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# MECHANISMS OF CLEAVAGE OF COBALT-CARBON BONDS IN ALKYLCOBALT(III) COMPLEXES

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# MECHANISMS OF CLEAVAGE OF COBALT-CARBON BONDS IN ALKYLCOBALT(III) COMPLEXES

（アルキルコバルト(III) 錯体におけるコバルトー炭素結合の開裂機構）

石川邦夫

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# GENERAL INTRODUCTION

Cleavage of metal-carbon bonds of transition-metal alkyls and the factors which control the reactivities have been subjects of much interest, since the cleavage is one of the most important steps in a variety of catalytic carbon-carbon bond formation reactions, catalyzed by organometallic compounds. Especially, significant attention has been devoted to the cleavage of cobalt-carbon bonds in alkylcobalt(III) complexes, which are frequently used as model compounds of naturally occurring coenzyme, vitamin $B_{12}$. However, cobalt-carbon bonds of alkylcobalt(III) complexes are rather stable, and thus, activation of the cobalt-carbon bond such as photo-excitation is required for the cleavage of the cobalt-carbon bond. In contrast, cobalt-carbon bonds of alkylcobalt(**IV**) complexes formed by the one-electron oxidation of alkylcobalt(**III**) complexes are known to be readily cleaved. Strong oxidants, however, are required for the oxidation of monoalkylcobalt(III) complexes because of the relatively weak reducing ability.

This study reports mechanisms for the cleavage of cobalt-carbon bonds with various oxidants, focusing on the reactivities of **dialkylcobalt(III) complexes** which have stronger reducing abilities than monoalkylcobalt(III) complexes. Cobalt-carbon bonds of dialkylcobalt(III) complexes are still stable towards weak oxidants such as dioxygen. However, cobalt-carbon bonds of cis-dialkylcobalt(III) complexes are readily cleaved by dioxygen in the presence of catalytic amounts of redox coenzyme analogues such as riboflavin and pterine derivatives in acetonitrile containing $HClO_4$. Mechanisms of the catalysis of coenzyme analogues in the presence of $HClO_4$ are discussed. Homolytic cleavage of cobalt-carbon bonds of cis-dialkylcobalt(III) complexes occurs also thermally or photochemically. Redox reactions of substrates associated with the homolytic cleavage of cobalt-carbon bonds are also reported.

In **chapter 1** are described the cleavage mechanisms of cobalt-carbon bonds of cis-dialkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]^+$, (R = Me, Et and $PhCH_2$; bpy = 2,2'-bipyridine) upon the one-electron oxidation by various strong oxidants such as $[Fe(phen)_3]^{3+}$ (phen = 1,10-phenanthroline), 2,3-dichloro-5,6-

dicyano-p-benzoquinone in acetonitrile.

In **chapter 2** are described mechanisms of coenzyme-catalyzed oxidation of cis-dialkylcobalt(III) complexes by dioxygen in the presence of perchloric acid in acetonitrile.

In **chapter 3**, the contribution of electron transfer processes in the electrophilic cleavage of cobalt-carbon bonds of alkylcobalt(III) complexes with iodine is evaluated based on the product distribution and the kinetic comparison with the electron-transfer from ferrocene derivatives to iodine with the aid of the Marcus theory of electron transfer.

In **chapter 4** are described the mechanisms of the photochemical reactions of alkylcobalt(III) complexes with iodine in $CCl_4$ under the conditions that thermal electrophilic cleavage can be neglected.

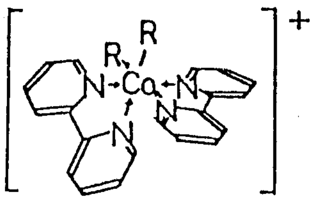
In **chapter 5**, photoredox reactions of cis-dialkylcobalt(III) complexes with benzyl and allyl bromides are reported. Mechanisms of the photoredox reactions are discussed based on the product distribution and the identification of the reactive intermediates detected by low-temperature ESR measurements and the quantum yield determinations.

In **chapter 6** are described redox reactions of cis-dialkylcobalt(III) complexes with benzyl and allyl bromides, induced by thermal cleavage of cobalt-carbon bonds. Mechanisms of the redox reactions of cis-$[R_2Co(bpy)_2]^+$ with benzyl and allyl bromides induced by the thermal cleavage of the cobalt-carbon bonds are compared with those induced by the corresponding photo-cleavage reactions.

Concluding remarks are presented at the end of this thesis.

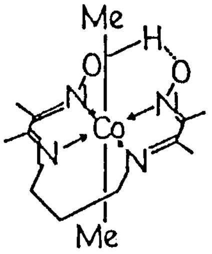
The alkylcobalt(III) complexes used in this study, cis-$[R_2Co(bpy)_2]^+$ (R = Me, Et, $PhCH_2$; bpy = 2,2'-bipyridine), trans-$[Me_2Co(DpnH)]$ (DpnH = 11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-1-olate), $[RCo(DH)_2py]$ (R = Me, Et, $PhCH_2$; $(DH)_2$ = bis(dimethylglyoximato); py = pyridine), as shown below.

**Alkylcobalt(III) Complexes**

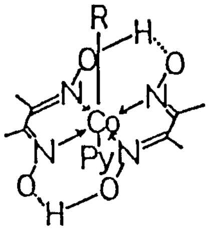


cis-$[R_2Co(bpy)_2]^+$

R = Me, Et, $PhCH_2$



trans-$[Me_2Co(DpnH)]$



$[RCo(DH)_2py]$

R = Me, Et, $PhCH_2$

The content of this thesis is composed of the following papers.

(1) Fukuzumi, S.; Ishikawa, K.; Tanaka, T., Activation of Cobalt(III)-Alkyl Bonds through Interaction with Organic Oxidants and the Catalytic Effect of $Mg^{2+}$ Ion on Alkyl Transfer Reactions from cis-Dialkylcobalt(III) Complexes to p-Benzoquinone Derivatives, Chem. Lett. **1984**, 421-424.

(2) Fukuzumi, S.; Ishikawa, K.; Tanaka, T., Cleavage of Cobalt-Alkyl Bonds of cis-Dialkylcobalt(III) Complexes with Organic Oxidants Catalyzed by $Mg(ClO_4)_2$ and $HClO_4$, Nippon Kagaku Kaishi **1985**, 62-69.

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(1) Fukuzumi, S.; Kuroda, S.; Goto, T.; Ishikawa, K.; Tanaka, T., Acid-catalysed Reduction of Flavin Analogues by an NADH Model Compound, 10-Methyl-9,10-dihydroacridine and *cis*-Dialkylcobalt(III) Complexes, *J. Chem. Soc., Perkin Trans. 2* **1989**, 1047-1053.

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# Chapter 1 ONE-ELECTRON OXIDATION OF cis-DIALKYLCOBALT(III) COMPLEXES

**Abstract:** One-electron oxidation of cis-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et, $PhCH_2$; bpy = 2,2'-bipyridine) by organic and inorganic oxidants such as 2,3-dichloro-5,6-dicyano-p-benzoquinone and $[Fe(phen)_3]^{3+}$ results in the cleavage of the cobalt-carbon bonds. In the absence of dioxygen, one-electron oxidation of cis-$[R_2Co(bpy)_2]^+$ yields exclusively the coupling products of the alkyl group (R-R). In the presence of dioxygen, as well, the same coupling products are obtained in the case of R = Me and Et. In the case of R = $PhCH_2$, however, no coupling products is obtained in the presence of dioxygen, but instead, oxygenated product, benzaldehyde, is obtained. The logarithm of the rate constants (log $k_{obs}$) for these electron-transfer reactions in acetonitrile at 298 K is linearly correlated with the difference in the redox potentials between cis-$[R_2Co(bpy)_2]^+$ and oxidants with a slope of approximately equal to -F/2.3RT (F is the Faraday constant). Based on the product distribution as well as kinetic analysis, mechanisms of cleavage of cobalt-carbon bond upon one-electron oxidation of cis-$[R_2Co(bpy)_2]^+$ are discussed.

## 1-1 Introduction

The mechanisms of cleavage of metal-carbon bonds have been of considerable interest owing to the importance in understanding the role of organometallic compounds in a variety of catalytic reactions.[1,2] Especially, cleavage of the cobalt-alkyl bonds in alkylcobalt(III) complexes upon oxidation has extensively been studied.[3-8] Although both mono- and dialkylcobalt(III) complexes are known, examples of the latter are fewer and relatively little is known concerning their reactivities towards oxidants.[9] For example, trans-dialkylcobalt(III) complexes are reported to be readily oxidized by inorganic oxidants such as $Hg^{2+}$, $Ag^+$, $Zn^{2+}$, $Pb^{2+}$, and $[IrCl_6]^{2-}$, resulting in the fission of only one cobalt-alkyl bond.[10-12] However, little is known of the cleavage of cobalt-alkyl bonds in cis-dialkylcobalt(III) complexes. Moreover, no cleavage of such bonds in trans- or cis-dialkylcobalt(III) complexes by organic oxidants has so far been reported.

In this work[13] we report the electron-transfer reactions of cis-dialkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]^+$ (R = Me, Et, $PhCH_2$; bpy = 2,2'-bipyridine), with various oxidants such as 2,3-dichloro-5,6-dicyano-p-benzoquinone and $[Fe(phen)_3]^{3+}$, where the cis-complexes have been found to undergo the cleavage of cobalt-carbon bonds in a stepwise manner. The mechanisms of these reactions in the absence and presence of dioxygen will be discussed based on the product distribution and kinetic analysis.

## 1-2 Experimental

**Materials.** The cis-dialkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et, $PhCH_2$), were prepared by the reaction of $CoCl_2 \cdot 6H_2O$ with an excess of $NaBH_4$ in the presence of the corresponding alkyl halide.[14] They were isolated as the perchlorate salts and recrystallized from methanol-water. The purities of the complexes were checked by the elemental analyses. Anal. Calcd for $C_{22}H_{22}N_4O_4CoCl$ (cis-$[Me_2Co(bpy)_2]ClO_4$): C,52.8; H,4.4; N,11.2 Found: C, 52.7; H,4.6; N,11.1. Anal. Calcd for $C_{24}H_{28}N_4O_4CoCl$ (cis-$[Et_2Co(bpy)_2]ClO_4$): C,52.7; H,5.2; N,10.2. Found: C,52.1; H,5.1; N,10.0. Anal. Calcd for $C_{34}H_{30}N_4O_4CoCl$ (cis-$[(PhCH_2)_2Co(bpy)_2]ClO_4$): C,63.0 ; H,4.7; N,8.7. Found: C,62.0; H,4.6; N,8.5. Tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDBQ), and 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) were obtained commercially and purified by the standard method.[15] 2,3-Dicyano-p-benzoquinone (DCBQ) was prepared from the corresponding hydroquinone according to the literature.[16] The preparation of $[Fe(phen)_3](ClO_4)_3$ (phen = 1, 10-phenanthroline) and $[Fe(bpy)_3]^{3+}$ was described elsewhere.[17] Ferrocenium, n-butylferrocenium, and 1,1'-dimethyl-ferrocenium ions were prepared by the oxidation of the corresponding ferrocene derivatives with p-benzoquinone in the presence of perchloric acid in acetonitrile,[18] and isolated as the hexafluorophophate salts. Reagent grade acetonitrile (MeCN) obtained from Wako Pure Chemicals was purified by the standard procedure,[15] followed by redistillation from calcium hydride.

**Oxidation of cis-Dialkylbis(2,2'-bipyridyl)cobalt(III) Complexes.** In a typical experiment, the oxidant 2,3-dichloro-5,6-dicyano-p-benzoquinone ($2.0 \times 10^{-5}$ mol) was weighed into a round-bottom flask (2.0 $cm^3$) containing MeCN (2.0 $cm^3$). The flask was capped with a rubber septum and filled with nitrogen by pumping and refilling through a syringe needle. Then, an MeCN solution (0.10 $cm^3$) of cis-[$Et_2Co(bpy)_2$]$ClO_4$ (3.8 x $10^{-6}$ mol) was introduced into the flask by using a hypodermic syringe. The contents were equilibrated at 298 K for 30 min and thoroughly mixed. The gaseous products were analyzed by gas chromatography using a Unibeads 1S column. After the addition of an equivalent amount of perchloric acid to the product mixture, the [$Co(bpy)_2$]$^{2+}$ complex was isolated as the perchlorate salt by the slow addition of diethylether (Anal. Calcd for $C_{20}H_{16}Cl_2CoN_4O_8$ ([$Co(bpy)_2$]$(ClO_4)_2$): C,42.1; H,2.8; N,9.8. Found: C,42.5; H,3.1; N,9.4.).

Spectral titrations were carried out by adding known quantities of a stock solution of cis-[$R_2Co(bpy)_2$]$^+$ to a quartz cuvette containing a known aliquot of the oxidant in excess. After the reaction was complete, the absorption spectrum was measured using a Union SM-401 spectrophotometer. The amounts of the radical anions of oxidants determined from the absorbances at $\lambda_{max}$ due to radical anions ($\lambda_{max}$ 475 nm, $\varepsilon_{max}$ 5.67 x $10^3$ $M^{-1}$ $cm^{-1}$ for radical anion of TCNE,[19] $\lambda_{max}$ 585 nm, $\varepsilon_{max}$ 3.63 x $10^3$ $M^{-1}$ $cm^{-1}$ for radical anion of DDBQ,[20] $\lambda_{max}$ 585 nm, $\varepsilon_{max}$ 3.65 x $10^4$ $M^{-1}$ $s^{-1}$ for radical anion of DCBQ,[20] $\lambda_{max}$ 842 nm, $\varepsilon_{max}$ 4.35 x $10^4$ $M^{-1}$ $s^{-1}$ for radical anion of TCNQ,[21]) were plotted against the amount of cis-[$R_2Co(bpy)_2$]$^+$ added. The least-squares slope was 1.0 ± 0.1.

**Kinetic Measurements.** Kinetic measurements were carried out by using a Union RA-103 stopped-flow spectrophotometer and a Union SM-401 spectrophotometer for electron-transfer reactions from cis-[$R_2Co(bpy)_2$]$^+$ to oxidants in the presence and absence of dioxygen with half-lives of shorter than 10 s and longer than 100 s, respectively. Reaction rates were monitored by the increase in the absorbances at $\lambda_{max}$ of the radical anions of organic oxidants[19-21] or the disappearance of absorbance at $\lambda_{max}$ due to cis-[$R_2Co(bpy)_2$]$^+$ in MeCN ($\lambda_{max}$ = 472, 495, 502 nm for R = Me, Et, $PhCH_2$, respectively) under pseudo-first-order conditions in the presence of more than a 10-fold excess of oxidant. Pseudo-first-order rate constants were determined by least-squares curve fitting using a Union System 77 microcomputer.

**Cyclic Voltammetry.** Redox potentials of cis-[$R_2Co(bpy)_2$]$^+$ in MeCN were determined by cyclic voltammetry at various sweep rates (20-1000 mV $s^{-1}$), based on the method described in detail elsewhere.[22,23] The cyclic voltammogram was recorded on a Hokuto Denko model HA-301 potentiostat/galvanostat at 298 K using a platinum microelectrode and a standard NaCl calomel reference electrode (SCE) under deaerated conditions. The platinum microelectrode was routinely cleaned by soaking in concentrated nitric acid, followed by repeated rinsing with water and acetone, and drying at 353 K prior to use. The anodic peak potential of *cis*-$[R_2Co(bpy)_2]^+$ at a constant sweep rate was reproducible within $\pm 20$ mV. Little deterioration of the electrode was observed upon repeated scans, indicating that anodic oxidation leads to products without fouling of the electrode surface.

## 1-3 Results and Discussion

**Cleavage Modes of Cobalt-Carbon Bonds upon the One-Electron Oxidation of Dialkylcobalt(III) Complexes.** The modes for the cleavage of cobalt-carbon bonds of alkylcobalt(IV) complexes are examined by determining the cleaved products in electron-transfer reactions from dialkylcobalt(III) complexes to strong one-electron oxidants such as $[Fe(bpy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ in the presence and absence of dioxygen (Table 1-1, 1-2). In the case of *cis*-$[R_2Co(bpy)_2]^+$ (R = Me, Et, $PhCH_2$), one-electron oxidation with $[Fe(bpy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ under deaerated conditions yields exclusively the coupling products of the alkyl groups (eq 1). When one-electron oxidation of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ is carried out in the presence of dioxygen, PhCHO is obtained instead of the coupling product, $PhC_2H_4Ph$ (Table 1-2). However, the same coupling products are obtained in the case of R = Me and Et in the absence and presence of dioxygen (Table 1-1, 1-2).

