Biomimetic Oxidation with Molecular Oxygen. Selective Carbon-Carbon Bond Cleavage of 1,2-Diols by Molecular Oxygen and Dihydropyridine in the Presence of Iron-Porphyrin Catalysts

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Abstract: The selective carbon-carbon bond cleavage of 1,2-diols in the presence of an iron-porphyrin complex, molecular oxygen, and 1-benzyl-3-carbamoyl-1,4-dihydropyridine is reported. The C-C bonds of aryl-substituted ethane-1,2-diols were cleaved exclusively to aldehydes or ketones as the oxidation products at room temperature. The reaction rates were influenced by the steric hindrance of the substituents both in the catalysts and diols, but no differences in the reactivities were observed between the two stereo isomers (meso and dl) of diols. A kinetic analysis of this bond cleavage reaction is consistent with the reaction mechanism consisting of the initial binding of diol on the active catalyst forming an intermediate complex and its subsequent breakdown in the rate-determining step of the catalytic cycle. The initial binding step is favorable for electron-deficient diols and is influenced by steric hindrance, whereas the rate-determining bond cleavage step is accelerated by electron-rich diols and unaffected by the steric effect. The mechanism of this diol cleavage reaction is discussed on the basis of these observations.

Transition-metal-catalyzed reactions of molecular oxygen with various organic compounds are important processes for the mimesis of metal-containing oxidases and oxygenases. Particularly, the reactions catalyzed by iron and manganese porphyrin complexes have attracted attention in relevance to the activation of molecular oxygen and oxygen atom transfer to organic substrates, which are processes dependent on cytochrome P-450 in biological systems.[1,2]

As models of the so-called shunt mechanism using exogenous oxidants several systems composed of synthetic metalloporphyrins and single-oxygen donors were reported.[2,3] High-valent oxo-iron-porphyrin complexes have been recognized as the active intermediates for the shunt cycles,[4] and the mechanism of oxygen atom transfer from iron to the substrates has been a subject of extensive investigation from various points of view such as kinetics,[5] stereoselectivity,[6] molecular rearrangement,[7] and deuterium isotope effects.[8] Cytochrome P-450 actually utilizes such single-oxygen donors as the oxygen source, and evidence supporting the participation of an oxometal intermediate in the catalysis by cytochrome P-450 is now increasing. Enzyme-like reactions by the catalysis of metal-porphyrin complexes have also been reported by using molecular oxygen as the oxygen source in the presence of reductants such as sodium ascorbate,[9] sodium tetrahydroborate,[10] H_2/Pt,[11] and FMN/MNAH,[12,13] as well as electrochemical reduction.[14] However, such a system utilizing molecular oxygen is complicated[15] and not suitable for kinetic analysis.

We reported previously[16] the aerobic carbon-carbon bond cleavage of 1,2-bis(*p*-methoxyphenyl)ethane-1,2-diol catalyzed by chloro(*meso*-tetraphenylporphyrinato)iron(III) ((TPP)FeCl) in the presence of 1-benzyl-3-carbamoyl-1,4-dihydropyridine (BNAH), an NAD(P)H analogue. This reaction simulates the final step of the side chain cleavage of cholesterol catalyzed by cytochrome P-450_{scc} in the steroidal hormone biosynthesis,[17] which induces successive hydroxylations of C-H groups at C-20 and C-22 followed by the fission of the C-C bond of the vicinal diol into two carbonyl compounds.[18] This kind of oxidative C-C bond scission is unique among the reactions of P-450 catalysis. Recently, Ortiz de Montellano suggested two mechanisms involving the intermediate formation of a high-valent oxoiron complex for the bond cleavage catalyzed by cytochrome P-450_{scc},[19] one of which proceeds through the addition of a hydroxyl group of diol to the activated oxygen atom coordinated on the iron center, and the other is the abstraction of a hydrogen atom or an electron and a proton from one of the hydroxyl groups of substrate. However, no evidence for these mechanisms has been presented either in

(1) For recent reviews see: (a) Ortiz de Montellano, P. R., Ed. *Cytochrome P-450, Structure, Mechanism, and Biochemistry*; Plenum: New York, 1986. (b) Guengerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9-16.

(2) (a) McMurry, T. J.; Groves, J. T., ref 1a, Chapter 1. (b) Meunier, B. *Bull. Soc. Chem. Fr.* **1986**, 578-594.

(3) For recent reports for the iron porphyrin-oxidant system see: (a) Traylor, T. G.; Nakano, T.; Miksztal, A. R.; Dunlap, B. E. *J. Am. Chem. Soc.* **1987**, *109*, 3625-3632. (b) Bruice, T. C.; Michael Dicken, C.; Balasubramanian, P. N.; Woon, T. C. *Ibid.* **1987**, *109*, 3436-3443. (c) Ostovic, D.; Knobler, C. B.; Bruice, T. C. *Ibid.* **1987**, *109*, 3444-3451.

(4) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884-2886.

(5) (a) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Brauman, J. I.; Papazian, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4343-4345. (b) Traylor, T. G.; Marsters, J. C.; Nakano, T.; Dunlap, B. E. *Ibid.* **1985**, *107*, 5537-5539. (c) Groves, J. T.; Watanabe, Y. *Ibid.* **1986**, *108*, 507-508.

(6) Traylor, T. G.; Nakano, T.; Dunlap, B. E.; Traylor, P. S.; Dolphin, D. *J. Am. Chem. Soc.* **1986**, *108*, 2782-2784.

(7) (a) Groves, J. T.; Subramanian, D. V. *J. Am. Chem. Soc.* **1984**, *106*, 2177-2181. (b) Collman, J. P.; Kodadek, T.; Brauman, J. I. *Ibid.* **1986**, *108*, 2558-2594. (c) Traylor, T. G.; Miksztral, A. R. *Ibid.* **1987**, *109*, 2270-2274 and references cited therein.

(8) Lindsay Smith, J. R.; Piggott, R. E.; Sleath, P. R. *J. Chem. Soc., Chem. Commun.* **1982**, 55-56.

(9) Munsuy, D.; Laclaire, J.; Fontecave, M.; Momenteau, M. *Tetrahedron* **1984**, *40*, 4297-4311.

(10) (a) Tabushi, I.; Koga, N. *J. Am. Chem. Soc.* **1979**, *101*, 6456-6458. (b) Perree-Fauvet, M.; Gaudemer, A. *J. Chem. Soc., Chem. Commun.* **1981**, 874-875.

(11) (a) Tabushi, I.; Yazaki, A. *J. Am. Chem. Soc.* **1981**, *103*, 7371-7373. (b) Tabushi, I.; Morimitu, K. *Ibid.* **1984**, *106*, 6871-6872.

(12) Tabushi, I.; Kodera, M. *J. Am. Chem. Soc.* **1986**, *108*, 1101-1103.

(13) Abbreviations used: TPP, 5,10,15,20-tetraphenylporphyrin dianion; TTP, 5,10,15,20-tetra(*o*-tolyl)porphyrin dianion; Tp-ClPP, 5,10,15,20-tetrakis(*p*-chlorophenyl)porphyrin dianion; TMP, 5,10,15,20-tetramesitylporphyrin dianion; acac, 2,4-pentanedione anion; BNAH, 1-benzyl-3-carbamoyl-1,4-dihydropyridine; MNAH, 1-methyl-3-carbamoyl-1,4-dihydropyridine; FMN, Flavin mono nucleoside; *N*-MeIm, 1-methylimidazole; py, pyridine; DMF, *N*,*N*-dimethylformamide.

(14) Creager, S. E.; Raybuck, S. A.; Murray, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 4225-4227.

(15) Tabushi, I.; Kodera, M.; Yokoyama, M. *J. Am. Chem. Soc.* **1985**, *107*, 4466-4473.

(16) Okamoto, T.; Sasaki, K.; Shimada, M.; Oka, S. *J. Chem. Soc., Chem. Commun.* **1985**, 381-383.

(17) Burstein, S.; Gut, M. C. *Recent Prog. Horm. Res.* **1971**, *27*, 303-349.

(18) (a) Shikita, M.; Hall, P. F. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 1441-1445. (b) Byon, C. Y.; Gut, M. *Biochem. Biophys. Res. Commun.* **1980**, *94*, 549-552.

(19) Ortiz de Montellano, P. R., ref 1a, p 250.

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Table I. Transition-Metal-Catalyzed Bond Cleavage of **1a**[a]

catalyst	solvent	reaction time, h	yield of **2a**,[b] %
(TPP)FeCl	Me_2SO	4[c]	18
	DMF	4[c]	19
	pyridine	4[c]	18
	CH_2Cl_2	4[c]	52
	CH_2Cl_2	8	99
(TPP)$FeClO_4$	CH_2Cl_2	8	99
$[(TPP)Fe]_2O$	CH_2Cl_2	8	0
(TTP)FeCl	CH_2Cl_2	4	99
(TMP)FeCl	CH_2Cl_2	8	64
(Tp-ClPP)FeCl	CH_2Cl_2	8	91
$(acac)_2Fe$	CH_2Cl_2	12[c]	10
(TPP)MnOAc	CH_2Cl_2	8	13
(TPP)Co	CH_2Cl_2	8	2[d]

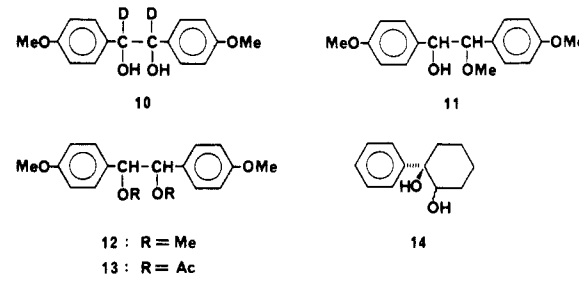
[a] Reactions were carried out under the following conditions by using a merry-go-round apparatus: (TPP)FeCl, 1.0×10^{-3} mmol; BNAH, 2.0×10^{-2} mmol; **1a**, 1.0×10^{-2} mmol; solvent, 1 mL under dry air irradiated by visible light with Fuji SC-42 cut-off filter at room temperature. [b] Yields were calculated on the basis of **1a** used. [c] Merry-go-round apparatus was not used. [d] *p,p'*-Dimethoxybenzoin was detected in a 20% yield as the main product.

