Table 2. The results of Si analysis in Al_2O_3 with matrix matching technique and matrix removal   unit : μg/mL

Sample	Matrix matching	Matrix separation
#1	15.5	12.0
#2	25.3	18.6
#3	91.8	81.9

ceramic samples using high pressure acid digestion bomb method.

The recovered percentages of Si over all acid concentrations prepared was over 90% with the relative standard deviation of less than 1.5%. Even there was some loss of Si for the acid concentration range of 0.08% to 2%, the recovery was fairly reproducible. The loss can cause the decrease of Si signal from the true value. Another thing to point out in this experiment is that about 20 to 40 mL of the front part of the collected solution from the separation column should be discarded because it was found that the recovery of Si increased from about 30% at first 20 mL of the solution to about 91% at 60 mL in the sulfuric acid concentration of 7%. Such results, i.e., loss of Si and dead volume occurring during the matrix elimination process, mean that large volume of sample was required for the quantitative analysis with good reproducibility and precision.

From the results, it should also be noted that acid concentrations have influence on not only the signal intensity in ICP-AES but also the efficiency of matrix removal. When sulfuric acid was added to decompose the fine ceramic powder of Al_2O_3, the volume should be controlled considerably. If too much acid was added, the decrease of removal efficiency would be expected besides the signal suppression due to the presence of sulfuric acid in ICP-AES. On the other hand, in case that too small amount of acid was used, much longer time is required to decompose sample powder and even no complete dissolution can be accomplished.

Application to Al_2O_3 ceramics. The Al matrix elimination method was applied to the real ceramic powder and the analytical results for Si are shown in Table 2. The result was compared with that of matrix matching technique. From the table it is general to say that matrix elimination technique gave less analytical value than matrix matching technique. However, this method does not require to prepare Al matrix matched standard solution that is known to be time consuming and laborious works in the laboratories. Therefore, it will be useful to apply this method to the industrial laboratories in which many samples are to be handled daily.

References

1. MacChesney, J. B.; Potter, J. F. *J. Am. Ceram. Soc.* 1965, 48(2), 81.
2. Sauer, H. A.; Fisher, J. R. *J. Am. Ceram. Soc.* 1960, 43(6),

297.
3. Matsuo, Y.; Fujimura, M.; Sasaki, H.; Nagase, K.; Hayakawa, S. *Ceramic Bulletin* 1967, 47(3), 292.
4. Goodman, G.; Buchanan, Relva.C.; Reynolds III, T.G. In *Ceramic Materials for Electronics*; Buchanan, Relva. C. Ed.; Marcel Dekker, Inc.: New York, U.S.A., 1990; p 79.
5. Broekaert, J. A. C.; Brandt, R.; Leis, F.; Pilger, C.; Pollmann, D.; Tschopel, P.; Tolg, G. *J. Anal. Atom. Spectrom.* 1994, 9, 1065.
6. Broekaert, J. A. C.; Tolg, G. *Fresenius Z. Anal. Chem.* 1987, 325, 495.
7. Broekaert, J. A. C.; Graule, T.; Jenett, H.; Tolg, G.; Tschopel, P. *Fresenius Z. Anal. Chem.* 1989, 322, 825.
8. Pollmann, D.; Leis, F.; Tolg, G.; Tschopel, P.; Broekaert, J. A. C. *Spectrochim. Acta* 1994, 49B(12-14), 1251.
9. Lim, H. B.; Han, J. R.; Lee, G. H.; Lee, K. W.; Yanagisawa, M. *J. of the Korean Chemical Society* 1994, 38(6), 411.

