

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.<sup>1)</sup> However, the reactions of oxygen with organometallic compounds have recently attracted growing attention,<sup>2)</sup> 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.<sup>3)</sup> 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.<sup>4)</sup> 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.

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).<sup>5)</sup> The rate of the decay of

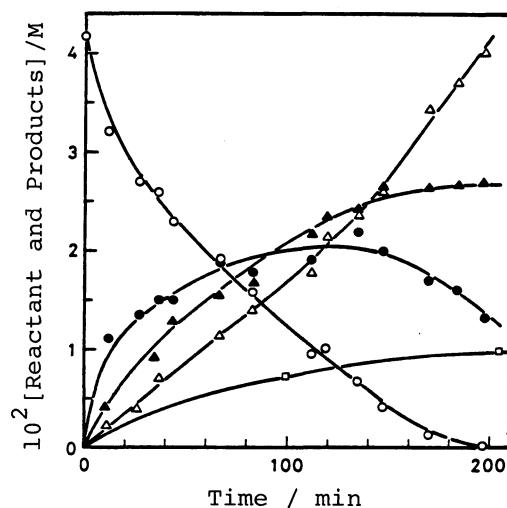


Fig. 1. Oxidation of  $cis$ - $[(PhCH_2)_2Co(bpy)_2]^+$  by oxygen in the presence of  $HCLO_4$  (0.12 M; 1 M = 1 mol  $dm^{-3}$ ) in  $CD_3CN$  at 273 K, monitored by  $^1H$  nmr;  $cis$ - $[(PhCH_2)_2Co(bpy)_2]^+$  ( $\circ$ ),  $PhCH_2-OOH$  ( $\bullet$ ),  $PhCHO$  ( $\triangle$ ),  $[PhCH_2Co(bpy)_2]^{2+}$  ( $\blacktriangle$ ),  $[Co(bpy)_3]^{2+}$  ( $\square$ ).

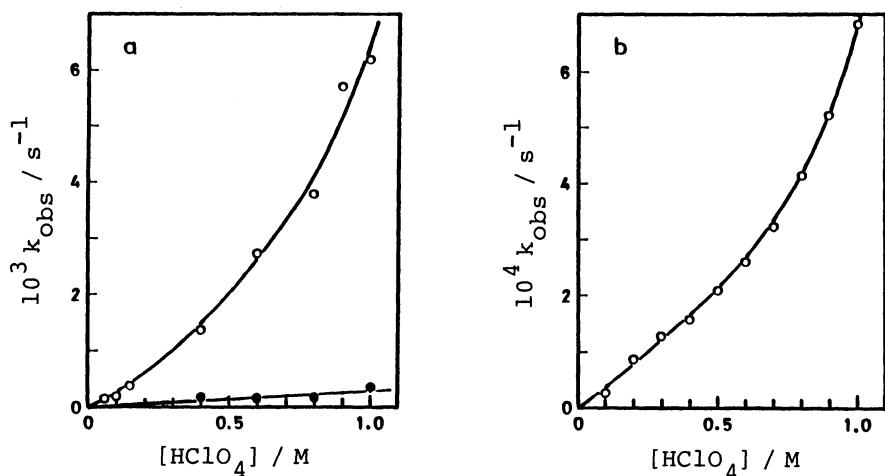
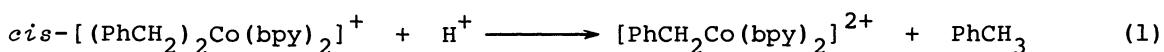


Fig. 2. (a) Dependence of the observed pseudo-first-order rate constant  $k_{\text{obs}}$  on the  $\text{HClO}_4$  concentration for the oxidation of  $\text{cis-}[(\text{PhCH}_2)_2\text{Co}(\text{bpy})_2]^+$  by oxygen in the presence of  $\text{HClO}_4$  (○) and for the reaction of  $\text{cis-}[(\text{PhCH}_2)_2\text{Co}(\text{bpy})_2]^+$  with  $\text{HClO}_4$  in the absence of oxygen (●) in MeCN at 298 K. (b) Dependence of  $k_{\text{obs}}$  on  $[\text{HClO}_4]$  for the one-electron oxidation of 1,1'-dimethylferrocene ( $\text{Me}_2\text{Fc}$ ) by oxygen in the presence of  $\text{HClO}_4$  in MeCN at 298 K.

$\text{cis-}[(\text{PhCH}_2)_2\text{Co}(\text{bpy})_2]^+$  in an oxygen saturated MeCN solution in the presence of  $\text{HClO}_4$  was first order with respect to  $\text{cis-}[(\text{PhCH}_2)_2\text{Co}(\text{bpy})_2]^+$  and the pseudo-first-order rate constant  $k_{\text{obs}}$  increases with increasing the  $\text{HClO}_4$  concentration as shown by the open circles in Fig. 2a. In the absence of oxygen, the cobalt-benzyl bond of  $\text{cis-}[(\text{PhCH}_2)_2\text{Co}(\text{bpy})_2]^+$  was cleaved by the electrophilic attack of proton to yield  $[\text{PhCH}_2\text{Co}(\text{bpy})_2]^{2+}$  and toluene (Eq. 1),<sup>6)</sup> although the rate of the

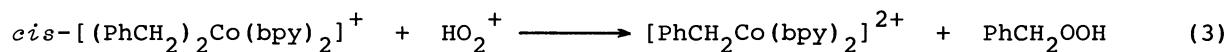


electrophilic cleavage reaction is much slower than the rate of oxidation of  $\text{cis-}[(\text{PhCH}_2)_2\text{Co}(\text{bpy})_2]^+$  by oxygen at the same concentration of  $\text{HClO}_4$  (Fig. 2a).