the native enzymic systems or in model studies. The diol cleavage reported here is also closely related to the lignin degradation by hemoprotein ligninase. Participation of the high-valent oxo–metal–porphyrin complex has been postulated in these biological degradation reactions of natural polyoxygen compounds.[20]

Sligar and co-worker reported that a non-enzymatic system consisting of (TPP)CrCl and *p*-cyano-*N,N*-dimethylaniline *N*-oxide was effective for this type of bond cleavage. The active species of the reaction is shown as a high-valent oxochromium complex.[21] However, since the rate-limiting step in this system is probably the formation of an oxochromium complex by oxygen transfer from the oxidant to chromium metal ion, no mechanistic information of the following C–C bond scission has been obtained so far for the catalytic bond cleavage.[22]

Herein, we report the scope, limitation, and kinetic results of the selective C–C bond cleavage of 1,2-diols to the corresponding aldehydes or ketones by the system composed of iron porphyrin, BNAH, and molecular oxygen. Our kinetic study indicated that the dependence of initial rates on the substrate concentrations had an asymptote at a high substrate concentration and that the relative order of reactivity of some para-substituted diphenylethanediols in separate reactions was reversed in competitive reactions. These observations are interpreted in terms of the Michaelis–Menten relationship and indicate the reversible binding of the diol to the iron catalyst, forming an iron–diol intermediate complex. The breakdown of this complex to the product is the rate-determining step of the catalytic cycle. Michaelis constants determined by the general procedure (Lineweaver–Burk plot) revealed that the former binding process is accelerated by electronegative substituents and is influenced by marked steric hindrance. On the contrary, the latter product-forming process is little affected by the steric effect and is slightly accelerated by electropositive substituents. This system closely resembles the system of epoxidation of olefins reported by Collman and coworkers with hypochlorite and the Mn(TPP)Cl catalyst,[23] which suggests that the two metal–porphyrin-catalyzed reactions, the aerobic C–C bond cleavage of diols and epoxidation of olefins with hypochlorite, proceed, at least in part, by similar mechanisms.

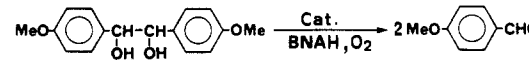
Chart I



To our knowledge, this bond cleavage is the first example suggesting the importance of selective coordination of substrate in the metalloporphyrin-catalyzed oxidation with molecular oxygen.

Results

General Scope of the Bond Cleavage of 1,2-Diols. 1,2-Bis(*p*-methoxyphenyl)-1,2-ethanediol (**1a**) (1.0×10^{-2} M) was converted to *p*-metoxybenzaldehyde (**2a**) in a quantitative yield via carbon–carbon bond cleavage in the presence of 10 mol % of (tetraarylporphyrinato)iron(III) and 200 mol % of BNAH in dichloromethane under dry air at room temperature. No other products such as *p,p'*-dimethoxybenzoin, *p,p'*-dimethoxybenzil, *p*-methoxybenzoic acid, and *p*-methoxybenzyl alcohol were formed. The catalyst, BNAH, and molecular oxygen were essential for the reaction and irradiation by visible light had an accelerating effect. Replacing air for the atmospheric pressure of oxygen also gave the same results, but accelerated the degradation of the catalyst. Dichloromethane was the most suitable solvent in both reactivity and selectivity for the C–C bond cleavage. Polar solvents such as DMSO and DMF as well as pyridine were less effective as shown in Table I.



1a **2a**

A number of iron(III)–porphyrin complexes were effective catalysts for the reaction (Table I). (TTP)FeCl was the most reactive catalyst examined, and sterically crowded (TMP)FeCl was less reactive. (TPP)Mn(OAc) showed low reactivity, and catalysis by (TPP)Co gave only negligible amounts of the cleavage product with concomitant formation of the dehydrogenation product, *p,p'*-dimethoxybenzoin, as the major product. The μ-oxo dimer, $[(TPP)Fe]_2O$, showed no detectable catalytic activity.

The reactions with various 1,2-diols by using (TPP)FeCl as the catalyst were examined under the following reaction conditions (standard reaction conditions): (TPP)FeCl, 1.0×10^{-3} M; diol, 1.0×10^{-2} M; BNAH, 2.0×10^{-2} M in CH_2Cl_2 at room temperature under irradiation of visible light. Table II shows the results. Diaryl- and tetraarylethane-1,2-diols were cleaved to the corresponding benzaldehydes and benzophenones in good yields. The reactivity of phenylethanediol (**4**), 1,4-diphenylbutane-2,3-diol (**8**), or 1,6-diphenylhexane-3,4-diol (**7**) was low compared with that of 1,2-diarylethanediols. The reaction of 1,2-dicyclopropyl-1,2-diphenylethane-1,2-diol (**6**) occurred very slowly and gave only cyclopropyl phenyl ketone as the product. No products such as propyl phenyl ketone and 1-propenyl phenyl ketone, formed via ring opening, were detected by HPLC.[24]

A deuteriated substrate, 1,2-bis(*p*-methoxyphenyl)ethane-1,2-diol-*1,2-d*$_2$ (**10**), was similarly cleaved to anisaldehyde quantitatively. The deuterium content of the aldehyde was determined by GC/MS analysis after trap-to-trap distillation of the reaction mixture (Table S1, supplementary material). The relative

(20) (a) Hammel, K. E.; Tien, M.; Kalyanaraman, B.; Kirk, T. K. *J. Biol. Chem.* **1985**, *260*, 8348–8355. (b) Shimada, M.; Habe, T.; Umezawa, T.; Higuchi, T.; Okamoto, T. *Biochem. Biophys. Res. Commun.* **1984**, *122*, 1247–1255. (c) Habe, T.; Shimada, M.; Okamoto, T.; Panijpan, B.; Higuchi, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1323–1324.

(21) Murray, R. I.; Sligar, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 2186–2187.

(22) Yuan, L.-C.; Calderwood, T. S.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 8273–8274.

(23) (a) Collman, J. P.; Brauman, J. I.; Meunier, B.; Raybuck, S. A.; Kodadek, T. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 3245–3248. (b) Collman, J. P.; Brauman, J. I.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 2000–2005.

(24) It is known that cyclopropylcarbinyl radicals rearrange to butenyl radicals at the diffusion-control rate.[25] In the case of phenylcyclopropylcarbinyl radical, however, it has also been reported that the release of a hydrogen atom from hydroxyl group competed with the rearrangement, the former process being 2.5 times faster than the latter.[26]

(25) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323.

(26) Neckers, D. C. *Tetrahedron Lett.* **1965**, 1889–1896.

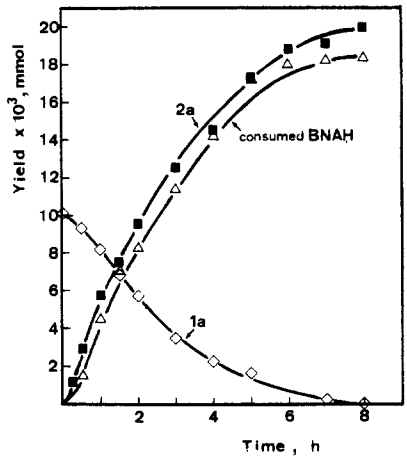
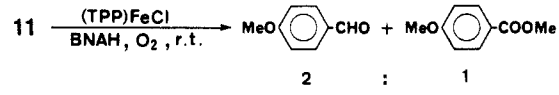


Figure 1. Time course of the reaction of **1a** (1.0×10^{-2} mmol) with BNAH (2.0×10^{-2} mmol) catalyzed by (TPP)FeCl (1.0×10^{-3} mmol) in CH_2Cl_2 (1 mL) under dry air at room temperature: (◇) **1a**, (■) **2a**, (△) consumed BNAH.

abundance of peaks around the parent ion was compared with those for the products in the oxidation of **10** with $NaIO_4$[27] and anisaldehyde-*1-d*, which was prepared separately according to Seebach's method.[28] The distribution of fragment ions of the aldehyde produced from **10** in the present catalytic reaction was quite similar to those of anisaldehyde-*1-d* prepared by the two independent procedures, indicating complete retention of the deuterium atoms. The most labile benzylic hydrogen atoms were not abstracted during the oxidative cleavage.

The reaction of the monomethyl ether of diol (**11**) proceeded more slowly than that of the corresponding diol, producing anisaldehyde and methyl *p*-methoxybenzoate at the ratio of 2 to 1 in an overall yield of 58% in 12 h.



On the contrary, masking of both of the two hydroxyl groups of diol by methyl or acetyl groups (**12**, **13**) suppressed the reaction and the substrates were recovered quantitatively. Monofunctional alcohols such as *p*-methoxybenzyl alcohol, methanol, and *p,p'*-dimethoxybenzoin as well as *p,p'*-dimethoxybenzil were also unreactive under these reaction conditions. Aldehydes were stable against further oxidation.