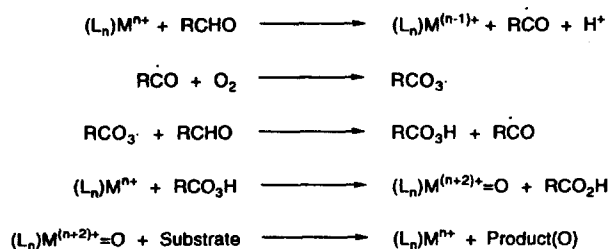# Nickel Complex as a Radical Inhibitor in the Oxidation Reactions by Dioxygen Plus Aldehyde

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Catalytic oxidation of hydrocarbons by dioxygen plus aldehyde catalyzed by metal complexes is of current interest in functionalization of organic compounds.[1] These reactions proceed *via* a free-radical type of mechanism in which radicals such as acyl and acylperoxy radicals are generated in the reaction media (Scheme 1).[1(a),2] While we have been studying the epoxidation of olefins by dioxygen plus aldehyde in the presence of metal complexes,[3] we found that nickel complexes of tetraazamacrocyclic ligands have the ability to inhibit the radical type of oxidation reactions.[4] We herein describe the inhibition of the radical reaction by a

$$(L_n)M^{n+} + RCHO \longrightarrow (L_n)M^{(n-1)+} + R\dot{C}O + H^+$$

$$R\dot{C}O + O_2 \longrightarrow RCO_3{}^{\cdot}$$

$$RCO_3{}^{\cdot} + RCHO \longrightarrow RCO_3H + R\dot{C}O$$

$$(L_n)M^{n+} + RCO_3H \longrightarrow (L_n)M^{(n+2)+}=O + RCO_2H$$

$$(L_n)M^{(n+2)+}=O + Substrate \longrightarrow (L_n)M^{n+} + Product(O)$$

Scheme 1.

Notes

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Table 1. Effect of a nickel complex in the epoxidation of cyclo-hexene by O_2 plus aldehyde[a]

| Metalloporphyrins	Yield of cyclohexene oxide (mmol)
Cr(TPP)Cl	1.0 (0)[b]
Mn(TPP)Cl	1.0 (0)[b]
Fe(TPP)Cl	1.0 (0)[b]
Co(TPP)	1.0 (0)[b]
Ni(TPP)	1.2 (0)[b]

[a] Reaction conditions: Metalloporphyrin (0.02 mmol), cyclohexene (3 mmol), and cyclohexanecarboxaldehyde (1 mL) in CH_3CN (5 mL). O_2 was bubbled through the reaction solution for 8 h. [b] Numbers in parentheses were obtained when the reaction was carried out in the presence of [1,2-bis(diphenylphosphino)-ethane]nickel(II) chloride (0.02 mmol).

nickel complex, [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride, and the oxidation of a cobalt porphyrin complex, $Co^{II}(TPP)$ (TPP=tetraphenylporphyrin), in the oxidation reaction by dioxygen plus aldehyde.

The epoxidation of cyclohexene by dioxygen plus aldehyde in the presence of metalloporphyrin complexes yielded cyclohexene oxide as the predominant product (Table 1).[3] When [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride was added to the metal porphyrin complex-mediated cyclohexene epoxidation, both the epoxidation of cyclohexene and the oxidation of aldehyde were not initiated at least for 8 h as shown in Table 1, clearly indicating that the nickel complex has the ability of inhibiting the radical reaction.[4] When either nickel chloride or 1,2-bis(diphenylphosphino)ethane alone was added to the iron porphyrin complex-mediated cyclohexene epoxidation, the epoxidation reaction was not inhibited.

We proposed previously that the role of the nickel complex is to trap an acylperoxy radical, $RC(O)OO\cdot$, generated in the oxidation of aldehyde by dioxygen (eq. 1).[4] In this case, radicals produced cannot build up sufficiently to