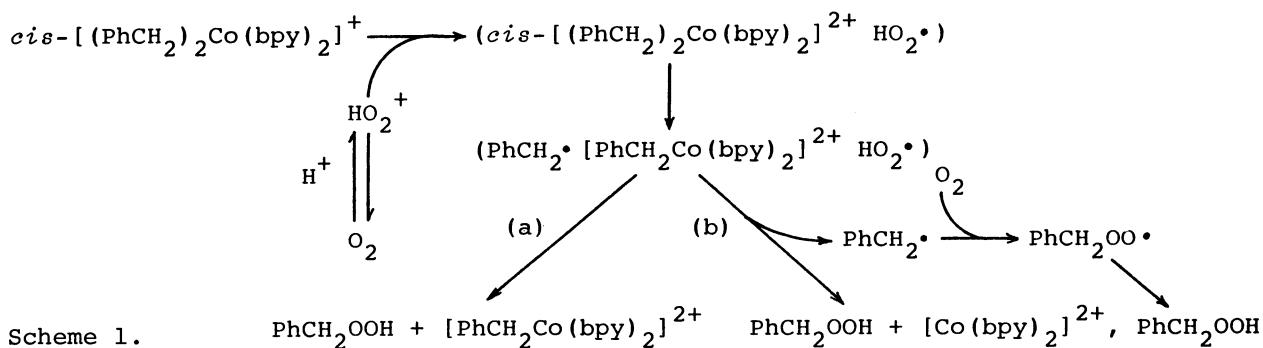
In the presence of acids, the reduction potential of oxygen is given by Eq. 2,

$$E(\text{O}_2/\text{HO}_2^\bullet) = E^0(\text{HO}_2^+/\text{HO}_2^\bullet) + \frac{2.3RT}{F} \log \left( \frac{K_{\text{red}} + [\text{H}^+]}{K_{\text{ox}} + [\text{H}^+]} \right) \quad (2)$$

where  $K_{\text{ox}}$  and  $K_{\text{red}}$  are the acid dissociation constants of hydroperoxonium ion ( $\text{HO}_2^+$ ) and hydroperoxyl radical ( $\text{HO}_2^\bullet$ ), respectively, and  $E^0(\text{HO}_2^+/\text{HO}_2^\bullet)$  is equal to  $E^0(\text{O}_2/\text{O}_2^-) + (2.3RT/F)(pK_{\text{red}} - pK_{\text{ox}})$ .<sup>7)</sup> According to Eq. 2, the reduction potential of oxygen in the presence of acids,  $E(\text{O}_2/\text{HO}_2^\bullet)$ , may be shifted to the positive direction with increasing the acid concentration compared with that in the absence of acid  $E^0(\text{O}_2/\text{O}_2^-)$  owing to the formation of the protonated oxygen, i.e.,  $\text{HO}_2^+$  when  $\text{pH} < pK_{\text{red}}$  ( $= 4.69$ ), and the one-electron reduction process gives way to an apparent irreversible two-electron reduction process.<sup>4)</sup> Thus, in the reaction of  $\text{cis-}[(\text{PhCH}_2)_2\text{Co}(\text{bpy})_2]^+$  with oxygen in the presence of  $\text{HClO}_4$ , the cobalt-benzyl bond may be cleaved by the electrophilic attack of hydroperoxonium ion to yield benzyl hydroperoxide and  $[\text{PhCH}_2\text{Co}(\text{bpy})_2]^{2+}$  (Eq. 3). However, the amount of

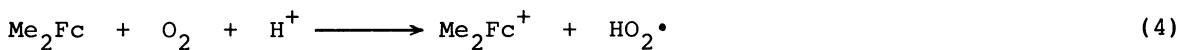


$[PhCH_2Co(bpy)_2]^{2+}$  formed is less than the initial amount of  $cis-[(PhCH_2)_2Co(bpy)_2]^+$  which is less than the total amount of oxidation products ( $PhCH_2OOH$  and  $PhCHO$ ) as shown in Fig. 1. Then, there may be a different pathway to cleave both the cobalt-benzyl bonds by  $HO_2^+$ , 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 benzylperoxy 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  $[Co(bpy)_2]^{2+}$ ,<sup>8)</sup> 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),<sup>4)</sup> 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.<sup>9)</sup>

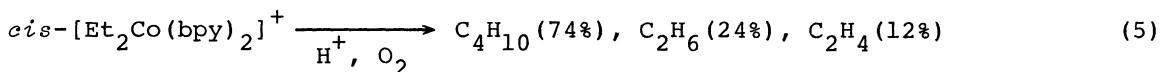
The enhancement of the one-electron oxidation process by oxygen in the presence of  $HClO_4$  is well demonstrated in the electron transfer reaction from 1,1'-dimethylferrocene ( $Me_2Fc$ ) to oxygen in the presence of  $HClO_4$  (Eq. 4) as shown



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).

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,<sup>9)</sup> 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<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>2+</sup> to



yield butane upon the one-electron oxidation by oxygen in the presence of  $HCLO_4$  may be much faster than the reaction with  $HO_2\cdot$  in contrast to the case of  $cis$ -[(PhCH<sub>2</sub>)<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> (Scheme 1). Such a difference may be ascribed to a much longer lifetime of  $cis$ -[(PhCH<sub>2</sub>)<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>2+</sup> than  $cis$ -[Et<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>2+</sup>.<sup>10</sup> 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.<sup>11</sup>

In the case of  $cis$ -[Me<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup>, the rate of the electrophilic cleavage reaction by  $H^+$  is the fastest among  $cis$ -[R<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> and no change in the products (methane and MeCo(bpy)<sub>2</sub>)<sup>2+</sup><sup>6</sup> or the rate has been observed between the reactions in the presence and absence of oxygen.

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