Effect of Substituent. The substituents on the aromatic rings such as methoxy, methyl, and chloro groups were unchanged under the reaction conditions. The diols (**1a–d**) having para substituents were cleaved with more than >99% selectivity to the corresponding benzaldehydes in high yields after 8–12 h, while ortho-substituted diarylethanediols (**1e–g**) were less reactive and slightly less selective. Figure 1 shows the time course of the reaction of **1a** under the standard reaction conditions. The bond cleavage product (**2a**) was formed simultaneously with the consumption of the starting diol (**1a**) and nearly two times as much BNAH. No intermediate products were detected by HPLC. After a short induction period of 5 to 10 min, the yield of aldehyde in the early stage of the reaction increased linearly, indicating zero-order dependence of the rate on substrate concentration. Figure 2 shows similar plots of the initial stages of the reactions with various para-substituted diols (**1a–d**). The electron-donating substituent on the aromatic ring enhanced the rate of aldehyde formation, although the overall difference in reactivity between methoxy and chloro derivatives was only threefold. On the contrary, competition experiments

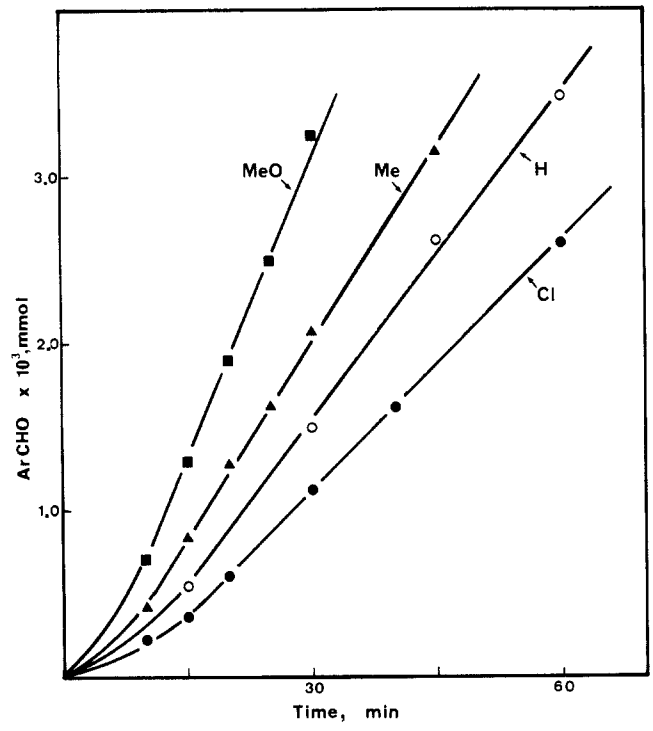


Figure 2. Initial time course of separate reactions of para-substituted diphenylethane-1,2-diols (1.0×10^{-2} mmol) in the presence of (TPP)FeCl (1.0×10^{-3} mmol) and BNAH (2.0×10^{-2} mmol) in CH_2Cl_2 (1 mL) at room temperature: (■) **2a**, (▲) **2b**, (○) **2c**, (●) **2d**.

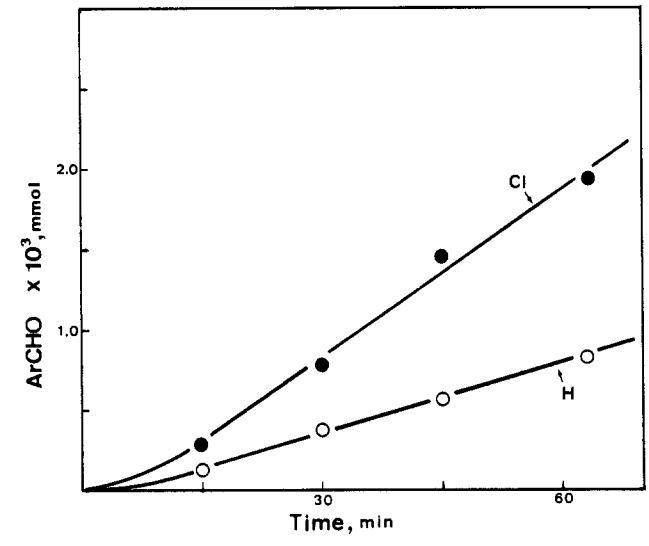


Figure 3. Initial time course of competitive reaction with an equimolar amount of **1c** and **1d** (1.0×10^{-2} mmol) in the presence of (TPP)FeCl (1.0×10^{-3} mmol) and BNAH (2.0×10^{-2} mmol) in CH_2Cl_2 (1 mL) at room temperature: (○) **2c**, (●) **2d**.

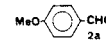
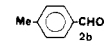
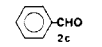
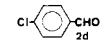
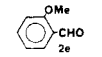
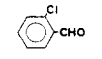
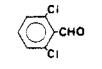
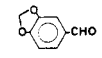
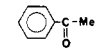
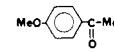
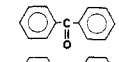
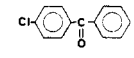
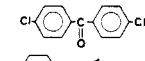
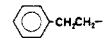
gave quite different results. The reaction with an equimolar mixture of **1c** (X = H) and **1d** (X = *p*-Cl) induced preferential formation of **2d** over **2c** (Figure 3) in sharp contrast to the separate reactions.

Stereochemistry. The effect of the stereochemistry of starting diols on the reactivity was examined with meso and dl forms of **1a**, **1c**, and 1-phenylcyclohexane-1,2-diol (**14**) (Table III). In contrast to the results of oxidation with $NaIO_4$, which induces cleavage of the C–C bond of dl isomer in preference to that of meso isomer,[27,29] none of the diols examined showed any significant difference in reactivity between the two stereochemical forms in our catalytic reaction.

Kinetic Study. Five typical substrates (**1a**, **1c**, **1d**, **1e**, and **3a**) were selected for the kinetic experiments to examine the polar and steric effects of the substituents. The catalyst concentration

(27) For reviews on the reaction of periodic acid and periodate see: Fatiadi, A. J. *Synthesis* **1974**, 229–272. Jackson, E. L. *Org. React.* **1944**, *2*, 341–375.
(28) Seebach, D.; Erickson, B. W.; Singh, G. *J. Org. Chem.* **1966**, *31*, 4303–4304.
(29) Trahanovsky, W. S.; Gilmore, J. R.; Heaton, P. C. *J. Org. Chem.* **1973**, *38*, 760–763.

Table II. Reactions of Various Diols Catalyzed by (TPP)FeCl[a]

	R	R_1	R_2	react time, h	convsn, %	product	%
1a		H	H	8	100	 2a	99
1b		H	H	12	100	 2b	99
1c		H	H	12	95	 2c	95
1d		H	H	12	95	 2d	95
1e		H	H	12	90	 2e	80
1f		H	H	12	–[b]		34
1g		H	H	12	–[b]		20
1h		H	H	12[c]	100		99
1i	H			12	100	2a	91
						2d	92
3a		Me	Me	12	100		95
3b		Me	Me	12	100		86
4	H		H	12	60	2c	55
5a				16	86		48[d]
5b				6	95		91
5c				6	–[b]		94
6				48	–[b]		5[e]
7		H	H	12	–[b]		11[f]
8		H	H	12	–[b]		1[f]
9	H	Et	H	12	0		0[f]

[a] Reactions were carried out under following conditions: (TPP)FeCl, 1.0×10^{-3} mmol; BNAH, 2.0×10^{-2} mmol; diol, 1.0×10^{-2} mmol; CH_2Cl_2, 1 mL under dry air at room temperature irradiated by visible light. Yields were determined by HPLC and calculated on the basis of substrate used. [b] Not determined. [c] At the initial stage of the reaction, starting diol was insoluble in dichloromethane. [d] The other products were not identified. [e] No ring opening product was observed. [f] Yields were determined by GLC.

Table III. Comparison of the Reactivities between Stereoisomers

		(TPP)FeCl–BNAH–O_2[a]		$NaIO_4$[b]	
substrate	dl/meso	time, h	yield,[c] %	time, h	yield,[c] %
1a	92/8	1	28		
	0/100	1	29		
1c	100/0	1	14	0.2	18
	0/100	1	17	0.2	2
14	100/0	12	29	2	11
	0/100	12	27	2	3

[a] Reaction conditions were the same as in Table I. [b] Reactions were carried out under the following conditions: substrate, 1.0×10^{-2} mmol; $NaIO_4$, 1.2×10^{-2} mmol; solvent, $EtOH/H_2O$ (4/1), 1 mL at room temperature. [c] Yields of bond cleavage products based on the used substrate.

under the standard reaction conditions used in the previous section was not suitable for the kinetic study because of the presence of an initial induction period and lack of linear correlation of the rate on the catalyst concentration. When the concentration of catalyst was decreased to about 1×10^{-5} M, however, the initial reaction rate showed first-order dependence on the catalyst concentration and the induction period disappeared. The reaction conditions used for the kinetic studies were as follows: [(TPP)-FeCl], 0.5×10^{-5} to 2.0×10^{-4} mmol; [BNAH], 2.0×10^{-2} mmol; [substrates], 2.0×10^{-4} to 1.0×10^{-2} mmol; in 1 mL of dichloromethane at 25.0 ± 0.5 °C under dry air with visible light irradiation. Under these reaction conditions, the initial rate was independent of BNAH concentration, and the absorption in the Solet region completely disappeared after about 2 h, which indicates gradual degradation of the catalyst. The overall catalyst turnover number was about 30. To eliminate the effect of the decomposition of catalyst, the rate of reaction was determined from the initial rate of formation of aldehyde in the first 10 min. Figure 4 shows the dependence of the rate on the catalyst concentration for the reaction of **1c**. At the lower concentration of catalyst ($<4 \times 10^{-5}$ M) the reaction rate was linearly dependent on the concentration of (TPP)FeCl. Thus, the bond cleavage reaction was a first-order process for the catalyst, at least, in the catalyst concentration range of 10^{-5} M. With increase of the catalyst concentration, the rate was leveled off to a constant value.

Dependence of the rate on the diol concentration was investigated in the concentration range of 0.5×10^{-4} to 1.0×10^{-2} M at a constant BNAH concentration with the catalyst concentration

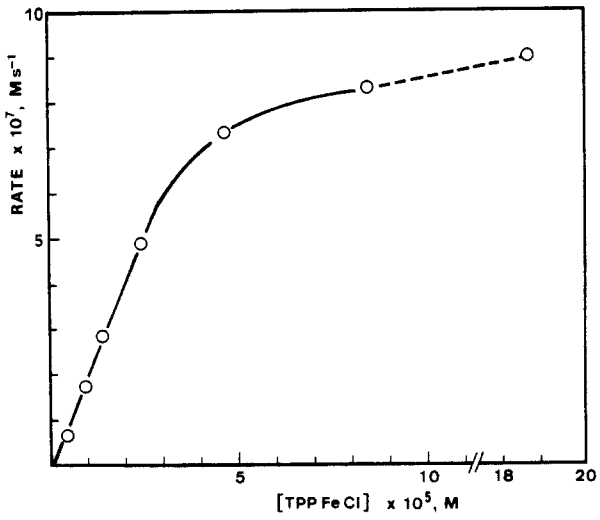


Figure 4. Dependence of catalyst concentration on the initial reaction rate of **1c**: (TPP)FeCl, 4.6×10^{-6} to 1.8×10^{-4} mmol; **1c**, 1.0×10^{-2} mmol; BNAH, 2.0×10^{-2} mmol; CH_2Cl_2 1 mL; 25.0 ± 0.5 °C.