$$Ni(II) + RC(O)OO\cdot \rightarrow Ni(III) + RC(O)OO^- \quad (1)$$
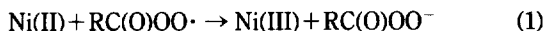
initiate the propagation of the radical reaction as shown in Scheme 1. A supporting evidence for this suggestion is that an organic peroxy radical scavenger, N-phenyl-1-naphthyl-amine,[5] added to the epoxidation of cyclohexene by dioxygen plus aldehyde carried out in the presence of a cobalt porphyrin complex also inhibited the radical reaction.[3] It has been proposed that the organic radical scavenger reduces a peroxy radical to the corresponding anion *via* an electron transfer from the nitrogen atom of N-phenyl-1-naphthylamine to the peroxy radical which is generated from *tert*-butyl hydroperoxide (eq. 2).[6] In the reactions of molecular oxygen plus aldehyde, the amine compound reacts with an acylperoxy radical and reduces it to the corresonding peroxy anion (eq. 3). We conclude based on these results that the nickel complex efficiently reacts with the acylperoxy radical and transfers one electron from nickel(II) to the radical species as shown in eq. 1,[4,7] thereby the radical chain reaction is delayed.
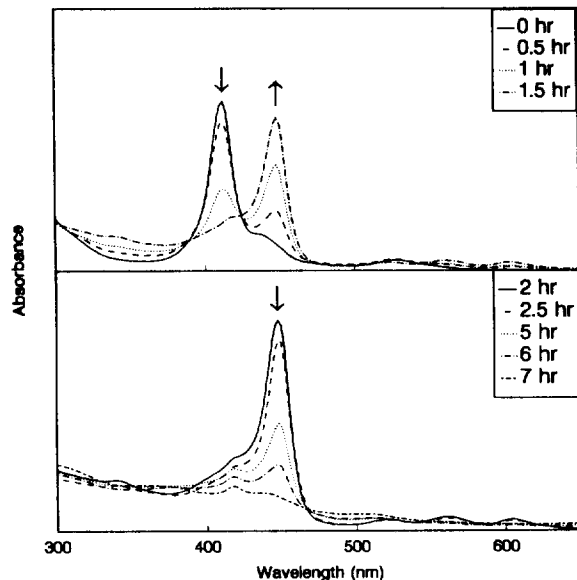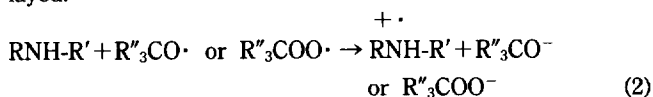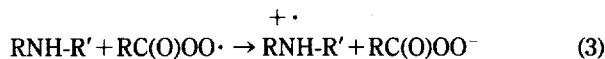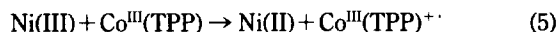
$$RNH\text{-}R' + R''_3CO\cdot \text{ or } R''_3COO\cdot \xrightarrow{+\cdot} RNH\text{-}R' + R''_3CO^-$$
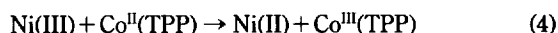$$\text{or } R''_3COO^- \quad (2)$$

Figure 1. UV-visible spectral changes of Co(TPP) (0.02 mmol) obtained during the oxidation reaction with O_2 plus cyclohexane-carboxaldehyde (1 mL) in the presence of [1,2-bis(diphenylphos-phino)ethane]nickel(II) chloride (0.02 mmol) in $ClCH_2CH_2Cl$ (5 mL).

$$RNH\text{-}R' + RC(O)OO\cdot \xrightarrow{+\cdot} RNH\text{-}R' + RC(O)OO^- \quad (3)$$

It was found that cobalt porphyrin complex, Co(TPP), was slowly oxidized during the oxidation reaction by dioxygen plus aldehyde, carried out in the presence of [1,2-bis(diphen-ylphosphino)ethane]nickel(II) chloride. UV/vis spectral changes of the Co(TPP) complex obtained during the oxidation reaction indicated that $Co^{II}(TPP)$ was completely oxidized to $Co^{III}(TPP)$,[8] then the $Co^{III}(TPP)$ species formed disappeared when the reaction proceeded further (see Figure 1). By taking EPR spectra of the cobalt porphyrin complex during the oxidation reaction, it was demonstrated that Co^{II} (TPP) was oxidized to $Co^{III}(TPP)$, and then to $Co^{III}(TPP)^{+\cdot}$ species (see Figure 2).[9] Since the oxidation potential of Co^{II} $(TPP)/Co^{III}(TPP)$ is smaller than that of $Co^{III}(TPP)/Co^{III}$ $(TPP)^{+\cdot}$,[10] $Co^{II}(TPP)$ was completely oxidized to $Co^{III}(TPP)$ before the oxidation of $Co^{III}(TPP)$ to $Co^{III}(TPP)^{+\cdot}$ took place in the reaction system. When Co(TPP) was oxidized in the absence of the nickel complex, the distinct spectral changes were not observed, but fast degeradation of the porphyrin ligand of the Co(TPP) complex occurred within 30 min. The UV/vis and EPR spectral changes of the cobalt porphyrin complex were summarized in Scheme 2.

