decomposes in hydrochloric acid with liberation of salicylic acid (ca. 75% within a period of 60 min at pH 2). For these reasons, CBS unlike any other bismuth-containing drug seems to arrive in the ulcus regions chemically mostly intact and is finally attached via sulfhydryl (-SH) groups. Chemical model experiments addressing this latter question are presently being performed in our laboratories.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters for non-hydrogen atoms, bond distances, bond angles, and root-mean-square amplitudes of thermal vibration (14 pages); a table of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page. These data, including additional drawings, have also been deposited at the Fachinformationszentrum Energie Mathematik Physik (FIZ), Eggenstein-Leopoldshafen, Germany, under the registery number CSD 54652.

Anorganisch-chemisches Institut der Technischen Universität München
Lichtenbergstrasse 4
D-8046 Garching bei München, Germany

Wolfgang A. Herrmann*
Eberhardt Herdtweck
Liba Pajdla

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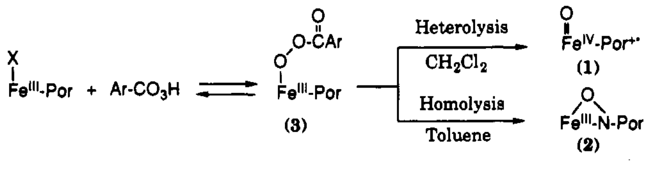
Remarkable Solvent Effect on the Shape-Selective Oxidation of Olefins Catalyzed by Iron(III) Porphyrins

Metalloporphyrin-catalyzed oxidations have been extensively studied, and higher valent oxo–metalloporphyrin intermediates are considered as reactive intermediates in many reactions.[1] In fact, the solid evidence for the formation of oxo–ferryl porphyrin cation radicals (**1**) was shown in the reaction of Fe^{III}TMP and *m*-CPBA in CH_2Cl_2.[2,3] Meanwhile, we have reported that the same reaction in an aromatic solvent such as toluene gave the *N*-oxide of Fe^{III}TMP (**2**) due to the homolytic O–O bond cleavage of a peracid–iron complex (**3**) (Scheme I).[4] We herein describe competitive epoxidation of norbornylene and α-methylstyrene by *m*-CPBA in the presence of a catalytic amount of iron porphyrins in CH_2Cl_2 and toluene. The results indicate possible participation of **3** in the epoxidation of olefins when the formation of **1** is a less favorable process.

Scheme I



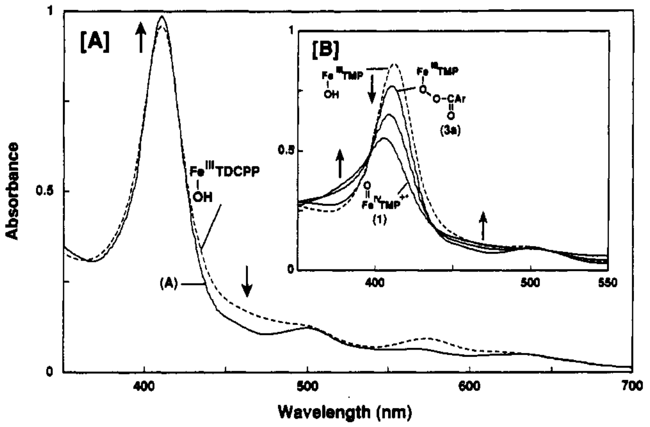


Figure 1. (A) Spectral change in the reaction of 1.0 × 10^{-5} M of Fe^{III}TDCPP(OH) (--) and *m*-CPBA in CH_2Cl_2 at −78 °C. (B) Time-dependent spectral changes of 0.85 × 10^{-5} M Fe^{III}TMP(OH) (--) upon the addition of *m*-CPBA in CH_2Cl_2 at −78 °C. Scan interval: 2 min.

In a typical reaction, oxidation of a mixture of norbornylene and α-methylstyrene (1:1, 300 equiv with respect to the catalyst) took place in CH_2Cl_2 (0.5 mL) at −78 °C for 3 h by employing a catalytic amount of Fe^{III}TMP(Cl) (1 mM). The reaction was initiated by adding *m*-CPBA (30 equiv), and preferable epoxidation of norbornylene over α-methylstyrene was observed in 63% yield (norbornylene oxide[5]:α-methylstyrene oxide[6] = 100:9; Table I, run 3). Change of the axial ligand from chloride to hydroxide did not cause any appreciable changes in the catalytic activity and selectivity (run 4). A similar result was also obtained in the oxidation catalyzed by Fe^{III}TDMPP(Cl) (run 6).[2] In these reactions, a rapid color change from brown to green by the addition of *m*-CPBA was observed. These color changes are indicative of oxo–ferryl porphyrin cation radical formation as shown in Figure 1B.[3a,b]

