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Photochemical Epoxidation of Olefins with Molecular Oxygen Activated by Niobium Porphyrin: A Functional Model of Cytochrome P-450

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The selective monooxygenation of hydrocarbons by synthetic catalysts have received a great deal of attention in connection with the chemistry of cytochrome P-450. The stereospecific epoxidation of olefins by iodosylbenzene was catalyzed by synthetic iron porphyrins, and $Fe^{IV}(O)(por^{+}\cdot)$, where por stands for the dianionic porphyrinate ligand, was claimed to be the reactive intermediate.[1] Olefins were also epoxidized by iodosylbenzene dispersed in organic solvents as mediated by several transition-metal salts.[2,3] Among those metal salts, a (μ-oxo)dicopper(III) species was suggested to be the active reagent for oxygenation. In spite of the fruitful results as regards the epoxidation of olefins by iodosylbenzene, a single oxygen atom source, the oxygen atom transfer to organic substrates via activation of dioxygen has not been successfully achieved. In this regard, Tabushi et al. reported the reductive activation of dioxygen by molecular hydrogen and colloidal platinum.[4] Stereospecific and regioselective epoxidation was catalytically performed under such conditions in the presence of $Mn^{III}(por)$.

We have previously found that irradiation of the tri-μ-oxo dimer of (5,10,15,20-tetra-p-tolylporphinato)niobium(V) (1) with the visible light in benzene afforded an oxygenated radical species at room temperature under aerobic conditions, the radical species giving an ESR signal consisting of ten hyperfine lines[5] (Figure 1a). The $\bar{A}_{Nb}$ value is 5.08×10^{-4} cm^{-1} for this species, while it is 175×10^{-4} cm^{-1} for $Nb^{IV}(O)(por)$ obtained by chemical,

$\bar{A} = 5.08 \times 10^{-4}$ cm^{-1}

a

$\frac{H}{10 \text{ G}}$

$g = 2.011$

b

$\frac{H}{10 \text{ G}}$

$g = 2.0$
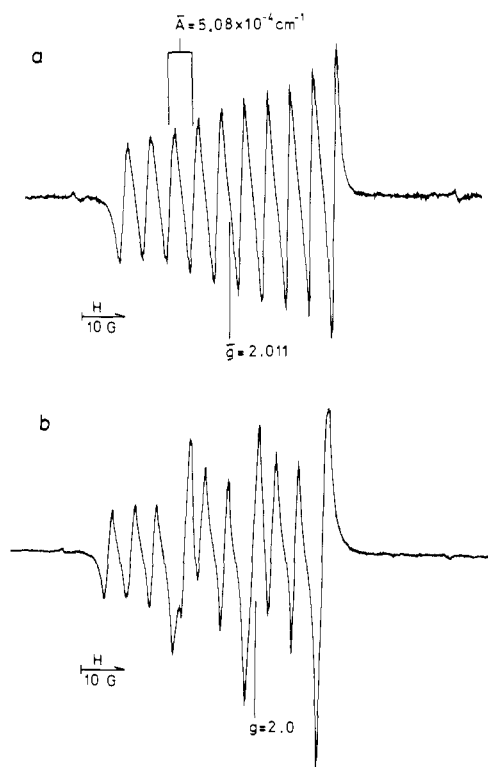
Figure 1. ESR spectra of paramagnetic species generated upon aerobic irradiation of 1 (ca. 1.0×10^{-3} M) with the visible light at room temperature: (a) in benzene; (b) in benzene containing 10% (v/v) 2,2,6,6-tetramethylpiperidine.
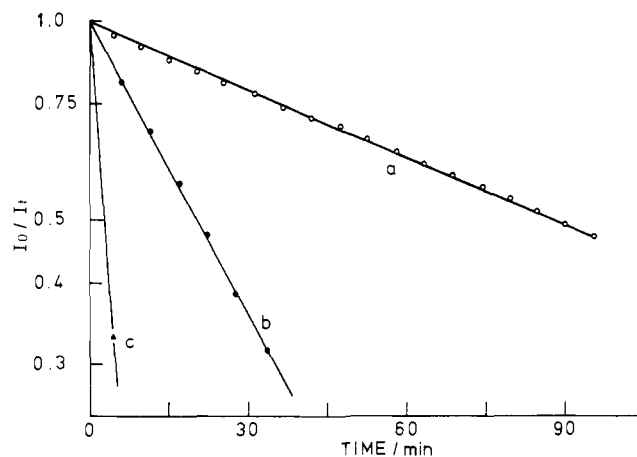
Figure 2. Time courses for decay of the ESR signal originated from 2 (ca. 1.0×10^{-3} M) in benzene after interruption of aerobic irradiation at room temperature: (a) pyridine added [10% (v/v)]; (b) 2,2,6,6-tetramethylpiperidine added [10% (v/v)]; (c) without base. I_0 and I_t denote the signal intensities at time zero and t after interruption of irradiation.