Table 1-1. Product Yields in the One-Electron Oxidation of *cis*-$[R_2Co(bpy)_2]^+$ (R = $PhCH_2$, Et, Me; $3.8 \times 10^{-6}$ mol) by Various Oxidants ($2.0 \times 10^{-5}$ mol) in Deaerated MeCN (2.0 $cm^3$) at 298 K

| *cis*-$[R_2Co(bpy)_2]^+$ R | oxidant | products (yield,[a] %) |
|---|---|---|
| $PhCH_2$ | $[Fe(phen)_3]^{3+}$ | $PhC_2H_4Ph$ (98) |
| $PhCH_2$ | $[Fe(bpy)_3]^{3+}$ | $PhC_2H_4Ph$ (99) |
| $PhCH_2$ | DDBQ | $PhC_2H_4Ph$ (99) |
| $PhCH_2$ | DCBQ | $PhC_2H_4Ph$ (97) |
| Et | $[Fe(phen)_3]^{3+}$ | $C_4H_{10}$ (98) |
| Et | $[Fe(bpy)_3]^{3+}$ | $C_4H_{10}$ (100) |
| Et | $[Fe(C_5H_5)_2]^+$ | $C_4H_{10}$ (99) |
| Et | $[Fe(MeC_5H_4)_2]^+$ | $C_4H_{10}$ (97) |
| Et | TCNE | $C_4H_{10}$ (97) |
| Et | DDBQ | $C_4H_{10}$ (99) |
| Et | DCBQ | $C_4H_{10}$ (100) |
| Me | $[Fe(phen)_3]^{3+}$ | $C_2H_6$ (100) |
| Me | $[Fe(bpy)_3]^{3+}$ | $C_2H_6$ (100) |
| Me | DDBQ | $C_2H_6$ (100) |
| Me | DCBQ | $C_2H_6$ (100) |

[a] Based on the amount of *cis*-$[R_2Co(bpy)_2]^+$.

$$\underline{cis}\text{-}[R_2Co(bpy)_2]^+ + Ox \longrightarrow R\text{-}R + [Co(bpy)_2]^{2+} + Ox^- \qquad (1)$$

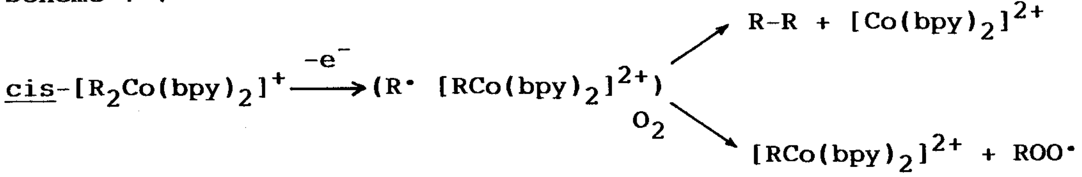
Such effects of dioxygen on the one-electron oxidation of $\underline{cis}$-$[R_2Co(bpy)_2]^+$ may be explained by Scheme 1-1, where the cleavage of the two cobalt-carbon bonds upon the one-electron oxidation occurs in a stepwise manner. Namely, one electron oxidation of $\underline{cis}$-$[R_2Co(bpy)_2]^+$ results in the cleavage of one cobalt-carbon bond, followed by the reaction of the resulting alkyl radical with $\underline{cis}$-$[RCo(bpy)_2]^{2+}$ in the cage to yield the coupling product, R-R. In the case of R = $PhCH_2$, the benzyl radical formed by the initial cleavage of the cobalt-benzyl bond upon the one-electron oxidation may be stable enough to be trapped by dioxygen to give the benzylperoxy radical ($PhCH_2OO\cdot$), as shown in Scheme 1-1. The benzylperoxy radical may decay by the bimolecular reaction to give benzaldehyde and benzyl alcohol, the latter of which may be further oxidized by the oxidants to yield benzaldehyde (PhCHO).[24,25]

Table 1-2. Product Yields in the One-Electron Oxidation of $\underline{cis}$-$[R_2Co(bpy)_2]^+$ (R = $PhCH_2$, Et, Me; $3.8 \times 10^{-6}$ mol) by Various Oxidants ($2.0 \times 10^{-5}$ mol) in Oxygen-Saturated MeCN (2.0 $cm^3$) at 298 K

| $\underline{cis}$-$[R_2Co(bpy)_2]^+$ R | oxidant | products (yield,[a] %) |
|---|---|---|
| $PhCH_2$ | $[Fe(phen)_3]^{3+}$ | PhCHO (99) |
| $PhCH_2$ | $[Fe(bpy)_3]^{3+}$ | PhCHO (99) |
| Et | $[Fe(phen)_3]^{3+}$ | $C_4H_{10}$ (100) |
| Et | $[Fe(bpy)_3]^{3+}$ | $C_4H_{10}$ (97) |
| Et | TCNE | $C_4H_{10}$ (96) |
| Et | DDBQ | $C_4H_{10}$ (97) |
| Et | DCBQ | $C_4H_{10}$ (100) |
| Me | $[Fe(phen)_3]^{3+}$ | $C_2H_6$ (100) |
| Me | $[Fe(bpy)_3]^{3+}$ | $C_2H_6$ (98) |
| Me | TCNE | $C_2H_6$ (94) |
| Me | DDBQ | $C_2H_6$ (99) |
| Me | DCBQ | $C_2H_6$ (100) |

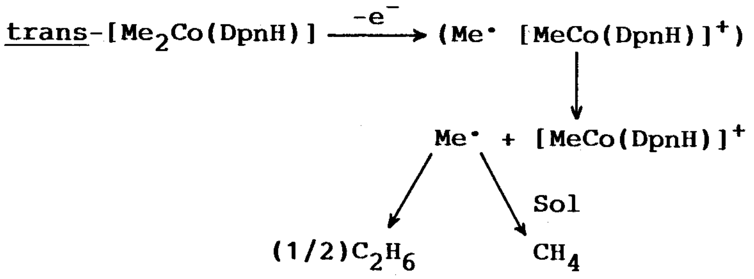
[a] Based on the amount of $\underline{cis}$-$[R_2Co(bpy)_2]^+$.

**Scheme 1-1**



One-electron oxidation of $\underline{trans}$-$[Me_2Co(DpnH)]$ is also known to give methyl radical and $[MeCo(DpnH)]^+$.[12,23,26] In this case, however, the reaction of methyl radical with another cobalt-methyl bond may be disfavored, compared with the case of $\underline{cis}$-$[R_2Co(bpy)_2]^+$, because of the $\underline{trans}$ configuration, and thereby methyl radical may diffuse outside of the cage to yield methane and ethane by the hydrogen abstraction from solvent and the radical coupling reaction, respectively (Scheme 1-2).[12,23,26]

**Scheme 1-2**



**Redox Potentials of $\underline{cis}$-$[R_2Co(bpy)_2]^+$.** In order to understand electron-transfer reactions from $\underline{cis}$-$[R_2Co(bpy)_2]^+$ to oxidants (eq 1), the redox potentials of both $\underline{cis}$-$[R_2Co(bpy)_2]^+$ and the oxidants are indispensable. The redox potentials of oxidants $E^\theta(Ox\text{-}Ox^-)$ used in this study are well known since the cathodic electrochemistry of these oxidants is reversible.[27,28] On the other hand, electrochemical oxidation of monoalkylcobalt(III) complexes with dimethylglyoxime and Schiff-base ligands is also known to proceed by a reversible one-electron process to afford relatively stable monoalkylcobalt(IV) complexes with a half-life of about several minutes at 298 K in MeCN, and thereby the redox potentials of monoalkylcobalt(III) complexes have been determined from the cyclic voltammograms.[29] In contrast, the anodic electrochemistry of dimethylcobalt(III) complexes with macrocyclic ligand is reported to be highly irreversible.[12] In the present case as well, the electrochemical oxidation of $\underline{cis}$-$[R_2Co(bpy)_2]^+$ was highly irreversible as characterized by the cyclic voltammogram which shows a cathodic wave with a well defined current maximum but no coupled anodic wave on the reverse scan even at sweep rates up to 1000 mV $s^{-1}$. Such an irreversible oxidation of $\underline{cis}$-$[R_2Co(bpy)_2]^+$ indicates that the follow-up reaction of $\underline{cis}$-$[R_2Co(bpy)_2]^{2+}$, i.e., the reductive coupling of the alkyl ligands (eq 1), may be fast on the time-scale of the cyclic voltammetry measurements.

A method of determining redox potentials in such irreversible systems has recently been established based on the Gibbs energy relationship for electron-transfer reactions,[22,23] which as given by Marcus[30] is shown in eq 2, where $\Delta G_{ex}{\ddagger}$ is the

$$\Delta G{\ddagger} = \Delta G_{ex}{\ddagger}[1 + (\Delta G_{et}{}^{\theta}/4\Delta G_{ex}{\ddagger})]^2 \qquad (2)$$

Gibbs activation energy for self-exchange of electrons between cis-$[R_2Co(bpy)_2]^+$ and cis-$[R_2Co(bpy)_2]^{2+}$ when the standard Gibbs energy of electron transfer, $\Delta G_{et}^{\theta}\{= F[E^{\theta}(R_2Co^{2+}-R_2Co^+) - E]\leq$, where F is the Faraday constant and E the electrode potential, is equal to zero. It should be noted that the application of eq 2 is limited to a region $-4\Delta G_{ex}^{\ddagger} < \Delta G_{et}^{\theta} < 4\Delta G_{ex}^{\ddagger}$.[31] In this region the transfer coefficient β is expressed as a function of $\Delta G_{et}^{\theta}$ by differentiating eq 2 with respect to $\Delta G_{et}^{\theta}$ yielding eq 3, from which can be derived a relation between the oxidation

$$\beta = 1/2 + (\Delta G_{et}^{\theta}/\Delta G_{ex}^{\ddagger})/8 \qquad (3)$$

peak potential $E^p(R_2Co^{2+}-R_2Co^+)$ and the standard redox potential $E^{\theta}(R_2Co^{2+}-R_2Co^+)$ when $E = E^p(R_2Co^{2+}-R_2Co^+)$, eq 4. According to eq 4, the standard redox potentials $E^{\theta}(R_2Co^{2+}-R_2Co^+)$ can be

$$E^p(R_2Co^{2+}-R_2Co^+) = E^{\theta}(R_2Co^{2+}-R_2Co^+) + 4(1 - 2\beta)\Delta G_{ex}^{\ddagger}/F \qquad (4)$$

evaluated from the intercept of the linear correlation between $E^p(R_2Co^{2+}-R_2Co^+)$ and $4(1 - 2\beta)$ and the β value is obtained from the width of the anodic wave, $E^p(R_2Co^{2+}-R_2Co^+) - E^{p/2}(R_2Co^{2+}-R_2Co^+)$, using eq 5.[32] Linear plots of $E^p(R_2Co^{2+}-R_2Co^+)$ vs. $4(1 - 2\beta)$ for cis-$[R_2Co(bpy)_2]^+$ (R = Me, Et, $PhCH_2$) in MeCN containing 0.10 $M^{-1}$ $NBu^n_4ClO_4$ are shown in Fig. 1-1. Then, from the intercepts and slopes in Fig. 1-1 the standard redox potentials $E^{\theta}(R_2Co2^+-R_2Co^+)$ vs. SCE and the $\Delta G_{ex}^{\ddagger}$ values were

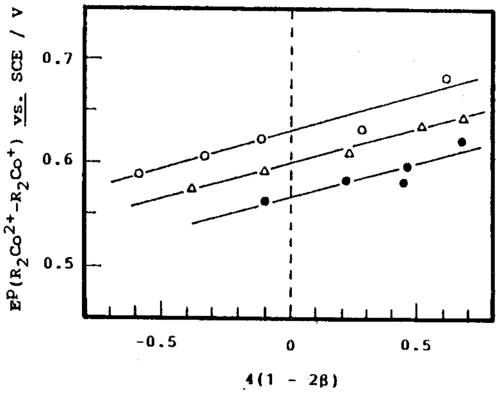


Fig. 1-1. Oxidation peak potentials $E^p(R_2Co^{2+}-R_2Co^+)$ vs. SCE of cis-$[R_2Co(bpy)_2]^+$ (R = Me (○), Et (●), $PhCH_2$ (△)) in MeCN containing 0.1 M $NBu^n_4ClO_4$ plotted as a function of the transfer coefficient β, 4(1 - 2β), based on the Marcus-Gibbs energy relationship.

$$E^p(R_2Co^{2+}-R_2Co^+) - E^{p/2}(R_2Co^{2+}-R_2Co^+) = 1.857RT/\beta F \qquad (5)$$

determined as follows: R = Me, $E^{\theta}(Me_2Co^{2+}-Me_2Co^+)$ 0.63V; R = Et, $E^{\theta}(Et_2Co^{2+}-Et_2Co^+)$ 0.57V; R = $PhCH_2$, $E^{\theta}((PhCH_2)_2Co^{2+}-(PhCH_2)_2Co^+)$ 0.60V, $\Delta G_{ex}^{\ddagger}$ of the cis-$[R_2Co(bpy)_2]^+$ (R = Me, Et, $PhCH_2$) are approximately the same $\Delta G_{ex}^{\ddagger}$ 9.8 ± 0.1 kJ $mol^{-1}$.

**Kinetics and Mechanism.** The rates of the electron-transfer reactions from cis-$[R_2Co(bpy)_2]^+$ to oxidants in MeCN at 298 K were monitored by the increase in the absorbance at $\lambda_{max}$ of the radical anions of oxidants[19-21] or the decrease of the $\lambda_{max}$ of cis-$[R_2Co(bpy)_2]^+$. The rate equation can be expressed in terms of the second-order kinetics, showing a first-order dependence on the concentration of each reactant (eq 6), which was

$$d[Ox^-]/dt = k_{obs}[R_2Co^+][Ox] \qquad (6)$$

confirmed under pseudo-first-order conditions in the presence of large excesses of the oxidants. The observed rate constants $k_{obs}$ were determined from 4 to 20 replicate measurements to give average deviations from the mean values within ± 5% (Table 1-3), together with the redox potentials of the oxidants[27,33] and cis-$[R_2Co(bpy)_2]^+$.

Table 1-3. Observed Second-Order Rate Constants $k_{obs}$ for Electron-Transfer Reactions from cis-$[R_2Co(bpy)_2]^+$ (R = $PhCH_2$, Et, Me) to Various One-Electron Oxidants in MeCN at 298 K, the One-Electron Reduction Potentials $E^0_{red}$ of Oxidants, and the One-Electron Oxidation Potentials of cis-$[R_2Co(bpy)_2]^+$

| | | $k_{obs}$[a] / $M^{-1}$ $s^{-1}$ of cis-$[R_2Co(bpy)_2]^+$ | | |
|---|---|---|---|---|
| oxidant | $E^0_{ox}$ / V | R = $PhCH_2$ (0.60V) | R = Et (0.57V) | R = Me (0.63V) |
| DDBQ | 0.51 | 7.8 | $5.5 \times 10^5$ | $3.2 \times 10^3$ |
| $[Fe(C_5H_5)_2]^+$ | 0.37 | - | $7.1 \times 10^2$ | - |
| $[Fe(BuC_5H_4)(C_5H_5)]^+$ | 0.31 | - | $3.3 \times 10^2$ | - |
| DCBQ | 0.28 | $2.3 \times 10^{-3}$ | $2.3 \times 10^2$ | 1.8 |
| $[Fe(MeC_5H_4)_2]^+$ | 0.26 | - | $4.6 \times 10$ | - |
| TCNE | 0.22 | - | $1.9 \times 10$ | $2.5 \times 10^{-1}$ |
| TCNQ | 0.19 | $3.5 \times 10^{-4}$ | 6.1 | - |

[a] The experimental errors are within ±10%.

From the temperature dependence of $k_{obs}$ for the reactions of cis-$[R_2Co(bpy)_2]^+$ with DCBQ, measured at 298, 308, and 318 K, the activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) have been determined: R = Me, $\Delta H^\ddagger$ 59 ± 5 kJ $mol^{-1}$, $\Delta S^\ddagger$ -13 ± 17 kJ $mol^{-1}$; R = Et, $\Delta H^\ddagger$ 49 ± 5 kJ $mol^{-1}$, $\Delta S^\ddagger$ -4 ± 17 kJ $mol^{-1}$. The $\Delta S^\ddagger$ values are close to zero, within the experimental errors, typical for electron-transfer reactions.[31]

The log $k_{obs}$ in Table 1-3 are plotted against the difference in the redox potentials of cis-$[R_2Co(bpy)_2]^+$ and the oxidants, $E^0_{ox} - E^0_{red}$, which correspond to the Gibbs free energy change of electron transfer $\Delta G_{et}{}^0$, as shown in Fig. 1-2. For each cis-$[R_2Co(bpy)_2]^+$, a linear correlation is observed between log $k_{obs}$ and $E^0_{ox} - E^0_{red}$ (eq 7). Each slope is about the same,

$$\log k_{obs} = -15.3[E^0(R_2Co^{2+}-R_2Co^+) - E^0(Ox-Ox^-)] + \text{Constant} \qquad (7)$$

ca. -15.3 which corresponds to -F/(2.3RT) at 298 K. Thus, the decrease in the $\Delta G_{et}^{\theta}$ value [$F(E^0_{ox} - E^0_{red})$] with an increase in the $E^0_{red}$ value of various oxidations is directly reflected in the increase in the rate constant [$\log k_{obs} = \log Z - \Delta G_{et}^{\ddagger}/(2.3RT)$].[34] The $k_{obs}$ value of cis-[$R_2Co(bpy)_2$]$^+$ at the same $E^0_{ox} - E^0_{red}$ value is in the order R = Et > Me >> $PhCH_2$ (Fig. 1-2). The lowest reactivity of cis-[$(PhCH_2)_2Co(bpy)_2$]$^+$ indicates that the rate of coupling reaction of R$^\bullet$ with [$RCo(bpy)_2$]$^{2+}$ (Scheme 1-1) is the slowest in the case of R = $PhCH_2$ since benzyl radical is much more stable than methyl and ethyl radicals. As such only benzyl radical is stable enough to be trapped by dioxygen to yields the oxygenated product(Table 1-2).

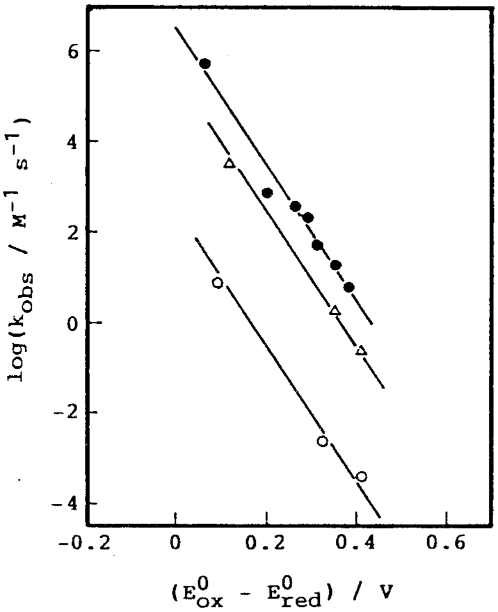


Fig. 1-2. Plots of log $k_{obs}$ for electron-transfer reactions from cis-[$R_2Co(bpy)_2$]$^+$ [R = $PhCH_2$ (○), Et (●), Me (△)] to oxidants vs. the difference in the redox potentials between $E^0_{ox}$ of cis-[$R_2Co(bpy)_2$]$^+$ and $E^0_{red}$ of the oxidants.

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(34) When the activation Gibbs free energy $\Delta G_{et}^{\ddagger}$ is proportional to $\Delta G_{et}^{0}$, $k_{obs}$ may be given by $k_{obs}$ = Const. + $F(E^0_{ox} - E^0_{red})/(2.3RT)$, in which the slope of the plot of log $k_{obs}$ *vs.* $E^0_{ox} - E^0_{red}$ would be equal to $-F/(2.3RT) = -16.9$ at 298 K.

# Chapter 2 OXIDATION OF cis-DIALKYLCOBALT(III) COMPLEXES WITH OXYGEN, CATALYZED BY COENZYME ANALOGUES

**Abstract:** Oxygenation of the benzyl ligand of cis-$[(PhCH_2)Co(bpy)_2]^+$ (bpy = 2,2'-bipyridine), occurs efficiently in the presence of a catalytic amount of a coenzyme analogue, riboflavin, riboflavin-2',3',4',5'-tetraacetate, lumazine, or aminopterin, in acetonitrile containing perchloric acid at 298 K to produce benzyl hydroperoxide which decomposes to yield benzaldehyde as the final oxygenated product. In the case of cis-$[R_2Co(bpy)_2]^+$ (R = Et, Me), however, no oxygenation of the ligands proceeds under the same conditions otherwise, but instead, oxidative coupling of alkyl ligands of cis-$[R_2Co(bpy)_2]^+$ undergoes in the coenzyme-catalyzed oxidation by dioxygen to yield ethane and butane, respectively, when dioxygen is reduced to hydrogen peroxide. The origin of such difference in the oxygenation and oxidative coupling pathways depending on the alkyl ligands is discussed based on the comparison of the products and kinetics with those of the one-electron oxidation of cis-$[R_2Co(bpy)_2]^+$ by various oxidants in the absence and presence of dioxygen in acetonitrile at 298 K.