Mechanistic studies on the iron porphyrin catalyzed epoxidations by Groves and his co-workers indicated that the side-on approach of olefins to the iron-bound oxo oxygen in **1** results in the preferable *cis*-olefin epoxidation over *trans*-olefins.[7] More recently, they have examined the crystal structure of an adduct of styrene oxide and Ru^{II}TDCPP(CO).[2,8] The structure clearly shows the coordination of the epoxide ring at 49° with respect to the porphyrin plane and the two oxirane protons protrude toward the pyrrole ring of the porphyrin with vertical distances of ca. 2.8 Å from the plane. Thus, it will be difficult for α-methylstyrene to have a position suitable for the epoxidation, consistent with our results.

When the same reactions were carried out in toluene, remarkable changes in the shape selectivity of the olefins were observed; i.e., comparable amounts of α-methylstyrene to norbornylene were oxidized (Table I, runs 5 and 7). As reported before, the formation of **2** is predominant if olefins are absent.[4] Further, the oxidation of the olefins under the same condition without catalysts gave less than 5% epoxides (based on the Fe^{III}TMP-catalyzed epoxide formation). Therefore, these very different shape selectivities in toluene and CH_2Cl_2 would be at-

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(2) Abbreviations used are: Fe^{III}TMP, (tetramesitylporphyrinato)iron(III); Fe^{III}TDMPP, (tetrakis(2,6-dimethoxyphenyl)porphyrinato)iron(III); Fe^{III}TDCPP, (tetrakis(2,6-dichlorophenyl)porphyrinato)iron(III); Fe^{III}TPFPP, (tetrakis(pentafluorophenyl)porphyrinato)iron(III); *m*-CPBA, *m*-chloroperbenzoic acid, *o*-CPBA, *o*-chloroperbenzoic acid.

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(5) A small amount of endo epoxide was observed in the iron porphyrin catalyzed oxidations.

(6) α-Methylstyrene oxide gives two peaks in the GLC analysis due to its thermal rearrangement to phenylpropionaldehyde. The ratio of two speices was not constant even when a purified oxide was analyzed. Thus, the yields of the oxide represent a total amount of two products.

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Table I. Competitive Epoxidation of α-Methylstyrene and Norbornylene with Peracids Catalyzed by Iron(III)

run	catalyst	oxidant	solvent	temp, °C	% yield	selectivity[a] (norbornylene oxide (endo %)/ α-methylstyrene oxide)[b]	ratio of selectivity in toluene/CH_2Cl_2
1	none	*m*-CPBA	CH_2Cl_2	*c*	76	100 (0):30	1.4
2	none	*m*-CPBA	toluene	*c*	62	100 (0):42	
3	FeTMP(Cl)	*m*-CPBA	CH_2Cl_2	−78	63	100 (4):9	8.2
4	FeTMP(OH)	*m*-CPBA	CH_2Cl_2	−78	65	100 (6):10	7.4
5	FeTMP(OH)	*m*-CPBA	toluene	−78	65	100 (2):74	
6	FeTDMPP(Cl)	*m*-CPBA	CH_2Cl_2	−78	98	100 (24):29	5.1
7	FeTDMPP(OH)	*m*-CPBA	toluene	−78	47	100 (<1):148	
8	FeTDCPP(Cl)	*m*-CPBA	CH_2Cl_2	−78	63	100 (6):59	1.4
9	FeTDCPP(OH)	*m*-CPBA	CH_2Cl_2	−78	72	100 (10):57	1.4
10	FeTDCPP(OH)	*m*-CPBA	toluene	−78	44	100 (1):82	
11	FeTPFPP(Cl)	*m*-CPBA	CH_2Cl_2	−78	98	100 (2):73	1.3
12	FeTPFPP(Cl)	*m*-CPBA	toluene	−78	42	100 (5):98	
13	none	*o*-CPBA	CH_2Cl_2	*c*	93	100 (0):22	1.8
14	none	*o*-CPBA	toluene	*c*	96	100 (0):39	
15	FeTMP(Cl)	*o*-CPBA	CH_2Cl_2	−78	53	100 (2):9	10.1
16	FeTMP(OH)	*o*-CPBA	toluene	−78	51	100 (<1):91	
17	FeTDMPP(Cl)	*o*-CPBA	CH_2Cl_2	−78	47	100 (22):30	
18	FeTDCPP(Cl)	*o*-CPBA	CH_2Cl_2	−78	96	100 (4):73	1.5
19	FeTDCPP(OH)	*o*-CPBA	toluene	−78	52	100 (3):113	

[a] Determined by GLC. [b] See ref 6. [c] Room temperature.

tributed to the alternation of the reactive species of the iron porphyrin.

