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New Reduction Catalysis of Metalloporphyrins. Catalytic Reduction of Nitrobenzene to Aniline with Tetraphenylporphyrinato-iron(III) Chloride-$NaBH_4$ System

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The (TPP)FeCl-$NaBH_4$ system performs remarkably efficient catalytic reduction of nitrobenzene to aniline. (TPP)Co and (TPP)MnCl also catalyze the reduction of p-chloronitrobenzene to p-chloroaniline, while their catalytic activities are much lower than that of (TPP)FeCl.

Because of the many interesting catalyses of cytochrome P-450,$^{1)}$ various attempts to perform its model reactions with metalloporphyrins have been actively made in the last decade.$^{2)}$ These attempts have been concentrated mainly on the modeling of the oxidation catalyses of cytochrome P-450. However, attempts to mimic reduction catalyses of cytochrome P-450 have been reported limitedly,$^{3-8)}$ whereas it also catalyzes reduction of nitro and azo compounds$^{9a)}$ and reductive dehalogenation of alkylhalides$^{9b)}$ when combined with NADPH (nicotineamide adenine dihydride). These reduction catalyses of cytochrome P-450 are not surprising because cytochrome P-450 reductively activates an oxygen molecule by accepting electrons from NADPH.$^{1,2a)}$ In this work, we examined catalytic reduction of nitrobenzene by using metalloporphyrin and $NaBH_4$ as the model reaction of cytochrome P-450 and NADPH.

In a typical run, (TPP)FeCl (0.05 mmol dm^{-3}), $NaBH_4$ (130 mmol dm^{-3}), and aromatic nitro compound (80 mmol dm^{-3}) were dissolved in a diglyme under nitrogen atmosphere, and the solution was stirred at 30 °C. This concentration of (TPP)FeCl was adopted by referring the previously reported model reduction of NO_2^- catalyzed with (TPPS)Fe(III)(H_2O),$^{5)}$ whereas the concentrations of the substrate and $NaBH_4$ were much higher than the previous ones$^{5)}$ because of the significantly higher turn over numbers of the present system (vide infra). An aliquot of 100 μl was taken from the reaction solution at an appropriate time-interval, and then the reactant and the product were monitored by HPLC (column: JASCO Finepak SIL C18-10, eluent: 60 vol% ethanol-water).

Although the reduction did not occur at all in the absence of (TPP)FeCl, the reduction of nitrobenzene by the (TPP)FeCl-$NaBH_4$ system rapidly proceeded, as shown in Fig. 1. Aniline was found as the sole product by HPLC analysis. Its yield was near to 100% after 24 h under a reaction condition described above. The turnover numbers of the catalyst were ca.500 after 0.5 h and ca.1700 after 24 h, as shown in Table 1. p-Chloronitrobenzene was also reduced by the same catalytic system. It has been known that for reduction of aromatic nitro compounds such a strong hydride reagent as $NaBH_2S_3$ and a higher temperature (e.g., reflux in THF) are necessary. The (TPP)FeCl-$NaBH_4$ system can reduce aromatic nitro compounds under mild condition (room temperature, weak hydride reagent, and very dilute concentration of catalyst). Therefore, the (TPP)FeCl-$NaBH_4$ system is a highly efficient reduction catalyst.

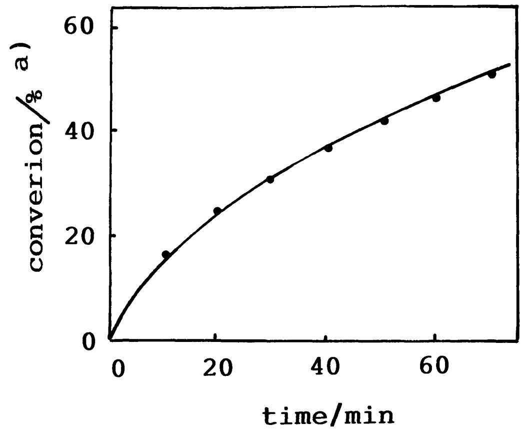

Fig. 1. Time-curve of reduction of nitrobenzene with (TPP)FeCl-$NaBH_4$.
a) Based on substrate. See text for reaction conditions.

The similar reduction was examined with (TPP)MnCl-$NaBH_4$ and (TPP)Co-$NaBH_4$ systems. Both systems, however, did not reduce nitrobenzene but p-chloronitrobenzene. As shown in Table 1, their catalytic activities were much lower than that of the (TPP)FeCl-$NaBH_4$ system.