## 2-1 Introduction

The interaction of dioxygen with transition-metal complexes has been extensively studied owing to the importance in understanding the mode of action of biological oxygen carriers.[1] In contrast, the contact of dioxygen with air-sensitive organometallic compounds has usually been avoided deliberately on their handling. Thus, relatively little is known about the reactions of dioxygen with such organometallic compounds, although dioxygenation reactions of alkyl Grignard reagents are known for a long time,[2,3] and the chemistry of organometallic compounds containing oxo and peroxo ligands formed in the reactions with dioxygen has recently attracted increasing interest with relevance to selective catalytic oxidation processes.[4-8] Moreover, reactions of most air-sensitive organometallic compounds with dioxygen are too rapid to study the mechanisms in detail.[9] However, some organometallic compounds such as alkylcobalt(III) complexes are rather stable to dioxygen. In such a case, oxygenation reactions of stable organometallic compounds require irradiation of light.[10-12] The oxygenation of alkyl ligands of monoalkylcobalt(III) complexes (RCo) are known to be induced also by thermal homolytic cleavage of cobalt-carbon bonds (eq 1),[13] followed by the reactions of the dissociated alkyl radicals with dioxygen (eq 2).[14] In other cases,

$$\mathrm{RCo} \longrightarrow (\mathrm{R^{\bullet}\ Co}) \tag{1}$$

$$(\mathrm{R^{\bullet}\ Co}) + \mathrm{O_2} \longrightarrow \mathrm{ROO^{\bullet}} + \mathrm{Co} \tag{2}$$

oxidation of dialkylmetal complexes ($R_2M$) by dioxygen leads to oxidative coupling of the alkyl ligands (eq 3).[15,16] In any

$$\mathrm{R_2M} + \mathrm{O_2} \longrightarrow \mathrm{R\text{-}R} + \mathrm{M^+} + \mathrm{O_2^-} \tag{3}$$

case, however, there has so far been no reports on catalytic systems to accelerate the reactions of organometallic compounds with dioxygen. In biological systems, redox coenzymes such as flavins and pterins are well known to play important roles in the enzymatic oxidation of substrates by dioxygen.[17,18]

In this study,[19] we report efficient catalytic systems for the reactions of cis-$[R_2Co(bpy)_2]^+$ (R = $PhCH_2$, Et, Me; bpy = 2,2'-bipyridine) with dioxygen using redox coenzyme analogues, riboflavin, riboflavin-2',3',4',5'-tetraacetate, lumazine (pteridine-2,4-diol), and aminopterin (4-aminofolic acid) as catalysts in the presence of $HClO_4$ in acetonitrile (MeCN). In the coenzyme-catalyzed oxidation of cis-$[R_2Co(bpy)_2]^+$ by dioxygen, both oxygenation and oxidative coupling processes occur depending on the difference in the alkyl ligands. The products as well as the kinetics are compared with those of electron transfer reactions from cis-$[R_2Co(bpy)_2]^+$ to various one-electron oxidants in order to elucidate the origin of the different oxidation pathways by dioxygen; oxygenation and oxidative coupling processes depending on the alkyl ligands of cis-$[R_2Co(bpy)_2]^+$.

## 2-2 Experimental

**Materials.** cis-Dialkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]^+$ (R = $PhCH_2$, Et, Me) used in this study are obtained by the method described in chapter 1.[20,21] Riboflavin-2',3',4',5'-

tetraacetate was prepared by the reaction of riboflavin with acetic anhydride in pyridine, and purified by recrystallization from the ethanol and chloroform mixture.[22] Riboflavin, lumazine, and aminopterin were obtained commercially and purified by the standard procedure. Perchloric acid (70 % aqueous solution) was purchased from Wako Pure Chemicals and stored under nitrogen. Benzyl hydroperoxide used as the authentic sample was prepared by the addition of benzylmagnesium chloride to dioxygen-saturated ether at -70 $^{o}C$.[4] The [Co-$(bpy)_3](ClO_4)_3$ was prepared by the reaction of $Co(ClO_4)_3 \cdot 6H_2O$ with an excess amount of 2,2'-bipyridine ligand. Reagent grade acetonitrile was purified by the standard procedure,[23] followed by redistillation from calcium hydride. Acetonitrile-$\underline{d}_3$ was stirred with freshly activated molecular sieve 4A (Wako Pure Chemicals) and then transferred under vacuum into a dry, glass-stoppered bottle. Other reagents used for the product analysis were obtained commercially.

**Product Analysis.** Typically, a catalytic amount of riboflavin-2',3',4',5'-tetraacetate ($1.0 \times 10^{-6}$ mol) was added to an NMR tube that contained an oxygen-saturated acetonitrile-$\underline{d}_3$ (0.6 $cm^3$) solution of $\underline{cis}$-$[R_2Co(bpy)_2]ClO_4$ ($1.8 \times 10^{-5}$ mol). The reaction was started by adding the $HClO_4$ ($6.0 \times 10^{-5}$ mol) using a micropipet under a stream of dioxygen. Then, the NMR tube was sealed by a rubber septum and the reaction was monitored by using a Japan Electron Optics JNM-PS-100 $^1H$ NMR spectrometer (100 MHz). The amounts of $PhCH_2OOH$ and $[PhCH_2Co(bpy)_2]^{2+}$ formed were determined by the appearance of new signals at $\delta$(ppm) 4.89 (2H, s) and 2.90 (2H, s) due to the methylene protons of the benzyl groups, respectively. After completion of the reaction, the products were analyzed also by GLC using a Unibeads 1-S or a Gaskropak 54 column.

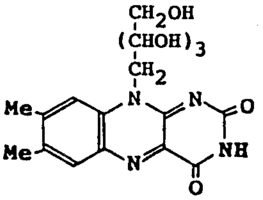
**Kinetic Measurements.** Kinetic measurements were carried out by using a Union RA-103 stopped-flow spectrophotometer and a Union SM-401 spectrophotometer for the oxidation of $\underline{cis}$-$[R_2Co(bpy)_2]^+$ with half-lives of shorter than 10 s and much longer than 10 s, respectively. Rates of the coenzyme-catalyzed oxidation of $\underline{cis}$-$[R_2Co(bpy)_2]^+$ by dioxygen were monitored by the rate of disappearance of absorbance at $\lambda_{max}$ due to $\underline{cis}$-$[R_2Co(bpy)_2]ClO_4$ in MeCN ($\lambda_{max}$ = 502, 495 and 472 nm for R = $PhCH_2$, Et and Me, respectively). All the kinetic measurements were carried out under pseudo-first-order conditions where the concentrations of oxidants and $HClO_4$ were maintained at >10-fold excess of the concentration of cis-$[R_2Co(bpy)_2]^+$ at 298 K. Pseudo-first-order rate constants were determined by least-squares curve fit using a Union System 77 or a NEC 9801 VM microcomputer.

**Electron Spin Resonance Measurements.** Typically, a small amount of cis-$[(R_2Co(bpy)_2]^+$ ($2.0 \times 10^{-7}$ mol) was added to a quartz ESR tube (1 mm i.d.) equipped with a side arm which contained an MeCN solution (0.20 $cm^3$) of Fl ($1.0 \times 10^{-3}$ M) and $HClO_4$ ($1.0 \times 10^{-2}$ M). After the ESR tube with a side arm was sealed and the reactant solution in the side arm was thoroughly degassed in vacuum by the successive freez-pump-thaw cycles, the solution was transferred to the ESR tube. Then, the ESR spectra were recorded under a non-saturating microwave power condition with a modulation amplitude $8.0 \times 10^{-2}$ mT using a JEOL-X band spectrometer (JES-ME-LX) at room temperature. The further reduction of modulation amplitude has not improved the hyperfine resolution. The g-value and the hyperfine coupling constants (hfc) of the ESR spectra were calibrated by using an $Mn^{2+}$ marker. The simulation of the ESR spectra was performed using a NEC 9801 VM microcomputer.

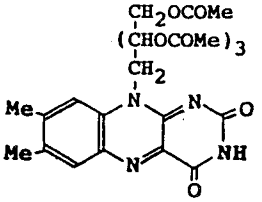
## 2-3 Results

**Coenzyme-Catalyzed Oxygenation of the Benzyl Ligand of cis-$[(PhCH_2)_2Co(bpy)_2]^+$.** The cis-$[(PhCH_2)_2Co(bpy)_2]ClO_4$ shows no reactivity towards dioxygen or redox coenzyme analogues, riboflavin (Fl), riboflavin-2',3',4',5'-tetraacetate (FlTA), lumazine (L), and aminopterin (AP), in MeCN at 298 K. When a strong acid such as perchloric acid ($HClO_4$) is added to an oxygen-saturated MeCN solution of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ in the presence of a catalytic amount of coenzyme analogue, however, cis-$[(PhCH_2)_2Co(bpy)_2]^+$ is readily oxidized by dioxygen to produce benzyl hydroperoxide (eq 4). A typical example of the coenzyme-catalyzed oxygenation reaction of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ is shown in Fig. 2-1, where cis-$[(PhCH_2)_2Co(bpy)_2]^+$ ($3.0 \times 10^{-2}$ M) reacts with dioxygen ($6.9 \times 10^{-5}$ mol) in the presence of catalytic amount of lumazine ($5.3 \times 10^{-3}$ M) in $CD_3CN$ (0.60 $cm^3$) containing $HClO_4$ (0.12 M) to produce $PhCH_2OOH$ which decomposes to yield benzaldehyde (PhCHO) as the final oxygenated

$$\underline{\text{cis}}\text{-}[(\mathrm{PhCH_2})_2\mathrm{Co(bpy)_2}]^+ + \mathrm{O_2} + \mathrm{H^+} \xrightarrow{\text{Fl, FlTA, L, or AP}} [\mathrm{PhCH_2Co(bpy)_2}]^{2+} + \mathrm{PhCH_2OOH} \qquad (4)$$

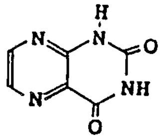


(Fl)

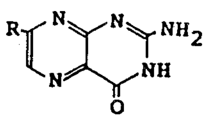


(FlTA)

R = $CH_2NHC_6H_4CONHCH(COOH)C_2H_4COOH$



(L)



(AP)

product.[24] The formation of $[PhCH_2Co(bpy)_2]^{2+}$ (eq 4) is also confirmed by the $^1H$ NMR spectrum (see Experimental). Other redox coenzyme analogues (FlTA, Fl, and AP) can also catalyze the oxygenation of the benzyl ligand of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ in the presence of $HClO_4$ in MeCN at 298 K and the yields of benzaldehyde are summarized in Table 2-1.

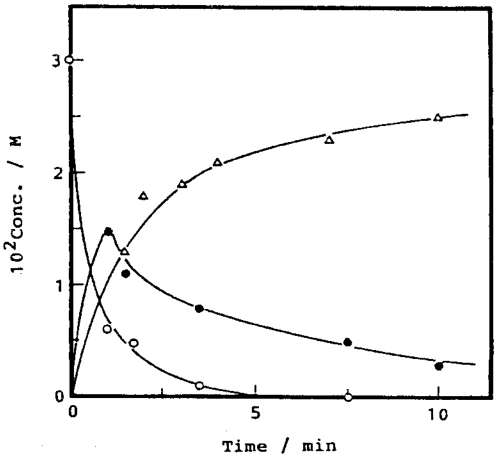


Fig. 2-1. Oxygenation of the benzyl ligand of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ ($3.0 \times 10^{-2}$ M) in the presence of $HClO_4$ ($1.2 \times 10^{-1}$ M) and a catalytic amount of lumazine ($5.3 \times 10^{-3}$ M) in $CD_3CN$ at 298 K; cis-$[(PhCH_2)_2Co(bpy)_2]^+$ ( ○ ), $PhCH_2OOH$ ( ● ), PhCHO ( △ ).

Flavin analogues are known to be protonated at the N(1) position in a strongly acidic aqueous solution ($pK_a$ = 0).[25] In MeCN, the protonation of flavin analogues occurs much more readily than that in $H_2O$.[18,26] The protonation equilibrium constant K of Fl in MeCN has been reported to be $2.7 \times 10^6$ $M^{-1}$.[26] Thus, the absorption band due to Fl and FlTA (ca. $10^{-4}$ M) in MeCN ($\lambda_{max}$ 439 and 442 nm) is blue-shifted in the presence of even slightly excess $HClO_4$ ($\lambda_{max}$ 388 and 390 nm, respectively). Such a blue shift due to the protonation is observed also for lumazine or aminopterin. Thus, all coenzyme analogues (Fl, FlTA, L, AP) exist in the protonated form ($FlH^+$, $FlTAH^+$, $LH^+$, $APH^+$) in the presence of an excess amount of $HClO_4$ in MeCN as shown in the case of Fl, eq 5.

$$\mathbf{Fl + H^+ \overset{K}{\rightleftarrows} FlH^+} \qquad (5)$$

Table 2-1. Product Yields in the Coenzyme-Catalyzed Oxidation of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ $[(1.8\text{-}2.5) \times 10^{-5}$ mol] by Dioxygen in the Presence and Absence of $HClO_4$ in $CD_3CN$ (0.60 $cm^3$) at 298 K

| $O_2$<br>$10^{-5}$ mol | catalyst[a]<br>$10^{-5}$ mol | $HClO_4$<br>$10^{-5}$ mol | products (yield,[b] %) |
|---|---|---|---|
| | FlTA | | |
| 6.9 | 0 | 0 | no reaction |
| 0 | 0.10 | 0 | no reaction |
| 6.9 | 0.10 | 0 | no reaction |
| 6.9 | 0.10 | 6.0 | PhCHO (99) $PhCH_2OOH$ (trace) |
| 0 | 0 | 6.0 | $PhCH_3$ (100) |
| | Fl | | |
| 6.9 | 0.10 | 6.0 | PhCHO (100) $PhCH_2OOH$ (trace) |
| 0 | 3.0 | 6.0 | $PhC_2H_4Ph$ (50) |
| | L | | |
| 6.9 | 0.32 | 7.2 | PhCHO (100) $PhCH_2OOH$ (trace) |
| | AP | | |
| 6.9 | 0.3 | 6.0 | PhCHO (100) $PhCH_2OOH$ (trace) |

[a] Catalyst: riboflavin-2',3',4',5'-tetraacetate (FlTA), riboflavin (Fl), lumazine (L), aminopterin (AP).

[b] Based on the amount of cis-$[(PhCH_2)_2Co(bpy)_2]^+$.

In the absence of dioxygen, the stoichiometric oxidation of cis-$[R_2Co(bpy)_2]^+$ ($R = PhCH_2$) by $FlH^+$ occurs in the presence of $HClO_4$ in MeCN to yield the coupling product, $PhC_2H_4Ph$ (Table 2-1). The stoichiometry of the reaction is given by eq 6, where formation of $FlH_2^{+\bullet}$ is confirmed by the

$$\underline{\text{cis}}\text{-}[R_2Co(bpy)_2]^+ + 2FlH^+ + 2H^+ \longrightarrow R\text{-}R + [Co(bpy)_2]^{3+} + 2FlH_2^{+\bullet} \qquad (6)$$

ESR spectrum as shown in Fig. 2-2 (part a). A computer simulation spectrum of $FlH_2^{+\bullet}$ is also shown in Fig. 2-2 (part b) with the best-fit parameters, the hyperfine coupling constant (hfc), $a_5(N)$ 0.585, $a_5(H)$ 1.170, $a_8(Me)$ 0.236, $a_{10}(N)$ 0.428, $a_{10}(CH_2)$ 0.431 mT and the maximum slope line width $\Delta H_{msl}$ 0.105 mT. The simulated spectrum agrees well with the observed spectrum, except for some line intensities. The large hfc value due to N-5 proton and the lack of appreciable hfc due to C-6 and C-9 protons are characteristic of a dihydroflavin radical cation.[27] The lack of appreciable hfc due to the C-7 proton, N-1, or N-3 is typical for flavin radical species [flavosemiquinone radical anion ($Fl^{-\bullet}$), neutral flavosemiquinone ($FlH^\bullet$), and dihydroflavin radical cation ($FlH_2^{+\bullet}$)][27] as confirmed by the MO calculation.[28] A similar ESR spectrum due to $FlTAH_2^{+\bullet}$ is obtained in the oxidation of cis-$[R_2Co(bpy)_2]^+$ by $FlTAH^+$ in the presence of $HClO_4$ in deaerated MeCN.[29] Both $FlH_2^{+\bullet}$ ($\lambda_{max}$ 500 nm) and $FlTAH_2^{+\bullet}$ ($\lambda_{max}$ 504 nm) are very stable in the presence of $HClO_4$ even in oxygen-saturated MeCN.

In the reaction of $LH^+$ with cis-$[(PhCH_2)_2Co(bpy)_2]^+$ as well, a transient new absorption band due to $LH_2^{+\bullet}$ ($\lambda_{max}$ 416 nm)[30] is observed. In the case of $APH^+$, however, no free radical species derived from $APH^+$ has been detected in the reaction with cis-$[(PhCH_2)_2Co(bpy)_2]^+$ in the presence of $HClO_4$ in deaerated MeCN.

In the absence of dioxygen and coenzyme analogues, the cobalt-carbon bond of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ is cleaved by the electrophilic attack of proton to yield $[PhCH_2Co(bpy)_2]^{2+}$ and toluene, eq 7 (Table 2-1).

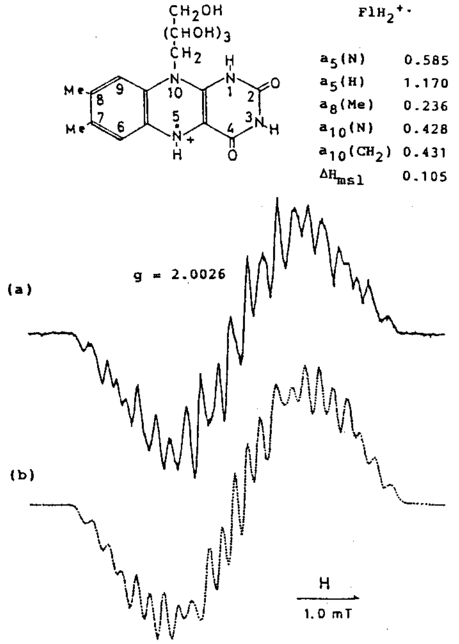


Fig. 2-2. (a) ESR spectrum of $FlH_2^{+\bullet}$ formed in the oxidation of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ ($1.0 \times 10^{-3}$ M) with $FlH^+$ ($1.0 \times 10^{-3}$ M) in the presence of $HClO_4$ ($1.0 \times 10^{-2}$ M) deaerated MeCN at 298 K, and (b) the computer simulation spectrum of $FlH_2^{+\bullet}$.

$$\textit{cis}\text{-}[(PhCH_2)_2Co(bpy)_2]^+ + H^+ \longrightarrow PhCH_3 + [PhCH_2Co(bpy)_2]^{2+} \qquad (7)$$

**Coenzyme-Catalyzed Oxidative Coupling of Alkyl Ligands of cis-$[R_2Co(bpy)_2]^+$ (R = Et, Me) by Dioxygen.** The coenzyme-catalyzed oxidation of other cis-dialkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]^+$ (R = Me, Et) by dioxygen also proceeds efficiently in the presence of $HClO_4$ in MeCN. In this case, however, no oxygenation of the alkyl ligands occurs, but instead coupling products of the alkyl groups are obtained upon the catalytic oxidation of cis-$[R_2Co(bpy)_2]^+$ by dioxygen in the presence of $HClO_4$. A typical example is shown in Fig. 2-3, where the ratios of the amount of the coupling product $C_4H_{10}$ formed in the $FlTAH^+$-catalyzed oxidation of cis-$[Et_2Co(bpy)_2]^+$ by dioxygen and the amount of cis-$[Et_2Co(bpy)_2]^+$ reacted to the initial amount of dioxygen are plotted against the reaction time. The reaction is carried out in the presence of a catalytic amount of FlTA ($2.9 \times 10^{-6}$ mol) in $CD_3CN$ containing $HClO_4$ ($6.8 \times 10^{-5}$ mol) and $H_2O$ ($5.40 \times 10^{-4}$ mol) under the conditions that the initial amount of <u>cis</u>-$[Et_2Co(bpy)_2]^+$ ($3.59 \times 10^{-5}$ mol) is excess to that of dioxygen ($1.38 \times 10^{-5}$ mol).[31] Fig. 2-3 indicates that the stoichiometry of the catalytic oxidation of <u>cis</u>-$[Et_2Co(bpy)_2]^+$ by dioxygen in the presence of $HClO_4$ is given by eq 8.[32] The yields of the coupling products in other coenzyme-catalyzed oxidation of <u>cis</u>-$[R_2Co(bpy)_2]^+$ (R = Et, Me; $(2.1\text{-}3.6) \times 10^{-5}$ mol) by an excess amount of dioxygen ($6.9 \times 10^{-5}$ mol) are shown in Table 2-2. In the case of R = Me, the coupling product, ethane, is the main product, but a small amount of methane is also produced by the competing electrophilic cleavage of cobalt-carbon bond with $HClO_4$.