Halogenated iron porphyrins such as $\mathrm{Fe^{III}}$TDCPP and $\mathrm{Fe^{III}}$TPFPP[2] are known as good catalysts for many oxidations;[1j,o,p,9] however, the reaction of *m*-CPBA with these iron porphyrins in CH_2Cl_2 at −78 °C failed to form the green intermediates even without olefins.[10] Thus, the reaction of $\mathrm{Fe^{III}}$TDCPP(OH) and *m*-CPBA in CH_2Cl_2 at −78 °C was examined by UV–vis spectroscopy. As shown in Figure 1A, introduction of *m*-CPBA gave a new species (A), which was stable under the condition. This new species is determined to be $\mathrm{Fe^{III}}$TDCPP(*m*-CPBA) (**3b**) since **3b** oxidized 2 equiv of tetra-*n*-butyl ammonium iodide. Replacement of the solvent with toluene yielded the *N*-oxide of $\mathrm{Fe^{III}}$TDCPP via a transient formation of (**3b**) under the same condition. Interestingly, while the oxidations of a mixture of norbornylene and α-methylstyrene were catalyzed by these halogenated iron porphyrins in CH_2Cl_2 and toluene at −78 °C, the shape selectivities were found to be similar in both solvents (Table I, runs 8–12). The ratios of selectivities of α-methylstyrene over norbornylene in toluene to CH_2Cl_2 were calculated to be 1.3–1.5. In addition, the epoxidation of the olefins by *m*-CPBA also showed a small solvent effect on the shape selectivity (ratio of selectivities was 1.4).

Comparable production of norbornylene oxide and α-methylstyrene oxide is rather indicative of the active species to be different from the oxo intermediate (**1**) even in CH_2Cl_2. As shown in Scheme I and Figure 1, a peracid–iron porphyrin complex (**3**) is the common intermediate certainly observed in both solvent systems. Further, peracid–manganese porphyrin complexes are known to oxidize olefins.[11] All these results suggest that the active species in the epoxidation is **3** when the formation of **1** is less favorable process. Recently, a very similar metal–oxidant adduct participation in the olefin epoxidations has been suggested.[12] If the adduct is responsible for the epoxidations, the shape selectivity would be dependent on the structure of peracids employed, while the selectivity must remain unchanged when **1** is the active species. Thus, the iron porphyrin catalyzed competitive epoxidations were carried out with *o*-CPBA.[2] As shown in Table I (runs 15–19), only the shape selectivity of norbornylene and α-methylstyrene catalyzed by FeTMP and FeTDMPP in CH_2Cl_2 was not affected by the structure of the peracid.

In conclusion, we have shown that there are two types of active species responsible for the epoxidation when a peracid–iron(III) porphyrin system was employed. Oxo–ferryl porphyrin cation radicals (**1**) preferably oxidized *cis*-olefin. A peracid–iron(III) porphyrin complex (**3**) was proposed to be an alternative reactive species in the oxidation where comparable epoxide formation of norbornylene and α-methylstyrene was observed.

Division of Molecular Engineering
Graduate School of Engineering
Kyoto University
Kyoto 606, Japan

Yoshihito Watanabe*
Kazuya Yamaguchi
Isao Morishima

National Chemical Laboratory for Industry
Tsukuba, Ibaraki 305, Japan

Katsuomi Takehira
Masao Shimizu
Takashi Hayakawa
Hideo Orita

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(10) While we failed to prepare higher-valent iron porphyrin derivatives of $\mathrm{Fe^{III}}$TDCPP and $\mathrm{Fe^{III}}$TPFPP under the conditions, Gold et al. reported the formation of $\mathrm{O{=}Fe^{IV}}$TDCPP in THF. Further, Sawyer et al. prepared $\mathrm{O{=}Fe^{IV}TDCPP^{\bullet +}}$ in acetonitrile. Gold, A.; Jayaraj, K.; Doppelt, P.; Weiss, R.; Chottard, G.; Bill, E.; Ding, X.; Trautwein, A. X. *J. Am. Chem. Soc.* **1988**, *110*, 5756–5761; Sugimoto, H.; Tung, H.-C.; Sawyer, D. T. *Ibid.* **1988**, *110*, 2465–2470.

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Mononuclear *cis*-Carbonyloxotungsten(IV) Complexes of Hydrotris(3,5-dimethyl-1-pyrazolyl)borate

Mononuclear complexes containing the cylindrically symmetrical but electronically disparate carbonyl π-acid and oxo π-base ligands are extremely rare. Prior to 1986, complexes of this type had been identified only in matrix-isolation and gas-phase experiments.[1-5] In 1986, Mayer and co-workers[6] reported the first

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