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Coenzyme-Catalyzed Cleavage of Cobalt-Carbon Bonds in the Oxidation of cis-Dialkylcobalt(III) Complexes by Oxygen

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Redox coenzyme analogues (riboflavin, aminopterin, and lumazine) catalyze the cleavage of cobalt-carbon bonds in the oxidation of cis-dialkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]ClO_4$ (R = $PhCH_2$, C_2H_5, CH_3; bpy = 2,2'-bipyridine) by oxygen in the presence of $HClO_4$ in acetonitrile.

The cleavage of the cobalt-carbon bond of methylcobalamin is believed to be a key step in a vitamin B_{12} dependent methyl transfer reaction, catalyzed by tetrahydrofolate methyltransferase which contains redox coenzymes, i.e., reduced forms of pterin and flavin coenzymes,1) although the exact mechanism has not been established. Thus, considerable interest has been focused on the cleavage of cobalt-carbon bonds in organocobalt complexes.2-6) However, no coenzyme-catalyzed cleavage of cobalt-carbon bonds has so far been reported. We report herein the first example of coenzyme-catalyzed cleavage of cobalt-carbon bonds in the oxidation of cis-dialkylcobalt(III) complexes by oxygen. The redox coenzymes used as catalysts in this study are a flavin (riboflavin) and pterin coenzyme analogues (aminopterin and lumazine).

The cis-dialkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]ClO_4$ (R = $PhCH_2$, C_2H_5, CH_3; bpy = 2,2'-bipyridine), are stable towards oxygen in acetonitrile at 298 K. However, cis-$[(PhCH_2)_2Co(bpy)_2]^+$ reacts with oxygen in the presence of a strong acid such as $HClO_4$ in acetonitrile to produce benzyl hydroperoxide which decomposes to yield benzaldehyde as the final product (Table 1).7) In the absence of oxygen, the cobalt-carbon bond was cleaved by the electrophilic attack of proton to yield toluene (Table 1). When a catalytic amount of riboflavin is added to an oxygen saturated acetonitrile solution of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ containing $HClO_4$, the oxidation rate to yield benzaldehyde was enhanced significantly. The oxidation rate, monitored by the decay of the absorption band due to cis-$[(PhCH_2)_2Co(bpy)_2]^+$, obeyed the pseudo-first-order kinetics. The observed rate constant increased linearly with increasing the catalyst concentration. Aminopterin and lumazine also exhibit the catalytic effect in the oxidation of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ by oxygen in the presence of $HClO_4$ (0.10 mol dm^{-3}).

The one-electron oxidation of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ by a strong one-electron oxidant, $[Fe(phen)_3]^{3+}$ (Phen = 1,10-phenanthroline), in the presence of oxygen gives the same product as the case of the coenzyme-catalyzed oxidation, i.e., benzaldehyde (Table 1).8) In the absence of oxygen, however, the one-electron

Table 1. Yields of the products for catalytic (or noncatalytic) cleavage of the cobalt-carbon bonds of cis-$[R_2Co(bpy)_2]^+$ by oxidants in the absence and presence of $HClO_4$ in acetonitrile (0.6 cm^3)

cis-$[R_2Co(bpy)_2]ClO_4$ (10^{-5} mol)	Oxidant (10^{-5} mol)		$HClO_4$ (10^{-5} mol)	Product (%), based on the cobalt complex[a)]
R = $PhCH_2$	O_2	Riboflavin		
2.5	6.9	0.10	6.0	PhCHO (100) $PhCH_2OOH$ (trace)
2.5	6.9	0	6.0	PhCHO (100) $PhCH_2OOH$ (trace)
2.0	0	0	6.0	$PhCH_3$ (100)
	O_2	$[Fe(phen)_3]^{3+}$		
2.4	6.9	94	0	PhCHO (99) $PhCH_2OOH$ (trace)
2.4	0	94	0	PhC_2H_4Ph (98)
R = C_2H_5	O_2	Riboflavin		
2.4	6.9	0.28	6.8[b)]	C_4H_{10} (100) C_2H_6 (trace)
2.1	6.9	0	20	C_4H_{10} (76) C_2H_6 (24) C_2H_4 (13)
2.1	0	0	6.3	C_4H_{10} (25) C_2H_6 (75) C_2H_4 (41)
	O_2	$[Fe(phen)_3]^{3+}$		
2.0	6.9	94	0	C_4H_{10} (100) C_2H_6 (trace)
2.0	6.9	0	0	C_4H_{10} (100) C_2H_6 (trace)
R = CH_3	O_2	Riboflavin		
3.6	6.9	3.6	12	C_2H_6 (89) CH_4 (11)
2.1	6.9	0	4.1	C_2H_6 (trace) CH_4 (100)
2.1	0	0	4.1	C_2H_6 (trace) CH_4 (100)

a) Determined by ^1H NMR and GLC. b) In the presence of 5.4 x 10^{-4} mol H_2O.