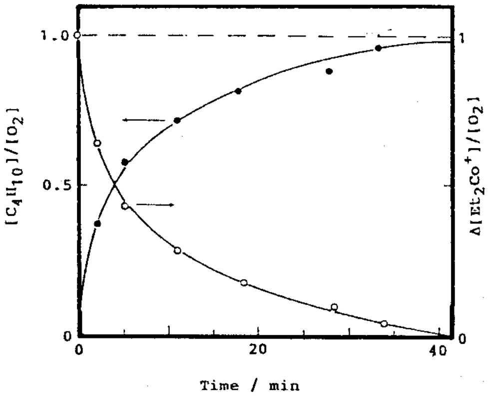


Fig. 2-3. Plots of the ratios of the amount of $C_4H_{10}$ formed in the $FlH^+$-catalyzed oxidation of <u>cis</u>-$[Et_2Co(bpy)_2]^+$ ($3.59 \times 10^{-5}$ mol) with dioxygen ($1.38 \times 10^{-5}$ mol) in the presence of $HClO_4$ ($6.8 \times 10^{-5}$ mol) and $H_2O$ ($5.4 \times 10^{-4}$ mol) in $CD_3CN$ (0.60 $cm^3$) and that of <u>cis</u>-$[Et_2Co(bpy)_2]^+$ reacted to the initial amount of $O_2$ <u>vs.</u> reaction time.

$$\underline{cis}\text{-}[(C_2H_5)_2Co(bpy)_2]^+ + O_2 + 2H^+ \xrightarrow{FlTA} C_4H_{10} + [Co(bpy)_2]^{3+} + H_2O_2 \qquad (8)$$

Table 2-2. Product Yields in the Coenzyme-Catalyzed Oxidation of <u>cis</u>-$[R_2Co(bpy)_2]^+$ (R = Et, Me) by Dioxygen in the Presence and Absence of $HClO_4$ in $CD_3CN$ (0.60 $cm^3$) at 298 K

| R | $O_2$<br>$10^{-5}$ mol | catalyst | $HClO_4$ | products (yield,[a] %) |
|---|---|---|---|---|
| Et | | | FlTA | |
| 2.1 | 6.9 | 0 | 0 | no reaction |
| 2.1 | 0 | 0.28 | 0 | no reaction |
| 2.4 | 6.9 | 0.28 | 6.8 | $C_4H_{10}$ (100) $C_2H_6$(trace) |
| | | | Fl | |
| 2.4 | 6.9 | 0.28 | 6.8 | $C_4H_{10}$ (100) $C_2H_6$(trace) |
| | | | L | |
| 2.4 | 6.9 | 0.28 | 6.8 | $C_4H_{10}$ (100) $C_2H_6$(trace) |
| Me | | | FlTA | |
| 2.1 | 0 | 3.60 | 0 | no reaction |
| | | | Fl | |
| 3.6 | 6.9 | 3.60 | 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] Based on the amount of <u>cis</u>-$[R_2Co(bpy)_2]^+$.

In the absence of a coenzyme analogue, the cobalt-carbon bond of <u>cis</u>-$[Me_2Co(bpy)_2]^+$ in both deaerated and oxygen-saturated MeCN is cleaved by the electrophilic attack of proton to yield $[MeCo(bpy)_2]^{2+}$ and $CH_4$, eq 9 (Table 2-2).

$$\underline{cis}\text{-}[Me_2Co(bpy)_2]^+ + H^+ \longrightarrow CH_4 + [RCo(bpy)_2]^{2+} \qquad (9)$$

**Kinetics of Coenzyme-Catalyzed Oxidation of $\underline{cis}$-$[R_2Co(bpy)_2]^+$ with Dioxygen.** Rates of the coenzyme-catalyzed oxidation of $\underline{cis}$-$[R_2Co(bpy)_2]^+$ by dioxygen in the presence of $HClO_4$ in MeCN obey pseudo-first-order kinetics when the concentrations of oxidants and $HClO_4$ are maintained at >10 fold excess of the concentration of $\underline{cis}$-$[R_2Co(bpy)_2]^+$. The pseudo-first-order rate constants $k^{(1)}$ increase linearly with an increase in the concentration of a coenzyme catalyst [Cat] as shown in Fig. 2-4. Thus, the rate of disappearance of $\underline{cis}$-$[R_2Co(bpy)_2]^+$ is given by eq 10. The $k_{obs}$ value in air-saturated MeCN was the same as that in oxygen-saturated MeCN.

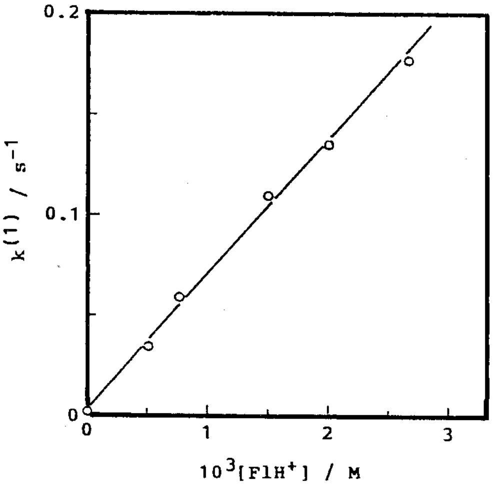


Fig. 2-4. Plot of the observed pseudo-first-order rate constant $k^{(1)}$ $\underline{vs.}$ the concentration of $FlH^+$ used as a catalyst for the catalytic oxidation of $\underline{cis}$-$[(PhCH_2)_2Co(bpy)_2]^+$ by dioxygen in the presence of $HClO_4$ (0.10 M) in MeCN at 298 K.

$$-d[R_2Co^+]/dt = k_{obs}[R_2Co^+][Cat] \qquad (10)$$

When $FlH^+$ or $LH^+$ is used as a catalyst for the catalytic oxidation of $\underline{cis}$-$[Et_2Co(bpy)_2]^+$ by dioxygen in the presence of $HClO_4$ in MeCN, the log $k_{obs}$ value increases linearly with an increase in the log$[HClO_4]$ value with a slope of unity as shown in Fig. 2-5. When $APH^+$ is used as a catalyst, however, the log $k_{obs}$ value remains constant with increasing $[HClO_4]$ in the low concentration region (log$[HClO_4]$ < 0) and increases linearly with an increase in the log$[HClO_4]$ value in the higher concentration region with a slope of unity (Fig. 2-5). The $HClO_4$ used in Fig. 2-5 contains 30% $H_2O$ (see Experimental). The addition of $H_2O$ to an MeCN solution of 0.10 M $HClO_4$ results in a significant decrease in the $k_{obs}$ value as shown in Fig. 2-6, where the log $k_{obs}$ values of the $FlH^+$-catalyzed oxidation of $\underline{cis}$-$[Et_2Co(bpy)_2]^+$ by dioxygen are plotted against the log$[H_2O]$ values.[38]

Fig. 2-7 shows the dependence of the pseudo-first-order

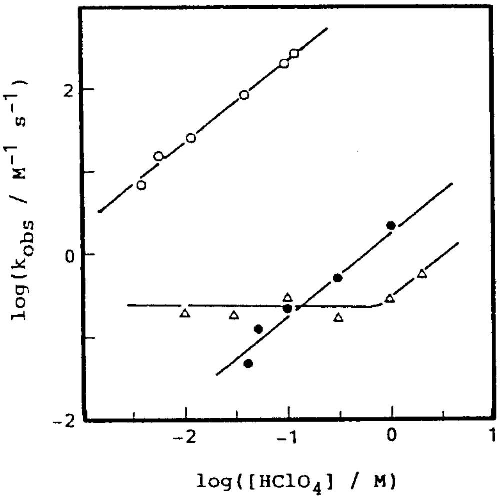


Fig. 2-5. Plots of the observed second-order rate constants log $k_{obs}$ vs. log[$HClO_4$] for the oxidation of cis-[$Et_2Co(bpy)_2$]$^+$ with dioxygen, catalyzed by $FlH^+$ (○), $LH^+$ (●), and $APH^+$ (△) in the presence of $HClO_4$ in MeCN at 298 K.

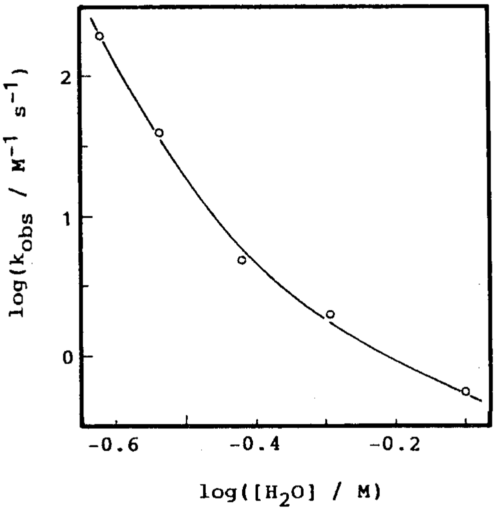


Fig. 2-6. Plots of the observed second-order rate constants log $k_{obs}$ vs. log[$H_2O$] for the $FlH^+$-catalyzed oxidation of cis-[$Et_2Co(bpy)_2$]$^+$ in the presence of $HClO_4$ (0.10 M) in MeCN containing various concentrations of $H_2O$ at 298 K.

rate constants log $k^{(1)}$ for the electrophilic cleavage of the cobalt-carbon bonds of cis-[$R_2Co(bpy)_2$]$^+$ in the absence of dioxygen and coenzyme analogues on the $HClO_4$ concentration, log[$HClO_4$]. Each $k^{(1)}$ value of cis-[$R_2Co(bpy)_2$]$^+$ shows a first-

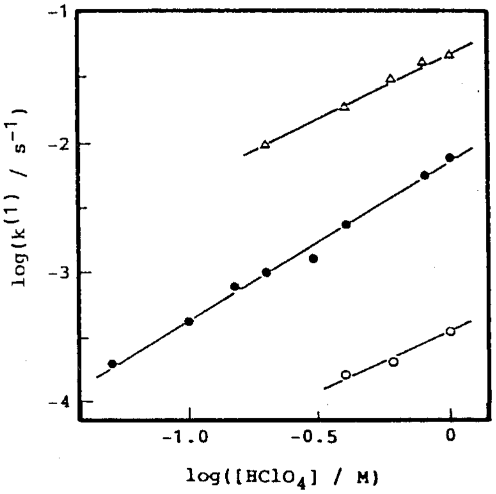


Fig. 2-7. Plots of the observed pseudo-first-order rate constants log $k^{(1)}$ vs. log[$HClO_4$] for the electrophilic cleavage of the cobalt-carbon bonds of cis-[$R_2Co(bpy)_2$]$^+$ [R = Me (△), Et (●), $PhCH_2$ (○)] by $HClO_4$ in deaerated MeCN at 298 K.

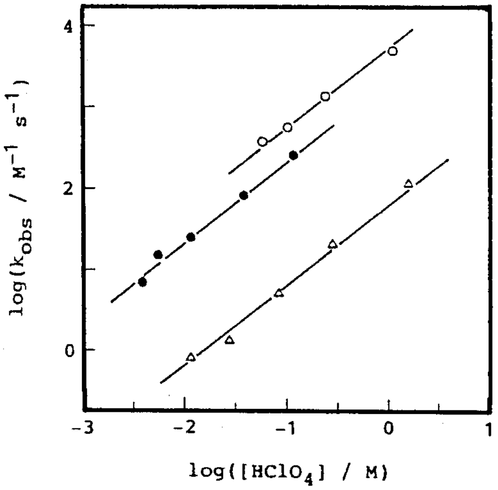


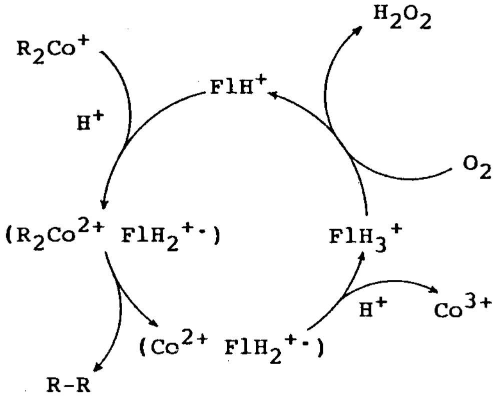
Fig. 2-8. Plots of the observed second-order rate constants log $k_{obs}$ vs. log[$HClO_4$] for the $FlH^+$-catalyzed oxidation of cis-[$R_2Co(bpy)_2$]$^+$ [R = $PhCH_2$ (○), Et (●), Me (△)] by dioxygen in the presence of $HClO_4$ in MeCN at 298 K.

order dependence on [$HClO_4$], and decreases in the order R = Me > Et > $PhCH_2$. Since the electrophilic cleavage of cis-[$R_2Co(bpy)_2$]$^+$ by $HClO_4$ is fastest for R = Me, the $k_{obs}$ values of the $FlH^+$-catalyzed reaction of cis-[$Me_2Co(bpy)_2$]$^+$ were determined under the conditions such that the contribution from the electrophilic cleavage reaction by $HClO_4$ can be neglected, using a large concentration of $FlH^+$ (> $1.0 \times 10^{-2}$ M). Then, the $k_{obs}$ values of cis-[$R_2Co(bpy)_2$]$^+$ (R = $PhCH_2$, Et, Me) are compared using the same catalyst ($FlH^+$) as shown in Fig. 2-8, where the log $k_{obs}$ values are plotted against the log[$HClO_4$] values. The $k_{obs}$ value at the same concentration of $HClO_4$ decreases in the order R = $PhCH_2$ > Et > Me.

## 2-4 Discussion

**Mechanism of Coenzyme-Catalyzed Oxidative Coupling of cis-[$R_2Co(bpy)_2$]$^+$ (R = Et, Me) by Dioxygen.** The formation of the coupling products of alkyl ligands of cis-[$R_2Co(bpy)_2$]$^+$ (R = Et, Me), which could only arise via the corresponding dialkylcobalt(IV) complexes, demonstrates clearly the involvement of an electron-transfer process in the coenzyme-catalyzed oxidation of cis-[$R_2Co(bpy)_2$]$^+$ (see Chapter 1). The catalytic cycle in the case of $FlH^+$ is shown in Scheme 2-1, where an acid-catalyzed electron transfer from the dialkylcobalt(III) complex ($R_2Co^+$) to $FlH^+$ occurs to give the corresponding dialkylcobalt(IV) complex ($R_2Co^{2+}$) and $FlH_2^{+\cdot}$, followed by the facile reductive elimination of the alkyl ligands to yield the coupling product R-R. The resulting cobalt(II) complex may reduce $FlH_2^{+\cdot}$ in the

**Scheme 2-1**



presence of $HClO_4$ to give $Co^{3+}$ and a protonated dihydroflavin $FlH_3{}^+$. The fully reduced form of flavin ($FlH_3{}^+$) is known to be readily oxidized by dioxygen to regenerate the oxidized form ($FlH^+$) accompanied by the formation of $H_2O_2$.[18,19] In the absence of dioxygen, the dihydroflavin radical cation $FlH_2{}^{+\cdot}$ is formed by the comproportionation reaction (eq 11) as shown in eq 6 (Fig. 2-2).[18,19]

$$FlH_3{}^+ + FlH^+ \rightleftharpoons 2FlH_2{}^{+\cdot} \qquad (11)$$

In Scheme 2-1, the acid-catalyzed electron transfer from $R_2Co^+$ to $FlH^+$ may be the rate-determining step, since the rate is proportional to $[R_2Co][FlH^+][H^+]$ and independent of the $O_2$ concentration (eq 10). Essentially the same reaction scheme may be applied for the $LH^+$-catalyzed oxidation of $R_2Co^+$ by dioxygen in the presence of $HClO_4$. In the case of $APH^+$, however, the rate is independent of $[HClO_4]$ in the low concentration region ($[\log[HClO_4] < 0$) as shown in Fig. 2-5. Such difference may be ascribed to the difference in the acid dissociation constant ($K_a$) of $APH_2{}^{+\cdot}$ and $FlH_2{}^{+\cdot}$ (or $LH_2{}^{+\cdot}$) as follows. The expression of Nernst equation of the one-electron reduction potential of $APH^+$ in the presence of $HClO_4$, $E_{red}$, may be given by eq 12,[27,33]

$$E_{red} = E^0_{red} + (2.3RT/F)\log(1 + K_a{}^{-1}[H^+]) \qquad (12)$$

where $E^0_{red}$ is the one-electron redox potential of the $APH^+/APH^\cdot$ couple, F is the Faraday constant, and 2.3RT/F is equal to 0.059 at 298 K. According to eq 12, $E_{red}$ is independent of $[HClO_4]$ in the low concentration region, $[HClO_4] \ll K_a$. In the higher concentration region, $[HClO_4] \gg K_a$, the reduced form of $APH^+$ may exist predominantly as $APH_2{}^{+\cdot}$, when the $E_{red}$ value is shifted to the positive direction with an increase in the $HClO_4$ concentration and thus, the one-electron reduction of $APH^+$ becomes energetically more favorable. If the activation Gibbs free energy change $\Delta G_{et}{}^\ddagger$ of electron transfer is directly related with the corresponding standard Gibbs free energy change, i.e., $\Delta G_{et}{}^\ddagger = \Delta G^0_{et} = F(E^0_{ox} - E^0_{red})$, from eq 12 is derived the dependence of the rate constant $k_{et}$ of electron transfer on $[HClO_4]$, as shown in eq 13, where C is a constant. Eq 13 agrees well with the experimental results in Fig. 2-5, where the

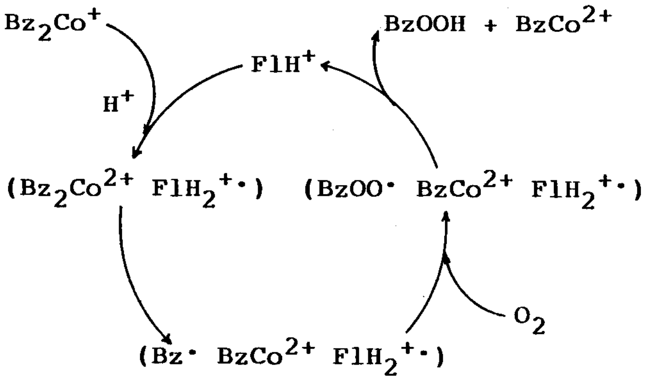
$$\log k_{et} = \log(1 + K_a^{-1}[H^+]) + C \qquad (13)$$

observed rate constant $k_{obs}$, which may be equal to $k_{et}$ of the rate-limiting electron-transfer step in eq 13, is independent of $[HClO_4]$ in the low concentration region ($\log [HClO_4] < 0$) but $k_{obs}$ increases showing the first-order dependence on $[HClO_4]$ in the higher concentration region. Thus, the log $K_a$ value of $APH_2^{+\bullet}$ is obtained as ca. 0 from the dependence of $k_{obs}$ on $[HClO_4]$. In the case of $FlH^+$ and $LH^+$, the log $K_a$ values of $FlH_2^{+\bullet}$ and $LH_2^{+\bullet}$ may be smaller than ca. -3 and -2, respectively. This may be the reason why $FlH_2^{+\bullet}$ and $LH_2^{+\bullet}$ radical cations are observed in electron-transfer reactions from cis-$[Et_2Co(bpy)_2]^+$ to $FlH^+$ and $LH^+$ in the presence of $HClO_4$ ($1.0 \times 10^{-2}$ M) in deaerated MeCN, but $APH_2^{+\bullet}$ radical cation is not observed (vide supra).