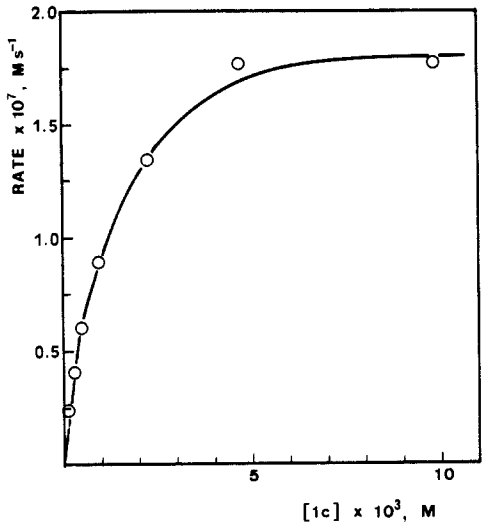


Figure 5. Dependence of diol concentration on the initial rate: diol, **1c**, 1.0×10^{-4} to 1.0×10^{-2} mmol; (TPP)FeCl, 9.4×10^{-6} mmol; BNAH, 2.0×10^{-2} mmol in CH_2Cl_2 (1 mL) at 25.0 ± 0.5 °C.

of 0.94×10^{-5} M. Figure 5 shows the plots of initial reaction rates versus diol concentrations for **1c**. The rates increased with a nearly first order dependency at a low diol concentration and approached the limiting value (1.8×10^{-7} M/s) at a high diol concentration. Molecular weight determination with the vapor pressure osmometer in CH_2Cl_2 eliminated the possibility of aggregation of the diol under the present reaction conditions (Table S2). Figure 6 shows the double reciprocal plot of 1/(rate) against 1/(diol concentration) for the five substrates.

Investigation of Catalytic Species. A. The Reduction of Iron(III) Porphyrin with BNAH. When a mixture of (TPP)FeCl and BNAH was stirred without oxygen and diols, no reduction of (TPP)Fe^{III}Cl to (TPP)Fe^{II} was observed in the absorption spectra either in the dark or under visible light. Nevertheless, addition of *N*-MeIm to the system caused rapid reduction of the catalyst from the iron(III) to the iron(II) state in the dark. The product was identified as (TPP)Fe^{II}(*N*-MeIm)$_2$ from its absorption spectra. Reduction of iron(III) was not observed in the absence of BNAH. In an analogous manner, addition of pyridine afforded (TPP)-$Fe^{II}(py)_2$, but only under visible light. The presence of CO also trapped Fe^{II} with the formation of Fe^{II}(CO)(TPP).

In the presence of molecular oxygen instead of a base or CO, (TPP)FeCl reacted with BNAH slowly to yield [(TPP)Fe]$_2$O in the dark. The reaction was significantly accelerated by visible light. However, the μ-oxo dimer was unchanged under our reaction conditions in the presence of BNAH even with the coexistence of 1-methylimidazole or pyridine either in the dark or under visible light.

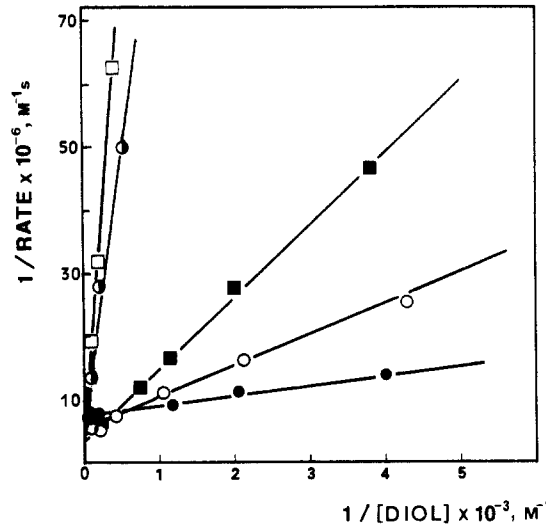


Figure 6. Plot of 1/rate vs 1/[diol] (Lineweaver–Burk plot): (■) **1a**, (○) **1c**, (●) **1d**, (◑) **1e**, (□) **3a**.

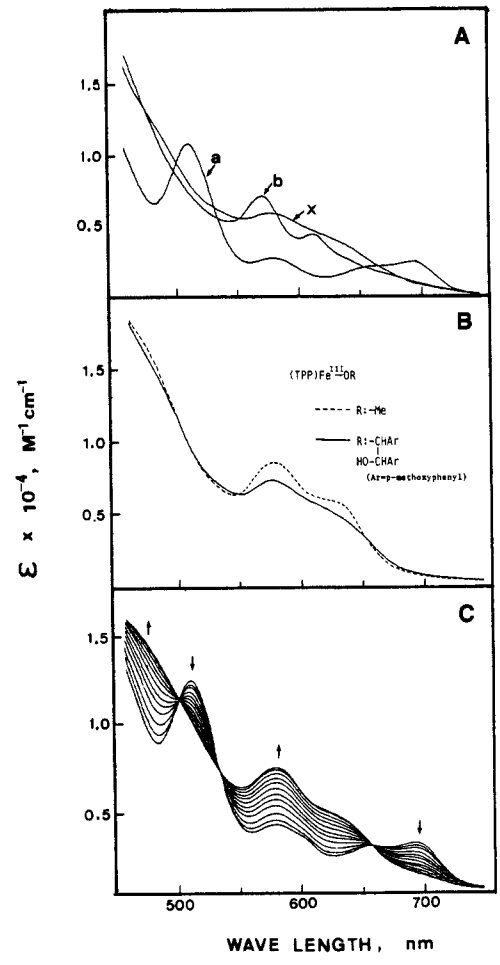


Figure 7. Electronic absorption spectra. (A) The reaction mixture under the catalytic reaction conditions. (TPP)FeCl, 1.0×10^{-3} mmol; BNAH, 2.0×10^{-2} mmol; diol **1a**, 1.0×10^{-2} mmol in CH_2Cl_2 (1 mL); trace a, initial; trace b, end of the reaction (6 h); trace x, after irradiation for 30 min. (B) (TPP)Fe(alkoxide): (—) **1a**–alkoxide; (---) methoxide. (C) (TPP)FeCl in the presence of methanol under catalytic reaction conditions; time interval, 3 min; (TPP)FeCl, 1.0×10^{-3} mmol; BNAH, 2.0×10^{-2} mmol; methanol, 5×10^{-2} mmol in CH_2Cl_2 (1 mL).

B. Spectroscopy. Under the standard reaction conditions the reaction mixture showed characteristic changes of absorption

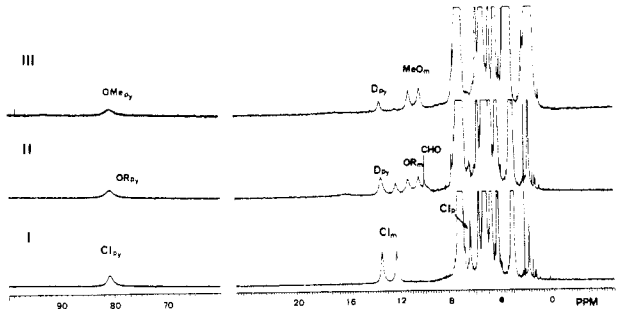


Figure 8. 200-MHz ^{1}H NMR spectra in dichloromethane-d_2 at 20 °C: trace I, the mixture of (TPP)FeCl, BNAH, and diphenylethanediol (**1c**); trace II, after irradiation of the above mixture for 45 min; trace III, the mixture of (TPP)FeCl, BNAH, and MeOH after irradiation for 60 min. Resonances are denoted by capital letters: Cl, (TPP)FeCl; OR, (TPP)Fe(**1c**–alkoxide); OMe, (TPP)FeOMe; D, $[(TPP)Fe]_2O$; CHO, aldehyde proton of the product. Subscripts refer to resonance assignment for the TPP ligand as follows: py, pyrrole; m, meta-H; p, para-H.

spectra during the course of reaction. Figure 7A shows typical spectra for the reaction of **1a**. The absorptions at 512 and 650–700 nm characteristic of (TPP)FeCl (trace a) disappeared within several minutes after irradiation of the reaction mixture accompanied by a concomitant increase of new absorptions at 580 and 635 (sh) nm due to an unknown species (X) (trace x). At the end of the reaction (6 h) the spectra of the reaction mixture was similar to those of the well-known μ-oxoiron(III) dimer, as seen in trace b. The unknown species (X) was assigned as an Fe^{III}–alkoxide complex in comparison with the spectra of the independently prepared (TPP)Fe^{III}–**1a** monoalkoxide shown in Figure 7B. Related spectral changes were also observed during the reaction with methanol (Figure 7C) or *p*-anisyl alcohol, giving rise to the spectra of corresponding (TPP)Fe^{III}(alkoxide)[30] although there was no further oxidation of alkoxides. The ^{1}H NMR spectra also support the assignment of X as (TPP)Fe^{III}(alkoxide)[31] as shown in Figure 8.

C. The Contribution of a High-Valent Iron Species. When the alkoxo–iron(IV) of diol[30] was independently prepared from **1a** at −50 °C and warmed to room temperature, the corresponding aldehyde was rapidly formed in a yield of 80% on the basis of an iron complex in the dark. The stoichiometric reaction of **1c** with (TPP)Fe^{II} [32] and O_2 also afforded benzaldehyde in toluene. (TPP)Fe^{III}(**1a** alkoxide) independently prepared from (TPP)FeClO_4 and sodium–**1a** alkoxide in dichloromethane (1.0 mM solution) gave a quantitative yield of anisaldehyde by irradiation of visible light under argon.

D. The Contribution of Active Oxygen Species. The systems generating singlet oxygen[33] such as $TPPH_2$–O_2 and Rose bengal–O_2 under visible light irradiation were ineffective for the bond cleavage of **1a**. Addition of diazabicyclo[2.2.2]octane (DABCO) as a $^1O_2$ quencher[34] in the (TPP)FeCl–BNAH–O_2 system brought about only negligible effects in the catalytic reaction of **1a**, and the reaction of **1a** with KO_2–18-crown-6 showed no detectable change in the starting diol.

Discussion

Kinetic Result. The initial rates of the reaction approach limiting values at a high concentration of both (TPP)FeCl and diol.

