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OXIDATION OF *cis*-DIALKYLCOBALT(III) COMPLEXES BY OXYGEN. ACTIVATION OF OXYGEN BY PERCHLORIC ACID

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The effects of protons on the reactions of *cis*-dialkylcobalt(III) complexes, *cis*-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et, $PhCH_2$; bpy = 2,2'-bipyridine), with oxygen are reported. Oxygen is shown to be activated in the presence of perchloric acid by forming hydroperoxonium ion which has a much stronger oxidizing ability than oxygen.

Oxidation of transition-metal alkyls by oxygen has usually been avoided carefully in their handling and thus, little is known about the oxidation processes.1) However, the reactions of oxygen with organometallic compounds have recently attracted growing attention,2) although some transition-metal alkyls are stable towards oxygen. Generally, oxygen is an unreactive molecule towards singlet organic compounds because of the triplet ground state and the low one-electron reduction potential.3) The two-electron reduction of oxygen in the presence of acids, however, is energetically much more favorable than the one-electron reduction in the absence of protons.4) Therefore, the presence of acid is expected to enhance the oxidizing ability of oxygen significantly. In this study, we report the first example of acid promoted reactions of oxygen with transition-metal alkyls which are stable towards oxygen in the absence of acids.

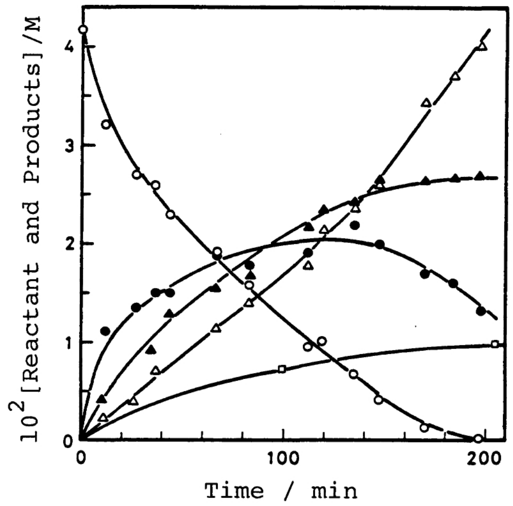


Fig. 1. Oxidation of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ by oxygen in the presence of $HClO_4$ (0.12 M; 1 M = 1 mol dm^{-3}) in CD_3CN at 273 K, monitored by ^1H nmr; *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (○), $PhCH_2$-OOH (●), PhCHO (△), $[PhCH_2Co(bpy)_2]^{2+}$ (▲), $[Co(bpy)_3]^{2+}$ (□).

The *cis*-dialkylcobalt(III) complexes, *cis*-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et, $PhCH_2$; bpy = 2,2'-bipyridine), are stable towards oxygen in acetonitrile (MeCN) at 298 K. However, *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ reacts readily with oxygen in the presence of perchloric acid ($HClO_4$) in CD_3CN even at 273 K to yield benzyl hydroperoxide which decomposes to produce benzaldehyde as a final oxidation product (Fig. 1).5) The rate of the decay of

