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t-BUTYLPEROXY COBALT(III) SCHIFF BASE COMPLEXES. PREPARATION AND PROPERTIES

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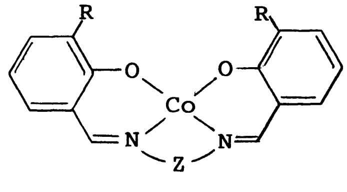
Treatment of t-butyl hydroperoxide with cobalt(II) Schiff base complexes in CH_2Cl_2 at room temperature gave the corresponding t-butylperoxy cobalt(III) complexes, which were isolated as crystals in good yield. The peroxy complexes oxidize Ph_3P to Ph_3PO and the Co-O bond in the peroxy complexes undergoes heterolysis with acids but homolysis in alcohols.

Reactions of organic hydroperoxides with cobalt(II) complexes bearing organic base ligands result normally in the one-electron reductive decomposition of the hydroperoxides, where the nature of decomposition products depends on the nature of the ligand of the complex and the solvent used.[1-3] In principle, formation of peroxy cobalt(III) complexes should be expected in the reaction of hydroperoxides with cobalt(II) complexes.[4] Little has, however, been reported on the preparation of peroxy cobalt(III) complexes from reactions between hydroperoxides and cobalt (II) complexes,[5] although the formation of a binary complex of cobalt(II) complex with hydroperoxide in cobalt(II)-catalyzed autoxidation of hydrocarbons has been suggested.[8] We now wish to report the preparation of t-butylperoxy cobalt(III) complexes from the reaction of t-butyl hydroperoxide with cobalt(II) Schiff base complexes and some properties of the peroxy complexes.

When t-butyl hydroperoxide (75 mmol)(commercially available 70% t-BuOOH) was added to a suspension of Co(Salen) (50 mmol) in dichloromethane (400 cm^3) at room temperature, a clear solution was obtained transiently. After a few minutes, t-BuOOCo(Salen) was deposited as fine crystals. A similar result was obtained from the reaction of t-butyl hydroperoxide with Co(MeOSalen), but evaporation of the



Co(Salen): R = H, Z = $(CH_2)_2$
Co(MeOSalen): R = OMe, Z = $(CH_2)_2$
Co(Salphen): R = H, Z = o-C_6H_4
Co(Salpr): R = H, Z = $(CH_2)_3NH(CH_2)_3$
Co(NMeSalpr): R = H, Z = $(CH_2)_3NMe(CH_2)_3$

solvent followed by addition of ether was required to isolate t-butylperoxy cobalt (III) complexes from Co(Salphen), Co(Salpr), and Co(NMeSalpr).9)

Spectrophotometric titration of t-butyl hydroperoxide with Co(Salen) showed an apparent 1 : 2 end point. Since the electronic spectrum of t-BuOOCo(Salen) is superimposable with that of HOCo(Salen) in the range of about 250 to 700 nm, the titration and the fact that t-BuOOCo(Salen) was isolated in 80% yield indicate that t-BuOOCo(Salen) is formed according to the following equations (1)-(3). The stoichiometry (4) is, thus, obtained, which is in good agreement with the preparative results.

$$\text{t-BuOOH} + 2\ \text{Co(Salen)} \longrightarrow \text{t-BuOCo(Salen)} + \text{HOCo(Salen)} \tag{1}$$

$$\text{t-BuOCo(Salen)} + \text{t-BuOOH} \longrightarrow \text{t-BuOOCo(Salen)} + \text{t-BuOH} \tag{2}$$

$$\text{HOCo(Salen)} + \text{t-BuOOH} \longrightarrow \text{t-BuOOCo(Salen)} + \text{H}_2\text{O} \tag{3}$$

$$2\ \text{Co(Salen)} + 3\ \text{t-BuOOH} \longrightarrow 2\ \text{t-BuOOCo(Salen)} + \text{t-BuOH} + \text{H}_2\text{O} \tag{4}$$

t-BuOOCo(Salen) oxidizes triphenylphosphine to triphenylphosphine oxide. Since the oxygen transfer reaction proceeds considerably fast and quantitatively at room temperature, this reaction can conveniently be applied for determination of the purity of the peroxy complex. In this reaction, the formation of t-BuOCo(Salen) should be expected, but isolable complex was only HOCo(Salen), obtainable by hydrolysis of the alkoxy complex *in situ* or during workup.

$$\text{Ph}_3\text{P} + \text{t-BuOOCo(Salen)} \longrightarrow \text{Ph}_3\text{PO} + \text{t-BuOCo(Salen)} \xrightarrow{\text{H}_2\text{O}} \text{HOCo(Salen)}$$

t-BuOOCo(Salen) reacted with acetic acid in dichloromethane rapidly to give AcOCo(Salen) and t-butyl hydroperoxide quantitatively,10) indicating an ionic nature of the Co-O bond in the peroxy complex as expected. The ionic nature of the Co-O bond in t-BuOOCo(Salen) was also confirmed by the reaction with other acids HX (X; CF_3COO, Cl) giving rise to XCo(Salen) and t-BuOOH.10)

Interestingly, however, when a solution of t-BuOOCo(Salen) in methanol was warmed gently under a nitrogen atmosphere, the peroxy complex was reduced to Co(Salen) quantitatively.11) The reduction also took place easily in other alcohols except tertiary alcohols. Since the reaction of the peroxy complex with benzyl alcohol gave benzaldehyde quantitatively (stoichiometry: Co/aldehyde = 1/1), the conversion of t-BuOOCo(Salen) to Co(Salen) should involve homolysis of the Co-O bond followed by hydrogen abstraction from the alcohol by the resulting t-butylperoxy radical. With other t-butylperoxy cobalt(III) complexes obtained in the present work, the similar reactivities towards triphenylphosphine, acids, and alcohols were observed.

