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Synthesis, characterization, and efficient catalytic activities of a nickel(II) porphyrin: remarkable solvent and substrate effects on participation of multiple active oxidants

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Abstract: A new nickel(II) porphyrin complex, [Ni^{II}(porp)] (1), has been synthesized and characterized by ¹H NMR, ¹³C NMR and mass spectrometry analysis. This Ni^{II} porphyrin complex 1 catalyzed quantitatively the epoxidation reaction of a wide range of olefins with meta-chloroperoxybenzoic acid (MCPBA) under mild conditions. Reactivity and Hammett studies, H218O-exchange experiments, and the use of PPAA (peroxyphenylacetic acid) as a mechanistic probe suggested that participation of multiple active oxidants Ni^{II}-OOC(O)R 2, Ni^{IV}-Oxo 3, and Ni^{III}-Oxo 4 in olefin epoxidation reactions by nickel porphyrin complex is markedly affected by solvent polarity and concentration and type of substrate. In aprotic solvent systems, such as toluene, CH₂Cl₂, and CH₃CN, multiple oxidants, Ni^{II}-OOC(O)R 2, Ni^{IV}-Oxo 3, and Ni^{III}-Oxo 4, operate simultaneously as the key active intermediates responsible for epoxidation reactions of easy-to-oxidize substrate cyclohexene, whereas Ni^{IV}-Oxo 3 and Ni^{III}-Oxo 4 species become the common reactive oxidant for difficult-to-oxidize substrate 1-octene. In protic solvent system, a mixture of CH₃CN and H₂O (95/5), the Ni^{II}-OOC(O)R 2 undergoes heterolytic or homolytic O-O bond cleavage to afford Ni^{IV}-Oxo 3 and Ni^{III}-Oxo 4 species by general-acid catalysis prior to direct interaction between 2 and olefin regardless of the type of substrate. In such case, only Ni^{IV}-Oxo 3 and Ni^{III}-Oxo 4 species were the common reactive oxidant responsible for olefin epoxidation reactions.

Introduction

Selective oxidation of organic substrates using metal-based catalysts is an exciting and challenging scientific goal and has received great attention in the field of bio-inorganic chemistry because it is selective, inexpensive, and closely related to the biomimetic oxidation reactions of metalloenzymes.^[1] Iron and manganese are the major metals found in oxygenases that

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perform efficient and selective hydrocarbon oxidations and for this reason, a large number of corresponding high-valent iron- and manganese-oxo intermediates have been investigated as biomimetic chemical models of cytochrome P450^[2-4] and as catalysts in alkane hydroxylation, alkene epoxidation, and sulfoxidation reactions in various oxygenation reactions.^[5-7]

In recent years, nickel has been found in the active sites of enzymes involved in oxidation processes. They include quercetin dioxygenases,[8] acireductone dioxygenases, СО dehydrogenase,^[9] acetyl-coenzyme A(CoA) synthase,^[10] and nickel superoxide dismutase.^[11] Moreover, high-valent nickel-oxo species have been postulated to be key reaction intermediates in the catalytic cycle of several oxidation reactions.^[12,13] However, a very few such species have been isolated and well-characterized to-date. For example, McDonald, Company, and Costas groups reported the characterization and reactivity of Ni^{III}-oxyl (or Ni^{IV}-Oxo), CIONi^{III}-ligand radical, and Ni^{III}-OR species, which could perform alkane hydroxylation, olefin epoxidation, and oxygenatom transfer to triphenyl phosphine.^[14] Furthermore, Kakazawa et al. obtained the crystal structure of a nickel(II)-acylperoxo complex and showed its reactivities toward alkene, alkane, and thioanisol.^[15] Our and other groups also proposed that Ni^{III}-Oxo and Ni^{IV}-Oxo species are involved in alkene or alkane oxidation reactions by studying reactivity via spectroscopic methods and using mechanistic probe.^[16] However, it is still not completely clear which reactive species are responsible for oxygen atom transfer in the catalytic oxygenation reactions and what factors influence the nature of the reactive intermediates in synthetic nickel complex systems.

Quite recently, we presented that multiple active oxidants, viz. Mn^V=O, Mn^{IV}=O, and Mn^{III}-OO(O)CR, operate simultaneously in olefin epoxidation via manganese porphyrin and Mn(nonheme) complexes, depending upon reaction conditions such as type of reaction solution and concentration of the substrate.^[17] In addition, it has been proposed that the nature of solvent might significantly affect partitioning between heterolysis and homolysis of the O-O bond of a Mn-acylperoxo intermediate (Mn-OOC(O)R), and that O-O bond cleavage of the Mn-OOC(O)R complex might proceed predominantly by heterolytic cleavage in protic solvents.