Table I. Aerobic Epoxidation of Olefins as Catalyzed by Niobium Porphyrin 1 upon Irradiation with Visible Light at 45 °C[a]

| olefin, mol	catalyst 1, mol	reaction time, h	yield,[b] %
cyclohexene			
2.96×10^{-3}	9.55×10^{-7}	3	5100
2.96×10^{-3}	$9.55 \times 10^{-7\,c}$	3	2830
2,3-dimethyl-2-butene			
4.20×10^{-3}	9.55×10^{-7}	5	5700
1-hexene			
2.40×10^{-2}	9.55×10^{-7}	4	220

[a] Benzene (1.5 mL) was used as the solvent. [b] Yields based on the niobium porphyrin dimer 1. Any products oxidized at the allyl site were not detected. [c] Pyridine [10% (v/v)] was added.

electrochemical, or photochemical reduction of 1.[5] Thus, the spin density at the niobium nucleus involved in the species responsible for the ESR signal is ca. 3% of that observed for $Nb^{IV}(O)(por)$. The ESR signal was rapidly quenched by any one of the following treatments: interruption of the irradiation, addition of a radical scavenger such as ethanol, and evacuation of dioxygen from the reaction system. On the basis of the above information, the paramagnetic species has been formulated as $Nb^{V}(O)(OO\cdot)(por)$ (2).

We describe here photochemical epoxidation of olefins as catalyzed by 1 under aerobic conditions without any reducing agents in the light of our previous results.[5] The ESR signal observed upon aerobic irradiation of 1 with the visible light was somewhat enhanced in intensity when heterocyclic bases such as pyridine and piperidine were added, and the rate of signal decay, caused by interruption of the aerobic irradiation, was reduced in the presence of the bases (Figure 2). Under these conditions, the heterocyclic bases were subjected to oxidation to afford the corresponding N-oxide radicals. The ESR spectrum, which was observed upon irradiation of 1 in the presence of 2,2,6,6-otetramethylpiperidine [10% (v/v)] in benzene, is composed of the signal due to the piperidine N-oxide radical overlapped with the one due to 2 (Figure 1b). Since the ESR signal intensity due to 2 was not reduced but rather enhanced upon addition of the heterocyclic bases, these bases must be oxidized by another niobium species

(1) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* 1983, *105*, 5786–5791.
(2) Franklin, C. C.; VanAtta, R. B.; Tai, A. F.; Valentine, J. S. *J. Am. Chem. Soc.* 1984, *106*, 814–816.
(3) VanAtta, R. B.; Franklin, C. C.; Valentine, J. S. *Inorg. Chem.* 1984, *23*, 4121–4123.
(4) Tabushi, I.; Morimitsu, K. *J. Am. Chem. Soc.* 1984, *106*, 6871–6872.
(5) Matsuda, Y.; Sakamoto, S.; Takaki, T.; Murakami, Y. *Chem. Lett.* 1985, *107*–110.

Scheme I
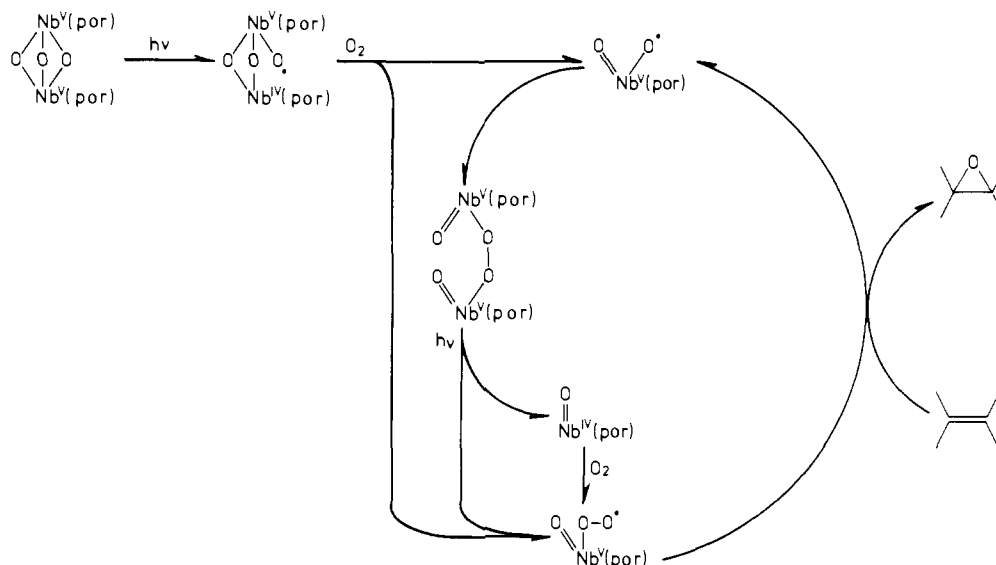
which is ESR silent. These observations are consistent with the photochemical homolysis of the Nb–O bond and the subsequent attack by dioxygen as shown by eq 1. Although both niobium
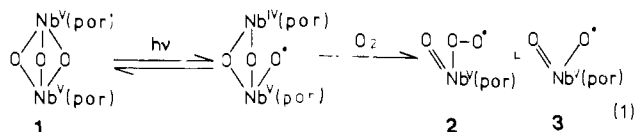
species **2** and **3** are considered to be paramagnetic, **3** seems to become ESR silent because it may have a short relaxation time due to the exchange process given by eq 2. As a consequence,
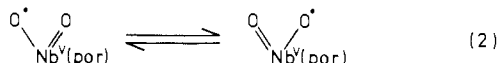
3 is responsible for oxidation of the heterocyclic bases, and the recombination of **2** and **3**, which takes place after interruption of aerobic irradiation, is disturbed due to loss of the latter; the lifetime of **2** becomes larger as shown in Figure 2.

