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Electrocatalytic Chemistry of the Transition Metal Complexes. III. Dehydrogenation of Cyclohexadienes Catalyzed by the Electro-reduced Cobalt Complex of $\alpha,\beta,\gamma,\delta$-Tetraphenylporphine

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Although there are some reports on the disproportionation of 1,3- and 1,4-cyclohexadiene (CHD) to produce benzene and cyclohexene,[1] only a few reports have appeared in which 1,3- and 1,4-CHD were dehydrogenated to produce benzene by using the homogeneous transition metal complexes such as the metal complexes of $\alpha,\beta,\gamma,\delta$-tetraphenylporphine (M(TPP)),[2] and dichloropalladium(II).[3]

In the previous papers,[4,5] the authors reported that the electro-reduced Co(TPP) had the catalytic activity of dehydrogenating cyclohexene to 1,3- and 1,4-CHD, and benzene (Bz). In this paper, the dehydrogenation reaction of 1,3- and 1,4-CHD by using the same catalyst will be described.

Experimental

Tetra-*n*-butylammonium perchlorate (TBAP),[6] Co(TPP),[7] 1,4-CHD,[8] and 1,3-CHD[9] were prepared according to the published methods. The conditions of electrolysis were: the concentration of Co(TPP), 1.0×10^{-3} mol/l; the concentration of TBAP, 2.0×10^{-1} mol/l; solvent, 10.0 ml; an anode, a platinum wire; a cathode, a platinum plate (the electrode area, 3.0 cm^2); a reference electrode, a silver wire; potential, −2.0 V; temperature, room temperature; reaction time, 24 hr; atmosphere, nitrogen; a electrolyzer, a Yanagimoto Controlled Potential Electrolyzer Model VE-3S; and an electrolytic cell, an H-type cell with a side arm to enable the insertion of an Ag wire reference electrode. The quantitative analysis of the products was performed by glc. The visible spectra of the reaction solution after electrolysis were measured using a Shimadzu Model MPS-50L Spectrophotometer.

Results and Discussion

Dehydrogenation of 1,3- and 1,4-CHD. The current efficiency for formation of benzene was defined as

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Table 1. Dehydrogenation of 1,3- and 1,4-cyclohexadiene catalyzed by the electro-reduced Co(TPP) in various solvents

Solvent	CHD	CHD/Co molar ratio	Composition of the products (%)					η'_{Bz} (%)[c]
			cC_6[a]	cC_6'[b]	1,3-CHD	1,4-CHD	Bz	
DMF	1,3	159	0	0	100	0	0	0
	1,4	128	0	6.1	15.5	68.9	6.0	104
HMPT	1,3	154	0	0	100	0	0	0
	1,4	131	0	0	0	93.0	7.0	81.2
PhCN	1,3	147	0	0	87.0	7.0	6.0	126
	1,4	121	4.5	0	0	75.7	19.8	408

Conditions: an anode, a Pt wire; a cathode, a Pt plate; a reference electrode, an Ag wire; the concentration of Co(TPP), 1.0×10^{-2} mol/l, the concentration of TBAP, 2.0×10^{-1} mol/l, potential, −2.0 V; solvent, 10.0 ml; temperature, r.t.; reaction time, 24 hr.

a) cyclohexane b) cyclohexene c) current efficiency for formation of benzene.

follows:

$$\eta'_{Bz}\,(\%) = (\text{Amount of Bz(mole)}) \times 200/\text{Current passage (Faraday)}$$

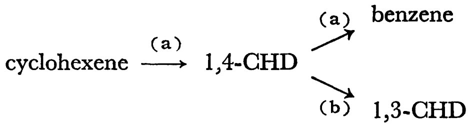
The results are shown in Table 1. In the electrolysis of 1,4-CHD with the use of dimethylformamide (DMF), hexamethylphosphoric triamide (HMPT), and benzonitrile (PhCN) as the solvent, the current efficiencies were higher than 100%, indicating that the dehydrogenation reaction is catalytic. The current efficiencies in the electrolysis of 1,3-CHD were much lower than those in the electrolysis of 1,4-CHD. Furthermore, the current efficiency in the case of PhCN used as the solvent was much higher than the current efficiencies in that of DMF and HMPT used.

In the 1,4-CHD–DMF system, 1,4-CHD was isomerized to produce 1,3-CHD. Cyclohexene and benzene were also produced in the same system, which are considered to be derived from the disproportionation of 1,4-CHD, since the amount of benzene was about equal to that of cyclohexene.[1] In the 1,4-CHD–HMPT system, 1,4-CHD was dehydrogenated to afford benzene, but 1,3-CHD was not observed in the reaction system.

In the 1,3-CHD–PhCN system, 1,3-CHD was isomerized to give 1,4-CHD, and was also dehydrogenated to produce benzene. However, in the 1,4-CHD–PhCN system, 1,4-CHD was not isomerized, but was dehydrogenated to produce benzene, and a little amount of cyclohexane was formed.

The reaction schemes in the case of the above three solvents used are summarized as follows:

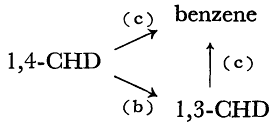
in the case of DMF used as the solvent;



in the case of HMPT used as the solvent;

$$1,4\text{-CHD} \xrightarrow{(c)} \text{benzene}$$

in the case of PhCN used as the solvent;



(a) disproportionation, (b) isomerization, (c) dehydrogenation

Effect of Addition of Methanol. The current efficiencies decreased with the addition of dry methanol to the reaction solution as shown in Table 2. The similar results have been reported in the dehydrogenation of cyclohexene catalyzed by the electro-reduced Co(TPP).[5] It may be reasonable to assume that added alcohol reacts with the conjugated ring of the catalytically active electro-reduced Co(TPP) to cleave or weaken the conjugated ring.

The Visible Spectra of the Reaction Solution after Electrolysis. In the visible spectrum of the HMPT solution containing 1,4-CHD after electrolysis, the new bands appeared at 620 and 417 nm, which were assigned to the Q-band and Soret-band, respectively, of the cobalt complex of $\alpha,\beta,\gamma,\delta$-tetraphenylchlorin (Co(TPC)) in which two hydrogen atoms are attached to a pyrrole

Table 2. Effect of addition of methanol

Solvent	CHD	CHD/Co molar ratio	MeOH/Co molar ratio	Composition of the products (%)					η'_{Bz} (%)
				cC_6	cC_6'	1,3-CHD	1,4-CHD	Bz	
DMF	1,3	102	138	0	0	100	0	0	0
	1,4	80	135	0	0.6	7.3	73.8	18.3	59.3
HMPT	1,3	101	131	0	0	100	0	0	0
	1,4	102	132	0	1.5	2.4	93.3	2.8	31.0
PhCN	1,3	99	137	0.1	0	56.9	0	43.0	72.6
	1,4	106	132	0	0	0	53.2	46.8	174

fragment of porphyrin skeleton.[10]

In a previous paper,[5] the authors reported that the active species for the dehydrogenation of cyclohexene could be the species electro-reduced at -2.0 V *vs.* Ag wire, *viz.*, $[\mathrm{Co^I(TPP)^{\dot{-}}}]^-$, and the formation of Co(TPC) was observed in the electrolysis of cyclohexene by using dioxane as the solvent.

From the above results, therefore, it may be reasonable to assume that the active species for the dehydrogenation of 1,3- and 1,4-CHD was analogous to that for the dehydrogenation of cyclohexene.

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