In the current study, we are concerned with the use of nickel(II) porphyrin complex for the catalytic epoxidation of olefins for three principal reasons: 1) catalytic olefin epoxidation with Ni porphyrin complex has not been reported to date. 2) Ni porphyrin complex might have a good solubility in various solvents, because most metal porphyrin complexes are usually soluble in various solvents such as non-polar, polar, and protic solvents. Therefore,

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it is possible to study solvent effects on the participation of multiple active oxidants generated from the reaction of a Ni(II) porphyrin complex with oxidant according to solvent variation. 3) Ni porphyrin complex with electron-donating groups might be susceptible to Ni⁺⁴/Ni³⁺/Ni²⁺ redox reactions rendering the oxidation reaction thermodynamically favorable, as Sadler *et al.* showed with nickel-peptide complexes.^[18]

Herein, we report a new nickel(II) porphyrin complex, [Ni^{II}(porp)] complex 1 (porp=tetrakis(2,6-di(nbutoxy)phenyl)porphyrinato), which catalyzed the epoxidation reaction of a wide range of olefins quantitatively in presence of meta-chloroperoxybenzoic acid (MCPBA) under mild conditions. Olefin epoxidation using this catalytic system is proposed to involve multiple active oxidants, viz. Ni^{II}-OOC(O)R, Ni^{IV}-Oxo, and Ni^{III}-Oxo species, based on reactivity and Hammett studies, H218O-exchange experiments, and the use of PPAA (peroxyphenylacetic acid) as a mechanistic probe. The participation of multiple active oxidants was found to be remarkably influenced by solvent polarity, concentration and type of substrate.

Results and Discussion

Synthesis and characterization of Ni (II) porphyrin 1

Ni(II) porphyrin complex was prepared by condensation between 2,6-dibutoxybenzaldehyde (L1) and pyrrole followed by metalation with NiCl₂ (Scheme 1).^[19] The final compound was successfully characterized by ¹H and ¹³C NMR and Matrix Assisted Laser Desorption Ionization-Time of Flight (MALDI-TOF) mass spectroscopy.



Scheme 1. Preparation of 1.

Epoxidation of various olefins catalyzed by a Ni (II) porphyrin complex 1

To study the reactivity of Ni (II) porphyrin **1** toward olefins, we performed catalytic epoxidation of cyclohexene with MCPBA as a oxidant in various solvent systems, such as toluene, CH_2CI_2 , CH_3CN and a mixture of CH_3CN and H_2O (95/5) (Table 1). All epoxidation reactions were complete within 2 min at room temperature, and control experiments confirmed that direct oxidation of the substrate by MCPBA was negligible. The best result (100% conversion and 99% yield) was obtained in CH_2CI_2 .

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 Table 1. Epoxidation of cyclohexene by Ni(II) porphyrin complex 1 with MCPBA in various solvent systems at room temperature.^[a]

Entry	Solvent	Product	Conversion [%] ^[b]	Yield [%] ^[b]
1	toluene	cyclohexene oxide	78.0±2.7	70.0±4.8
		2-cyclohexenol		-
		2-cyclohexenone		-
2	CH ₂ Cl ₂	cyclohexene oxide	100.0	98.7±1.3
		2-cyclohexenol		-
		2-cyclohexenone		trace
3	CH₃CN	cyclohexene oxide	66.4±11.7	34.2±2.9
A		2-cyclohexenol		-
		2-cyclohexenone		-
4	CH ₃ CN/H ₂ O	cyclohexene oxide	58.5±2.1	15.5±1.4
	(95/5)	2-cyclohexenol		-
		2-cyclohexenone		-

[a] Reaction conditions: cyclohexene (0.035 mmol), catalyst (0.8x10⁻³ mmol), and MCPBA (0.07 mmol). [b] Based on cyclohexene.

Therefore, we carried out the catalytic epoxidation reactions of various olefins by catalyst 1 in CH₂Cl₂. The results of the epoxidation reactions have been summarized in Table 2. Under mild reaction conditions, cyclic olefins such as cyclopentene, cycloheptene, and cyclooctene were oxidized to the corresponding epoxides in excellent yields (99.2-100%, entries 1-3), with conversions of 100%. Surprisingly, such quantitative conversion is very rare in olefin epoxidation reactions catalyzed by metal porphyrin complexes.^[20] For cyclohexene (entry 4), it afforded cyclohexene oxide (98.7%) as the major product along with trace amount of 2-cyclohexenone. This suggested that free radical oxidation process scarcely occurs in the epoxidation of cyclohexene.^[21] On the other hand, terminal olefins such as 1hexene and 1-octene, which are well-known as notably challenging substrates to epoxidize,[22,23] were less efficiently oxidized to the corresponding 1-hexene oxide and 1-octene oxide respectively (17.5% and 25.5%, entries 5 and 6).