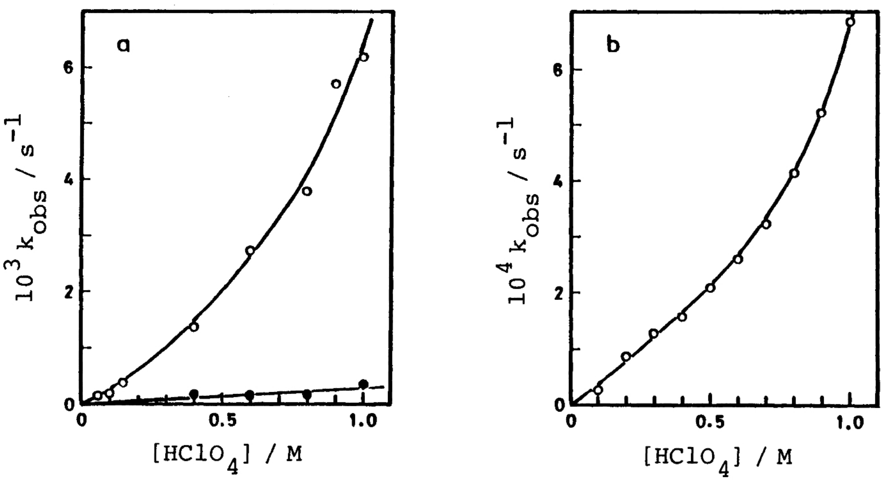


Fig. 2. (a) Dependence of the observed pseudo-first-order rate constant k_{obs} on the $HClO_4$ concentration for the oxidation of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ by oxygen in the presence of $HClO_4$ (○) and for the reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with $HClO_4$ in the absence of oxygen (●) in MeCN at 298 K. (b) Dependence of k_{obs} on $[HClO_4]$ for the one-electron oxidation of 1,1'-dimethylferrocene (Me_2Fc) by oxygen in the presence of $HClO_4$ in MeCN at 298 K.

cis-$[(PhCH_2)_2Co(bpy)_2]^+$ in an oxygen saturated MeCN solution in the presence of $HClO_4$ was first order with respect to *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ and the pseudo-first-order rate constant k_{obs} increases with increasing the $HClO_4$ concentration as shown by the open circles in Fig. 2a. In the absence of oxygen, the cobalt-benzyl bond of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ was cleaved by the electrophilic attack of proton to yield $[PhCH_2Co(bpy)_2]^{2+}$ and toluene (Eq. 1),[6] although the rate of the

$$\textit{cis}\text{-}[(PhCH_2)_2Co(bpy)_2]^+ + H^+ \longrightarrow [PhCH_2Co(bpy)_2]^{2+} + PhCH_3 \qquad (1)$$

electrophilic cleavage reaction is much slower than the rate of oxidation of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ by oxygen at the same concentration of $HClO_4$ (Fig. 2a).

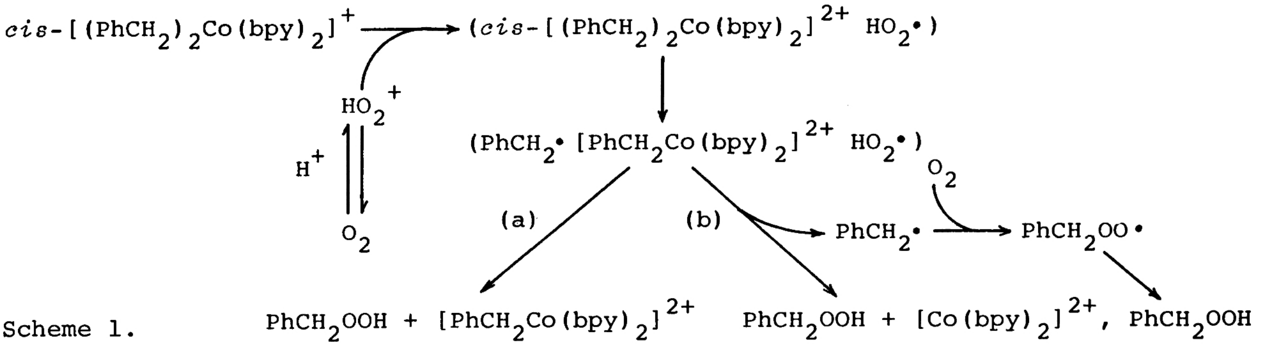
In the presence of acids, the reduction potential of oxygen is given by Eq. 2,

$$E(O_2/HO_2\cdot) = E^0(HO_2{}^+/HO_2\cdot) + \frac{2.3RT}{F}\log\left(\frac{K_{red} + [H^+]}{K_{ox} + [H^+]}\right) \qquad (2)$$