Visible and ESR spectra were measured for analysis of the active species of the catalytic system. In the ESR spectra, the typical high spin signals due to (TPP)Fe(III)Cl disappeared upon addition of $NaBH_4$ and no signal was observed at liq. N_2 temperature. It has been known that

Table 1. Turnover numbers in catalytic reduction of nitrobenzene, **1**, and p-chloronitrobenzene, **2**, with the metalloporphyrin-$NaBH_4$ system

Catalyst	(mmol dm^{-3})	$NaBH_4$ (mmol dm^{-3})	Substrate (mmol dm^{-3})	Time / h	Turn over numbers **1**	**2**
(TPP)FeCl	5.0×10^{-2}	130	80	0.5	500	450
				1	740	630
				24	1700	
(TPP)Co	5.0×10^{-1}	130	80	24	unknown product	90
(TPP)MnCl	5.0×10^{-1}	130	80	24	0	30

porphyrinato-iron(II) shows no ESR signal at liq. N_2 temperature,[10a)] while porphyrinato-iron(I) has been reported to be ESR active.[11)] Therefore, no ESR signal observed in this catalytic system suggests that only porphyrinato-iron(II) exists probably as an active species. Visible spectra offered additional informations about the porphyrinato-iron(II) complex. Addition of $NaBH_4$ to (TPP)FeCl significantly changed the visible spectrum, as shown in Fig. 2. Although $NaBH_4$ has been known to reduce porphyrinato-iron(III) to porphyrinato-iron(II),[12)] the spectrum obtained here differed from that of (TPP)Fe(II)$(THF)_2$ reported before.[10b)] This difference strongly suggests that (TPP)Fe(II) is coordinated by either H^- or BH_4^-. Further addition of nitrobenzene to the (TPP)FeCl-$NaBH_4$ system significantly enlarged an absorption around 610 nm, while an absorption of 500 - 550 nm hardly changed upon addition of nitrobenzene. This result suggests that a new species is formed. Because an absorption around 550 nm of porphyrinato-iron(II) has been reported to grow larger upon amine coordination,[13)] the enlargement of the absorption around 610 nm would be interpreted in terms of coordination of aniline which is formed from nitrobenzene. A difference in λ_{max} of the absorption between the present catalytic system (about 610 nm) and the previously reported bis(pyridine)porphyrinato-iron(II) complex (around 550 nm)[13)] is not surprising because coordination of either the H^- or BH_4^- ligand would cause red-shift of the absorption. In the case of (TPP)Co, a clear change of visible spectra was not observed upon adding $NaBH_4$ and substrate, but the absorptions grew slightly larger. In the case of (TPP)MnCl, addition of $NaBH_4$ yielded visible absorptions very similar to those of (TPP)Mn(II).[14,15)] This result indicate that (TPP)Mn(II) would be an active species.

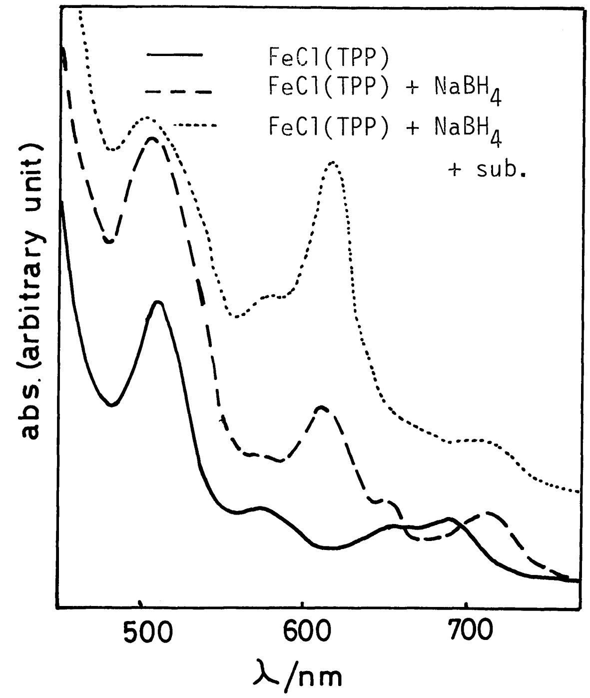

Fig. 2. Visible spectra of the (TPP)FeCl catalytic system.

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15) The absorption increases upon addition of nitrobenzene. This is probably due to coordination of aniline produced by (TPP)Mn(II), like in the case of (TPP)FeCl-$NaBH_4$ system.

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