cis-2-Hexene, utilized to probe the epoxidation stereochemistry, was predominantly converted to *cis*-2-hexene oxide (96.0%; entry 9) and a small amount of *trans*-2-hexene oxide (4.0%), indicating the high stereochemical retention (96%). On the other hand, *trans*-2-hexene generated exclusively *trans*-2-hexene oxide (85.7%; entry 8). The preference test for a mixture of *cis*- and *trans*-2-hexene showed a ratio of 1.2, indicating a similar preference to *cis*- and *trans*-0efin. The epoxidation reactions using *cis*-2-octene and *trans*-2-hexene (entries 9 and 10).

For styrene having an aromatic ring, styrene epoxide was produced in a low yield (17.5%; entry 11), along with some phenylacetaldehyde (39.2%) and trace amount of benzaldehyde

(0.5%). *cis*-Stilbene afforded both *cis*-stilbene oxide (16.8%; entry 12) and *trans*-stilbene oxide (21.0%) along with minor amounts of benzaldehyde (1.0%) and 2-phenylacetophenone (7.5%), whereas *trans*-stilbene formed *trans*-stilbene oxide (43.1%; entry 13) as the only major product in addition to small amounts of benzaldehyde (3.2%) and 2-phenylacetophenone (5.6%). For aromatic olefin epoxidation reaction, the formation of aldehyde and ketone by-products indicated that either peroxo radical or nickel(III)-Oxo species as the epoxidizing agent might be responsible for the epoxidation of aromatic olefins. To the best of our knowledge, **1** is the first nickel(II) porphyrin catalyst capable of epoxidizing olefins and the most efficient among metal-porphyrin complexes that showed quantitative conversions and high epoxide yields.

Table 2. Olefin epoxidations by Ni(II) porphyrin complex 1 with MCPBA in CH_2CI_2 at room temperature. $^{[a]}$

Entry	Substrate	Product	Conversion [%] ^[b]	Yield [%] ^[b]
1	cyclopentene	epoxide	~100	~100
2	cycloheptene	epoxide	~100	~100
3	cyclooctene	epoxide	~100	99.2±1.5
4	cyclohexene	epoxide ~100		98.7±1.3
		2-cyclohexenol		-
		2-cyclohexenone		trace
5	1-hexene	epoxide	23.2±2.2	17.5±0.5
6	1-octene	epoxide	24.8±1.3	25.5±0.8
7	cis-2-hexene	<i>cis</i> -oxide	~100	96.0±1.5
		trans-oxide		4.0±0.1
8	trans-2-hexene	trans-oxide	96.8±0.2	85.7±0.5
9	cis-2-octene	<i>cis</i> -oxide	99.6±0.2	95.2±0.1
		trans-oxide		3.9±0.2
10	trans-2-octene	trans-oxide	95.9±0.4	93.3±0.9
11	styrene	epoxide 67.6±1.2		17.5±0.3
		benzaldehyde		0.5±0.1
		phenylacetaldehyde		39.2±0.3
12	<i>cis</i> -stilbene	cis-stilbene oxide	75.3±0.8	16.8±0.0
		trans-stilbene oxide	v	21.0±0.0
		benzaldehyde		1.0±0.4
		2-phenylacetophenone		7.5±0.6
13	trans-stilbene	trans-stilbene oxide	81.5±3.9	43.1±1.1
		benzaldehyde		3.2±1.2
		2-phenylacetophenone		5.6±0.5

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[a] Reaction conditions: olefins (0.035 mmol), Ni(II) porphyrin complex (0.8x10 3 mmol), and MCPBA (0.07 mmol). [b] Based on substrate.

Competition experiments of styrene and *para*-substituted styrenes for Hammett study

To understand the nature of reactive intermediates responsible for the olefin epoxidation, competitive reactions of four *para*substituted styrenes were carried out (Fig. 1). Results showed that the rates of the epoxidation reactions with electron-rich olefins were faster than those with electron-deficient ones. The Hammett analysis gave a good linear relationship with ρ value of -0.45, which indicated electrophilic character of the reactive oxidant. This value is somewhat lower than those reported for the epoxidation of styrene with [Ni(cyclam)](NO₃)₂ (ρ = -0.82),^[24] [Ni(bisamidate)] (ρ = -0.86),^[14a] [Ni(II)(dpaq)CI] (dpaq=2-(bis(pyridin-2-ylmethyl)amino)-N-(quinolin-8-yl)acetamide) (ρ = -0.72)^[16a] and [Ni(Tp^{CF3Me})(κ ²-mCPBA)] (Tp^{CF3Me} = hydrotris(3trifluoromethyl-5-methylpyrazolyl)borate) (ρ = -1.35).^[15a]



Figure 1. Hammett plot for selective reactivities of styrene to *para*-substituted styrenes by 1 with MCPBA.

