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THE ELECTROCATALYTIC CHEMISTRY OF TRANSITION METAL COMPLEXES I. DEHYDROGENATION OF CYCLOHEXENE BY THE ELECTROREDUCED METAL COMPLEXES OF α,β,γ,δ-TETRAPHENYLPORPHINE I.

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The cobalt complex of α,β,γ,δ-tetraphenylporphine reduced by electrolysis had the catalytic activity of dehydrogenating cyclohexene to 1,3- and 1,4-cyclohexadiene and benzene. The composition of the dehydrogenated products depended upon the solvents used. An anion radical of Co(I) complex was assumed the intermediate based on e.s.r. and polarographic data.

The reduction and oxidation of metal complexes of α,β,γ,δ-tetraphenylporphine (TPP) by electrolysis, chemical reaction or photoreaction have been extensively studied.

We have now investigated the electrolysis of transition metal TPP complexes M(TPP) (M=Co(II), Ni(II), Fe(III), Pd(II), Pt(II), Cu(II), Mn(III) and V(IV)), which were prepared by the Calvin's method[1] in the presence of excess cyclohexene and found that 1,3-cyclohexadiene, 1,4-cyclohexadiene and benzene were electrocatalytically formed by using cobalt TPP complex. Other transition metal TPP complexes did not give any dehydrogenated products. The composition of the products depended upon the solvents used as shown in Table 1. When dimethylformamide (DMF), dioxane or hexamethylphosphoric triamide (HMPT) was used as the solvent, 1,3- and 1,4-cyclohexadiene were formed. On the other hand, by using benzonitrile or dimethyl sulfoxide (DMSO), benzene was yielded and cyclohexadienes were not observed in the reaction solution. The current efficiencies of the dehydrogenated products were much higher than 100%, indicating that this reaction is catalytic. However, there was found no direct relation between the dielectric constants of solvent and the current efficiencies of the products. The current efficiency, $\eta_{CHD}+\eta_{Bz}$ increased with increasing the reaction temperature, and the composition of the products was markedly varied. The electrolysis of Co(TPP) in a DMF solution of cyclohexene at 20° gave only cyclohexadienes. However the reaction at 55° yielded cyclohexadienes and benzene, while the reaction at 75° produced only benzene. These results were shown in Figure 1. The polarography of the Co(TPP) shows the first half wave potential at -0.82 v and the second at -1.87 v vs SCE[2].

The dehydrogenated products were yielded only when the reaction solution was electrolyzed at -2.0 v vs Ag/Ag^+. The products were not formed when the reaction solution was kept at room temperature under nitrogen or oxygen and not electrolyzed or when the electrolysis was carried out at -1.5 v vs Ag/Ag^+. Therefore,

Table 1. Dehydrogenation of cyclohexene catalyzed by the electroreduced Co(TPP) in a variety of solvents.[a)]

Solvent	cC_6'/Co	Yield(%) CHD[b)]	Yield(%) Bz	CHD/Co	Bz/Co	η_{CHD}	η_{Bz}	Dielectric constant
dioxane	195	6.88	0	14.3	0	277	0	2.28
pyridine	204	trace	trace	~0	~0	~0	~0	12.3
PhCN	212	trace	11.0	~0	23.3	~0	872	25.2
HMPT	204	2.02	0	4.11	0	180	0	30
DMF	202	4.73	0	9.52	0	160	0	36.7
DMSO	204	trace	3.23	~0	6.58	~0	274	49

a) conditions: anode, Pt coil; cathode, Pt plate(the electrode area, 2.7 cm^2); reference electrode, Ag coil; supporting electrolyte $(n\text{-}Bu)_4NClO_4$, 2.0×10^{-1} mol/l; concentration of Co(TPP), 1.0×10^{-2} mol/l; electrolysis at -2.0 V vs Ag/Ag$^+$; time, 24 hours; temperature, room temp.(19-23°C).

b) the total amount of 1,3- and 1,4-cyclohexadiene.

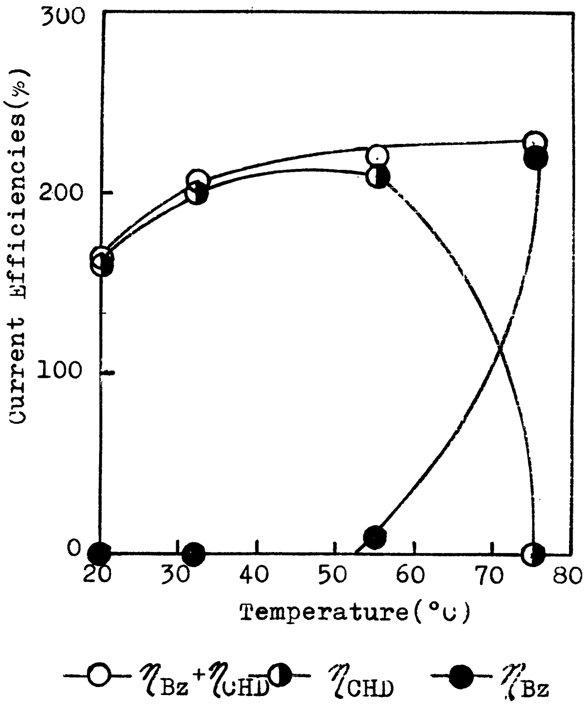

Fig. 1. Effects of reaction temperature

these results indicates that this reaction is not catalyzed by the Co^{I}(TPP) or Co^{II}(TPP). The electrolysis by using cell with diaphragm gave the products only in the dark green solution of catholyte.

The e.s.r. spectra of the reaction solution under electrolysis showed no signal at the first half wave potential, but a signal(g=2.003; peak-to-peak width, 5.7 gauss; total width, 12 gauss) at the second half wave potential similar to those ascribed to [M(TPP)]$^{\cdot-}$ (M=Zn, Cd, Mg or H_2).[2)]

Felton et al.[2)] reported that the electrolysis of Co^{II}(TPP) at the first half wave potential yields Co^{I}(TPP).

On the other hand, the e.s.r. characteristics of the signal observed at the second half wave potential indicates that electron delocalizes on the conjugated ring of the porphyrin. Therefore, it may be reasonable to conclude that the signal at g=2.003 observed at the second half wave potential is due to [Co^{I}(TPP)]$^{\cdot-}$ and this species is an intermediate for dehydrogenating cyclohexene to cyclohexadienes and benzene.

References

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