylene glycol	H_2O	H_2[b]	Butenes (mol %)[c]			Yield[d]
No.	(ml)	(ml)	(ml)	1-	trans-2-	cis-2-	(mmole)
1	0	50	74	95	4	1	11.14
2	10	40	72	93	5	2	12.50
3	20	30	69	85	7	8	7.56
4	30	20	64	65	10	25	5.10
5	40	10	60	46	9	45	2.81

a) CN/Co=6.0, 20°C, $CoCl_2$=10 mmol, Hydrogen was absorbed prior to the introduction of butadiene.

b) Volume of hydrogen absorbed by pentacyanocobaltate(II) before the introduction of butadiene.

c) Composition of after 3 hours from the start of the hydrogenation

d) Relative yield of after 3 hours from the start of the hydrogenation

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