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## PHOTOCATALYTIC CLEAVAGE OF 1,2-DIOLS BY A COFACIALLY HINDERED WATER-SOLUBLE IRON(III) PORPHYRIN

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Summary: The photocatalytic decompositions of 1,2-diols by newly synthesized [meso-tetrakis(3,5-dichloro-1-methyl-4-pyridiniumyl)porphyrinato]iron(III) FeIIITCl2MPyP were compared with those by [meso-tetrakis(1-methyl-4-pyridiniumyl)porphyrinato]iron(III) FeIIITMPyP. Cofacially hindered FeTCl2MPyP was more robust and substrate-specific than FeTMPyP.

Although photocatalysis by porphyrins and metalloporphyrins is inherently attractive, its application to organic chemistry is relatively little studied. Oxidation of organic substrates by photochemically produced active oxygen species such as oxo-metal complexes and a hydroxyl radical (water could be a source of the oxygen atom)<sup>1</sup> and accomplishment of multi-electron transfer organic phototransformations such as reduction of  $C02^2$  are still challenging problems. For these purposes we have recently undertaken to explore new photocatalytic reactions by using water-soluble redox-active metalloporphyrin complexes. $^3$ As a part of our study for cultivating new porphyrin photocatalysts, we now examined the photocatalytic reactivities of cofacially hindered  $Fe^{III}TC1_2MPyP$  toward 1,2-diols 1 - 4and the results were compared with those of FeIIITMPyP. By analogy with metal complexes of ortho halogen-substituted meso-tetraphenylporphyrins, 4 we expected FeTCl<sub>2</sub>MPyP to be tougher as a catalyst than FeTMPyP. Furthermore, we aimed to avoid the possible complications that may be caused by formation of a  $\mu$ -oxo dimer. The  $\mu$ -oxo dimer, which possibly has a very low photodisproportionation reactivity,<sup>5</sup> will not be formed from FeTClpMPyP owing to the steric hindrance by the chloro substituents.<sup>6</sup> To the best of our knowledge, synthess and reactivities of substituted HoTMPyP's and their metal complexes are as-yet not reported. CH<sub>3</sub>



Meso-tetrakis(3.5-dichloro-4-pyridyl)porphyrin H2TCl2PyP was synthesized by Lindsey's method<sup>7</sup> (4 % yield) from pyrrole and 3.5-dichloropsonicotinaldehyde, which in turn had been prepared by formylation of 3.5-dichloropyridine by treatment with LDA and ethyl formate at -78 °C (71 %). Insertion of zinc with Zn(OAc)<sub>2</sub>, methylation with MeOTs, demetallation with conc HCl, and finally insertion of iron with FeCl<sub>2</sub> afforded Fe<sup>III</sup>TCl<sub>2</sub>MPyP(Cl)<sub>5</sub> (overall 27 % yield from H<sub>2</sub>TCl<sub>2</sub>PyP).<sup>8</sup>

Solutions of diols 1 – 4 in aerated MeCN-H<sub>2</sub>O or H<sub>2</sub>O containing the porphyrin catalyst  $Fe^{III}TMPyP$  (A) or  $Fe^{III}TCl_2MPyP$  (B) were irradiated with visible-light (> 400 nm) and the products were analyzed by HPLC or GC. Benzopinacol (4) was cleaved even in the dark with a speed about half that of the reaction under irradiation. The results are summarized in Table I. Other products than those listed in Table I were undetectable under our HPLC and GC conditions. Except run 6, all experiments were done until most of the catalysts was consumed. A possible mechanism for the diol cleavage is described in eq 1. A detailed discussion of the mechanism will be published elsewhere.<sup>3</sup>

Inspection of Table I readily demonstrates that, in the cleavage of each diol, the catalyst B afforded a higher product yield than the catalyst A. Thus, as was predicted,  $^4$  B is more robust than A. However, the cleavage reactions of some diols meso-1, dl-1, and  $_4$  by B were considerably slower than those by A.

run	substrate	catalyst solvent MeCN-H <sub>2</sub> 0,v/v			ırradn tıme,h	products, % <sup>b</sup>		recovered porphyrin,%	
							PhCHO	PhCOOH	
1	meso- <u>1</u>	А	1	:	1	12	2100	350	none
2	meso-1	В	1	:	1	40	3100	110	none
3	d]−1	А	1	:	1	12	2100	380	none
4	d1- <u>1</u>	В	1	:	1	40	4100	140	none
5	2	А	H <sub>2</sub> 0	01	nly	20	860	0	$\sim 5$
6	2	В	H <sub>2</sub> 0	0	nly	20	1700	56	~50
							Me <sub>2</sub>		
7	3	А	1	:	1¢	40	21	00	none
8	3	В	1	:	1	40	2600		none
						dark,h	Ph2	со	
9d	4	А	4	:	1	8	10	00	none
10d	4	В	4	:	1	150	1600		$\sim 5$