Table IV. Kinetic Parameters of the Reaction Catalyzed by (TPP)FeCl–BNAH–O_2[a]

diol	K_m, 10^{-3} M	V_{max}, 10^{-7} M/s
1a	3.1	2.7
1c	1.2	1.8
1d	0.3	1.5
1e	41.4	3.0
3a	19.0	2.2

[a] (TPP)FeCl, 0.94×10^{-5} mmol; BNAH, 2.0×10^{-2} mmol; diol, 1×10^{-4} to 1×10^{-2} mmol in CH_2Cl_2 (1 mL) at 25.0 ± 0.5 °C under irradiation of visible light.

Collman and co-workers reported[23] a similar finding for the epoxidation of olefins with the (TPP)MnCl–ClO^- system. They suggested the association of metalloporphyrins as the reason for the saturation of the rate at a high catalyst concentration. As for the dependence on the diol concentration, molecular weight determination showed that no aggregation occurred even at 1×10^{-2} M of diol in CH_2Cl_2. A trace amount of inhibitors in the diol may also give a similar result, but since the substrates prepared by different procedures gave the same results, this is not the case. Formation of a less reactive catalyst complex coordinated by two diol ligands[30a] would be another possibility for the decrease in the rate at a high diol concentration. However, a preliminary finding with Baldwin's capped porphyrin complex[35] that the dependence on diol concentration was similar even with the hindered catalyst argues against this possibility.[36] Then the dependence of the rate on the substrate concentration is interpreted by the Michaelis–Menten relationship as shown in eq 1.[37] Complex I reversibly

$$\underset{\text{complex I}}{FeL_m} + \text{diol} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{complex II}}{FeL_n(\text{diol})} \xrightarrow{k_2} FeL_0 + \text{product} \quad (1)$$

reacts with the diol leading to an iron–diol complex II, which irreversibly decomposes to the product in the rate-determining step. The rate expression is described by eq 2.

$$\text{rate} = \frac{d[P]}{dt} = \frac{V_{max}[\text{diol}]}{K_m + [\text{diol}]} \quad (2)$$

$$K_m = \frac{k_{-1} + k_2}{k_1}, \qquad V_{max} = k_2[Fe]_T$$

where K_m is a measure of the observed dissociation constant of complex II, and the V_{max} value is equal to the product of k_2 multiplied by the total catalyst concentration, a measure of the rate-determining decay of complex II.

The values of V_{max} and K_m were estimated from the intercept and the slope of the double reciprocal plot of the rate vs diol concentration (Lineweaver–Burk plot, eq 3)[38] as shown in Figure 6 for several diols. Table IV shows a summary of these values. Inspection of the K_m and V_{max} values for para-substituted 1,2-

$$\frac{1}{\text{rate}} = \frac{1}{V_{max}} + \frac{K_m}{V_{max}[\text{diol}]} \quad (3)$$

diarylethane-1,2-diols revealed that electron-deficient diols bind more efficiently (lower K_m value) than electron-rich diols. These K_m values are proportional to the pK_as of corresponding benzyl alcohols and suggest the development of negative charge on the substrates by the coordination. The high-valent oxo–metal–porphyrin complex has been reported to bind predominantly with electron-rich substrates.[5a,23b] The observed opposite binding affinity of substrates compared with other oxygenation systems involving metal–porphyrin complexes is a characteristic feature of the present reaction. In contrast to the K_m values, the V_{max} values are larger for electron-rich substrates than for electron-

(30) (a) Groves, J. T.; Quinn, R.; McMurry, T. J.; Nakamura, M.; Lang, G.; Boso, B. *J. Am. Chem. Soc.* **1985**, *107*, 354–360. (b) Kobayashi, H.; Higuchi, T.; Kaizu, Y.; Osada, H.; Aoki, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3137–3141. (c) Behere, D. V.; Goff, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 4945–4950.

(31) ^{1}H NMR spectra were measured for a CD_2Cl_2 (1 mL) solution of (TPP)FeCl (5.0×10^{-3} mmol), BNAH (7.0×10^{-2} mmol), and **1c** (2.3×10^{-2} mmol) or MeOH (3.1×10^{-2} mmol) with Varian VXR 200 spectrometer. The spectra are identical with those of the alkoxide complex obtained in the (TPP)FeCl–quinine system.[30c]

(32) Chin, D. H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 4344–4350.

(33) For reviews see: Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104–110.

(34) Ouannes, C.; Wilson, T. *J. Am. Chem. Soc.* **1968**, *90*, 6527–6528.

(35) Almog, J.; Baldwin, J. E.; Huff, J. *J. Am. Chem. Soc.* **1975**, *97*, 227–228.

(36) Okamoto, T.; Sasaki, K.; Oka, S., unpublished results.

(37) Michaelis, L.; Menten, M. L. *Biochem. Z.* **1913**, *49*, 1333.

(38) Lineweaver, H.; Burk, D. *J. Am. Chem. Soc.* **1934**, *56*, 658–666.

deficient ones. Thus the rate for decomposition of complex II is accelerated by the electron-donating substituent. This observation suggests that the bond cleavage reaction proceeds through electron release from the diol part to the iron ion.

The steric effect of substituents also showed a clear difference in the response to K_m and V_{max} values. The V_{max} value showed a negligible difference when the steric hindrance of the catalyst–substrate complex (complex II) was increased by substitution of the ortho hydrogen atoms of aromatic rings or α-positions of hydroxyl groups in the substrate with methoxy or methyl groups. In other words, the decomposition of complex II is little affected by the steric bulkiness. On the contrary, the K_m value increased more than a factor of 10 by introduction of two *o*-methoxy groups. Methyl groups on the α-carbons of OH groups showed a similar effect. Thus the initial binding process suffers a large steric hindrance.

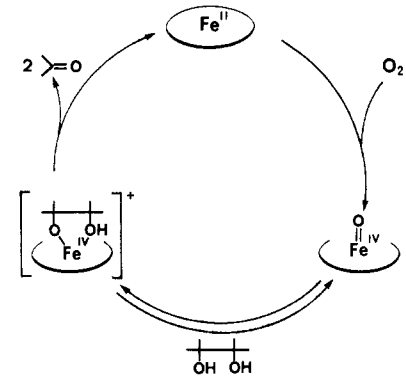
The K_m and V_{max} values thus obtained account for the qualitative tendencies of the substituent effect under the standard reaction conditions of high catalyst and diol concentrations: the different order of relative reactivities in separate and competitive reactions (see Figures 2 and 3), which are consistent with the presence of the iron–diol intermediate complex. Under the reaction conditions of a high concentration of substrate, the catalyst is almost completely converted to the coordinated form, complex II ([FeL]/[FeL(diol)] $\approx 10^{-5}$ for **1a–d**). Then in the separate reactions, the overall rate of reaction is controlled by the rate of decomposition of the intermediate complex II with preference for electron-rich diols having larger V_{max} values. Whereas, in competitive reactions, the relative reactivity is determined largely by the relative binding affinity of diols to the iron complex (K_m control), because the catalyst is still almost completely converted to complex II but with the distribution of those of the two substrates proportional to their K_m values, and the variation of V_{max} depending on the substituents (ca. two times) is smaller than that of K_m (ca. 13 times). In other words, the relative reactivity of the diols in the competitive reaction is determined by the thermodynamic distribution of complex II rather than their kinetic reactivities. It is notable that the substrate specificity in many biological systems has been controlled by these binding affinities.[39] The alternative possibility for the relative reactivity in the competitive reaction is that the relative rates of two substrates are determined by the difference in the activation energy for decomposition of two intermediates (V_{max} control).[40] However, from the discussion presented above on the K_m and V_{max} values the latter possibility is excluded in the present case.

Reaction Mechanism. In the initial step of the catalysis, we propose that (TPP)FeCl is reduced to the (TPP)Fe^{II} state. Although the Fe^{II} complex was not detectable in the visible spectra of a mixture of (TPP)FeCl and BNAH under Ar, the Fe^{II} complex was trapped by CO and nitrogen base in the form of (TPP)Fe(CO) and (TPP)$Fe(Base)_2$, respectively. These findings suggest that an equilibrium lies in the reactant side, as shown in the following equation, in relevance to the reduction of iron(III) porphyrins by amines[41] and ferricyanide ion by BNAH.[42] The interpretation is that the equilibrium moves to the Fe^{II} side when Fe^{II} or $BNAH^{\bullet+}$ is trapped irreversibly.

$$(TPP)Fe^{III}Cl + BNAH \rightleftarrows (TPP)Fe^{II} + Cl^- + BNAH^{\bullet+}$$

Because the reduction of iron(III)–porphyrin complex to the iron(II) state is accelerated by visible light irradiation, light contributes at least to accelerate electron transfer by activating the BNAH–iron encounter complex.