Product distribution of the O–O bond cleavage of PPAA with catalyst 1

We used phenylperacetic acid (PPAA)^[17,21a,25] as a mechanistic probe to gain insight into the reactive intermediates involved in olefin epoxidation, because a quantitative determination of degradation products derived from PPAA is very informative for distinguishing heterolytic from homolytic cleavage of the peracid O-O bond.^[17,21a,26] When the O-O bond of the Ni(II)-acylperoxo species (Ni^{III}-OOC(O)R **2**), formed from the reaction of Ni(II) porphyrin with peracid, was cleaved heterolytically, phenylacetic acid (PAA (**5**), pathway (a) of Scheme 2) was generated. The direct epoxidation of olefin by **2** also produced PAA (pathway (b)) and apparently varied the O-O bond cleavage mode. By contrast, a homolytic cleavage of the O-O bond of **2** afforded benzyl alcohol

(6), benzaldehyde (7) and toluene (8) through a rapid β -scission of the acyloxy radical (pathway (c)).

First, a degradation experiment of PPAA with Ni(II) porphyrin complex **1** was carried out in the absence of substrate in nonpolar solvent toluene (entry 1 in Table 3 and entry 1 in Table S1). The heterolytic cleavage product PAA was the dominant degradation product of PPAA (71.6% based on PPAA), along with some amounts of benzaldehyde (18.2%) and benzyl alcohol (4.2%) formed via a homolytic O-O bond cleavage. These results indicated that Ni^{II}-OOC(O)R species **2** generated from the reaction of **1** and PPAA underwent 76.2% heterolysis and 23.8% homolysis to produce high-valent Ni^{IV}-Oxo **3** and Ni^{III}-Oxo **4** species. Importantly, these results indicated, for the first time, that Ni^{IV}-Oxo species can be generated from the reaction of a nickel porphyrin complex and peracids as an oxidant, whereas in only a few cases in the past, Ni^{IV}-Oxo species s^[12,14a,c,16]

Table 3. Olefin epoxidation by Ni(II) porphyrin complex 1 with PPAA as oxidant in various solvent systems at room temperature.^[a]

Entry	Solvent (dielectric constant)	Concentration of olefin	Hetero/Homo in cyclohexene ^[b]	Hetero/Homo in 1-octene ^[b]		
1	toluene	0 mM	3.2 (76.2/23.8)	3.2 (76.2/23.8)		
2	(2.4)	20 mM	3.9 (79.6/20.4)	3.8 (79.2/20.8)		
3		40 mM	4.6 (82.1/17.9)	3.9 (79.6/20.4)		
4		80 mM	5.4 (84.4/15.6)	3.8 (79.2/20.8)		
5		160 mM	8.0 (88.9/11.1)	3.9 (79.6/20.4)		
6	CH_2Cl_2	0 mM	4.4 (81.5/18.5)	4.4 (81.5/18.5)		
7	(3.1)	20 mM	4.7 (82.5/17.5)	3.5 (77.8/22.2)		
8		40 mM	7.7 (88.5/11.5)	3.7 (78.7/21.3)		
9		80 mM	13.1 (92.9/7.1)	3.8 (79.2/20.8)		
10		160 mM	22.7 (95.8/4.2)	4.0 (80.0/20.0)		
11	CH ₃ CN	0 mM	2.7 (73.0/27.0)	2.7 (73.0/27.0)		
12	(5.8)	20 mM	2.8 (73.7/26.3)	2.6 (72.2/27.7)		
13		40 mM	3.4 (77.3/22.7)	2.5 (71.4/28.6)		
14		80 mM	3.6 (78.3/21.7)	2.0 (66.7/73.3)		
15		160 mM	4.1 (80.4/19.6)	2.4 (70.6/29.4)		
16	CH ₃ CN/H ₂ O	0 mM	3.8 (79.2/20.8)	3.8 (79.2/20.8)		
17	(CH ₃ CN : 5.8,	20 mM	4.4 (81.5/18.5)	3.5 (77.8/22.2)		
18	H ₂ O . 9.0)	40 mM	4.2 (80.8/19.2)	4.1 (80.4/19/6)		
19		80 mM	5.2 (83.9/16.1)	3.8 (79.2/20.8)		
20		160 mM	4.7 (82.5/17.5)	3.9 (79.6/20.4)		

[a] See Experimental section for details. [b] **Hetero/Homo** means the ratio of heterolysis and homolysis.