Table I. Cleavage of 1,2-Diols by Fe<sup>III</sup>TMPyP (A) and Fe<sup>III</sup>TC1<sub>2</sub>MPyP (B) under air.<sup>a,d</sup>

<sup>a</sup>For runs 1 – 8, aerated solutions containing diols and porphyrin catalysts at pH  $\sim$  7 (except run 7) were irradiated at >400 nm; [diol] = 0.01 M except runs 5 and 6 (0.07 M) and runs 7 and 8 (0.7 M); [catalyst] = 1 x 10<sup>-4</sup> M except runs 7 and 8 (1 x 10<sup>-3</sup> M). <sup>b</sup>(product/cat) x 100. <sup>c</sup>pH = 12 with NaOH. <sup>d</sup>For runs 9 and 10, aerated solutions containing 0.007 M diol 4 and 1 x 10<sup>-4</sup> M catalyst A or B at pH  $\sim$  7 were stored in the dark and the reaction was followed by HPLC.



Efficiency for Cleavage of 1,2-Diols by Fe<sup>III</sup>TMPyP Table II. (A) and Fe^III\_TCl\_2MPyP (B) under air at pH  $\sim$  7.ª

aUnless otherwise specified,				L. V			
[diol] = 0.012 M and [cat] = 1.2 x 10 <sup>-4</sup> M. <sup>b</sup> Relative quantum yield ( $\Phi_{rel}$ = 1.00 for the PhCHO formation from		sub- strate	cata- lyst	solvent MeCN-H <sub>2</sub> O,v/v	Φ	rel <sup>b</sup>	A/B <sup>c</sup>
						DI 00011	
macn=1) CThe officiency of	-				PhCHO	PhCOUH	
meso-i). The entrency of	1	meso-l	A	1:1	1.00a	0.24	
product formation catalyzed	2	meso–l∕	В	1:1	0.22	J <b>.0090</b>	5.5
by A divided by that cata-							
lyzed by B. $d\Phi = 0.064$ .	3	d1-1	А	1:1	1.2	0,28	
e[3] = 0.42  M,  [cat] = 2.6  x	4	d]-1	В	1 • 1	0.23	0.0091	6.0
$10^{-4}$ M, $f[4] = 0.0068$ M,		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	-				
$[cat] = 1 \times 10^{-4} M.$	5	2	А	H <sub>2</sub> O only	0.032	0	
9Bimolecular rate constants	6	$\tilde{2}$	В	H <sub>2</sub> O only	0.021	0.0020	1.4
between 4 and A or B at		~		<u>2</u> - 5			
room temperature.					Me		
	7	3	А	1 : 1	0 (	163	
	ge	a a a a a a a a a a a a a a a a a a a	Δ	1.1	0.0	54	
	0e	ž	P	1.1	0.0	27 20	0.0
	3~	2	D	1 : 1	0.	12	0.9
					k, M	-1 <sub>5</sub> -1 g	
	10f	4	А	4:1	0.1	18	
	11f	4	В	4	2 (	 1×10−3	89
	• •	~	-	· • •			

Cleavage efficiencies for diols 1 - 4 by A or B are listed in Table II: the quantum yield ( $\Phi$ ) was measured for 1 - 3, whereas the rate constant was measured for 4, since 4 underwent the cleavage without light. As Table II shows,  $\Phi_{rel}$  by A increased in the order 2 (0.032) < 3 (0.063) < meso-1 (1.24) < d1-1 (1.48) and 4 was reactive even in the dark. This finding suggests that the C-C bond of 1,2-diol is more easily cleaved, when it is more highly substituted with the Me or Ph group, especially, with the Ph group. As is

postulated in eq 1, the (photochemical) electron transfer from diol to iron(III) is a crucial step of this cleavage reaction. Therefore, a correlation between the cleavage efficiencies of diols and their oxidation potentials is not surprising. [Indeed, dio] 4 has a very low oxidation potential (-0.58 V in 0.1 N NaOH vs SCE) $^9$  and the oxidation potential of dl-1 was estimated by us to be slightly lower than that of meso-1 (1.02 and 1.09 V, respectively, in MeCN vs SCE).

An interesting steric effect by the protruding chloro substituents of FeTC12MPyP is evident from analysis of the last column of Table II, where the ratio of the cleavage efficiencies catalyzed by A and B (A/B) is listed for each diol. In the case of 2.3-dimethyl-2.3-butanediol (3) having no bulky phenyl groups, the value for A/B is 0.9. In the case of the very bulky diol 4, it is 89. The value changed as much as 100 times in going through 3, 2, 1, and 4. Such a large change in the A/B value may be understood by reasoning that, owing to the steric hindrance by the chloro substituents, the reaction by B will be more sensitive to the bulkiness of the diol molecule than that by A. In other words, B is more substrate-specific than A, i.e., B carries an increased ability for molecular recognition as compared with A.

In summary, B is more robust and more substrate-specific than A.

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