Scheme I



Recently, Balch and co-workers clarified irreversible oxidation of (TMP)Fe^{II} by molecular oxygen at a low temperature[43] and confirmed the previous proposal.[44] The oxygen-bound iron–porphyrin complex reacts with another (TPP)Fe^{II} which leads to the μ-peroxo-iron(III) complex. Successive O–O bond cleave gives the oxoiron(IV)–porphyrin complex, (TPP)Fe^{IV}=O. This complex reacts further with (TPP)Fe^{II}, finally forming the μ-oxo dimer. Formation of $[(TPP)Fe]_2O$ in the reaction of (TPP)FeCl with BNAH in an oxygen atmosphere probably proceeds according to similar reaction pathways.

$$(TPP)Fe^{II} + O_2 \rightarrow (TPP)Fe(O_2) \xrightarrow{(TPP)Fe^{II}}$$
$$(TPP)Fe\text{-}O\text{-}O\text{-}Fe(TPP) \rightarrow 2\,(TPP)Fe^{IV}{=}O \xrightarrow{(TPP)Fe^{II}} [(TPP)Fe^{III}]_2O$$

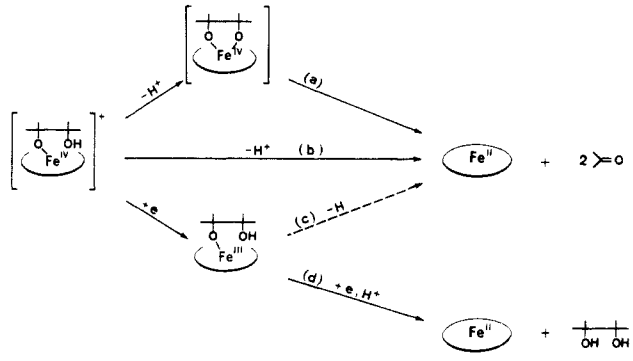
$$(TPP)Fe^{III}Cl + BNAH \rightleftarrows (TPP)Fe^{II} + Cl^- + (BNAH)^{\bullet+} \xrightarrow{O_2} [(TPP)Fe]_2O + BNA^+Cl^- + H_2O$$

In the intermediate state during the present catalytic reaction, a diol–iron complex, (TPP)Fe^{III}(alkoxide), was identified by spectroscopy. However, this species was only detectable in the dark and was stable under room light. Therefore, it does not necessarily follow that this is a "true intermediate" under irradiation of visible light. In other words, (TPP)Fe^{III}(alkoxide) may not be important in the catalytic cycle, but it may be a product of the side reactions.[45] (TPP)Fe^{III}(alkoxide) has been identified independently in the reaction of (TPP)Fe^{II} with alcohols under O_2.[36] Formation of benzaldehyde from **1c** has also been confirmed in toluene when the catalyst concentration was low. The alkoxide complex was not formed in the absence of O_2, or when a mixture of (TPP)FeCl and diol was stirred in the light under an atmosphere of O_2 or Ar.[36] These findings suggest that the interaction between the diol and the iron complex occurs in the presence of Fe^{II}, O_2, and diol, probably via participation of iron(IV).

As an active complex leading to the C–C cleavage, we previously proposed the participation of an alkoxo complex of iron(IV).[16] Groves and co-workers synthesized and characterized such an alkoxo–iron(IV) complex, which is stable ony at a low temperature. By warming to room temperature, alkoxo–iron(IV) decomposes to iron(III)(alkoxide).[30a] In our reaction system at room temperature, alkoxo–iron(IV) was not detectable, but the formation of iron(III)(alkoxide) was identified as described above.[46] The

(39) For example, see: Fersht, A. In *Enzyme Structure and Mechanism*, 2nd ed.; Freeman: New York, 1985; pp 347–354.
(40) Halpern, J. *Science* **1982**, *217*, 401–407.
(41) Castro, C. E.; Jamin, M.; Yokoyama, W.; Wade, R. *J. Am. Chem. Soc.* **1986**, *108*, 4179–4187.
(42) (a) Okamoto, T.; Ohno, A.; Oka, S. *J. Chem. Soc., Chem. Commun.* **1977**, 181–182. (b) Okamoto, T.; Ohno, A.; Oka, S. *J. Chem. Soc., Chem. Commun.* **1977**, 784–786. (c) Powell, M. F.; Wu, J. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 3850–3856. (d) Sinha, A.; Bruice, T. C. *Ibid.* **1984**, *106*, 7291–7292.
(43) (a) Balch, A. L.; Chan, Y.-W.; Cheng, R.-J.; La Mar, G. N.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7779–7785. (b) Balch, A. L.; La Mar, G. N.; Latos-Grazynski, L.; Renner, M. W.; Thanabal, V. *Ibid.* **1985**, *107*, 3003–3007.
(44) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 265–272.
(45) A preliminary result of flash photolysis supported the assumption: (TPP)Fe^{III}(alkoxide) was rapidly changed to other species of low extinction coefficient at 420 nm and the original optical density was recovered gradually under the catalytic reaction conditions.
(46) Direct formation of (TPP)Fe^{III}(alkoxide) from (TPP)Fe^{II} or (TPP)Fe^{III}Cl with O_2 is also a possible mechanism to be considered.[30c,47] Although the possibility of this type of reaction could not be eliminated completely, the contribution should be small because of quite different basicity of the reaction system.

Scheme II



bond cleavage product was formed in the thermal decomposition of an independently prepared alkoxo–iron(IV) complex at room temperature, suggesting the participation of the species as the intermediate.

Scheme I shows a plausible mechanism consisting of the formation of the alkoxo–iron(IV) complex during the C–C cleavage. The reversible binding between the diol and oxo–iron(IV) leads to alkoxo–iron(IV) which corresponds to complex II in eq 1.[48] The higher binding affinity of the iron complex for electron-poor diols suggests the generation of a negative charge on the diol moiety on coordination, thus supporting the alkoxide formation. However, another possible route leading to alkoxo–iron(IV) such as the oxidation of coordinated alcohol by molecular oxygen[50] cannot be excluded. The steric effect of substituents to the equilibrium constant K_m can be examined by inspection of the molecular model. The steric requirement of the formation of an alkoxide complex is rather stringent even for unsubstituted (TPP)Fe(**1c** alkoxide). Construction of the model of corresponding alkoxide complex for 2,3-diphenyl-2,3-butanediol (**3a**) was difficult if iron ion stayed in the plane of the porphyrin ligand and the length of the Fe–O bond was shorter than 2 Å.

In addition to the proposed noncyclic monodiol complex, the cyclic chelating dialkoxide complex might also be considered as a structure of the alkoxo–iron(IV) species. However, the participation of the cyclic dialkoxide complex is less probable because there was no difference in reactivity between the dl and meso isomers of **1a**, **1c**, or **14**, which has been used as one of the criteria to establish the cyclic intermediate for oxidative bond cleavage of 1,2-diols by $NaIO_4$[27] and $Pb(OAc)_4$.[29,51]

Scheme II shows some possible pathways for decomposition of alkoxo–iron(IV), the product-forming steps. The first two pathways (a and b) involve the two-electron oxidation processes of diol monoalkoxide, and path c is the conversion to iron(III)(alkoxide) by the reduction with BNAH, followed by the C–C bond cleavage of diol. Path d is a nonproductive reduction of iron(IV) competing with the oxidation reaction. In the case of alcohols such as methanol or benzyl alcohol, only path d predominates because of the high barrier to the oxidation of alcohols. The two-electron oxidation processes (paths a and b) have been well recognized in oxidation of diols by $Pb(OAc)_4$[29] and $NaIO_4$.[27] Successful formation of aldehyde by the thermal decomposition of the independently prepared **1a**–alkoxo complex of (TPP)Fe^{IV} and the reaction of diol with (TPP)Fe^{II} and O_2 (see Experimental Section for details) in the absence of a reducing reagent indicate that either path a or b could indeed take place. However, as stated above the lack of dependence of the rate between stereoisomers (dl and meso) of diols is an indication against the cyclic intermediate of path a. Path c obviously takes place under the present reaction condition since the intermediary of the Fe(III) alkoxide complex was observed spectroscopically during the reaction. Nevertheless its contribution to the overall catalytic reaction may be small because the C–C bond cleavage reaction via Fe(IV) complex (vide antre) took place very quickly in the presence of BNAH.

The formation of methyl ester from the monomethyl ether of diol is noted from the mechanistic point of view. It seem reasonable to consider a large contribution of path c in the reaction of monoether because of the high activation energy required for removal of a methyl group in paths a and b. In this case, the bond cleavage reaction may proceed via electron release from the coordinated substrate to iron, affording the aldehyde and phenyl methoxymethyl radical as the precursor of methyl ester.[52]

The contribution of active oxygen species, singlet oxygen and superoxide, is excuded by the results of control experiments. Because no dehydrogenation to benzoins and benzils took place in the present reaction and because deuterium atoms were retained on the α-carbons of the hydroxyl groups, there is no participation of the free radical chain processes. Richman and co-workers have reported that (TPP)Fe^{IV}=O generated by photodisproportionation of μ-oxo dimer under UV light irradiation induces radical-type abstraction of hydrogen atoms from olefins to produce allylic oxidation products.[49] However, $[(TPP)Fe]_2O$ had no catalytic activity in this reaction.

The contribution of a direct single-electron-transfer (SET) process should also be a possible mechanism for the bond cleavage. Shimada and co-workers proposed such a SET process for the cleavage of a highly electron rich 1,3-diol with *t*-BuOOH in the presence of iron–porphyrin catalysts.[53] Diol cleavage by single-electron-transfer reagents such as Ag^{2+} [54] or ammonium hexa(nitrato)cerate(IV) (CAN)[29] has many precedents, and the electrophilic high valent oxoiron complex is also expected to have similar reactivity.[55] In fact, very recently Traylor and co-workers clearly showed that this type of reaction participates in a high-valent oxo–iron–porphyrin catalysis.[7e] If reversible electron transfer between the iron complex and the diol should take place before the rate-determining bond cleavage, however, positive charge will develop in the diol part of the radical ion pair. On the contrary, kinetic results indicate the generation of a negative charge during the reversible binding process. Furthermore photooxidation sensitized by dicyanonaphthalene (DCN),[56] a well-known single-electron-transfer system, and stoichiometric oxidation with single-electron oxidants such as Ag(II)[54] have been reported to induce the bond cleavage of the dimethyl ether of diol as well as the diol itself. In our system, however, dimethyl ether was unreactive, disfavoring the contribution of the SET process between the high-valent iron complex and the uncoordinated diol.

Conclusion. Aerobic C–C bond cleavage of aryl-substituted 1,2-diols in the presence of molecular oxygen, a dihydropyridine, and an iron–porphyrin catalyst proceeded selectively producing aldehydes and ketones. This C–C bond cleavage simulates the biological glycol cleavage catalyzed by cytochrome $P\text{-}450_{scc}$. We propose that the mechanism of the catalytic reaction consists of the reversible reduction of the iron catalyst by dihydropyridine, the reaction of reduced catalyst with molecular oxygen to yield

(47) (a) Maldotti, A.; Bartocci, C.; Chiorboli, C.; Ferri, A.; Carassiti, V. *J. Chem. Soc., Chem. Commun.* **1985**, 881–882. (b) Bartocci, C.; Scandola, F.; Ferri, A.; Carassiti, V. *J. Am. Chem. Soc.* **1980**, *102*, 7067–7072.

