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SELECTIVE FORMATION OF PEROXY-*p*-QUINOLATO Co(III) COMPLEXES IN THE OXYGENATION OF 4-ALKYL-2,6-DI-*t*-BUTYLPHENOLS WITH Co(II)-SCHIFF'S BASE COMPLEXES

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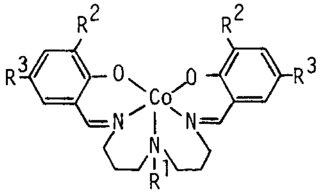
The oxygenation of 4-alkyl-2,6-di-*t*-butylphenols (**2**) with Co(II)-Schiff's base complexes in aprotic solvents such as CH_2Cl_2, THF, Py, and DMF leads to highly selective formation of the corresponding peroxy-*p*-quinolato Co(III) complexes. The reaction proceeds by mechanism involving a rate determining hydrogen abstraction by superoxo Co(III) species from **2** giving phenoxy radical, rapid step of electron transfer from Co(II) complex to the phenoxy radical, and dioxygen incorporation into phenolato Co(III) complex thus formed.

Selective oxidation of organic substrates catalyzed by transition metal complexes capable of activating dioxygen is of current interest from viewpoints of synthetic problems[1-4] and biological oxygenations.[5-8] In a previous report on the oxygenation of 4-alkyl-2,6-di-*t*-butylphenols (**2**) catalyzed by Co(II)-Schiff's base complexes in methanol leading to the corresponding *p*-quinols, peroxy-*p*-quinolato Co(III) complex has been suggested as a reaction intermediate.[9] We now report that the oxygenation of **2** with Co(II)-Schiff's base complexes **1** proceeds stoichiometrically in aprotic solvents such as CH_2Cl_2, THF, Py, and DMF resulting in the exclusive formation of peroxy-*p*-quinolato Co(III) complexes **3** in contrast to the case of 4-aryl-2,6-di-*t*-butylphenols, where only peroxy-*o*-quinolato complexes **4** are formed.[10]

Peroxy-*p*-quinolato Co(III) complexes **3a**-**f** were isolated as crystals (Table 1), whose ^{1}H NMR spectra display two signals for *t*-Bu groups and a signal for the alkyl group R shifted unusually to high field, which are characteristic for **3** (Table 1). Acid hydrolysis of **3** gave the corresponding hydroperoxides **5** quantitatively. Attempts to isolate **3** other than those given in Table 1 were not undertaken, but ^{1}H NMR spectra of the oxygenation mixtures confirm exclusive formation of the corresponding **3**. Table 2 shows relation between O_2-uptake and formation of **3**. Time course of the oxygenation of **2d** with **1b** shows that the formation of **3d** corresponds to the consumption of **1b**



1

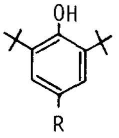
a; $R^1=R^2=R^3$ =H; Co(Salpr)

b; R^1=Me, $R^2=R^3$=H; Co(NMeSalpr)

c; R^1=Me, R^2=OMe, R^3=H; Co(3-MeONMeSalpr)

d; R^1=Me, $R^2=R^3$=Cl; Co(3,5-Cl_2NMeSalpr)

e; R^1=Me, R^2=H, $R^3=NO_2$; Co(5-NO_2NMeSalpr)



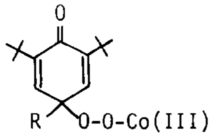
2

a; R=t-Bu

b; R=i-Pr

c; R=Et

d; R=Me



3

a; R=t-Bu, Co(Salpr)

b; R=i-Pr, Co(Salpr)

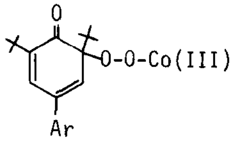
c; R=Et, Co(Salpr)

d; R=Me, Co(Salpr)

e; R=Me, Co(3-MeONMeSalpr)

f; R=Me, Co(3,5-Cl_2NMeSalpr)

g, R=Me, Co(5-NO_2NMeSalpr)



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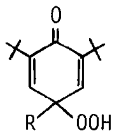

5

Table 1. Peroxy-p-quinolato Co(III) Complexes **3**[a]

3[b]	Yield[c] (%)	mp(dec) (°C)	^{1}H NMR($CDCl_3$) δ(ppm) t-Bu		R^d
3a	64	160~162	1.28	1.30	0.60
3b	60	130~131	1.18	1.30	0.57[e]
3c	62	110~112	1.10	1.27	0.50[f]
3d	64	136~137	1.07	1.25	
3e	81	95~96	0.95	1.05	0.72
3f	73	103~105	1.00	1.06	0.82
3g	60	> 200	1.23	1.27	0.91

[a] Synthetic Conditions: Oxygen was bubbled through a solution of **1** (3 mmol) and **2** (6 mmol) in CH_2Cl_2 at 0 °C for 3 h. The reaction mixture was concd and addition of petrol. ether gave **3** as crystals. [b] All products show satisfactory analytical results: C,±0.31%; H,±0.29%; N,±0.25%; Co,±0.21%. [c] Yield by isolation based on **1**: product selectivity;ca. 100%. [d] Me group. [e] d,J=7 Hz. [f] t,J=7.5 Hz.