A possible explanation for the oxidation of the cobalt complexes is that the cobalt complex is to reduce the Ni(III) species which is formed by the reaction of Ni(II) and an acylperoxy radical (eq. 1).[11] In this case, Ni(II) species is regenerated by the reduction of the Ni(III) by an electron transfer from the cobalt complexes (eqs. 4 and 5).

$$Ni(III) + Co^{II}(TPP) \rightarrow Ni(II) + Co^{III}(TPP) \quad (4)$$

$$Ni(III) + Co^{III}(TPP) \rightarrow Ni(II) + Co^{III}(TPP)^{+\cdot} \quad (5)$$

In summary, we have shown that [1,2-Bis(diphenylphos-
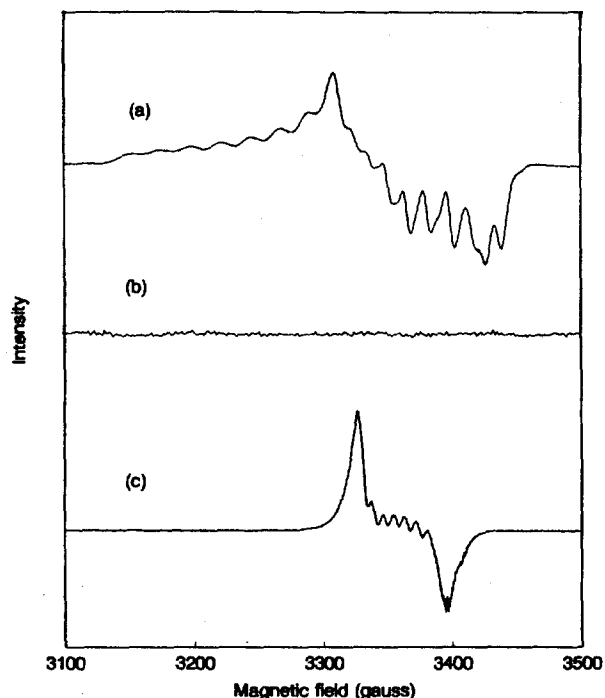
Figure 2. EPR spectra of cobalt porphyrin complexes at 77 K, (a) (TPP)Co^{II}·O$_2$, (b) Co^{III}(TPP), (c) Co^{III}(TPP)$^{+·}$.

$$Co^{II}(TPP) \xrightarrow{-e^-} Co^{III}(TPP) \xrightarrow{-e^-} Co^{III}(TPP)^{+·}$$

EPR signal   EPR silent   EPR signal (g = 2.0047)

UV/vis

Soret band = 412 nm   448 nm

Q bands = 528 nm   522, 562, 604 nm
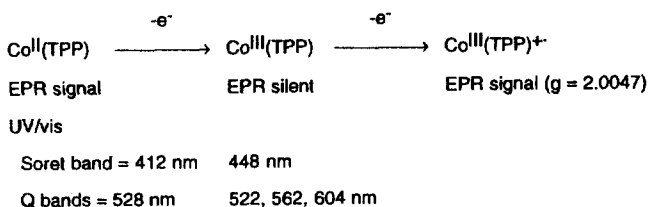
Scheme 2.