**Mechanism of Catalytic Oxygenation of Benzyl Ligand of cis-$[(PhCH_2)_2Co(bpy)_2]^+$.** The product in the coenzyme-catalyzed oxidation of cis-$[R_2Co(bpy)_2]^+$ by dioxygen in the case of R = $PHCH_2$ is drastically changed from R-R in the case of R = Et or Me (Table 2-2) to the oxygenated product PhCHO (Table 2-1). Such a change in the products depending on the alkyl ligands is also observed in the one-electron oxidation of cis-$[R_2Co(bpy)_2]^+$ in the presence of dioxygen as described in Chapter 1.

Based on the above discussion and the discussion in Chapter 1, the catalytic cycle for the coenzyme-catalyzed oxygenation of benzyl ligand of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ ($Bz_2Co^+$) in the case of $FlH^+$ may be shown in Scheme 2-2. At first, an acid-catalyzed

**Scheme 2-2**



electron transfer from $Bz_2Co^+$ to $FlH^+$ occurs to give ($Bz_2Co^{2+}$ $FlH_2^{+\bullet}$). One cobalt-benzyl bond in $Bz_2Co^{2+}$ may be readily cleaved to give benzyl radical ($Bz^\bullet$), followed by the facile trap by dioxygen to produce benzylperoxy radical ($BzOO^\bullet$) which then gives benzyl hydroperoxide (BzOOH) by the abstraction of hydrogen atom from $FlH_2^{+\bullet}$, accompanied by regeneration of $FlH^+$. The benzyl hydroperoxide may decompose to give the final product, benzaldehyde.[30] Essentially the same reaction scheme may be applied for the case of $LH^+$. In the case of $APH^+$, however, the initial electron transfer from $Bz_2Co^+$ to $APH^+$ produces $APH^\bullet$ instead of $APH_2^{+\bullet}$ as indicated by the dependence of log $k_{obs}$ on [$HClO_4$] (Fig. 2-5).

Comparison between Scheme 2-1 and Scheme 2-2 reveals the origin of the difference in the oxygenation and oxidative coupling processes, that is the much less reactivity of benzyl radicals as compared to methyl or ethyl radicals in the coupling reactions, resulting in the trap of benzyl radical by dioxygen to lead to the oxygenated product, benzyl hydroperoxide. As such, *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ is the least reactive in the one-electron oxidation in the absence of dioxygen because of the slow coupling process in Scheme 1-1 (Fig. 1-2), but it becomes the most reactive in the coenzyme catalyzed reaction in the presence of dioxygen in Scheme 2-2 because of the facile trap of benzyl radical by dioxygen (Fig. 2-8).

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# Chapter 3 MECHANISMS OF ELECTROPHILIC CLEAVAGE OF COBALT-CARBON BONDS IN ALKYLCOBALT(III) COMPLEXES WITH IODINE

**Abstract:** Contribution of the electron-transfer processes in the cleavage of cobalt-carbon bonds of alkylcobalt(III) complexes, (cis-$[R_2Co(bpy)_2]^+$; R = Me, Et and $PhCH_2$; bpy = 2,2'-bipyridine, trans-$[Me_2Co(DpnH)]$ (DpnH = 11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1-olate), and $[RCo(DH)_2py]$ (R = Me, Et and $PhCH_2$; $(DH)_2$ = bis-(dimethylglyoximato); py = pyridine) with iodine has been studied by detecting the products that could arise only via electron-transfer processes as well as by the kinetic comparison between the electrophilic reactions of iodine with alkylcobalt(III) complexes and the electron transfer reactions of iodine with ferrocene derivatives in acetonitrile. The coupling products of alkyl groups of dialkylcobalt(III) complexes, derived from the corresponding dialkylcobalt(IV) complexes, are obtained in the cleavage reactions of dialkylcobalt(III) complexes with iodine, besides alkyl iodide being the main products. The observed second-order rate constants for the cleavage reactions of alkylcobalt(III) complexes with iodine in acetonitrile at 298 K are compared with those of electron transfer from ferrocene derivatives to iodine, based on the Marcus theory of electron-transfer.

## 3-1 Introduction

The mechanisms for electrophilic cleavage of cobalt-carbon bonds have been of considerable interest owning to the importance in understanding the enzymatic cleavage of those bonds.[1,2] The cleavage of the cobalt-carbon bond by electrophiles which generally leads to the alkylation of attacking electrophiles, has generally been considered as a direct displacement of the cobalt atom by the attack of electrophiles at the α-carbon.[3-7] Recently some electrophilic cleavage reactions of cobalt-carbon bonds have been reconsidered as proceeding via electron-transfer processes.[8-10] However, it is often difficult to distinguish between these two mechanisms unless attempts are made to identify the products that could arise only via intermediates produced by electron-transfer processes. In this context, Fanchiang[11a] has recently reported the formation of $CH_3Cl$ in the demethylation of methylcobalamin ($CH_3$-$B_{12}$) by iodine performed in the presence of $Cl^-$, suggesting that the $CH_3Co(IV)$ complex, formed by electron transfer from $CH_3$-$B_{12}$ to $I_2$, is quenched by $Cl^-$ to yield $CH_3Cl$ instead of $CH_3I$. More direct evidence for the involvement of alkylcobalt(IV) complexes may be obtained by using <u>cis</u>-dialkylcobalt(III) complexes, <u>cis</u>-$[R_2Co(bpy)_2]^+$ (R = Me, Et; bpy = 2,2'-bipyridine), since the corresponding <u>cis</u>-dialkylcobalt(IV) complexes are known to be subjected to the unique reductive elimination of the alkyl groups to yield the coupling products R-R exclusively as shown in chapter 1 (eq 1).[12] Thus, the alkyl coupling products of <u>cis</u>-dialkylcobalt(III) complexes

$$\text{cis-}[R_2Co(bpy)_2]^+ \xrightarrow{-e^-} R\text{-}R + [Co(bpy)_2]^{2+} \qquad (1)$$

in the electrophilic cleavage of the cobalt-carbon bonds with iodine may be used as a nice probe to investigate the contribution of electron-transfer processes.

In this work,[13] we report evidence for the contribution of electron-transfer processes in the cleavage of cobalt-carbon bonds of dialkylcobalt(III) complexes with iodine by identifying the alkyl coupling products which could arise only <u>via</u> dialkylcobalt(IV) complexes. The degree of the contribution of electron-transfer processes is evaluated by the kinetic comparison between the cleavage reactions of various alkylcobalt(III) complexes with iodine and the electron-transfer reactions of ferrocene derivatives with iodine in acetonitrile (MeCN) using the Marcus theory of electron-transfer.[14]

## 3-2 Experimental

**Materials.** Alkylcobalt(III) complexes; <u>cis</u>-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et and $PhCH_2$),[12,15] <u>trans</u>-$[Me_2Co(DpnH)]$,[16-18] and $[RCo(DH)_2py]$ (R = Me, Et and $PhCH_2$),[19] were prepared as described previously. The purity of the complexes was checked by the elemental analysis. Anal. Calcd for $C_{13}H_{25}N_4O_2Co$ (<u>trans</u>-$[Me_2Co(DpnH)]$): C,47.6; H,7.7; N,17.1. Found: C,47.5; H,7.7; N,17.0. Anal. Calcd for $C_{14}H_{22}N_5O_4Co$ ($[MeCo(DH)_2py]$): C,43.9; H,5.8; N,18.3. Found: C,43.8; H,5.8; N,18.3. Anal. Calcd for $C_{15}H_{24}N_5O_4Co$ ($[EtCo(DH)_2py]$): C,45.4; H,6.1; N,17.6. Found: C,45.2; H,6.0; N,17.8. For <u>cis</u>-dialkylcobalt(III) complexes, see Experimental in Chapter 1. Ferrocene derivatives; ferrocene, butylferrocene, amylferrocene, *tert*-amylferrocene, 1,1'-dimethylferrocene, 1,1'-dibutylferrocene, were obtained commercially and purified by sublimation or recrystallization from ethanol. Iodine was purified by vacuum sublimation three times. Bromine was refluxed and distilled with solid KBr, and dried by shaking with an equal volume of concentrated $H_2SO_4$, then distilled after the separation from $H_2SO_4$.[20] Reagent grade acetonitrile was purified by the standard procedure,[20] followed by redistillation from calcium hydride. Acetonitrile-$\underline{d}_3$ was stirred with freshly activated molecular sieve 4A (Wako Pure Chemicals) and then transferred under vacuum into a dry, glass-stoppered bottle. Other reagents used for the product analyses were obtained commercially.

**Product Analysis.** Typically, iodine ($3.0 \times 10^{-5}$ mol) was added to an NMR tube that contained an acetonitrile-$\underline{d}_3$ (0.5 $cm^3$) solution of alkylcobalt(III) complex ($3.0 \times 10^{-5}$ mol). The cleavage reaction of cobalt-carbon bond of the alkylcobalt(III) complex was monitored by using a Japan Electron Optics JNM-PS-100 $^1H$ NMR spectrometer (100 MHz). After completion of the reaction, the products were analyzed also by GLC using a Unibeads 1-S or a Gaskropak 54 column.

**Stoichiometry** Spectral titrations were carried out by adding known quantities of a stock solution of iodine to a quartz cuvette containing a known aliquot of the alkylcobalt(III) complexes or ferrocene derivatives. After the reaction was complete, the electronic absorption spectrum was measured using a Union SM-401 spectrophotometer. The amount of the triiodide ion ($I_3^-$) determined from the absorption band at $\lambda_{max}$ = 361 nm ($\varepsilon = 2.50 \times 10^4$ $M^{-1}$ $cm^{-1}$),[21] which was much more intense than those of the other absorbing species present in the solution, were plotted against the amount of $I_2$ added.

**Kinetic Measurements.** Kinetic measurements were carried out by using a Union-RA-103 stopped-flow spectrophotometer and a Union SM-401 spectrophotometer for the cleavage reactions of cobalt-carbon bond of alkylcobalt(III) complexes with iodine or the electron-transfer reactions of ferrocene derivatives with iodine under deaerated conditions with half-lives of shorter than 10s and longer than 10s, respectively. The rates in MeCN at 298K were determined by the increase in the absorbances at

$\lambda_{max}$ of the triiodide ion. All the kinetic measurements were carried out under the pseudo-first-order conditions where the concentrations of iodine were maintained at > 10-fold excess of the concentration of alkylcobalt(III) complexes or ferrocene derivatives. Pseudo-first-order plots for the reaction of iodine with alkylcobalt(III) complexes and ferrocene derivatives in MeCN were linear for more than five half-lives and the pseudo-first-order rate constants were determined by the least-squares curve fit, using a Union System 77 or NEC 9801 VM microcomputer.

**Cyclic Voltammetry.** Redox potentials of alkylcobalt(III) complexes and ferrocene derivatives in MeCN were determined by cyclic voltammetry at various sweep rates (20-1000 mV $s^{-1}$). The cyclic voltammograms were recorded on a Hokuto Denko model HA-301 potentiostat/galvanostat at 298 K using a platinum microelectrode and a standard NaCl calomel reference electrode (SCE) under deaerated conditions. The platinum microelectrode was routinely cleaned by soaking it in concentrated nitric acid, followed by repeated rinsing with water and acetone, and dried at 353 K prior to use. The anodic peak potential of alkylcobalt(III) complexes at a constant sweep rate was reproducible within ±20 mV. Little deterioration of the electrode was observed upon repeated scans, indicating that anodic oxidation leads to products without fouling of the electrode surface.

The redox potentials of ferrocene derivatives and [RCo(DH)$_2$py] were determined as the average of anodic and cathodic peak potentials, since their electrochemical oxidation proceeds by reversible one-electron processes.

## 3-3 Results and Discussion

**Electron-Transfer Processes in the Reactions of Alkylcobalt(III) Complexes with Iodine.** All alkylcobalt(III) complexes react readily with iodine in MeCN to yield mainly alkyl iodide, cobalt(III) complexes, and triiodide ion. The stoichiometry of the cleavage reaction of cobalt-carbon bonds of alkylcobalt(III) complexes with iodine (Fig. 3-1) is given by eq 2.

$$RCo^{III} + 2I_2 \longrightarrow RI + Co^{III+} + I_3^- \qquad (2)$$

This 1 : 2 stoichiometry indicates that the cleavage of the cobalt-carbon bond of alkylcobalt(III) complexes by iodine occurs to yield RI and $I^-$ (eq 3), the latter of which

$$RCo^{III} + I_2 \longrightarrow RI + Co^{III+} + I^- \quad (3)$$

reacts further with excess $I_2$ to produce $I_3^-$ (eq 4).[22] In

$$I^- + I_2 \longrightarrow I_3^- \quad (4)$$

the case of cis-[$R_2Co(bpy)_2$]$^+$ (R = Me, Et) and trans-[$Me_2Co$(DpnH)], minor gaseous products are produced in the cleavage of cobalt-carbon bonds with iodine as well as bromine. The yields are listed in Table 3-1, where the main gaseous products from cis-[$R_2Co(bpy)_2$]$^+$ are the coupling products of the alkyl groups, *i.e.*, ethane and butane for R = Me and Et, respectively, while trans-[$Me_2Co$(DpnH)] yields more methane than the coupling product, ethane. In the case of cis-[$(PhCH_2)_2Co(bpy)_2$]$^+$, however, the cleavage of the cobalt-carbon bonds with iodine and bromide yields only $PhCH_2I$ and $PhCH_2Br$, respectively (Table 3-1). No gaseous products have been observed in the case of monoalkylcobalt(III) complexes, [$RCo(DH)_2py$] (R = Me, Et). With increasing mole ratio of iodine to cis-[$R_2Co(bpy)_2$]$^+$ (R = Me, Et), the yields of R-R decrease as shown in Fig. 3-2. Similarly, the yields of methane and ethane decrease with an increase

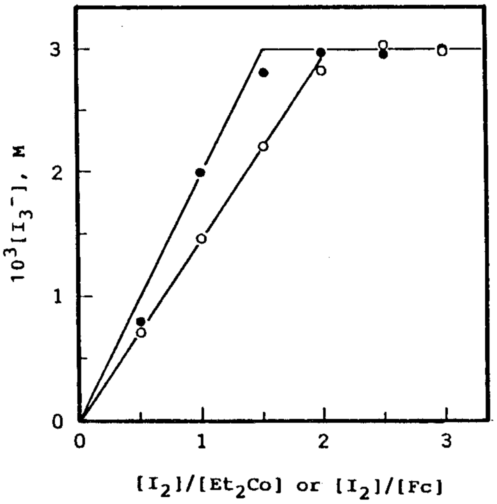


**Fig. 3-1.** Plots of the concentration of tiiodide ion, $[I_3^-]$, formed by the cleavage reaction of cobalt-carbon bond of cis-[$R_2Co(bpy)_2$]$^+$ ($Et_2Co$) with iodine (○), and by the electron-transfer reaction from 1,1'-dimethylferrocene (Fc) to iodine (●) in MeCN *vs.* the ratio of iodine to $Et_2Co$, $[I_2]/[Et_2Co]$, and the ratio of iodine to Fc, $[I_2]/[Fc]$, respectively.

Table 3-1. Product Yields in the Reactions of Alkylcobalt(III) Complexes ($4.0 \times 10^{-2}$ M) with Halogen ($X_2$: $4.0 \times 10^{-2}$ M) in MeCN at 298 K

| alkylcobalt(III) complex | $X_2$ | product yield, %[a] |
|---|---|---|
| cis-[$Me_2Co(bpy)_2$]$^+$ | $I_2$ | $CH_3I$(99) $CH_4$(trace) $C_2H_6$(0.60) |
| cis-[$Me_2Co(bpy)_2$]$^+$ | $Br_2$ | $CH_3Br$(99) $CH_4$(trace) $C_2H_6$(0.24) |
| cis-[$Et_2Co(bpy)_2$]$^+$ | $I_2$ | $C_2H_5I$(97) $C_2H_6$(trace) $C_2H_4$(trace) $C_4H_{10}$(3.2) |
| cis-[$Et_2Co(bpy)_2$]$^+$ | $Br_2$ | $C_2H_5Br$(97) $C_2H_6$(trace) $C_4H_{10}$(3.8) |
| cis-[$(PhCH_2)_2Co(bpy)_2$]$^+$ | $I_2$ | $PhCH_2I$(100) |
| cis-[$(PhCH_2)_2Co(bpy)_2$]$^+$ | $Br_2$ | $PhCH_2Br$(100) |
| trans-[$Me_2Co$(DpnH)] | $I_2$ | $CH_3I$(99) $CH_4$(0.34) $C_2H_6$(0.06) |
| trans-[$Me_2Co$(DpnH)] | $Br_2$ | $CH_3Br$(99) $CH_4$(0.15) $C_2H_6$(trace) |
| [$MeCo(DH)_2py$] | $I_2$ | $CH_3I$ (100) |
| [$EtCo(DH)_2py$] | $I_2$ | $C_2H_5I$ (100) |

[a] Based on the amount of the alkylcobalt(III) complex.

in the mol ratio of $I_2$ to trans-[$Me_2Co(DpnH)$] as shown in Fig. 3-3.

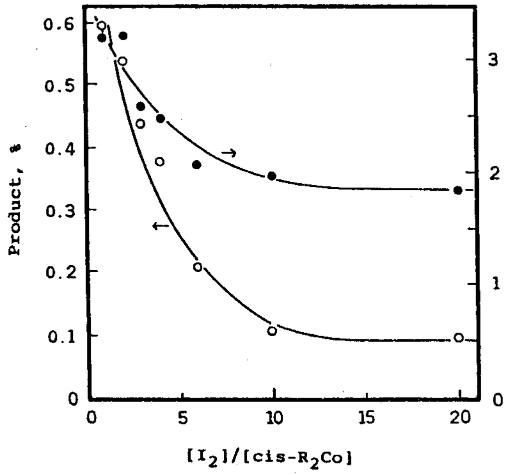


Fig. 3-2. Plots of the gaseous products produced by the reaction of cis-[$R_2Co(bpy)_2$]$^+$ (cis-$R_2Co$) with iodine in MeCN vs. the ratio of iodine to cis-$R_2Co$: R = Me, ethane (○); R = Et, butane (●).