where K_{ox} and K_{red} are the acid dissociation constants of hydroperoxonium ion ($HO_2{}^+$) and hydroperoxyl radical ($HO_2\cdot$), respectively, and $E^0(HO_2{}^+/HO_2\cdot)$ is equal to $E^0(O_2/O_2{}^-) + (2.3RT/F)(pK_{red} - pK_{ox})$.[7] According to Eq. 2, the reduction potential of oxygen in the presence of acids, $E(O_2/HO_2\cdot)$, may be shifted to the positive direction with increasing the acid concentration compared with that in the absence of acid $E^0(O_2/O_2{}^-)$ owing to the formation of the protonated oxygen, i.e., $HO_2{}^+$ when pH < pK_{red} (= 4.69), and the one-electron reduction process gives way to an apparent irreversible two-electron reduction process.[4] Thus, in the reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with oxygen in the presence of $HClO_4$, the cobalt-benzyl bond may be cleaved by the electrophilic attack of hydroperoxonium ion to yield benzyl hydroperoxide and $[PhCH_2Co(bpy)_2]^{2+}$ (Eq. 3). However, the amount of

$$\mathit{cis}\text{-}[(PhCH_2)_2Co(bpy)_2]^+ + HO_2^+ \longrightarrow [PhCH_2Co(bpy)_2]^{2+} + PhCH_2OOH \qquad (3)$$

$[PhCH_2Co(bpy)_2]^{2+}$ formed is less than the initial amount of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ which is less than the total amount of oxidation products ($PhCH_2OOH$ and PhCHO) as shown in Fig. 1. Then, there may be a different pathway to cleave both the cobalt-benzyl bonds by HO_2^+, which accounts for the stoichiometry observed in Fig. 1. The most plausible reaction pathway is shown in Scheme 1, where electron transfer from *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ to HO_2^+ may occur to produce *cis*-$[(PhCH_2)_2Co(bpy)_2]^{2+}$ which may readily dissociate to give $PhCH_2\cdot$ and $[PhCH_2Co(bpy)_2]^{2+}$, followed by either (a) the recombination of radicals between $PhCH_2\cdot$ and $HO_2\cdot$ to yield $PhCH_2OOH$ or (b) the attack of $HO_2\cdot$ on $[PhCH_2Co(bpy)_2]^{2+}$ resulting in the formation of $PhCH_2OOH$ and $[Co(bpy)_2]^{2+}$ as well as $PhCH_2\cdot$ which may be trapped by oxygen immediately to give benzylperoxyl radical, yielding additional benzyl hydroperoxide by the abstraction of hydrogen from a solvent. At present, the former process (a) is indistinguishable from the electrophilic pathway (Eq. 3). The formation of Co^{II} species was confirmed by the ^1H nmr spectrum where about one-third of the 2,2'-bipyridine ligand of the reactant was detected as the form $[Co(bpy)_3]^{2+}$ which may be produced from $[Co(bpy)_2]^{2+}$,8) and the rest as $[PhCH_2Co(bpy)_2]^{2+}$, which agrees with the stoichiometry observed in Fig. 1. The electron transfer process from *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ to HO_2^+ may be energetically possible since electron transfer from *cis*-$[R_2Co(bpy)_2]^+$ to *p*-benzoquinone derivatives (Q), whose reduction potentials are similar to that of oxygen ($E^0(O_2/O_2^-) = -0.8$ V *vs*. SCE),4) is known to occur in the presence of $HClO_4$ when Q is partially protonated to form QH^+ which has a much stronger oxidizing ability than Q.9)



Scheme 1.

The enhancement of the one-electron oxidation process by oxygen in the presence of $HClO_4$ is well demonstrated in the electron transfer reaction from 1,1'-dimethylferrocene (Me_2Fc) to oxygen in the presence of $HClO_4$ (Eq. 4) as shown in Fig. 2b, where the dependence of k_{obs} on the $HClO_4$ concentration is similar to that observed in the oxidation of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ by oxygen in the presence of $HClO_4$ in MeCN (the open circles in Fig. 2a).