To further investigate the direct relation between the O-O bond cleavage and olefin epoxidation, concentration effect of an easy-to-oxidize substrate, cyclohexene, was studied.[17,21a,26a-c] If Ni^{II}-OOR species 2 was involved in the epoxidation reaction, the ratio of heterolysis to homolysis would increase with increase in the concentration of cyclohexene.^[26] This is because PAA as heterolysis product is produced from the direct olefin epoxidation by Ni^{II}-OOR species 2. When the concentration of cyclohexene was increased from 0 to 160 mM, the ratio of the heterolysis to homolysis also increased gradually from 3.2 (76.2/23.8) to 8.0 (88.9/11.1) (entries 1-5 in the fourth column of Table 3 and entries 1-5 in Table S1). This increase signified that Ni^{II}-OOC(O)R species 2 contributed to the epoxidation with increasing concentration of cyclohexene in toluene. To examine the type effect of substrate on the cleavage mode of peracid, we further changed the substrate from cyclohexene to 1-octene, more difficult-to-oxidize substrate. The ratio did not vary within experimental error (entries 1-5 in the fifth column of Table 3 and entries 1-5 in Table S2). These results suggested that Ni^{II}-OOR species 2 might not be a competent oxidant capable of oxidizing the difficult-to-oxidize olefin.

We also studied the solvent effects on participation of multiple active oxidants, because it has been demonstrated previously in Mn(porphyrin) complexes that multiple oxidants, Mn^{III}-OOC(O)R, Mn^V=O, and Mn^{IV}=O, operate simultaneously as the key active intermediates in aprotic solvents and that Mn^V=O species becomes the common reactive intermediate in protic solvents.^[17c] A variety of solvents with different polarities for a detailed study was used, ranging from toluene (dielectric constant: 2.4) to CH₂Cl₂ (dielectric constant: 3.1) to CH₃CN (dielectric constant: 5.8) to a mixture of H₂O (dielectric constant: 9.0) and CH₃CN (5/95).

When a slightly more polar solvent (CH₂Cl₂) than toluene was used, the partitioning of Ni^{II}-OOC(O)R species 2 in the absence of cyclohexene was 81.5 vs. 18.5 (heterolysis vs. homolysis) (entry 6 in the fourth column of Table 3 and entry 1 in Table S3). An increase in concentration of cyclohexene showed a similar pattern for the ratio of heterolysis to homolysis as shown in toluene (entries 6-10 in the fourth column of Table 3 and entries 1-5 in Table S3). When the substrate was changed from cyclohexene to 1-octene, the ratio did not vary within an experimental error as shown in toluene (entries 6-10 in the fifth column of Table 3 and entries 1-5 in Table S4). In the more polar solvent CH₃CN, the ratio (73.0/27.0) of heterolysis to homolyis in the absence of cyclohexene was somewhat lower than those in toluene and CH₂Cl₂ (entry 11 in the fourth column of Table 3 and entry 1 in Table S5).^[17c] Similarly, increasing the concentrations of cyclohexene increased the ratios of heterolysis to homolysis (entries 11-15 in the fourth column of Table 3 and entries 1-5 in Table S5). With 1-octene, the ratio did not vary within the experimental error (entries 11-15 in the fifth column of Table 3 and entries 1-5 in Table S6). These results suggested that Ni^{II}-OOR species 2 might not be a competent oxidant capable of oxidizing

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the difficult-to-oxidize olefin in CH_2Cl_2 and CH_3CN as shown in toluene.

In the most polar and protic solvent system, e.g. a mixture of H₂O/CH₃CN (5/95), the partitioning of Ni^{II}-OOC(O)R 2 in absence of cyclohexene gave 79.2% heterolysis and 20.8% homolysis (entry 16 in the fourth column of Table 3 and entry 1 in Table S7). An increase in the concentration of cyclohexene showed, surprisingly, no increase in the ratio of heterolysis to homolysis unlike in aprotic solvents, toluene, CH₂Cl₂, and CH₃CN (entries 16-20 in the fourth column of Table 3 and entries 1-5 in Table S7). This result indicated that a protic solvent might induce the Ni^{II}-OOC(O)R intermediate 2 to undergo O-O bond cleavage by general-acid catalysis prior to direct interaction between 2 and olefin.^[27] With 1-octene, a nearly identical O-O bond cleavage pattern was also observed as shown with cyclohexene (entries 16-20 in the fifth column of Table 3 and entries 1-5 in Table S8). These results demonstrated again that the Ni^{II}-OOC(O)R intermediate undergoes O-O bond cleavage by general-acid catalysis prior to direct interaction between 2 and olefin regardless of the type of substrate in the protic solvent system, and that Ni^{IV}-Oxo 3 and Ni^{III}-Oxo 4 species produced from the O-O bond cleavage of Ni^{II}-OOC(O)R intermediate might be the common reactive intermediate.