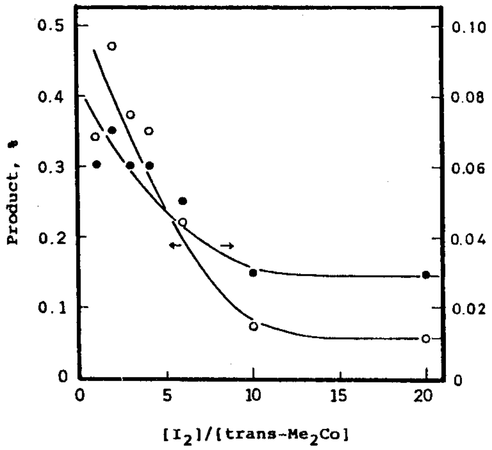
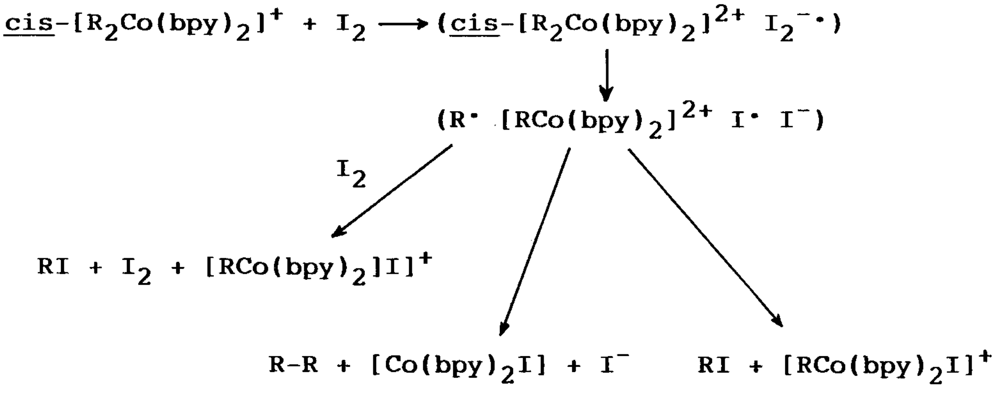


Fig. 3-3. Plots of the gaseous products produced by the reaction of trans-[$Me_2Co(DpnH)$] (trans-$Me_2Co$) with iodine in MeCN vs. the ratio of iodine to trans-$Me_2Co$: methane (○); ethane (●).

The formation of the coupling products of alkyl groups of cis-[$R_2Co(bpy)_2$]$^+$ demonstrates clearly the involvement of an electron-transfer process in the cleavage of the cobalt-carbon bonds with iodine and bromine. Although the apparent quantities of the coupling products are small (Table 3-1), the product distribution depending on the alkyl group as well as the dependence on the excess $I_2$ concentration (Fig. 3-2, 3-3) suggests that the electron-transfer process is the main pathway for the cleavage of the cobalt-carbon bond as discussed below. As shown in Scheme 3-1, electron transfer from cis-[$R_2Co(bpy)_2$]$^+$ to $I_2$

**Scheme 3-1**



occurs to give the radical ion pair, in which one cobalt-carbon bond of cis-[$R_2Co(bpy)_2]^{2+}$ as well as I-I bond of $I_2^{-\cdot}$ is cleaved readily to produce the radical pair ($R^\cdot$ $[RCo(bpy)_2]^{2+}$ $I^\cdot$ $I^-$). In the case of R = Me and Et, the facile reaction of $R^\cdot$ with $[RCo(bpy)_2]^{2+}$ may give the coupling product R-R in competition with the radical coupling between $R^\cdot$ and $I^\cdot$ in the cage to yield RI (Scheme 3-1). In the presence of excess $I_2$, the formation of the coupling product may be suppressed by the radical trap by $I_2$ to yield RI and $I^\cdot$,[23] the latter of which combines with $I^\cdot$ to regenerate $I_2$. In the case of R = $PhCH_2$, the reaction of $PhCH_2^\cdot$ with $[PhCH_2Co(bpy)_2]^{2+}$ to yield $PhC_2H_4Ph$ may be too slow to compete with the radical coupling reaction between $PhCH_2^\cdot$ and $I^\cdot$, when benzyl iodide becomes the sole product, since the reaction of $PhCH_2^\cdot$ with $[PhCH_2Co(bpy)_2]^{2+}$ may be much slower than the corresponding reactions for R = Me and Et, judging from the effect of oxygen on the one-electron oxidation of cis-$[R_2Co(bpy)_2]^+$ (Scheme 1-1).[24]

In the case of trans-[$Me_2Co(DpnH)$], the reaction of $Me^\cdot$ with $[MeCo(DpnH)]^+$ in the cage may be disfavored geometrically, compared with the case of cis-$[R_2Co(bpy)_2]^+$, and thereby a free radical ($Me^\cdot$) is escaped from the cage to yield methane and ethane (Scheme 1-2) in competition with the radical coupling between $Me^\cdot$ and $I^\cdot$ in the cage to yield MeI. The escaped $Me^\cdot$ radical may be trapped by $I_2$ as shown in Scheme 3-1 for the case of cis-$[R_2Co(bpy)_2]^+$, and thus the yields of methane and ethane decrease with an increase in the mol ratio of $I_2$ to trans-[$Me_2Co(DpnH)$] as observed in Fig. 3-3.

At this stage, however, a possibility of the competition between the one-electron-transfer process (Scheme 3-1) and the direct displacement of the cobalt atom by the attack of iodine at the α-carbon cannot be ruled out. Thus, in order to evaluate the degree of contribution of the electron-transfer processes (Scheme 3-1) quantitatively, we have performed the kinetic comparison between the cleavage reactions of alkylcobalt(III) complexes with iodine and the electron-transfer reactions of ferrocene derivatives with iodine in MeCN at 298 K with the aid of the Marcus theory of electron transfer.

**Kinetic Comparison between Cleavage Reactions of Cobalt-Carbon Bonds with Iodine and Electron-Transfer Reactions from Ferrocene Derivatives to Iodine.** The rates of the cleavage reactions of alkylcobalt(III) complexes with iodine in MeCN at 298 K were monitored by the increase in the absorbance at $\lambda_{max}$ (= 361 nm) of the triiodide ion. The rate of formation of $I_3^-$ obeyed the pseudo-first-order kinetics in the presence of large excess $I_2$, and the pseudo-first-order rate constant is proportional to the $I_2$ concentration as shown in Fig. 3-4. Thus, the rate can be expressed in terms of the clean second-order kinetics, showing a first-order dependence on the concentration of each reactant (eq 5), although the rates of reactions of halogen often include a second-order term in the halogen concentration.[25] The observed second-order rate constants $k_{obs}$ were determined from 4 to 20 rate measurements to give average deviations from the mean values within ±5%, and the $k_{obs}$ values are listed in Table 3-2, together with the redox potentials of the alkylcobalt(III) complexes (see Experimental).[12]

$$d[I_3^-]/dt = k_{obs}[RCo^{III}][I_2] \quad (5)$$

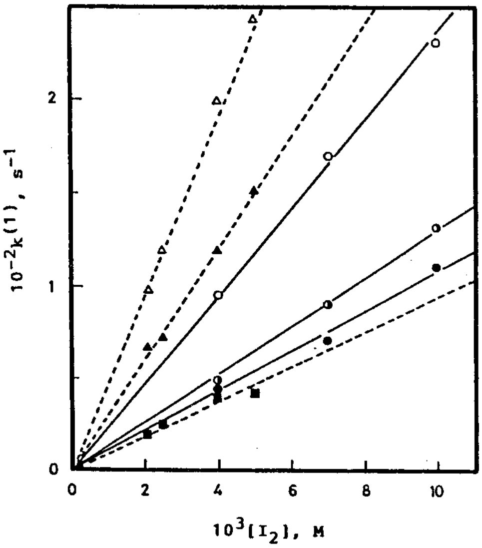


**Fig. 3-4. Plots of the observed first-order rate constants, $k^{(1)}$ for the cleavage reactions of alkylcobalt(III) complexes with iodine (——) and electron-transfer reactions from ferrocene derivatives to iodine (----) in MeCN at 298 K _vs._ the concentration of iodine: _cis_-$[Me_2Co(bpy)_2]^+$ (○); _cis_-$[Et_2Co(bpy)_2]^+$ (○); _cis_-$[(PhCH_2)_2Co(bpy)_2]^+$ (◑); buthylferrocene (△); _tert_-amylferrocene (▲); ferrocene (■).**

Ferrocene and its derivatives (Fc) are also oxidized readily to the corresponding ferrocenium ions ($Fc^+$), and the stoichiometry of the electron-transfer reaction (eq 6) has been determined from the spectroscopic measurements

Table 3-2. Observed Second-Order Rate constants ($k_{obs}$) for Cleavage Reactions of Alkylcobalt(III) Complexes with Iodide in MeCN at 298 K and the One-Electron Oxidation Potentials ($E^0_{ox}$ _vs._ SCE) of Alkylcobalt(III) Complexes, and the Calculated Rate Constants ($k_{calc}$) for the Corresponding Electron-Transfer Reactions Based on the Marcus Theory

| alkylcobalt(III) complex | $E^0_{ox}$ V | $k_{obs}$ $M^{-1}$ $s^{-1}$ | $k_{calc}$[a] $M^{-1}$ $s^{-1}$ |
|---|---|---|---|
| _cis_-$[Me_2Co(bpy)_2]^+$ | 0.63 | $2.4 \times 10^4$ | $8.8 \times 10^2$ |
| _cis_-$[Et_2Co(bpy)_2]^+$ | 0.57 | $1.2 \times 10^4$ | $5.0 \times 10^3$ |
| _cis_-$[(PhCH_2)_2Co(bpy)_2]^+$ | 0.60 | $1.2 \times 10^4$ | $2.1 \times 10^3$ |
| _trans_-$[Me_2Co(DpnH)]$ | 0.53 | $2.5 \times 10^6$ | $4.1 \times 10^2$ |
| $[MeCo(DH)_2py]$ | 0.88 | $3.1 \times 10^{-2}$ | $2.2 \times 10^{-2}$ |
| $[EtCo(DH)_2py]$ | 0.82 | $2.7 \times 10^{-1}$ | $1.3 \times 10^{-1}$ |

[a] Calculated based on the Marcus theory.

$$2Fc + 3I_2 \longrightarrow 2Fc^+ + 2I_3^- \qquad (6)$$

of the concentration of ferrocenium ion produced with changing the mole ratio of Fc to $I_2$ as shown in Fig. 3-1. Such a stoichiometry indicates that the electron-transfer from Fc to $I_2$ occurs to give $Fc^+$ (eq 7) and $I_2^{-\bullet}$, the latter of which is known to dissociate to produce $I^\bullet$ and $I^-$ (eq 8),[26,27] followed by the facile second electron-transfer reaction from Fc to $I^\bullet$ (eq 9).[28] The iodide ion reacts with excess $I_2$ to yield $I_3^-$ (eq 4).

$$Fc + I_2 \xrightarrow{k_{obs}} Fc^+ + I_2^{-\bullet} \qquad (7)$$

$$I_2^{-\bullet} \longrightarrow I^\bullet + I^- \qquad (8)$$

$$Fc + I^\bullet \longrightarrow Fc^+ + I^- \qquad (9)$$

The rate of formation of $I_3^-$ can also be expressed in terms of the second-order kinetics, showing a first-order dependence on the concentration of each reactant (eq 10) as shown in Fig.

$$d[I_3^-]/dt = k_{obs}[Fc][I_2] \qquad (10)$$

3-4. The observed second-order constants $k_{obs}$ were determined from 10 to 20 rate measurements to give average deviations from the mean values within ±5%, and the $k_{obs}$ values are listed in Table 3-3, together with the one-electron oxidation potentials of the ferrocene derivatives.

Table 3-3. Observed Second-Order Rate Constants ($k_{obs}$) for Electron-Transfer Reactions from Ferrocene Derivatives to Iodine in MeCN at 298 K and the One-Electron Oxidation Potentials of Ferrocene Derivatives ($E^0_{ox}$ *vs.* SCE), and the Corresponding Calculated Rate Constants ($k_{calc}$) Based on the Marcus Theory

| ferrocene derivative | $E^0_{ox}$ V | $k_{obs}$ $M^{-1}$ $s^{-1}$ | $k_{calc}$[a] $M^{-1}$ $s^{-1}$ |
|---|---|---|---|
| 1,1'-dibutylferrocene | 0.25 | $1.7 \times 10^5$ | $3.0 \times 10^5$ |
| 1,1'-dimethylferrocene | 0.26 | $1.5 \times 10^5$ | $2.5 \times 10^5$ |
| buthylferrocene | 0.31 | $4.6 \times 10^4$ | $8.9 \times 10^4$ |
| amylferrocene | 0.32 | $3.2 \times 10^4$ | $7.2 \times 10^4$ |
| *tert*-amylferrocene | 0.33 | $3.1 \times 10^4$ | $5.8 \times 10^4$ |
| ferrocene | 0.37 | $9.4 \times 10^3$ | $2.4 \times 10^4$ |

[a] Calculated based on the Marcus theory.

A quantitative comparison between the cleavage of the cobalt-carbon bonds with $I_2$ and the electron-transfer reactions from Fc to $I_2$ can be achieved by comparing the $k_{obs}$ values with those predicted by the Marcus theory for the rates of outer-sphere electron-transfer reactions.[14] The Marcus relation for the rate constant of electron transfer from a reductant (1) to an oxidant (2), $k_{12}$, is given by eq 11,[14] where $k_{11}$ and $k_{22}$

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{11}$$

are the rate constants for the corresponding self-exchanges of (1) and (2), and $K_{12}$ is the equilibrium constant for the electron-transfer reaction. The $K_{12}$ value is obtained from the one-electron oxidation potential of the reductant (1), $E^0_{ox}$, and the one-electron reduction potential of the oxidant (2), $E^0_{red}$, by using eq 12, where $w_p$ is the work term required to bring the

$$\log K_{12} = [F/(-2.3RT)](E^0_{ox} - E^0_{red} + w_p) \tag{12}$$

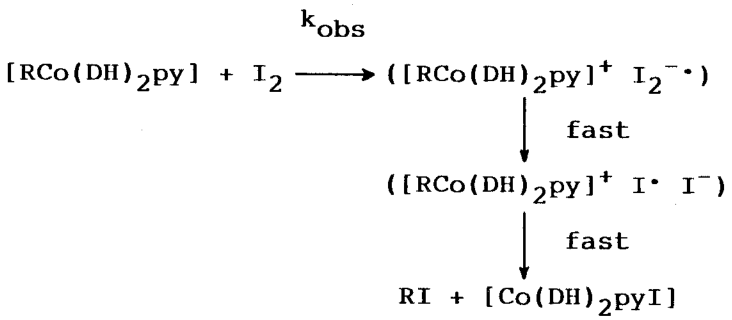
products together to the mean separation in the activation complex.[29-31] The parameter f in eq 11 is given by eq 13, in

$$\log f = (\log K_{12})^2/[4\log(k_{11}k_{22}/Z^2)] \tag{13}$$

which Z, the frequency factor, is taken as $10^{11}$ $M^{-1}$ $s^{-1}$.[14] The reported values of self-exchange rate constants for $Fc/Fc^+$ ($k_{11} = 5.3 \times 10^6$ $M^{-1}$ $s^{-1}$)[32] and $I_2/I_2^{-\cdot}$ ($k_{22} = 8.5 \times 10^4$ $M^{-1}$ $s^{-1}$)[33] together with the equilibrium constant $K_{12}$, obtained from the one-electron oxidation potentials of Fc (Table 3-3), and the one-electron reduction potential of $I_2$ ($E^0_{red}$ = 0.19 V vs. SCE)[33] constitute a satisfactory basis for accounting for the $k_{obs}$ values in light of the Marcus relation, eqs 11-13. The calculated electron-transfer rate constants ($k_{calc} = k_{12}$ in eq 11) are also listed in Table 3-3, where $k_{obs}$ values agree well with the $k_{calc}$ values. Such agreement indicates that the electron transfer from Fc to $I_2$ proceeds by an outer-sphere mechanism.

Similarly, the rate constants of electron transfer from alkylcobalt(III) complexes to $I_2$ can be calculated from the reported $k_{11}$ values of alkylcobalt(III) complexes[12,34] and the one-electron-oxidation potentials in Table 3-2 by using eqs 11-13. The calculated values ($k_{calc}$) are also listed in Table 3-2, where the $k_{obs}$ values of $[RCo(DH)_2py]$ (R = Me, Et) agree well with the corresponding $k_{calc}$ values. Such agreement indicates that the rate-determining step for the cleavage of the cobalt-carbon bonds with $I_2$ is the electron transfer from $[RCo(DH)_2py]$ to $I_2$ as shown in Scheme 3-2. In contrast with the case of dialkylcobalt(IV) complexes, the $[RCo^{IV}(DH)_2py]^+$ complex is known to be rather stable,[35] and thus the cleavage of the

Scheme 3-2



cobalt-carbon bond may occur by the reaction with $I^\cdot$ in the cage to yield RI (Scheme 3-2).[36-38] In the case of dialkylcobalt(III) complexes, the $k_{obs}$ values agree reasonably well with the corresponding $k_{calc}$ value (Table 3-2),[39] indicating that the electron-transfer process in Scheme 3-1 is the main pathway for the cleavage of the cobalt-carbon bonds with $I_2$, despite the small quantity of the coupling product of the alkyl group, derived from cis-$[R_2Co^{IV}(bpy)_2]^{2+}$. In the case of trans-$[Me_2Co(DpnH)]$, however, the $k_{obs}$ value is significantly larger than the corresponding $k_{calc}$ value (Table 3-2).[40,41] Such a discrepancy between the observed and calculated values may indicate the contribution of an inner-sphere pathway for the electron-transfer process. At present, however, the contribution of the direct displacement of the cobalt atom by the attack of $I_2$ at the $\alpha$-carbon[42] cannot be ruled out in such a case.

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(29) The work term for the reactants may be neglected since the reactants in the present case include neutral species. The importance of the work term for the charged species has been well documented.[34] In the present case, $w_p$ is taken as -0.05 eV.[30,31]

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(40) When the reported lowest limit of the $k_{11}$ value of trans-$[Me_2Co(DpnH)]$ (the corresponding activation free energy is 2.1 kcal $mol^{-1}$)[41] is used, the $k_{calc}$ vlaue is obtained as $1.0 \times 10^4$ $M^{-1}$ $s^{-1}$ which is still $2.4 \times 10^2$ times smaller than the $k_{obs}$ value.

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(42) In this case, electron transfer may be viewed as occurring in concert with bond formation.

# Chapter 4 PHOTOCHEMICAL REACTIONS OF ALKYLCOBALT(III) COMPLEXES WITH IODINE

**Abstract:** Cobalt-carbon bonds of various alkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et, $PhCH_2$; bpy = 2,2'-bipyridine), trans-$[Me_2Co(DpnH)]$ (DpnH = 11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1-olate) and $[RCo(DH)_2py]$ (R = Me, Et, $PhCH_2$; $(DH)_2$ = bis(dimethylglyoximato); py = pyridine), are readily cleaved by iodine in carbon tetrachloride to yield alkyl iodides via photoinduced radical chain reactions with the large quantum yields (e.g., $\Phi = 7.0 \times 10^3$) under low energy irradiation ($\lambda$ 517 nm). The rate-determining step in the radical chain reactions is suggested to be electron transfer from alkylcobalt(III) complexes to iodine atom ($I^\bullet$) which is produced by the photo-dissociation of $I_2$, based on the formation of by-products that could arise only via electron-transfer processes as well as the kinetic comparison between alkylcobalt(III) complexes and tetraalkyltin compounds for the reactions with iodine atom.