Co(Salen) has been found to catalyze the oxidative deamination of 4-amino-1,2,4-triazin-5(4H)-ones, important herbicides, with t-butyl hydroperoxide, which provides an interesting model for the metabolism of the herbicides,13) and the oxidative t-butylperoxylation of hindered phenols14) and hydrazones.15) In these reactions, t-BuOOCo(Salen) is now found to be the real catalytically active species, which iniciates the reactions by hydrogen abstraction from the substrates.

Although t-butylperoxy palladium(II) complexes have been reported to catalyze the oxidation of terminal olefins with t-butyl hydroperoxide,16) no catalytic activity of t-BuOOCo(Salen) was observed for oxidation of olefins with t-butyl hydroperoxide in dichloromethane, where an inactive complex, ClCo(Salen) was formed and deposited unexpectedly.17)

t-BuOOCo(Salen) as well as other five coordinate peroxy cobalt(III) complexes is found to be unstable in general in chlorinated solvents such as dichloromethane and chloroform resulting in the formation of the corresponding chloro cobalt(III) complexes. In the presence of a base ligand such as pyridine or N-methylimidazole, however, the peroxy cobalt(III) complexes become stable in the chlorinated solvents. Since Co(Salen) itself was quite stable in dichloromethane, the t-butylperoxy group should take part in the formation of the chloro cobalt(III) complex. Detailed mechanism of the formation of ClCo(Salen) and of the reduction of t-butylperoxy cobalt(III) complexes in alcohols are currently investigated.

References

1) W. H. Richardson, J. Am. Chem. Soc., 87, 247 (1965).
2) J. H. Espenson and A. H. Martin, J. Am. Chem. Soc., 99, 5953 (1977).
3) R. W. Brandon and C. S. Elliot, Tetrahedron Lett., 1967, 4375.
4) Coupling of a peroxy radical with a cobalt(II) species and/or reaction between hydroperoxide and hydroxo cobalt(III) species formed in the one-electron reduction of hydroperoxide with cobalt(II) species could be expected to give peroxy cobalt(III) complexes. Actually, the reaction of Co(Salpr) with 2,4,6-tri-t-butyl-4-hydroperoxy-2,5-cyclohexadienone gives peroxy-p-quinolato Co(Salpr) along with one-electron reductive decomposition products from the hydroperoxide: A. Nishinaga, H. Tomita, K. Nishizawa, T. Matsuura, S. Ooi, and K. Hirotsu, J. Chem. Soc., Dalton Trans., 1981, 1504.
5) Alkylperoxy cobalt(III) complexes are normally prepared by insertion of dioxygen into the Co-C bond of alkylcobalt complexes,6) or by photochemical replacement of the alkyl group in organocobalt complexes with a hydroperoxide.7) Oxygenation of hindered phenols with Co(Salpr) also gives peroxyquinolato Co(Salpr).4) Very recently, it is reported that the reaction of cobaloxime with t-butyl hydroperoxide in benzene gives t-butylperoxy cobaloxime and hydroxo cobaloxime: J. H. Espenson and J. D. Melton, Inorg. Chem., in press.
6) D. Dodd and M. D. Johnson, Organometal. Chem. Rev., 52, 1 (1973).
7) C. Gianotti, C. Fontaine, A. Chiaroni, and C. Riche, J. Organometal. Chem., 113, 57 (1976).
8) J. F. Black, J. Am. Chem. Soc., 100, 527 (1978).
9) t-BuOOCo(Salen) and t-BuOOCo(MeOSalen) were deposited as crystals directly from the reaction mixture in 80% and 71% yield, respectively. The complexes showed satisfactory analytical results (C, ±0.5%; H, ±0.5%; N, ±0.3%). t-BuOOCo(Salphen), t-BuOOCo(Salpr), and t-BuOOCo(NMeSalpr) were not deposited directly from the reaction mixtures, but after evaporation of the solvent followed by addition of ether (yield, 70%, 40%, 41%, respectively).

In the oxidation of Co(Salphen) with t-BuOOH in dichloromethane, the resulting t-BuOOCo(Salphen) was always contaminated by ClCo(Salphen) formed by the reaction of t-BuOOCo(Salphen) with CH_2Cl_2. Elemental analysis and determination with PPh_3 showed that a sample obtained after a 1.5 h reaction includes about 20% of ClCo(Salphen).

10) t-BuOOH was determined by the reaction with PPh_3 giving rise to Ph_3PO. XCo(Salen) complexes (X; AcO, CF_3COO, Cl) were isolated as crystals, which showed satisfactory analytical results (C, H, N; ±0.5%).

11) HOCo(Salen) was obtained quantitatively in the air. This is due to the oxidation of Co(Salen) generated *in situ* with O_2.[12)]

12) G. Costa, G. Mestroni, and G. Pellizer, J. Organometal. Chem., **15**, 187 (1965).

13) Y. Nakayama, Y. Sanemitsu, H. Yoshioka, and A. Nishinaga, Tetrahedron Lett., **23**, 2499 (1982).

14) A. Nishinaga, H. Nogusa, and T. Matsuura, to be published.

15) A. Nishinaga, S. Yamazaki, and T. Matsuura, to be published.

16) H. Mimoun, J. Mol. Catal., **7**, 1 (1980).

17) In a few preliminary experiments, we find that Co(Salpr) catalyzes oxidative t-butylperoxylation of styrene with t-BuOOH in CH_2Cl_2, and that Co(Salen) can catalyze oxidation of styrene with t-BuOOH in methanol to give acetophenone. These interesting problems are currently investigated.

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