Scheme 2. Possible reactive intermediates formed from the reaction of PPAA with nickel(II) complex.

Mechanism

Based on our mechanistic studies, Scheme 3 shows the most plausible mechanism for the formation of the reactive species responsible for olefin epoxidation reaction catalyzed by Ni(II) porphyrin complex. An initial nickel-acylperoxo intermediate (Ni^{II}-OOC(O)R; **2**), derived from reaction of a Ni(II) porphyrin complex and peracid, undergoes either a heterolytic or homolytic O-O bond cleavage to afford Ni^{IV}-Oxo **3** or Ni^{III}-Oxo **4** species, or transfers its oxygen atom directly to the substrate under the following two conditions. In aprotic solvent systems such as toluene, CH_2CI_2 , and CH_3CN , the multiple oxidants, Ni^{II}-OOC(O)R **2**, Ni^{IV}-Oxo **3**, and Ni^{III}-Oxo **4**, operate simultaneously as the key active intermediates responsible for the epoxidation reactions of the easy-to-oxidize olefin (pathways A, B, and C), whereas Ni^{IV}-Oxo

3 and Ni^{III}-Oxo **4** species become the common reactive oxidant to the difficult-to-oxidize olefin due to incompetent oxidizing power of **2** (pathways A and C). In protic solvent system, the Ni^{II}-OOC(O)R undergoes heterolytic and homolytic O-O bond cleavage simultaneously to afford Ni^{IV}-Oxo **3** and Ni^{III}-Oxo **4** species by general-acid catalysis prior to direct interaction between **2** and olefin regardless of the type of substrate (pathways D and E). In such case, only Ni^{IV}-Oxo **3** and Ni^{III}-Oxo **4** species are the common reactive oxidant responsible for olefin epoxidation reactions.

In order to observe the proposed reactive intermediates Ni-Oxo, isotope labeling experiments were carried out to understand the source of oxygen atoms found in epoxide products.^[28] Epoxidation of cyclohexene (10 equiv) by nickel complex **1** (0.8 mmol) and MCPBA (20 equiv) was conducted in presence of excess H₂¹⁸O (1111 equiv) in a mixture of H₂O/CH₃CN (5/95). The cyclohexene oxide product contained a small amount (ca. 3%) of ¹⁸O derived from H₂¹⁸O, demonstrating that high-valent Ni-Oxo species are involved in the reactions of the catalysts with MCPBA, but oxygen exchange between Ni-Oxo species and H₂¹⁸O might be much slower than oxygen-atom transfer of Ni-Oxo species to the substrate.



Scheme 3. Plausible mechanism for the formation of the reactive oxidants responsible for the olefin epoxidation from the reaction of nickel porphyrin complex 1 with peracid.

Conclusions

We have synthesized and characterized the nickel porphyrin complex 1, which efficiently and quantitatively catalyzed a wide range of olefin epoxidation under mild conditions. To the best of our knowledge, 1 is the first nickel(II) porphyrin catalyst capable of epoxidizing olefins and the most efficient among all the metalporphyrin complexes reported to-date that showed quantitative conversions and epoxide yields. Therefore, the present results provide important information for designing of new oxidation catalysts consisting of nickel porphyrin. On the other hand, reactivity and Hammett studies, H218O exchange experiments, and the use of PPAA as a mechanistic probe suggested that participation of multiple active oxidants Ni^{IV}-Oxo 3, Ni^{III}-Oxo 4, and Ni^{II}-OOC(O)R 2 in olefin epoxidation reactions by nickel porphyrin complex was markedly affected by several factors, such as solvent polarity and concentration and type of substrate. In aprotic solvent systems, such as toluene, CH₂Cl₂, and CH₃CN, multiple

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oxidants, Ni^{II}-OOC(O)R, Ni^{III}-Oxo, and Ni^{IV}-Oxo, operate simultaneously as the key active intermediates responsible for the epoxidation reactions of the easy-to-oxidize olefin, whereas Ni^{IV}-Oxo and Ni^{III}-Oxo species become the common reactive oxidant to the difficult-to-oxidize olefin due to incompetent oxidizing power of **2**. In protic solvent system, the Ni^{II}-OOC(O)R undergoes heterolytic and homolytic O-O bond cleavage simultaneously to afford Ni^{IV}-Oxo and Ni^{III}-Oxo species by general-acid catalysis prior to direct interaction between **2** and olefin regardless of the type of substrate. In such case, only Ni^{IV}-Oxo and Ni^{III}-Oxo species are the common reactive oxidant responsible for olefin epoxidation reactions.