oxidation results in the cleavage of both cobalt-benzyl bonds to yield the coupling product, 1,2-diphenylethane (Table 1).[9)] In the case of cis-$[(C_2H_5)_2Co(bpy)_2]^+$, the riboflavin-catalyzed oxidation by oxygen in the presence of $HClO_4$ gives exclusively the coupling product, butane (Table 1). Without riboflavin, the cobalt-ethyl bond is slowly cleaved by $HClO_4$ to yield butane, ethane and ethylene in both the absence and presence of oxygen. The yield of coupling product, butane, is larger in the presence of oxygen, compared with the case in the absence of oxygen (Table 1). The one-electron oxidation by $[Fe(phen)_3]^{3+}$ in both the absence and presence of oxygen also gives the coupling product, butane, in contrast with the case of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ (Table 1).[4)] In the case of cis-$[(CH_3)_2Co(bpy)_2]^+$ as well, the riboflavin-catalyzed oxidation gives the coupling product, ethane, but small amount of methane is also formed because of the facile electrophilic cleavage of the cobalt-carbon bond by $HClO_4$ (Table 1). Without riboflavin, the cobalt-methyl bond is slowly cleaved to yield exclusively methane (Table 1).

Without $HClO_4$, the redox coenzyme analogue (riboflavin, aminopterin, or lumazine) showed no catalytic activity. The effects of $HClO_4$ on the second-order rate constants for the cleavage of the cobalt-carbon bonds by the redox coenzyme analogues are shown in Fig. 1, together with the pseudo-first-order rate constants for the electrophilic cleavage of the cobalt-carbon bonds in the absence of the redox coenzyme analogue for comparison. The log k_{obsd} values increase linearly with increasing the log[$HClO_4$] value, except for the cis-[$(C_2H_5)_2$-Co(bpy)$_2$]$^+$-aminopterin system (Fig. 1). In the present systems, each coenzyme is protonated in the presence of $HClO_4$ in MeCN. Thus, upon the one-electron reduction, riboflavin semiquinone (FlH$^•$) and lumazine semiquinone (LH$^•$) may be further protonated to produce dihydroriboflavin radical cation ($FlH_2^{+•}$) and dihydrolumazine radical cation ($LH_2^{+•}$), respectively. Such protonation upon one-electron reduction is known to cause the positive shift of the one-electron reduction potential and thus, accelerates the electron transfer reaction.[10] In the case of aminopterin (P), the protonation of PH$^•$ may occur at high $HClO_4$ concentrations (> 1 mol dm^{-3}) and thus, the rate constant is constant with increasing the $HClO_4$ concentration up to 1 mol dm^{-3} (Fig. 1). In fact, the formation of dihydroriboflavin radical cation in the reaction of cis-[$(C_2H_5)_2$Co(bpy)$_2$]$^+$ with riboflavin in the presence of $HClO_4$ under a degassed condition was confirmed by the ESR spectrum (g = 2.0026).[11] In the case of the reaction with aminopterin, no radical cation has been detected.