(48) The formation of an alkoxo–iron(IV) complex by the reaction of a high-valent oxoiron complex with alcohol was not known. However, our preliminary result of the reaction of **1a** with $(TPPFe)_2O$ under irradiation of a high-pressure Hg lamp ($\lambda > 420$ nm), in which the formation of TPP-Fe^{IV}=O was proposed by Richman and others,[49] indicated the production of anisaldehyde under unaerobic conditions, whereas in similar conditions without $[(TPP)Fe]_2O$ no oxidation product was detected.[36]

(49) Peterson, M. W.; Rivers, D. S.; Richman, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 2907–2915 and references cited therein.

(50) (a) Tovrog, B. S.; Diamond, S. E.; Mares, F. *J. Am. Chem. Soc.* **1979**, *101*, 5067–5069. (b) Hamilton, G. A.; Adolf, P. K.; Jersey, J. D.; DuBois, G. C.; Dyrkacz, G. R.; Daniel Libby, R. *Ibid.* **1978**, *100*, 1899–1912.

(51) Criegee, R.; Buchner, E.; Walter, W. *Chem. Ber.* **1940**, *73*, 571–575.

(52) Plesnicar, B. In *The Chemistry of Peroxide*; Patai, S., Ed.; Wiley: New York, 1986; pp 574–575.

(53) Shimada, M.; Habe, T.; Higuchi, T.; Okamoto, T.; Panijpan, B. *Holtzforshung* **1987**, *41*, 277–285.

(54) (a) Greenspan, F. P.; Woodburn, H. M. *J. Am. Chem. Soc.* **1954**, *76*, 6345–6349. (b) Walling, C.; Camaioni, D. M. *J. Org. Chem.* **1978**, *43*, 3266–3271.

(55) Burka, L. T.; Guengerich, F. P.; Willard, R. J.; Macdonald, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 2549–2551.

(56) Davis, H. F.; Das, P. K.; Reichel, L. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 6968–6973.

active catalyst (probably oxo–iron(IV) complex), the reversible formation of an alkoxide complex by the reaction of diol with the active iron catalyst, and the rate-determining oxidation of alkoxide into two carbonyl compounds on the basis of the experimental findings. Formation of the alkoxide complex was facilitated by the electron-withdrawing substituents in the diol and influenced by steric hindrance, while the rate-determining bond-cleavage reaction was accelerated by electron-releasing substituents and not influenced by steric hindrance.

Experimental Section

Instruments. The electronic absorption spectra were recorded with a Union Giken SM-401 spectrometer. ^{1}H NMR spectra were obtained by a JEOL JNM FX-100, GX-400, or Varian VXR-200 spectrometer. The chemical shifts are determined relative to tetramethylsilane as the internal standard. Mass spectra were obtained by a JEOL JMSO-1SG mass spectrometer or a Hewlett-Packard 5992B gas chromatograph/mass spectrometer (EI 70 eV) equipped with either a 30 m × 0.93 mm silicon OV 101 or Carbowax 20M capillary column. Analyses by gas chromatography were made on Yanaco G-2800 gas chromatograph fitted with a 1 m × 3 mm column of Carbowax 20M or 30 m × 0.93 mm silicon OV 1701 capillary column. HPLC analyses were performed on a Hitachi 655 liquid chromatograph over a 15 cm × 0.46 cm Cosmosil 5ph or 5C_{18} column (Nakarai Chemical Co.) eluted with H_2O–MeOH (1:1) mixed solvent. Vapor pressure osmometric analyses were performed on a Corona 117 molecular weight apparatus in dichloromethane at 30.0 °C. Irradiation of visible light during the C–C bond cleavage was performed by using a merry-go-round apparatus at 25.0 °C with a Ushio 650 W tungsten halogen lamp at 70 V. The ultraviolet light was filtered off with a Fuji SC-42 cutoff filter ($\lambda > 420$ nm).

Materials. (TPP)FeCl, (TPP)MnOAc, and (TPP)Co (Sigma) were commercial products and were used as received. Other porphyrin ligands were prepared by known procedures[57] and metalated by conventional methods.[58] (TPP)$FeClO_4$,[59] (TMP)$FeClO_4$,[59] (TMP)$Fe(ClO_4)_2$,[60] and [(TPP)Fe]$_2O$ were prepared as previously reported. 1-Benzyl-3-carbamoyl-1,4-dihydropyridine (BNAH) was prepared from corresponding pyridinium salts by the reduction with sodium dithionite.[61]

Substrates. Substituted 1,2-diphenylethane-1,2-diols (**1a–g,i,j**) were prepared by the reduction of the corresponding benzoins or benzils with sodium tetrahydroborate in alcoholic solvents.[65] These diols were recrystallized from ethanol as white crystals. 1,2-Bis(*p*-methoxyphenyl)-ethane-1,2-diol-*1,2-d*$_2$ (**10**) was prepared by the reduction of 4,4′-dimethoxybenzil with $LiAlD_4$ as previously reported.[62] Deuterium content in the product was higher than 99% from the ^{1}H NMR spectra at benzylic positions and MS spectra. The stereochemical structure of these diols was assigned to meso forms from ^{1}H NMR chemical shifts. In the case of **1a**, a dl-rich mixture (dl:meso = 92:8) was obtained by crystallization of the residual mother liquid from $CHCl_3$–hexane followed by two fractional crystallizations from EtOH. *dl*-Diphenylethane-1,2-diol (*dl*-**1c**) was prepared from *trans*-stilben oxide[63] as previously reported.

1,2-Dicyclopropyl-1,2-diphenylethane-1,2-diol (**6**) was prepared by Grignard reaction of benzil with the corresponding alkylmagnesium bromide in THF.[64] 2,3-Diphenylbutane-2,3-diol (**3a**), 2,3-bis(*p*-methoxyphenyl)butane-2,3-diol (**3b**), 1,6-diphenylhexane-3,4-diol (**7**), 1,4-diphenylbutane-2,3-diol (**8**), 1,2-bis(*o*-chlorophenyl)ethane-1,2-diol (**1f**), and 1,2-bis(2,6-dichlorophenyl)ethane-1,2-diol (**1g**) were obtained as isomeric mixtures by the reductive condensation of corresponding aldehydes or ketones according to the literature.[65] Tetraphenylethanediol (**5a**), 1,2-bis(*p*-chlorophenyl)diphenylethanediol (**5b**), and tetrakis(*p*-chlorophenyl)ethanediol (**5c**) were prepared by a reductive coupling of the corresponding benzophenones with Mg–I_2.[66]

dl- and *meso*-phenylcyclohexane-1,2-diols (**14**) and phenylethanediol (**4**) were prepared from the corresponding epoxide[67] and mandelic acid,[68] respectively, by methods already reported. Commercial 1,2-butanediol (**9**) was distilled over CaH_2 in vacuo.

Dimethyl ether (**12**) and diacetate (**13**) of 1,2-bis(*p*-methoxyphenyl)ethane-1,2-diol were prepared by methylation with MeI–Ag_2O and acetylation with acetyl chloride in pyridine, respectively. Monomethyl ether (**11**) was prepared by the reduction of anisoin methyl ether with sodium tetrahydroborate.

All the complexes and substrates thus prepared gave satisfactory results on elemental analyses (Table S3, supplementary material).

Solvent. Reagent grade dichloromethane was purified by the conventional method and distilled over CaH_2 before use under dry air. Toluene and tetrahydrofurane (THF) were distilled from sodium metal and sodium benzophenone ketyl, respectively, and stored under argon. The other solvents were purified by standard methods and distilled before use.

Oxidation Procedure and Product Analyses. The catalytic reaction under aerobic condition was carried out as follows: A CH_2Cl_2 solution (1 mL) of the (TPP)FeCl complex (1.0×10^{-3} mmol), BNAH (2.0×10^{-2} mmol), diol (1.0×10^{-2} mmol), and an internal standard was placed in a 10-mL Pyrex reaction tube which was previously filled with dry air. The reaction tubes were put into a merry-go-round apparatus and irradiated continuously by visible light at room temperature. The progress of the reaction was monitored by HPLC for aliquots pretreated by Sep-Pack C_{18} cartridge (Waters Associates). Reactions of 1,4-diphenyl-2,3-hexanediol, 1,6-diphenyl-3,4-hexanediol, and 1,2-butanediol were analyzed by GLC.

Kinetic Study. The initial rates of the reaction were determined from the increase of the products with HPLC analyses. The following reaction conditions were mainly used: [(TPP)FeCl] 0.94×10^{-5} mmol, [BNAH] 2.0×10^{-2} mmol, [substrates] 2.0×10^{-4} to 1.0×10^{-2} mmol in CH_2Cl_2 (1 mL), under irradiation by visible light at 25.0 ± 0.5 °C.

Photodecomposition of the Alkoxide Complex of (TPP)Fe^{III}. The iron(III) monoalkoxide complex of porphyrin, (TPP)Fe(OR), was prepared as reported previously.[30] To a solution of (TPP)$FeClO_4$ (1.0 mM in CH_2Cl_2), 2 equiv of sodium monoalkoxide of **1a** (0.1 M) in THF which was prepared from **1a** with sodium metal (1.1 equiv) was added in a 0.1-cm quartz cell under argon. The color of the iron–porphyrin solution was immediately changed from red-brown to greenish-brown, characteristic of (TPP)Fe^{III}(alkoxide), with the absorption maxima at 580 and 635 (sh) nm. Irradiation of this alkoxide complex for 1.5 h resulted in the quantitative formation of anisaldehyde **2a** on the basis of Fe complex. In the control reaction of sodium monoalkoxide of diol without Fe complex or that of diol in the presence of (TPP)FeCl, no oxidation product was detected by HPLC.

Reaction of (TMP)Fe$(ClO_4)_2$ with the Sodium Monoalkoxide of 1a. The thermal decomposition of the alkoxo–(TMP)Fe^{IV} complex was examined for the complex prepared in situ according to the method of Groves et al.[30a] A solution of 5 equiv of sodium monoalkoxide of **1a** in THF was added to a solution of (TMP)Fe$(ClO_4)_2$ in CH_2Cl_2 at −50 °C under argon. A deep red solution characteristic of the alkoxo complex of (TMP)Fe^{IV} was immediately formed. The solution was rapidly warmed to the ambient temperature to obtain a greenish-brown solution characteristic of (TMP)Fe^{III}(alkoxide). HPLC analysis of the solution after the complete change of spectra showed formation of anisaldehyde **2a** in a 80% yield based on Fe complex without any other oxidation product. The control reaction of sodium **1a** monoalkoxide without an iron complex gave a negligible amount of anisaldehyde.