$$Me_2Fc + O_2 + H^+ \longrightarrow Me_2Fc^+ + HO_2\cdot \qquad (4)$$

The reaction of *cis*-$[Et_2Co(bpy)_2]^+$ with oxygen in the presence of $HClO_4$ gave significant amount of the coupling product butane, as observed in the acid catalysed electron transfer reactions from *cis*-$[Et_2Co(bpy)_2]^+$ to Q,9) as well as ethane and ethylene which may be produced by the electrophilic cleavage reaction by H^+ (Eq. 5). In this case, the reductive elimination from *cis*-$[Et_2Co(bpy)_2]^{2+}$ to

$$cis\text{-}[Et_2Co(bpy)_2]^+ \xrightarrow[H^+,\ O_2]{} C_4H_{10}(74\%),\ C_2H_6(24\%),\ C_2H_4(12\%) \tag{5}$$

yield butane upon the one-electron oxidation by oxygen in the presence of $HClO_4$ may be much faster than the reaction with $HO_2\bullet$ in contrast to the case of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (Scheme 1). Such a difference may be ascribed to a much longer lifetime of *cis*-$[(PhCH_2)_2Co(bpy)_2]^{2+}$ than *cis*-$[Et_2Co(bpy)_2]^{2+}$.10) A similar reductive coupling of the alkyl ligands of transition-metal alkyls is known to be induced by electron transfer reactions from transition-metal alkyls to oxygen.11)

In the case of *cis*-$[Me_2Co(bpy)_2]^+$, the rate of the electrophilic cleavage reaction by H^+ is the fastest among *cis*-$[R_2Co(bpy)_2]^+$ and no change in the products (methane and $MeCo(bpy)_2]^{2+}$)6) or the rate has been observed between the reactions in the presence and absence of oxygen.

References

1) J. K. Kochi, "Organometallic Mechanisms and Catalysis," Academic Press, New York (1978), pp. 517-522.
2) D. Astruc, J.-R. Hamon, E. Román, and P. Michaud, *J. Am. Chem. Soc.*, 103, 7502 (1981); A. M. Madonik and D. Astruc, *ibid.*, 106, 2437 (1984); N. A. Vol'kenau and V. A. Petrakova, *J. Organomet. Chem.*, 233, C7 (1982); C. Bied-Charreton and A. Gaudemer, *ibid.*, 124, 299 (1977); K. Jacob, K.-H. Thiele and B. Mohai, *Z. Anorg. Allg. Chem.*, 511, 89 (1984); A. Nishinaga, K. Nishizawa, Y. Nakayama, and T. Matsuura, *Tetrahedron Lett.*, 1977, 85.
3) R. Bonnett, *Essays in Biochemistry*, 17, 1 (1981).
4) D. T. Sawyer and J. S. Valentine, *Acc. Chem. Res.*, 14, 393 (1981); D.-H. Chin, G. Chiericato, Jr., E. J. Nanni, Jr., and D. T. Sawyer, *J. Am. Chem. Soc.*, 104, 1296 (1982); E. Ruff, *Chem. Soc. Rev.*, 6, 195 (1977).
5) In order to confirm the formation of benzyl hydroperoxide, the authentic sample was prepared by the addition of benzylmagnesium chloride to oxygen saturated ether at -70 °C; C. Walling and S. A. Bucker, *J. Am. Chem. Soc.*, 77, 6032 (1955).
6) Formation of equal amounts of $[RCo(bpy)_2]^{2+}$ and RH (R = $PhCH_2$ and Me) was confirmed by ^1H nmr and glc, respectively. ^1H nmr (CD_3CN) δ(ppm): CH_2, 2.90 (2H,s) for $[PhCH_2Co(bpy)_2]^{2+}$; CH_3, 3.37 (3H,s) for $[MeCo(bpy)_2]^{2+}$.
7) D. Meisel and G. Czapski, *J. Phys. Chem.*, 79, 1503 (1975).
8) S. Fukuzumi, K. Ishikawa, and T. Tanaka, *Chem. Lett.*, 1985, 1355.
9) S. Fukuzumi, K. Ishikawa, and T. Tanaka, *Nippon Kagaku Kaishi*, 1985, 62.
10) S. Fukuzumi, K. Ishikawa, and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1985, 899.
11) D. G. Morrell and J. K. Kochi, *J. Am. Chem. Soc.*, 97, 7262 (1975); S. Komiya, T. A. Albright, R. Hoffman, and J. K. Kochi, *Ibid.*, 99, 8440 (1977); W. Wada, K. Kusabe, and K. Oguro, *Inorg. Chem.*, 16, 446 (1977).

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