phino)ethane] nickel(II) chloride was found to be an efficient radical inhibitor in the oxidation reactions by molecular oxygen plus aldehyde catalyzed by metalloporphyrin complexes. A cobalt porphyrin complex, Co^{II}(TPP), was oxidized to Co^{III} (TPP), and then to Co^{III}(TPP)$^{+·}$ species during the oxidation reaction in the presence of the nickel complex. More detailed mechanistic studies are currently under investigation in connection with the chemistry of the known antioxidants.[12]

Experimental

Materials and Instrumentation. Reagents and solvents were purchased from Aldrich Chemical Co. and used without further purification unless otherwise indicated. Product analyses were performed on Donam Systems DS6200 gas chromatograph equipped with an HP-1 capillary column. UV/vis spectra were recorded on Hewlett Packard 5890 spectrophotometer. EPR spectra were obtainded on Bruker ESP 300 spectrometer.

General Oxidation Reactions. In a typical procedure, metal porphyrin complex (0.02 mmol), cyclohexene (3 mmol), and cyclohexanecarboxaldehyde (1 mL) were dissolved in ClCH$_2$CH$_2$Cl (5 mL). [1,2-Bis(diphenylphosphino) ethane] nickel(II) chloride (0.02 mmol) was added to the above reaction solution. Dioxygen (2 mL/min) was bubbled through the reaction solution, and then the products were analyzed by GC. EPR and UV/vis spectral studies of Co(TPP) were carried out in ClCH$_2$CH$_2$Cl (5 mL) containing Co(TPP) (0.02 mmol), [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride (0.02 mmol), and cyclohexanecarboxaldehyde (1 mL).

References

1. (a) Murahashi, S.-I.; Oda, Y.; Naota, T. *J. Am. Chem. Soc.* **1992**, *114*, 7913. (b) Mukaiyama, T.; Yamada, T.; Nagata, T.; Imagawa, K. *Chem. Lett.* **1993**, 327. (c) Takai, T.; Hata, E.; Yamada, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2513. (d) Yamada, T.; Takai, T.; Rhode, O.; Mukaiyama, T. *Chem. Lett.* **1991**, 1. (e) Mlodnicka, T. *J. Mol. Cat.* **1986**, *36*, 205.

2. (a) Simandi, L. I., Ed. *Catalytic Activation of Dioxygen by Metal Complexes*; Kluwer Academic Publishers: Dordrecht, 1992; pp 318-331. (b) Sheldon, R. A.; Kochi, J. K., Eds., *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; pp 359-363.

3. Nam, W.; Kim, H. J.; Kim, S. H.; Baek, S. J.; Ho, R.; Valentine, J. S. *Inorg. Chem.*, submitted for publication.

4. Nam, W.; Baek, S. J.; Lee, K. A.; Ahn, B. T.; Valentine, J. S. *Inorg. Chem.*, submitted for publication.

5. Hamilton, D. E.; Drago, R. S.; Zombeck, A. *J. Am. Chem. Soc.* **1987**, *109*, 374.

6. Maruyama, K.; Kusukawa, T.; Higuchi, Y.; Nishinaga, A. in *Dioxygen Activation and Homogeneous Catalytic Oxidation*; Simandi, L. I., Ed., Kluwer Academic Publishers: Dordrecht, 1991; pp 489-495.

7. Meshulam, A.; Cohen, H.; Eldik, R. V.; Meyerstein, D. *Inorg. Chem.* **1992**, *31*, 2151.

8. (a) Lee, W. A.; Bruice, T. C. *Inorg. Chem.* **1986**, *25*, 131. (b) Sugimoto, H.; Ueda, N.; Mori, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3425.

9. (a) Wayland, B. B.; Mohajer, D. *J. Chem. Soc., Chem. Commun.* **1972**, 776. (b) Kadish, K. M.; Mu, X. H.; Lin, X. Q. *Inorg. Chem.* **1988**, *27*, 1489.

10. Smith, K. M., Ed., *Porphyrins and Metalloporphyrins*; Elsevier: Amsterdam, 1975.

11. Kumar, K.; Rotzinger, F. P.; Endicott, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 7064.

12. Ingold, K. U. *Acc. Chem. Res.* **1969**, *2*, 1.