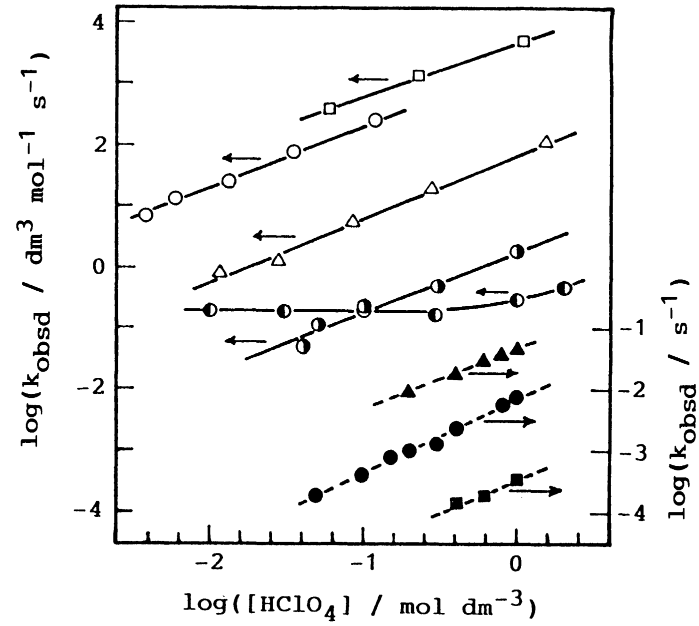
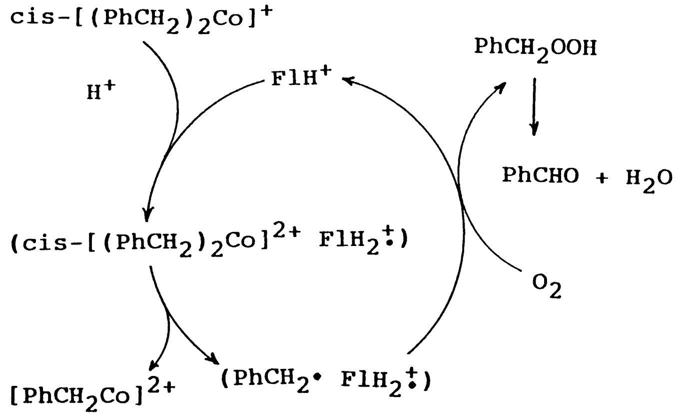


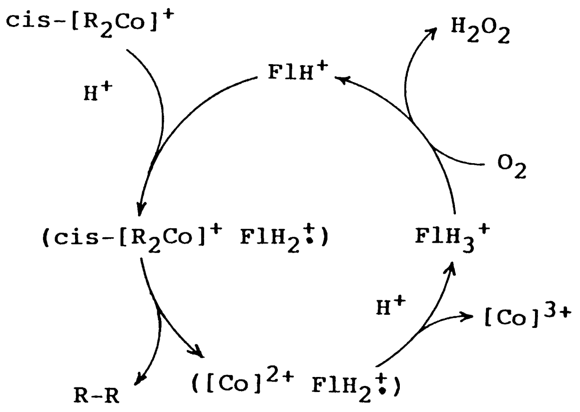
Fig. 1. Plots of log k_{obsd} vs. log[$HClO_4$] for the reactions of cis-[R_2Co(bpy)$_2$]$^+$ [R = $PhCH_2$ (□), C_2H_5 (○), CH_3 (△)] with riboflavin, for the reaction of cis-[$(C_2H_5)_2$Co(bpy)$_2$]$^+$ with aminopterin (◐) and lumazine (◑) in the presence of $HClO_4$, and for the reactions of cis-[R_2-Co(bpy)$_2$]$^+$ [R = CH_3 (▲), C_2H_5 (●), $PhCH_2$ (■)] with $HClO_4$ in MeCN at 298 K.

Based on the above results, the catalytic mechanisms are shown in Schemes 1 and 2, where the protonated riboflavin (FlH$^+$) can be replaced by the protonated lumazine (LH$^+$) or aminopterin (P). In Scheme 1, the electron transfer from cis-[$(PhCH_2)_2$Co(bpy)$_2$]$^+$ to FlH$^+$ occurs in the presence of $HClO_4$ to produce cis-[$(PhCH_2)_2$Co(bpy)$_2$]$^{2+}$ and $FlH_2^{+•}$. The cobalt-benzyl bond in the dibenzylcobalt(IV) complex may be readily cleaved to give benzyl radical, followed by the radical trap by oxygen to produce benzyl peroxy radical which then gives benzyl hydroperoxide by the abstraction of hydrogen atom from $FlH_2^{+•}$, accompanied by regeneration of FlH$^+$. The benzyl hydroperoxide decomposes to give the final product, benzaldehyde.

In the case of cis-[R_2Co(bpy)$_2$]$^+$ (R = CH_3 and C_2H_5), the alkyl radical formed upon the one-electron oxidation by FlH$^+$ may undergo the facile coupling reaction with [RCo(bpy)$_2$]$^{2+}$ to yield the coupling product R-R before the radical trap by oxygen (Scheme 2). The dihydroriboflavin radical cation $FlH_2^{+•}$ may be further reduced by [Co(bpy)$_2$]$^{2+}$ in the presence of $HClO_4$ to produce FlH_3^+ which is known to



Scheme 1.



Scheme 2.

be readily oxidized by oxygen to regenerate FlH$^+$.[12] The mechanistic difference between Schemes 1 and 2 may be ascribed to the difference in the reactivity between the alkyl radicals; benzyl radical is much more stable than methyl or ethyl radical in the coupling reaction with [RCo(bpy)$_2$]$^{2+}$.[7]

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