## 4-1 Introduction

The mechanisms for electrophilic cleavage of cobalt-carbon bonds have been extensively studied in relation with enzymatic cleavage of the cobalt-carbon bonds.[1-7] In this context, direct photo-cleavage of cobalt-carbon bonds of alkylcobalt(III) complexes, used as coenzyme $B_{12}$ models, has also been subjected to detailed scrutiny.[8-11] However, very little is known of the mechanisms of the photochemical cleavage of cobalt-carbon bonds by electrophiles. On the other hand, it has been well established that the photochemical cleavage of tetraalkyltin compounds ($R_4Sn$) by iodine proceeds via photoinduced radical chain reactions,[12] in which the Sn-C bonds are cleaved by electron transfer from $R_4Sn$ to iodine atom produced by the photo-dissociation of $I_2$.[13]

In this study,[14] we report that the photoinduced cleavage of the Co-C bonds of various alkylcobalt(III) complexes by iodine also proceeds via photoinduced electron-transfer radical chain reactions with large quantum yields (e.g., $\Phi$ $7.0 \times 10^3$) under the conditions that thermal cleavage of the Co-C bonds by iodine can be neglected. This study provides a unique opportunity to compare directly the reactivities of alkylcobalt(III) complexes towards iodine atom with those of tetraalkyltin compounds.

## 4-2 Experimental

**Materials.** Alkylcobalt(III) complexes, cis-[$R_2$Co(bpy)$_2$]-$ClO_4$ (R = Me, Et and $PhCH_2$), trans-[$Me_2$Co(DpnH)] and [RCo(DH)$_2$-py] (R = Me and Et) were prepared as described previously (see Chapters 1 and 3).[11,15] Potassium ferrioxalate used as an actinometer was prepared according to the literature[16] and purified by recrystallization from hot water. Reagent grade $CCl_4$ was shaken vigorously with solid KOH, washed with water. Then $CCl_4$ is shaken with concentrated $H_2SO_4$ until there is no further coloration, and washed with water, dried with $CaCl_2$, and distilled.[17] Other reagents used for the product analyses were obtained commercially.

**Product Analysis.** Typically, a $CCl_4$ solution (0.30 $cm^3$) of iodine (3.0 x $10^{-5}$ mol) was added to an NMR tube containing a $CCl_4$ solution (0.30 $cm^3$) of a monoalkylcobalt(III) complex (3.0 x $10^{-5}$ mol). After the reactant solution in the NMR tube was mixed and deaerated with a stream of argon, the sample was irradiated with visible light from a Ushio Model U1-501 Xenon lamp through a Toshiba glass filter cutting off the light below 460 nm. After the completion of the reaction, the products were analyzed by using a Japan Electron Optics JNM-PS-100 $^1H$ NMR spectrometer (100 MHz) as well as by using a Shimadzu GC-7A GLC equipped with a Gaskropak 54 column. In the case of dialkylcobalt(III) complexes, the thermal reactions with iodine occurred slowly in $CCl_4$.[7] In addition, the solubilities of cis-[$R_2$Co(bpy)$_2$]$ClO_4$ in $CCl_4$ were much poorer than those of monoalkylcobalt(III) complexes. Thus, as soon as an MeCN solution (5.0 x $10^{-2}$ $cm^3$) of a dialkylcobalt(III) complex (2.0 x $10^{-6}$ mol) was added to a Pyrex tube containing a $CCl_4$ solution (0.45 $cm^3$) of $I_2$ (2.0 x $10^{-6}$ mol), the sample was irradiated with the visible light. The reaction was completed in a few seconds. In such a short period, the contribution from the thermal reactions can be neglected. The gaseous products were analyzed by GLC using a Unibeads 1-S column.

Spectral titrations were carried out by adding known quantities of a stock solution of iodine to a quartz cuvette containing a known aliquot of the alkylcobalt(III) complexes in $CCl_4$, followed by irradiation of visible light ($\lambda$ > 460 nm). After the reaction was complete, the absorption spectrum was measured using a Union SM-401 spectrophotometer. The amounts of cobalt(III) complex $[Co(DH)_2py]I$ were determined from the absorption band at $\lambda_{max}$ 450 nm ($\varepsilon$ 1.35 x $10^3$ $M^{-1}$ $cm^{-1}$)[7].

**Quantum Yield Determinations.** The rates of photochemical reactions of monoalkylcobalt(III) complexes with iodine were determined from the disappearance of the absorption band due to iodine in $CCl_4$ ($\lambda_{max}$ = 517 nm, $\varepsilon$ = 9.03 x $10^2$ $M^{-1}$ $cm^{-1}$)[13] under irradiation of a monochromatized light ($\lambda$ = 517 nm) from a Xenon lamp through a Nikon Model G250 monochrometor. The light intensity of a monochromatized light ($\lambda$ = 350 nm) was determined by using a a standard actinometer (potassium ferrioxalate) under the conditions that the actinometer absorbed essentially all the incident light,[16] Then, the light intensity at 517 nm was obtained from the known ratios of the light intensities of the Xenon lamp between 350 and 517 nm. The light intensity was varied by changing the slit width of the monochrometor.

In the case of dialkylcobalt(III) complexes, the much higher light intensity was required to avoid the contribution from the thermal electrophilic cleavage of the cobalt-carbon bonds by iodine even in a non-polar solvent.[7] Thus, the quantum yields of dialkylcobalt(III) complexes were determined by a competition method as follows. A monoalkylcobalt(III) complex [RCo] which has different alkyl groups with a dialkylcobalt(III) complex $[R'_2Co]$ was employed as a standard. Typically, a deaerated $CCl_4$ solution (1.0 $cm^3$) containing iodine (5.0 x $10^{-7}$ mol) and large excess $[EtCo(DH)_2py]$ (2.0 x $10^{-5}$ mol) was placed in a Pyrex tube after the tube was flushed with a stream of argon. As soon as a deaerated MeCN solution (5.0 x $10^{-2}$ $cm^3$) of cis-$[Me_2Co(bpy)_2]ClO_4$ (2.0 x $10^{-6}$ mol) was added to the reaction tube, the sample was photolyzed with a Xenon lamp through a filter cutting off below 460 nm. The reaction was completed in a few seconds, judging by the decoloration of iodine. Under such conditions, the contribution from the thermal reactions between dialkylcobalt(III) complexes with iodine can be neglected. The ratio of the quantum yield of cis-$[Me_2Co(bpy)_2]ClO_4$ to $[EtCo(DH)_2py]$ at the same concentration was determined from the ratio of the products, i.e., EtI to MeI by taking account for the dependence of the quantum yield on the concentration of alkylcobalt(III) complexes. It was confirmed that essentially the same ratio of the quantum yields at the same concentration of alkylcobalt(III) complexes was obtained when the initial ratios of monoalkylcobalt(III) complexes to dialkylcobalt(III) complexes were varied.

## 4-3 Results

**Photochemical Reactions of Alkylcobalt(III) Complexes with Iodine.** Irradiation of the absorption band of iodine ($\lambda_{max}$ = 517 nm) in $CCl_4$ solution containing a monoalkylcobalt(III) complex [RCo(DH)$_2$py] at 298 K results in the decrease in the absorption band due to $I_2$, accompanied by the increase in the absorption band due to [Co(DH)$_2$py]I ($\lambda_{max}$ 450 nm)[7] with an isosbestic point at 498 nm (Fig. 4-1). The alkyl iodide formed in the reaction was identified by $^1$H NMR and GLC (see Experimental). A typical example of the spectral titration is shown in Fig. 4-2, where the concentrations of [Co(DH)$_2$py]I formed in the photochemical reaction are plotted against the mol ratios of iodine to the alkylcobalt(III) complex, revealing the stoichiometry given by eq 1. Any competition from the

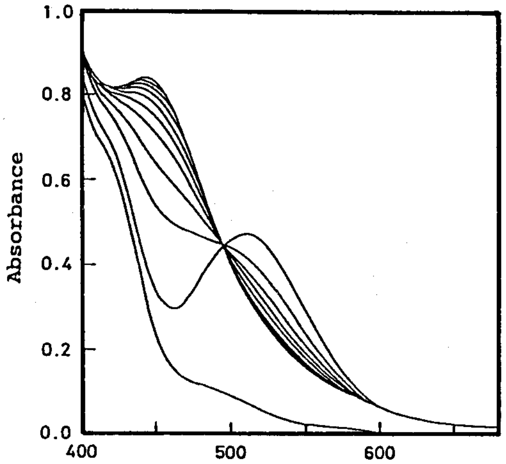


Fig. 4-1. Electronic spectra observed in the photochemical reaction of [MeCo(DH)$_2$py] (8.0 x $10^{-4}$ M) with iodine (8.0 x $10^{-4}$ M) in carbon tetrachloride at 298 K under irradiation of a monochromatized light λ 517 nm. The lowest spectrum corresponds to that of [MeCo(DH)$_2$py] in the absence of iodine.

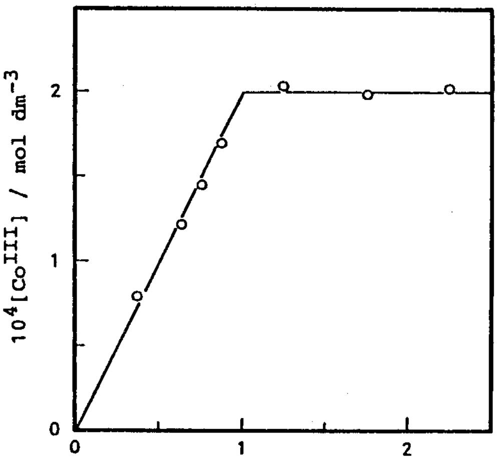


Fig. 4-2. Plot of the concentration of [Co(DH)$_2$py]I formed in the photochemical reaction of [MeCo(DH)$_2$py] with iodine vs. the mol ratio of iodine to [MeCo(DH)$_2$py] (2.0 x $10^{-4}$ M) in carbon tetrachloride at 298 K.

$$[\mathrm{RCo(DH)_2py}] + \mathrm{I_2} \xrightarrow[\mathrm{CCl_4}]{h\nu} [\mathrm{Co(DH)_2py}]\mathrm{I} + \mathrm{RI} \qquad (1)$$

electrophilic cleavage of the monoalkylcobalt(III) complex by $I_2$ (eq 2)[7] is too slow to be a significant complication in a nonpolar solvent such as $CCl_4$ at this temperature. In addition,

$$[\mathrm{RCo(DH)_2py}] + \mathrm{I_2} \xrightarrow[\mathrm{CCl_4}]{\Delta} [\mathrm{Co(DH)_2py}]\mathrm{I} + \mathrm{RI} \qquad (2)$$

irradiation of monochromatized light ($\lambda$ 517 nm) results in mainly the activation of molecular iodine, since the absorbance due to monoalkylcobalt(III) complexes in $CCl_4$ at this wavelength is much smaller than that due to the same concentration of iodine (Fig. 4-1), and the quantum yield for the photodissociation of iodine ($\Phi$ = 0.14)[18] is known to be much larger than those for the photo-dissociation of cobalt-carbon bonds of $[RCo(DH)_2py]$ ($\Phi$ = 0.0054 and 0.0101 for R = Me and Et, respectively).[19]

In the case of dialkylcobalt(III) complexes as well, the quantum yields for the photo-dissociation of cobalt-carbon bonds (*e.g.*, $\Phi$ = 0.012 for *cis*-$[Me_2Co(bpy)_2]^+$)[11] are known to be smaller than that for the photo-dissociation of iodine. In the photochemical reactions of dialkylcobalt(III) complexes, *cis*-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et) and *trans*-$[Me_2Co(DpnH)]$, with iodine, the minor gaseous products were produced beside the alkyl iodides being the main products. The yields are listed in Table 4-1, where the minor gaseous products from *cis*-$[R_2Co(bpy)_2]ClO_4$ are the coupling products of the alkyl groups, *i.e.*, ethane and butane for R = Me and Et, respectively (Table 4-1). In the case of R = $PhCH_2$, however, the photochemical reaction with iodine yields only $PhCH_2I$ with no coupling product, $PhC_2H_4Ph$ (Table 4-1). On the other hand, *trans*-$[Me_2Co(DpnH)]$ yields

Table 4-1. Product Distributions of the Photochemical Reactions of Alkylcobalt(III) Complexes ($2.0 \times 10^{-6}$ mol) with $I_2$ ($2.0 \times 10^{-6}$ mol) in $CCl_4$ at 298 K

| alkylcobalt(III) complex | yield(%)[a] |
|---|---|
| $[MeCo(DH)_2py]$ | $CH_3I$ (100) |
| $[EtCo(DH)_2py]$ | $C_2H_5I$ (100) |
| *cis*-$[Me_2Co(bpy)_2]^+$ | $CH_3I$ (99) $C_2H_6$ (0.9) $CH_4$ (trace) |
| *cis*-$[Et_2Co(bpy)_2]^+$ | $C_2H_5I$ (90) $C_4H_{10}$ (10) $C_2H_6$ (trace) |
| *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ | $PhCH_2I$ (100) $PhC_2H_4Ph$ (0) |
| *trans*-$[Me_2Co(DpnH)]$ | $CH_3I$ (100) $CH_4$ (0.02) $C_2H_6$ (trace) |

[a] Determined by GLC.

a small quantity of methane (0.02%) with a trace amount of the coupling product, ethane (Table 4-1).

**Quantum Yields for the Photochemical Reactions of Alkylcobalt(III) Complexes with Iodine.** Quantum yields $\Phi$ for the photochemical reactions of monoalkylcobalt(III) complexes with iodine were determined from the decay of the absorption band due to iodine ($\lambda_{max}$ = 517 nm) or the increase in the absorption band due to $[Co(DH)_2py]I$ ($\lambda_{max}$ = 450 nm)[7]. In the presence of large excess iodine, the quantum yield increased linearly with an increase in the concentration of alkylcobalt(III) complexes [RCo], eq 3. Thus, the time dependence of the quantum yields is given by eq 4, where the subscript 0 denotes the initial value.

$$\Phi \propto [\mathrm{RCo}] \qquad (3)$$

$$\ln[\mathrm{RCo}]/[\mathrm{RCo}]_0 = \ln(\Phi/\Phi_0) = -k_{obs}t \qquad (4)$$

Typical linear plots according to eq 4 are shown in Fig. 4-3. On the other hand, the quantum yield varied depending on the light intensity (In) absorbed by $I_2$, and the $\Phi$ value was proportional to $In^{-1/2}$, eq 5, as reported for the photochemical reactions of tetraalkyltin compounds with iodine.[13] The $\Phi$ values of

$$\Phi \propto In^{-1/2} \qquad (5)$$

$[RCo(DH)_2py]$ (R = Me, Et) at $[RCo(DH)_2py] = [I_2] = 5.0 \times 10^{-4}$ M with In = $1.29 \times 10^{-8}$ einstein $dm^{-3}$ $s^{-1}$ are listed in Table 4-2.

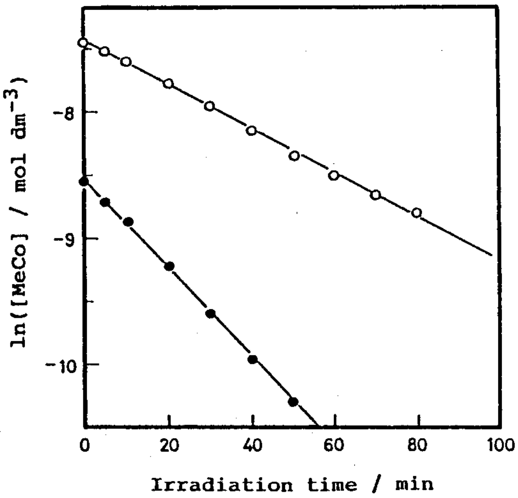


Fig. 4-3. Pseudo-first-order plots for the photochemical reaction of $[MeCo(DH)_2py]$ with iodine in $CCl_4$ at 298 K: $[MeCo(DH)_2py]$ 5.7 x $10^{-4}$ M, $[I_2]$ 3.8 x $10^{-3}$ M (○); $[MeCo(DH)_2py]$ 2.0 x $10^{-4}$ M, $[I_2]$ 2.0 x $10^{-3}$ M (●).

In the case of photochemical reactions of dialkylcobalt(III) complexes with iodine, much higher light intensity than monochromatized light was required in order to avoid the contribution of thermal electrophilic cleavage of the cobalt-carbon bonds of dialkylcobalt(III) complexes.[7] Thus, the quantum yields were determined by the competition method (see

Table 4-2. Quantum Yields of the Photochemical Reactions of Alkylcobalt(III) Complexes ($5.0 \times 10^{-4}$ M) with Iodine ($5.0 \times 10^{-4}$ M) in Carbon Tetrachoride at 298 K

| alkylcobalt(III) complex | quantum yield[a] |
|---|---|
| [MeCo(DH)$_2$py] | $2.3 \times 10^2$ |
| [EtCo(DH)$_2$py] | $3.0 \times 10^2$ |
| cis-[Me$_2$Co(bpy)$_2$]$^+$ | $4.4 \times 10^3$ |
| cis-[(PhCH$_2$)$_2$Co(bpy)$_2$]$^+$ | $1.6 \times 10^3$ |
| trans-[Me$_2$Co(DpnH)] | $7.0 \times 10^3$ |

[a] Detemined by a ferrioxalate actinometry for [RCo(DH)$_2$py] under irradiation of a monochromatized light (λ 517 nm) with the light intensity of $1.29 \times 10^{-8}$ einstein dm$^{-3}$ s$^{-1}$ (the experimental errors are within ±5%). The quantum yields of dialkylcobalt(III) complexes relative to [RCo(DH)$_2$py] were determined by the competition between dialkylcobalt(III) complexes and [RCo(DH)$_2$py] in the photochemical reactions with iodine under irradiation of light of λ > 460 nm (the experimental errors are within ±10%).

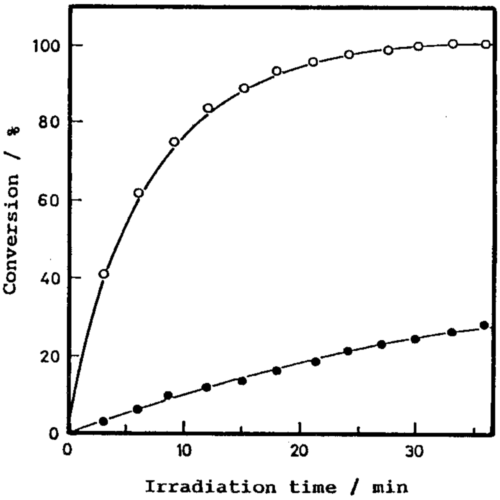
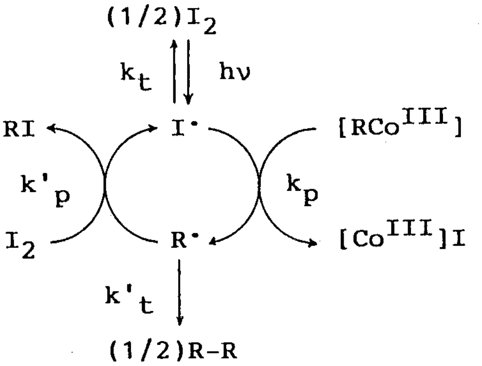


Fig. 4-4. Effect of a radical scavenger isoamyl nitrite on the the photochemical reaction of [MeCo(DH)$_2$py] ($5.1 \times 10^{-4}$ M) with iodine ($6.2 \times 10^{-4}$ M) in carbon tetrachloride at 298 K under irradiation of a monochromatized light λ 517 nm; no isoamyl nitrite (○), $7.4 \times 10^{-3}$ M isoamyl nitrite (●).