Table 2. Relation Between O_2-Uptake and Formation of **3**[a]

1	**2**	$t^b_{1/2}$ (min)	**3**[c] (%)	O_2-uptake/**1** (mol/mol)	**3**/**1** (mol/mol)
1a	**2a**		100	1.25	1.0
1a	**2d**	14	100	1.25	1.0
1e	**2d**	10	100	1.25	1.0
1d	**2d**	10	100	1.0	–[d]
1c	**2d**	11	100	1.0	0.5
1b	**2d**	10	100	1.0	0.5

[a] O_2-uptake was determined by gas volumetric analysis with a solution of **1** (1 mmol) and **2** (10 mmol) in CH_2Cl_2 (25 ml) at 5 °C at a constant O_2 pressure (780 mmHg). [b] Half conversion time. [c] Selectivity. [d] Not determined.

with two times O_2-uptake (Figure 1). No hydrogen peroxide is contained in any oxygenation mixture. In the case of O_2-uptake/**1** = 1, however, acidification of the oxygenation mixture releases hydrogen peroxide, indicating the formation of Co(III)O_2H. The following stoichiometries (i) and

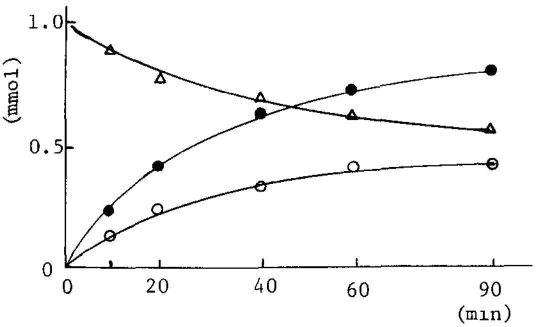

Figure 1. Time course of the oxygenation of **2d** with **1b**. Conditions: [**1b**]=[**2d**]=$2.5\text{X}10^{-2}$M in CH_2Cl_2 (40 ml), 5 °C. ○;**3**, ●;O_2, △;**2**.

(ii) are therefore describable for the cases of O_2-uptake/**1** = 1 and 1.25,[10] respectively.

$$2\ \text{Co(II)} + 2\ O_2 + \mathbf{2} \longrightarrow \mathbf{3} + \text{Co(III)}O_2H \qquad \text{(i)}$$

$$\text{Co(II)} + 5/4\ O_2 + \mathbf{2} \longrightarrow \mathbf{3} + 1/2\ H_2O \qquad \text{(ii)}$$

Obviously, the present oxygenation requires activation of dioxygen by **1**, and superoxo (CoO_2) complex thus formed initiates the reaction by hydrogen abstraction from **2**.[10,11] Rate of the oxygenation depends on the concentration of **2**. The reaction with ten times excess of **2d** follows pseudo first order kinetics with respect to **1b** up to more than 90% conversion (rate constant, $7.8 \text{ X } 10^{-4}$ sec^{-1} at 5 °C).

These results are reasonably explained in terms of the following reaction mechanism involving rate determining steps (1) and (2).

$$\begin{array}{lllll}
\underset{\mathbf{1}}{\text{Co(II)}} + O_2 & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & CoO_2\ [\text{Co(III)}O_2^-] & & (1) \\
CoO_2 + \underset{\mathbf{2}}{PH} & \xrightarrow{k_2} & \text{Co(III)}O_2H & + \ P\cdot & (2) \\
\text{Co(III)}O_2H & \xrightarrow{k_3} & \text{Co(III)OH} & + \ 1/2\ O_2 & (3) \\
P\cdot + \text{Co(II)} & \xrightarrow{\text{fast}} & P^-\text{Co(III)} & & (4) \\
PH + \text{Co(III)OH} & \xrightarrow{\text{fast}} & P^-\text{Co(III)} & + \ H_2O & (5) \\
P^-\text{Co(III)} + O_2 & \xrightarrow{k_6} & \underset{\mathbf{3}}{\text{POOCo(III)}} & & (6)
\end{array}$$

A kinetic analysis with **1b** and **2d**, applying a steady state approximation for the reactions (1) and (2),[14] has allowed us to estimate values of k_1 and k_{-1}/k_2 as $1.43 \text{ X } 10^{-1}sec^{-1}M^{-1}$ and $3.59 \text{ X } 10^{-2}$(5 °C), respectively. Decomposition reaction of hydroperoxo Co(III) complex [reaction (3)] has been known with an analogous compound.[15] Phenoxy radical (P·) is rapidly reduced by **1b** to give phenolato Co(III) complex,[16] which is also formed by the reaction (5) in the case of O_2-uptake/**3** = 1.25. Assumption of the phenolato Co(III) complex formation is quite reasonable taking account of the results obtained in the dioxygen incorporation into free phenolate anions.[17] The high regioselective dioxygen incorporation giving the peroxy-*p*-quinolato Co(III) complexes is due to the rapid phenolato Co(III) complex formation. Although no information about structure of the phenolato Co(III) complex is available for the moment, a π-complex may be reasonably assumed as deduced from mechanism of the oxygenation of phenolate anions.[18] Rate constant k_6 has been estimated to be 5.0×10^{-1} sec^{-1} M^{-1} (5 °C) with phenolato Co(III) complex derived from 1b and phenoxy radical of 2a, which is about 30 times larger than the rate constant of dioxygen incorporation into free phenolate anions, providing a support of one step ionic mechanism for the oxygenation of phenolate anions.[17]

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