More detailed mechanistic studies to elucidate the factors such as general-acid and -base catalysis that influence the partitioning of heterolysis versus homolysis of the Ni^{II}-OOC(O)R intermediate are currently underway in this laboratory.

Experimental Section

General: Olefins, epoxides, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, benzaldehyde, acetonitrile, dichloromethane, dodecane and MCPBA (65%) were purchased from Aldrich Chemical Co. and were used without further purification. PPAA^[17,21a,26a,b] and 2,6-dibutoxybenzaldehyde^[29] were synthesized according to the literature method. All other chemicals were obtained from commercial sources and used without further purification. All the reactions and manipulations of the porphyrin building blocks were carried out under N₂ with the use of standard inert-atmosphere and Schlenk techniques unless otherwise noted. Solvents used in inert-atmosphere reactions were dried and degassed using standard procedures. Flash column chromatography was performed with 230-400 mesh silica gel using wet-packing method.

Instruments: ¹H NMR spectra were recorded on a Varian AS400 (399.937 MHz for ¹H and 100.573 MHz for ¹³C) spectrometer. ¹H chemical shifts are referenced to the proton resonance resulting from protic residue in deuterated solvent and ¹³C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Matrix Assisted Laser Desorption Ionization–Time of Flight (MALDI-TOF) mass spectra were obtained on a Bruker Daltonics LPF20 MALDI TOF Mass Spectrometer Industry-Academic Cooperation Foundation, Yonsei University. Product analysis for olefin epoxidation and PPAA experiment were conducted by using a YL6500 gas chromatograph equipped with a FID detector and a 30 m capillary column (Hewlett-Packard, DB-5 or HP-FFAP). IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. UV/Vis spectra were carried out with a Perkin Elmer model Lambda 2S UV/Vis spectrometer.

2,6-Dibutoxybenzaldehyde (L1): To a solution TMEDA (7.1 mL, 71.71 mmol) and 1,3-dibutoxybenzene (13.37 g, 60.16 mmol) in diethyl ether was added n-BuLi (2.5M in hexane, 26.14 mL, 65.33 mmol) at 0 °C over a 30 min period. The reaction mixture was stirred for 3 h under N₂. After warming up to room temperature, DMF (8.88 mL) was added drop wise and the reaction was stirred for an additional 2 h. The mixture was quenched with water and the product was extracted with ethyl acetate 4 times. The solution was evaporated to dryness using a rotary evaporator to yield a yellow residue, which was recrystallized with hexane to afford the product as pure white solid (8.6 g, 73.6 % yield). ¹H NMR (CDCl₃): δ 10.46 (s, 1H), 7.41 (t, ³J_{H+H} = 8.2 Hz, 1H), 6.64(d, ³J_{H+H} = 8.2 Hz, 2H), 4.08 (q, ³J_{H+H} = 7.1 Hz, 4H), 1.78 (m, 4H), 1.41 (m, 4H), 1.01 (t, ³J_{H+H} = 7.1 Hz, 6H).

5,10,15,20-Tetrakis[2,6-di(*n*-butoxy)phenyl]porphyrin (L2): 2.6-Dibutoxybenzaldehyde (749 mg, 2.93 mmol) and pyrrole (428 mg, 2.93 mmol) were dissolved in dichloromethane (516 mL) in a 1-L Schlenk flask equipped with a magnetic stirrer and degassed for 10 min. TFA (142.2 µL) was added drop-wise, the flask was shield from light, and the resulting mixture was stirred for 3 h at room temperature. After DDQ (800 mg) was added, the solution was stirred for an additional 1 h. TEA (3.04 mL) was then added and the reaction mixture was evaporated to dryness using a rotary evaporator to yield a dark residue, which was purified by silica-gel column chromatography (CH₂Cl₂) to afford pure product as a purple solid (284 mg, 28.35 % yield). ¹H NMR (CDCl₃): δ 8.66 (s, 8H), 7.64 (t, ³J_{H-H} = 8.2 Hz, 4H), 6.95 (d, ³J_{H-H} = 8.2 Hz, 8H), 3.77 (t, ³J_{H-H} = 6.6 Hz, 16H), 1.00-0.91 (m, 16H), 0.64-0.53 (m, 16H), 0.33-0.28 (m, 24H). ¹³C NMR (100 MHz CDCl₃): ō (ppm) 144.4, 132.6, 129.2, 121.7, 102.3, 97.6, 91.3, 68.4, 30.8, 18.6, 13.4. MS (MALDI-TOF): m/z= 1191.79 for M+; Calcd. 1191.58.

