Solvent Effect on the Reduction of Butenyl Chlorides by Pentacyanocobaltate(II)

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We studied the reaction of the two butenyl chlorides with pentacyanocobaltate(II) in several solvents in the absence of hydrogen.

The reaction was carried out in a similar manner to that reported previously,[1] except that chlorides were added by an injection-syringe through a gum-stopper. Composition of the products was generally constant, although the reaction was rapid in water solution and slow in other solutions. Some of these results are shown in Tables 1 (CN/Co=6.0) and 2 (CN/Co=5.0). The data in the tables are those of after 3 hr from the start of the reaction. We obtain the following results; 1) At CN/Co=5.0, *trans*-2-butene is the main product in all solvents. 2) At CN/Co=6.0, mole fraction of 1-butene decreases and that of 2-butene increases in the solvents in which *cis*-2-butene is produced selectively in the butadiene hydrogenation. 3) Two chlorides bring the same results in each solvent. From this result we should consider a common intermediate for the reaction of the two chlorides. 4) Yield of butadiene is generally very low and does not vary in the course of the reaction. This result is differs largely from that by Kwiatek and Seyler. 5) Yield of butenes is larger in H_2O than in other solvents at CN/Co=6.0, and *vice versa* at CN/Co=5.0.

We consider these results are important in the study on pentacyanocobaltate(II). The detailed mechanism of this reaction and the role of the solvent will be discussed later.

TABLE 1. EFFECT OF SOLVENT ON PRODUCTS OF THE REDUCTION OF BUTENYL CHLORIDES AT CN/Co=6.0 ($CoCl_2$=10 mmol) (20°C)

Solvent	*trans*-1-Chloro-2-butene, product (mol %)			butd.[b]	3-Chloro-1-butene, product (mol %)			butd.[b]
	1-b	*t*-2-b	c-2-b		1-b	*t*-2-b	c-2-b	
H_2O (50 m*l*)	89 (41.6)[c]	9 (4.2)	2 (0.7)	0.6 (0.3)	92 (34.3)	7 (2.7)	1 (0.5)	2.0 (0.8)
glycerol (35 m*l*) +MeOH (15 m*l*)	60 (13.1)	27 (5.9)	13 (0.3)	0.9 (0.2)	63 (12.3)	22 (4.3)	15 (3.0)	0.4 (0.1)
Ethylene glycol (40 m*l*) +H_2O (10 m*l*)	61 (16.3)	28 (7.4)	11 (2.7)	0.1 (0.02)	67 (18.1)	22 (5.9)	11 (2.8)	0.2 (0.1)
H_2O[a]	87	10	3	89	90	8	2	86

a) By Kwiatek and Seyler[2]; CN/Co=7.0, 200 m*l* H_2O, 0.15 M cobalt, 0.15 M KOH
b) Butadiene assuming that total yield of butenes is 100.
c) The data in parentheses are relative yields of butenes and butadiene.

TABLE 2. EFFECT OF SOLVENT ON PRODUCTS OF THE REDUCTION OF BUTENYL CHLORIDES AT CN/Co=5.0 ($CoCl_2$=10 mmol) (20°C)

Solvent	*trans*-1-Chloro-2-butene, product (mol %)			butd.[b]	3-Chloro-1-butene, product (mol %)			butd.[b]
	1-b	*t*-2-b	c-2-b		1-b	*t*-2-b	c-2-b	
H_2O (50 m*l*)	15 (1.8)[c]	83 (9.8)	2 (0.2)	9.8 (1.2)	14 (1.9)	84 (11.7)	2 (0.3)	6.6 (0.9)
Glycerol (35 m*l*) +MeOH (15 m*l*)	10 (3.3)	87 (27.1)	3 (0.9)	0.5 (0.2)	11 (3.5)	86 (27.5)	3 (1.0)	0.4 (0.1)
H_2O[a]	16	82	2	114	17	81	2	112

a) By Kwiatek and Seyler[2]; CN/Co=5.1, 200 m*l* H_2O, 0.15 M cobalt, 0.15 M KOH
b), c) See footnotes b) and c) in Table 1

1) K. Tarama and T. Funabiki, This Bulletin, **41**, 1744 (1968).

2) J. Kwiatek and J. K. Seyler, *Advan. Chem. Ser.*, **70**, 207 (1968).