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# An Electrochemical Evidence for the Participation of Iron(IV) Porpyrin Species in the C-C Bond Cleavage of 1,2-Diaryl-1,2-ethanediol

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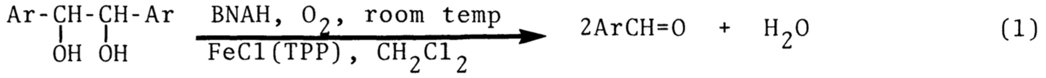
Cyclic voltammogram of a mixture of tetraphenylporphrinato-iron(III) and 1,2-bis(4-methoxyphenyl)ethane-1,2-diol in dichloromethane showed a catalytic wave at the potential corresponding to the oxidation of Fe(III) to Fe(IV). The rate of reaction of Fe(IV) with the diol following the electrochemical process was determined.

As a model system mimicking cytochrome P-450$_{scc}$, which catalyzes the physiologically important C-C cleavage of diol on the cholesterol side chain in the adrenal cortex, we reported the related cleavage of 1,2-diol to aldehyde in the presence of molecular oxygen, meso-tetraphenylporphyrinatoiron(III), (**1**), and 1-benzyl-1,4-dihydronicotinamide, (BNAH), an NADPH analogue.$^{1)}$ In those reports,



$$\underset{\text{OH}}{\text{Ar-CH}}\text{-}\underset{\text{OH}}{\text{CH}}\text{-Ar} \xrightarrow[\text{FeCl(TPP), CH}_2\text{Cl}_2]{\text{BNAH, O}_2\text{, room temp}} \text{2ArCH=O} + \text{H}_2\text{O} \qquad (1)$$

the iron(IV) species was proposed as the active species of the catalytic process. Although supporting evidence for diol cleavage by iron(IV) porphyrin complex was presented by using a stoichiometric amount of iron(IV) complex,$^{1b)}$ its participation in the catalytic process was still unconvincing. In this report, we communicate the electrochemical evidence for the participation of iron(IV) complex as the active catalyst of the reaction by cyclic voltammetry.

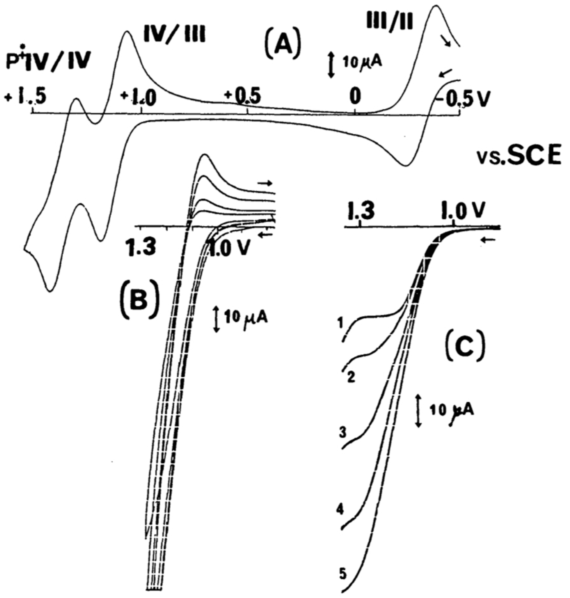


Fig. 1.
(A); **1**, 6x10$^{-4}$ M, 44 mV/s. (B); **1** + **2** (0.2 M). Scan rate, 80, 57, 23, and 11 mV/s.
(C); Dependence of limiting current on concn of **2** (from 1 to 5, 0.73, 1.58, 2.80, 5.36, and 6.69x10$^{-3}$ M), 5 mV/s.

The cyclic voltammogram was measured in a dichloromethane solution of **1** (6.0 x 10$^{-4}$ M) containing tetrabutylammonium perchlorate (0.1 M) with using glassy carbon as the working electrode, platinum wire as the counter electrode, and a saturated calomel electrode as the reference at 25.0 °C under nitrogen atmosphere. The voltammogram of Fe(TPP)Cl is shown in Fig. 1A. In accordance with the results in literature,$^{2)}$ reversible peaks are present at -0.31 V, 1.14 V, and 1.39 V to SCE, which correspond to the redox couples of

Fe(III)/Fe(II), Fe(IV)/Fe(III), and Fe(IV)P(+.)/Fe(IV), respectively. Addition of 0.2 M of benzyl alcohol to this solution had influence on the last redox couple without any significant change in the region of Fe(IV)/Fe(III). However, when 1,2-bis(4-methoxyphenyl)ethanediol, (**2**), the substrate of the model reaction, was added to the solution of **1**, the peaks of the Fe(IV)/Fe(III) redox couple showed distinct changes as shown in Fig. 1B: A catalytic reaction (EC' mechanism)3) occurred in the oxidation step of Fe(III) to Fe(IV), and the corresponding reductive wave eventually disappeared at the slow scan speed. The voltammogram of **2** measured in the absence of **1** was irreversible and the oxidative wave is observed at a higher potential (1.35 V) without the participation of a catalytic reaction.

The results presented above clearly indicate that the chemical reduction of Fe(IV) by **2** takes place with Fe(IV) electrochemically generated on the electrode, supporting the participation of Fe(IV) in the catalytic aerobic C-C bond cleavage of diol. The rate of the chemical process estimated from Eq. 24)

$$i_\infty = nFAC_r^*(DC_z^*k)^{1/2} \qquad (2)$$

was 65 $M^{-1}s^{-1}$. This catalytic reaction was not observed in the voltammogram of **1** in the presence of monometyl ether of **2**, (**3**). Together with the fact that the catalytic C-C bond cleavage of **3** proceeds very slowly compared with **2**,1) this observation suggests that the cleavage of **3** proceeds by a different mechanism to that of diol itself, such as photochemical decomposition of Fe(III) diolate complex,1b) for example. The facts that conversion of Fe(II) to Fe(III)alkoxide proceeds quickly by treatment with $O_2$ in the presence of alcohol,5) that the reaction of Fe(II)P with $O_2$ produces Fe(IV)P at low temperature,6) and that $Fe(IV)P(OR)_2$ is converted to FeP(OR)(III) spontaneously at room temperature,7) all present support for the participation of Fe(IV) species in the catalytic glycol cleavage of Eq. 1. Since epoxidation of olefin does not proceed with our system, it seems likely that Fe(TPP)Cl-BNAH-$O_2$ is a pure system of producing Fe(IV) without contamination of Fe(IV)P(+.).

References
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2) K. M. Kadish, M. M. Morrison, L. A. Constant, L. Dickens, and D. G. Davis, J. Am. Chem. Soc., **98**, 8387 (1976).
3) A. J. Bard and L. R. Faulkner, "Electrochemical Methods, Fundamentals and Applications," John Wiley and Sons, Inc., New York (1980), p.455.
4) Reference 3, p.457; $i_\infty$ = limiting current, A = area of electrode, $C_r^*$ = concn of **1**, D = diffusion constant, $C_z^*$ = concn of **2**, and k = rate of reaction.
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