[5,10,15,20-Tetrakis(2,6-di(n-butoxy)phenyl)porphyrinato]nickel(II)

(1): To a solution of L2 (100 mg, 83.8 mmol) in DMF (25.0 mL) was added NiCl₂ (419 mmol) and the resulting solution was refluxed for 24 h. After cooling, the reaction mixture was diluted with CHCl₃ and washed with water The organic layer was collected and dried over anhydrous Na₂SO₄, and the volatile was removed under reduced pressure. The resulting residue was purified by silica-gel column chromatography (DCM) to afford pure **1** as a reddish purple solid (80 mg, 76.5 % yield). ¹H NMR (CDCl₃): δ 8.57 (s, 8H), 7.58 (t, ³J_{H+H} = 8.2 Hz, 4H), 6.90 (d, ³J_{H+H} = 8.2 Hz, 8H), 3.75 (t, ³J_{H+H} = 6.6 Hz, 16H), 1.05-0.95 (m, 16H), 0.56-0.48 (m, 16H), 0.24-0.19 (m, 24H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 145.7, 131.8, 128.6, 121.7, 101.7, 96.7, 91.3, 68.4, 30.5, 18.3, 13.2. MS (MALDI-TOF): *m/z*= 1249.40 for M⁺; Calcd. 1248.26

Catalytic olefin epoxidations by MCPBA in the presence of Ni porphyrin complex: MCPBA (0.07 mmol) was added to a mixture of substrate (0.035 mmol), Ni porphyrin complex (0.8×10^{-3} mmol), and solvent (CH₂Cl₂; 1 mL). The mixture was stirred for 10 min at room temperature. Each reaction was monitored by GC/mass analysis of 20 µL aliquots withdrawn periodically from the reaction mixture. Dodecane as an internal standard was used to quantify the yields of products and conversions of substrates. All reactions were run at least in triplicate, and the average conversions and product yields are presented. Conversions and product yields were based on substrate.

Competitive reactions of styrene and *para***-substituted styrenes for Hammett plot in the presence of Ni porphyrin complex:** MCPBA (0.03 mmol) was added to a mixture of styrene (0.02 mmol) and *para*(X)-substituted styrene (0.02 mmol, X = -OCH₃, -CH₃, -CI, and -CN), Ni porphyrin complex (0.8x10⁻³ mmol), and solvent (CH₂Cl₂; 1 mL). The mixture was stirred for 10 min at room temperature. The amounts of styrenes before and after reactions were measured by GC. The relative reactivities were determined using the following equation: $k_x/k_y = \log(X_{i}/X_{i})/\log(Y_{i}/Y_{i})$ where X_i and X_f are the initial and final concentration of *para*-substituted styrenes and Y_i and Y_f are the initial and final concentration of styrene.^[26b,28c]

Analysis of the O–O bond cleavage products from the oxidation reactions of substrates by PPAA in the presence of Ni porphyrin complex: PPAA (0.04 mmol) was added to a mixture of substrate (0-0.16 mmol), Ni porphyrin complex (0.8×10^{-3} mmol), and various solvents (toluene, CH₂Cl₂, distilled CH₃CN, distilled CH₃CN/H₂O(95/5, 1 mL), respectively. The mixture was stirred for 10 min at room temperature. Each reaction was monitored by GC/mass analysis of 20 µL aliquots withdrawn periodically from the reaction mixture. Dodecane as an internal standard was used to quantify the yields of products and conversions of substrates. All reactions were run at least in triplicate, and the average conversions

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and product yields are presented. Conversions and product yields were based on substrate or PPAA.

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Supplementary data

Supplementary data related to this article can be found at http://

Keywords: Ni(II) porphyrin complex • olefin epoxidation • multiple active oxidants • Ni-Oxo species • Ni(II)-OOC(O)R species

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Multiple active oxidants: In the oxidation reactions catalyzed by a new nickel(II) porphyrin complex, participation of the active oxidants is markedly influenced by solvent polarity, and concentration and type of substrate. Three active oxidants, Ni^{IV}-Oxo, Ni^{III}-Oxo, and Ni^{II}-OOC(O)R, operate simultaneously in aprotic solvents, whereas two active oxidants, Ni^{IV}-Oxo and Ni^{III}-Oxo, operate in protic solvents.

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Synthesis, characterization, and efficient catalytic activities of a nickel(II) porphyrin: remarkable solvent and substrate effects on participation of multiple active oxidants