Reaction of Diphenylethane-1,2-diol with Dioxygen and (TPP)Fe^{II}. (TPP)Fe^{II} was prepared in toluene by the reduction of (TPP)FeCl (1.4×10^{-5} mmol) with zinc dust (20 mg) in a sealed tube.[32] Introduction of dry oxygen to a solution of (TPP)Fe^{II} and diphenylethane-1,2-diol (**1c**) (3 mg) resulted in a rapid reaction indicated by the change of color of the solution from original red to green-brown. The product complex was identified as [(TPP)Fe]$_2O$ from the absorption spectra. HPLC analysis of the resulting mixture indicated the formation of benzaldehyde (0.046 mg, 31%) without any other oxidation products.

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(57) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.
(58) (a) Chang, C. K.; DilNello, R. K.; Dolphin, D. *Inorg. Synth.* **1980**, *20*, 147–155. (b) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2445.
(59) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, R. W.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948–2958.
(60) Buisson, G.; Deronzier, A.; Duee, E.; Gans, P.; Marchon, J.-C.; Regnard, J.-R. *J. Am. Chem. Soc.* **1982**, *104*, 6793–6796. See also ref 30.
(61) Mauzerall, D.; Westheimer, F. H. *J. Am. Chem. Soc.* **1955**, *77*, 2261–2264.
(62) Wiberg, K. B. *J. Am. Chem. Soc.* **1954**, *76*, 5371–5375.
(63) Berti, G.; Bottari, F. *J. Org. Chem.* **1960**, *25*, 1286–1292.
(64) Mandell, L.; Johnston, J. C.; Day, R. A., Jr. *J. Org. Chem.* **1978**, *43*, 1616–1618.
(65) (a) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S. *J. Org. Chem.* **1976**, *41*, 260–265. (b) Mukaiyama, T.; Sano, T.; Hanna, J. *Chem. Lett.* **1973**, 1041–1044.
(66) Gomberg, M.; Bachmann, W. E. *J. Am. Chem. Soc.* **1927**, *49*, 236–254.
(67) Berti, G.; Bottari, F.; Macchia, B.; Macchia, F. *Tetrahedron* **1965**, *21*, 3277–3283.
(68) King, R. B.; Bakos, J.; Hoff, C. D.; Marko, L. *J. Org. Chem.* **1979**, *44*, 1729–1731.

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Supplementary Material Available: Data of GC/MS analyses for the products of reactions of **10** and anisaldehyde-*1-d* independently prepared, molecular weight measurement of diol **1c** by a vapor pressure osmometer, and combustion analyses of the substrate and catalysts (Tables S1, S2, and S3, respectively) (5 pages). Ordering information is given on any current masthead page.

Dioxygen-Copper Reactivity. Models for Hemocyanin: Reversible O_2 and CO Binding to Structurally Characterized Dicopper(I) Complexes Containing Hydrocarbon-Linked Bis[2-(2-pyridyl)ethyl]amine Units

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Abstract: A chemical system is described that mimics to a significant extent a number of properties of the copper-containing dioxygen carrier hemocyanin (Hc), including the reversible binding of CO and O_2 and major features of the UV-vis spectroscopy. A neutral dinucleating ligand, N4PY2, in which two tridenate PY2 units (PY2 = bis[2-(2-pyridyl)ethyl]amine) are connected by a tetramethylenealkyl chain, forms tetracoordinate dicopper(I) complexes, $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**) and $[Cu_2(N4PY2)(CH_3CN)_2]^{2+}$ (**1a**), as well as the pseudotricoordinate complex $[Cu_2(N4PY2)]^{2+}$ (**2**). Compounds **1** and **2** can be readily interconverted, indicating that **2** can bind carbon monoxide reversibly. Complexes **1a** or **2**, as ClO_4^- (i.e. **1a**-$(ClO_4)_2$ or **2**-$(ClO_4)_2$), PF_6^-, or BF_4^- salts (λ_{max} 350 nm (ϵ 3500 M^{-1} cm^{-1})), can be oxygenated at -80 °C in dichloromethane to produce intensely brown-colored solutions of dioxygen complexes, **3**, which are characterized by extremely strong and multiple electronic spectral absorptions (360 nm (ϵ 14 000-18 700 M^{-1} cm^{-1}), 458 (4500-6300), 550 (1200)) in the visible region. The reaction of **2** (or **1a**) with O_2 is reversible, and the application of a vacuum to the dioxygen adduct formed, **3**, removes the bound O_2 and regenerates the dicopper(I) complex, **2**. This *vacuum cycling* can be followed spectrophotometrically over several cycles. In addition, saturating a -80 °C solution of the dioxygen complex **3** with carbon monoxide (CO) results in the displacement of the dioxygen ligand with the formation of the dicopper(I) dicarbonyl complex, **1**. This behavior lends further support to the existence of the reversible binding equilibrium, **2** + O_2 ⇔ **3**. *Carbonyl cycling*, where **2** reacts with O_2 to produce **3**, O_2 is displaced by CO to give **1**, and **1** is decarbonylated to regenerate **2**, can also be followed spectrophotometrically over several cycles. Since (a) manometric measurements indicate that the stoichiometry of the reaction of **2** (and **1a**) with dioxygen is Cu:O_2 = 2:1, thus formulating **3** as $[Cu_2(N4PY2)(O_2)]^{2+}$, and (b) other evidence (e.g. the presence of a d-d band; λ_{max} 775 nm (ϵ 200 M^{-1} cm^{-1})) suggests that **3** possesses Cu(II) ions, **3** is best described as a peroxo-dicopper(II) complex. Crystallographic studies have been completed for both $[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (**1a**-$(ClO_4)_2$) and $[Cu_2(N4PY2)](ClO_4)_2$ (**2**-$(ClO_4)_2$). Compound **1a**-$(ClO_4)_2$ ($C_{36}H_{46}Cl_2Cu_2N_8O_8$) crystallizes in the monoclinic space group $A2/a$, with Z = 4 and a = 13.755 (4) Å, b = 20.071 (5) Å, c = 18.017 (4) Å, and β = 121.39 (2)°. Complex **2**-$(ClO_4)_2$ ($C_{32}H_{40}Cl_2Cu_2N_6O_8$) crystallizes in the monoclinic space group $A2/a$, with Z = 4, a = 19.437 (4) Å, b = 10.162 (3) Å, c = 23.231 (6) Å, and β = 128.14 (2)°. **1a**-$(ClO_4)_2$ possesses well-separated (Cu···Cu = 7.449 Å) equivalent Cu(I)-N_4 moieties with pseudotetrahedral ligation to the three nitrogen atoms of the PY2 unit and the acetonitrile molecule. In addition to the PY2 coordination in **2**-$(ClO_4)_2$, a weak Cu-O(ClO_4^-) interaction is observed; the bonding parameters for this complex suggest that the bonding is closer to that observed for other similar tricoordinate complexes with the Cu(I)-PY2 unit. The biological relevance of the dioxygen adducts described here and comparisons to oxy-Hc are discussed.

As part of our overall efforts in developing copper coordination chemistry of relevance to copper proteins and enzymes,[1-3] we are examining the binding, interaction, and subsequent reactivity of dioxygen (O_2) and its reduced forms at copper ion centers. Interest in such investigations stems in part from the occurrence of copper-containing proteins such as hemocyanins (Hc's), which bind and transport dioxygen,[4-6] the monooxygenases tyrosinase[1-4,5b,7] and dopamine β-hydroxylase[1-4,5b,8] which incorporate an oxygen atom from O_2 into organic substrates,[9] and copper oxidases such as galactose oxidase[10] and laccase,[11] which reduce dioxygen to either hydrogen peroxide or water, respectively. Also of relevance are cytochrome *c* oxidase,[12] which reduces O_2 to water at an iron-copper center, and the Cu/Zn-containing superoxide dismutase,[13] which effects the conversion of 2 mol of superoxide anion to hydrogen peroxide and dioxygen. Copper compounds have also been established to be essential catalysts in oxidation and O_2-

(1) Karlin, K. D.; Gultneh, Y. *J. Chem. Educ.* **1985**, *62*(11), 983-990.
(2) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219-327.
(3) Karlin, K. D., Zubieta, J., Eds. *Biological & Inorganic Copper Chemistry*; Adenine: Guilderland, NY, 1986; Vol. 1 & 2.
(4) (a) Solomon, E. I. In *Metal Ions in Biology*; Spiro, T. G., Ed.° Wiley-Interscience: New York, 1981; Vol. 3, pp 44-108. (b) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding (Berlin)* **1983**, *53*, 1-57.
(5) (a) Lontie, R.; Witters, R. *Met. Ions Biol. Syst.* **1981**, *13*, 229-258. (b) Lerch, K. *Met. Ions Biol. Syst.* **1981**, *13*, 143-186.
(6) Solomon, E. I. In *Copper Coordination Chemistry: Biochemical & Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1983; pp 1-22.
(7) Robb, D. A. In *Copper Proteins and Copper Enzymes*; Lontie, R., Ed.; CRC: Boca Raton, FL, 1984; Vol. 2, pp 207-241.
(8) Villafranca, J. J. In *Metal Ions in Biology*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1981; Vol. 3, pp 263-290.
(9) Recently, a pterin and copper ion dependent phenylalanine hydroxylase from *Chromobacterium violaceum* has been described. Pember, S. O.; Villafranca, J. J.; Benkovic, S. J. *Biochemistry* **1986**, *25*, 6611-6619.
(10) Kosman, D. J. In *Copper Proteins and Copper Enzymes*; Lontie, R., Ed.; CRC: Boca Raton, FL, 1984; Vol. 2, pp 1-26.
(11) (a) Farver, O.; Pecht, I. In *Metal Ions in Biology*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1981; Vol. 3, pp 151-192. (b) Reinhammar, B. *Adv. Inorg. Biochem.* **1979**, *1*, 91-118.
(12) Naqui, A.; Chance, B.; Cadenas, E. *Annu. Rev. Biochem.* **1986**, *55*, 137-166.
(13) Valentine, J. S.; Mota de Freitas, D. *J. Chem. Educ.* **1985**, *62*, 990-997.

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