The ESR signal was immediately quenched when olefins were added to a benzene solution of **1** under the aerobic irradiation conditions, indicating that the reaction of olefins with **2** takes place. The products were analyzed by GLC as summarized in Table I. Cyclohexene, 2,3-dimethyl-2-butene, and 1-hexene afforded exclusively the corresponding epoxides, and any products oxidized at the allyl site were not detected by GLC analysis after the reaction periods shown in Table I. Since the product yields were well over quantitative after certain reaction periods studied here, the reaction must proceed catalytically. The substrate with a terminal double bond, 1-hexene, shows lower reactivity relative to the others. This seems to be attributed to the lower oxygen affinity of terminal olefins. 2,3-Dimethyl-2-butene was transformed into the corresponding epoxide in a good yield, while 2,3-dimethyl-2-hydroperoxybutane was recovered without any transformation under the identical experimental conditions. This strongly indicates that singlet oxygen, which produces allylic oxidation products, is not involved during the present oxygenation reaction. The epoxidation of cyclohexene was somewhat depressed upon addition of pyridine to the reaction system, while addition of pyridine resulted in enhancement of the ESR signal originated from **2** under the comparable conditions without the substrate. Thus, the ESR silent species (**3**) presumably participates in the catalytic cycle, and its inactivation by the reaction with pyridine (vide supra) disturbs regeneration of the catalytically active species. The catalytic cycle is plausibly illustrated by Scheme I in the light of the present observations. The advantageous aspects of the

present catalyst system are as follows: (i) The atmospheric oxygen molecule can be utilized as a single oxygen atom source for selective epoxidation; (ii) molecular oxygen can be activated without any additional reductants. The preparation of niobium catalysts with other organic ligands is under current investigation.

Disilylation of Acetylenes with Si–Mn Reagent

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Previously reported reaction of Si–Mg, Si–Al, or Si–Zn reagents with an acetylenic linkage affords simple and general access to the cis-addition products of the component atoms.[1] The regiochemistry is dependent on the transition-metal catalysts employed and the reaction is useful in synthetic work.[2] In further extension of this technique, we have examined the reaction of Si–Mn reagent with acetylenes to observe rather unexpected formation of disilylated products.[3]

Typical experimental procedure is as follows. Methyllithium (1.4 M, 3.2 mL, 4.5 mmol) was added to a solution of hexamethyldisilane (0.93 mL, 4.5 mmol) in THF (8 mL)–HMPA (2 mL) at 0 °C. After the mixture was stirred for 15 min, methylmagnesium iodide (1.5 M, 3.0 mL, 4.5 mmol) was added to the resulting solution of (trimethylsilyl)lithium. The mixture was stirred for another 15 min and anhydrous manganese(II) chloride (0.19 g, 1.5 mmol) was added in one portion.[4,5] Then a solution

(1) Hayami, H.; Sato, M.; Kanemoto, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 4491.

(2) Morizawa, Y.; Oda, H.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 1163. Okuda, Y.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Ibid.* **1984**, *25*, 2483.

(3) Palladium(0)-catalyzed double silylation of acetylenes with disilanes of special substituents such as hydro, fluoro, and methoxy group gave the corresponding silyl olefins in good yield. In contrast, hexamethyldisilane gave very poor yields of double-silylated products. Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, 149 and references cited therein.

(4) The addition of 3 equiv of BuLi to MnCl₂ is known to give Bu₃MnLi (Normant, J.-F.; Cahiez, G. "Modern Synthetic Methods 1983"; Salle Verlag: Frankfurt/M, 1983; pp 173–216. Kauffmann, T.; Bisling, M. *Tetrahedron Lett.* **1984**, *25*, 293). We are tempted to assume that the active reagent in our new method could be (Me₃Si)₃MnMgMe derived from 3 equiv of Me₃SiMgMe and MnCl₂. The addition of PhCHO to the reagent provided only phenyl(trimethylsilyl)carbinol and no trace of 1-phenylethanol.