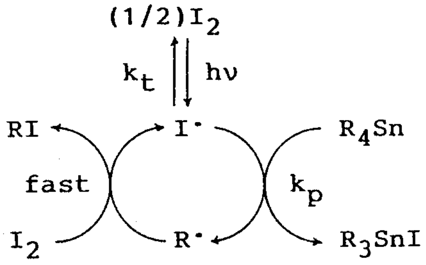
Experimental). The quantum yields thus determined are also listed in Table 4-2, where all the Φ values are much larger than unity. The largest quantum yield is obtained as $7.0 \times 10^3$ for trans-[Me$_2$Co(DpnH)] (Table 4-2). Such large quantum yields indicate the photochemical cleavage of the cobalt-carbon bonds to be a chain process. In fact, the radical chain character is demonstrated by the effect of radical inhibitor. As shown in Fig. 4-4, the addition of isoamyl nitrite, which is known as an efficient radical scavenger of iodine atom,[13,20] results in a significant decrease in the rate of the photochemical reaction of [MeCo(DH)$_2$py] ($5.1 \times 10^{-4}$ M) with iodine ($6.2 \times 10^{-4}$ M).

**Photoinduced Radical Chain Reactions.** The high quantum yields exceeding unity (Table 4-2) together with the inhibition of the photochemical reactions by isoamyl nitrite, which is known as a radical scavenger of iodine atom,[13,20] (Fig. 4-4) clearly indicate a radical chain mechanism for the photoinduced cleavage of the Co-C bonds by iodine. We have previously reported that the photoinduced cleavage of the Sn-C bonds of tetraalkyltin compounds (R$_4$Sn) by iodine proceeds via the radical chain reactions as shown in Scheme 4-1.[13] As applied to the photochemical reactions of alkylcobalt(III) complexes [RCo], the chain mechanism may be given as shown in Scheme 4-2. Since

Scheme 4-1



Schme 4-2



the reaction of of R· with $I_2$ is known to be diffusion-limited,[21] the reaction of $[RCo^{III}]$ with I· may be the rate-determining step in the chain propagation. In such a case, by applying the steady-state approximation to the chain-carrier radical (I·) in Scheme 4-2, the quantum yield may be derived as given by eq 6, where $\Phi_i$ is the quantum yield for the photo-

$$\Phi = k_p[\Phi_i/(k_t In)]^{1/2}[RCo] \tag{6}$$

dissociation of $I_2$ being the initiation step, $k_p$ is the propagation rate constant for the reaction of $[RCo^{III}]$ with I·, and $k_t$ is the termination rate constant for the bimolecular reaction of I·. According to eq 6, the quantum yield is proportional to [RCo] and $In^{-1/2}$, in agreement with the experimental results as shown in eqs 3 and 5, respectively. Since $\Phi_i$ and $k_t$ are known; $\Phi_i$ = 0.14[18] and $k_t = 7.2 \times 10^9$ $M^{-1}$ $s^{-1}$,[22] respectively, the propagation rate constants $k_p$ can be evaluated from the values of $\Phi$, $\Phi_i$, $k_t$, In, and [RCo] using eq 6. The $k_p$ values thus determined are listed in Table 4-3, together with the reported $k_p$ values of tetraalkyltin compounds,[13] and the one-electron oxidation potentials $E^0_{ox}$ of the

Table 4-3. Rate Constants $k_p$ for the Reactions of Alkylmetals (Alkylcobalt(III) Complexes and Tetraalkyltin Compounds) with Iodine Atom in $CCl_4$ at 298 K and the One-electron Oxidation Potentials $E^0_{ox}$ (vs. SCE) of Alkylmetals in MeCN

| alkylmetal | $E^0_{ox}$ V | $k_p$[a] $dm^3\ mol^{-1}\ s^{-1}$ |
|---|---|---|
| trans-$[Me_2Co(DpnH)]$ | 0.53[b] | $3.6 \times 10^8$ |
| cis-$[Me_2Co(bpy)_2]^+$ | 0.63[c] | $2.3 \times 10^8$ |
| cis-$[(PhCH_2)_2Co(bpy)_2]^+$ | 0.60[c] | $8.2 \times 10^7$ |
| $[EtCo(DH)_2Py]$ | 0.82[c] | $1.5 \times 10^7$ |
| $[MeCo(DH)_2Py]$ | 0.88[c] | $1.2 \times 10^7$ |
| $Bu_4Sn$ | 1.04[d] | $2.7 \times 10^6$ |
| $Pr_4Sn$ | 1.08[d] | $2.6 \times 10^6$ |
| $Et_4Sn$ | 1.12[d] | $2.7 \times 10^6$ |
| $Me_4Sn$ | 1.56[d] | $5.3 \times 10^4$ |

[a] The $k_p$ values of alkylcobalt(III) complexes were determined from eq 6, and those of tetraalkyltin compounds were taken from ref. 13. [b] ref. 23. [c] refs. 7 and 15. [d] refs. 24 and 25.

alkylmetals (alkylcobalt(III) complexes[7,15,23] and tetraalkyltin compounds[24,25]).

## 4-4 Discussion

**Electron-Transfer Processes in the $S_H2$ Reactions.** The simplest reaction scheme for the propagation step ($k_p$), the reaction of alkylcobalt(III) complexes [RCo] with iodine atom ($I^\bullet$), would be the single-step abstraction of R from [RCo] by $I^\bullet$. In such a case, the smaller the cobalt-alkyl bond dissociation energy ($D_{Co-R}$) is, the larger will the $k_p$ value be. In fact, however, the $k_p$ value of <u>cis</u>-$[(PhCH_2)_2Co(bpy)_2]^+$ is the smallest among the dialkylcobalt(III) complexes (Table 4-3), while the $D_{Co-R}$ value (22 kcal $mol^{-1}$) is known to be the smallest.[26] Thus, it seems appropriate to consider a multi-step mechanism rather than a single-step mechanism for the reactions of [RCo] with $I^\bullet$.

In this context, It has already been established that the reactions of $R_4Sn$ with $I^\bullet$, which are designated as bimolecular homolytic substitution ($S_H2$) of $R_4Sn$ by $I^\bullet$,[12] proceeds <u>via</u> electron transfer from $R_4Sn$ to $I^\bullet$, as given by eq 7.[13]

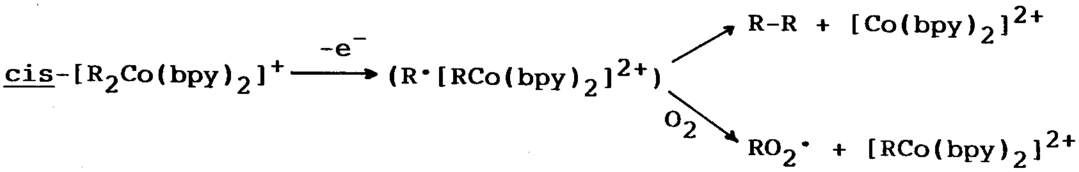
$$R_4Sn + I^\bullet \longrightarrow (R_4Sn^{+\bullet}\ I^-) \longrightarrow R^\bullet + R_3SnI \tag{7}$$

The formation of the ion pair as a reactive intermediate in the $S_H2$ reactions has been supported by selectivity studies, in which intramolecular competition in the homolytic displacement of the alkyl ligands from unsymmetrical tetraalkyltin compounds ($R_nSnR'_{4-n}$; n = 1-3) is the same as that observed in the fragmentation of $R_nSnR'_{4-n}{}^{+\bullet}$ generated independently, eqs 8 and 9.[13,27]

$$\begin{tikzcd}[column sep=small] & R^\bullet + R_{n-1}SnR'_{4-n}{}^{+} \qquad (8) \\ R_nSnR'_{4-n}{}^{+\bullet} \arrow[ur] \arrow[dr] & \\ & R'^\bullet + R_nSnR'_{3-n}{}^{+} \qquad (9) \end{tikzcd}$$

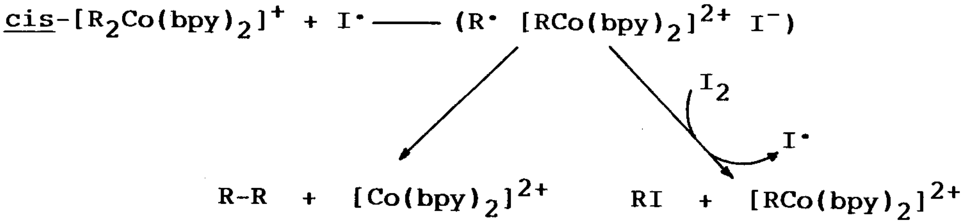
The cleavage mode of the Co-C bonds of dialkylcobalt(III) complexes upon the one-electron oxidation has also been established as shown in Chapter 1.[7] The one-electron oxidation of <u>cis</u>-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et) with $[Fe(bpy)_3]^{3+}$ (bpy = 2,2'-bipyridine) in the presence of oxygen yields exclusively the coupling products of the alkyl groups (R-R).[7] In the case of R = $PhCH_2$, however, the oxidation with $[Fe(bpy)_3]^{3+}$ is known to produce $PhCH_2O_2\cdot$ instead of the coupling product, $PhC_2H_4Ph$.[7,26] Such effects of oxygen on the one-electron oxidation of cis-$[R_2Co(bpy)_2]^+$ has been well explained by Scheme 4-3,

**Scheme 4-3**



where the cleavage of the two cobalt-carbon bonds upon the one-electron oxidation occurs in a stepwise manner.[7] Namely, the one-electron oxidation of cis-$[R_2Co(bpy)_2]^+$ (R = Me and Et) results in the cleavage of the one cobalt-carbon bond, followed by the reaction of the resulting alkyl radical with $[RCo(bpy)_2]^{2+}$ in the cage to yield the coupling product, R-R.[7,28] In the case of R = $PhCH_2$, the benzyl radical formed by the initial cleavage of the cobalt-benzyl bond upon the one-electron oxidation is stable enough to be trapped by oxygen to give benzylperoxyl radical ($PhCH_2O_2\cdot$) which is further oxidized to yield the final oxidized product, benzaldehyde.[7,28] Such difference in the stability of the resulting radicals produced by the oxidative cleavage of the Co-C bonds may account for the difference in the yields of the coupling products depending on the alkyl group in the photochemical reactions of cis-$[R_2Co(bpy)_2]^+$ with $I_2$ (Table 4-1) as shown in Scheme 4-4. In the

**Scheme 4-4**



case of R = Me and Et, the facile coupling reactions of $R\cdot$ with $[RCo(bpy)_2]^{2+}$ can compete well with the trap of $R\cdot$ by $I_2$, yielding the observed coupling products, R-R (Table 4-1). In the case of R = $PhCH_2$, the benzyl radicals $PhCH_2\cdot$ being more stable than $Me\cdot$ or $Et\cdot$ may be readily trapped by $I_2$ before the reaction with $[PhCH_2Co(bpy)_2]^{2+}$ as observed in the one-electron oxidation in the presence of oxygen (Scheme 4-3). This may be the reason why no coupling product has been detected in the case of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ (Table 4-1).

The one-electron oxidation of trans-$[Me_2Co(DpnH)]$ is also known to result in the cleavage of the one cobalt-carbon bond to give methyl radical (eq 10).[23,29] In this case, the reaction of

$$\text{trans-}[\mathrm{Me_2Co(DpnH)}] \xrightarrow{-e^-} \mathrm{Me}^{\bullet} + [\mathrm{MeCo(DpnH)}]^+ \qquad (10)$$

methyl radical with another cobalt-methyl bond is disfavoured, compared with the case of cis-$[R_2Co(bpy)_2]^+$, because of the trans-configuration, and thereby methyl radical diffuses outside of the cage.[23,29] Thus, electron transfer from trans-$[Me_2Co(DpnH)]$ with $I^{\bullet}$ may produce free methyl radical, followed by the reaction with $I_2$ to yield methyl iodide, accompanied by the regeneration of $I^{\bullet}$. Such involvement of free methyl radicals in the radical chain reactions may be responsible for the detection of a small quantity of methane (Table 4-1), formed by the hydrogen abstraction of methyl radical from solvent.[23,29]

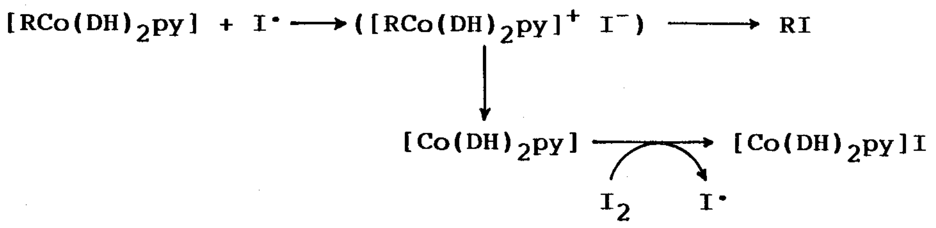
Alternatively, the minor gaseous products from dialkylcobalt(III) complexes may be produced by another termination step, i.e., the bimolecular coupling reactions of alkyl radicals ($k'_t$) in Scheme 4-2. However, the chain length, which is designated by $\Phi/\Phi_i$ ($\Phi_i$ = 0.14)[18], is as large as $3.1 \times 10^4$ for cis-$[Me_2Co(bpy)_2]^+$ under the experimental conditions in Table 4-2. Thus, even if the bimolecular coupling reaction of alkyl radicals is the sole termination step, the maximum yield of the coupling product from the termination step would be 0.003 %, which is much smaller than the observed yield (0.9 % in Table 4-1). Moreover, when the bimolecular coupling reaction of alkyl radicals is the sole termination step, the chain carrier radical should be alkyl radicals. In such a case, the quantum yield would be given by eq 11, instead of eq 6. Clearly, eq 11

$$\Phi = k'_p[\Phi_i/(k'_t\mathrm{In})]^{1/2}[I_2] \qquad (11)$$

disagrees with the experimental results in Fig. 4-3. Thus, it can be concluded that the minor gaseous products in Table 4-1 are formed via dialkylcobalt(IV) complexes (Scheme 4-4).

In the case of monoalkylcobalt(III) complexes, $[RCo(DH)_2py]$,[30] the one-electron oxidation is known to produce rather stable monoalkylcobalt(IV) complexes, $[RCo(DH)_2py]^+$, in which the Co-C bond is known to be cleaved by a nucleophile such as $I^-$.[31,32] Thus, the reaction of $[RCo(DH)_2py]$ with $I^\bullet$ may proceed as shown in Scheme 4-5, where the cleavage of the Co-C bond may

**Scheme 4-5**



occur by the nucleophilic attack of $I^-$ towards the alkylcobalt(IV) complexes to yield RI and $[Co(DH)_2py]$; the latter being the cobalt(II) complex may reduce $I_2$ to yield $[Co(DH)_2py]I$ accompanied by the regeneration of $I^\bullet$. This may be the reason where the cleavage of the Co-C bond may occur by the nucleophilic attack of $I^-$ towards the alkylcobalt(IV) complexes to yield RI and $[Co(DH)_2py]$; the latter being the cobalt(II) complex may reduce $I_2$ to yield $[Co(DH)_2py]I$ accompanied by the regeneration of $I^\bullet$. This may be the reason why no gaseous products derived from alkyl radicals have been detected in the case of $[RCo(DH)_2py]$ (Table 4-1).

As discussed above, the photoinduced cleavage of the Co-C bonds by iodine consists of the radical chain reactions in which the $S_H2$ reaction of the alkylcobalt(III) complex with $I^\bullet$ is the rate-determining step which is suggested to proceed <u>via</u> electron transfer from the alkylcobalt(III) complex to iodine atom. Thus, the reaction mechanism for the photoinduced cleavage of alkylcobalt(III) complexes by iodine may be essentially the same as that of tetraalkyltin compounds.[13] In fact, the propagation rate constant $k_p$ for electron transfer from alkylcobalt(III) complexes to iodine atom are correlated well with those of tetraalkyltin compounds as shown in Fig. 4-5, where the log $k_p$ values increase linearly with a negative shift in the one-electron oxidation potentials $E^0_{ox}$ of the alkylmetals (alkylcobalt(III) complexes and tetraalkyltin compounds) in MeCN when electron transfer from the alkylmetals to iodine atom becomes energetically more favourable. Although the energetics of electron transfer from alkylmetals to iodine atom in $CCl_4$ and the structures for the resulting ion pair intermediates are not known at present, such a linear correlation including both alkylcobalt(III) complexes and tetraalkyltin compounds indicates their coincidence of the reaction mechanism, i.e., photoinduced electron-transfer radical chain mechanism, in which the ease of the one-electron oxidation determines the reactivities of alkylmetals.

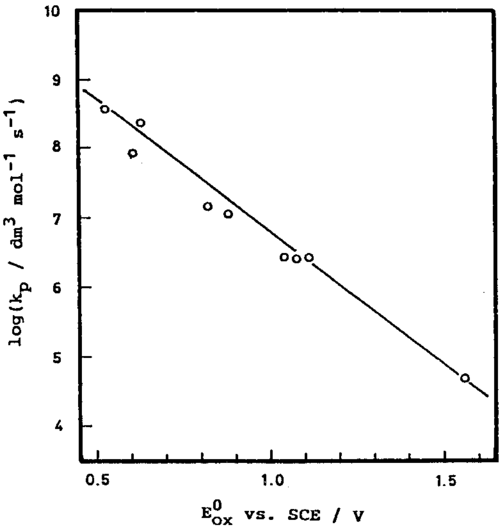


**Fig. 4-5.** Plot of logarithm of the rate constants $k_p$ for the reactions of alkylmetals (alkylcobalt(III) complexes and tetraalkyltin compounds) with iodine atom in $CCl_4$ at 298 K vs. the one-electron oxidation potentials $E^0_{ox}$ of alkylmetals in MeCN.

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# Chapter 5 PHOTOREDOX REACTIONS OF cis-DIALKYLCOBALT(III) COMPLEXES WITH BENZYL AND ALLYL BROMIDES

**Abstract:** When the photolysis of an acetonitrile solution of cis-dialkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]ClO_4$ (R = Me and Et; bpy = 2,2'-bipyridine), was carried out in the presence of benzyl or allyl bromide by using the visible light, cis-$[R_2Co(bpy)_2]ClO_4$ reacted with approximately three equivalent amounts of benzyl or allyl bromide to yield mainly the homo-coupling products 1,2-diphenylethane or 1,5-hexadiene as well as a small amount of the cross-coupling product between the alkyl group of cis-$[R_2Co(bpy)_2]ClO_4$ and benzyl or allyl group of the bromide. On the other hand, in the photoredox reaction of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ with benzyl or allyl bromide, cis-$[(PhCH_2)_2Co(bpy)_2]^+$ reacted with an equivalent amount of benzyl or allyl bromide to yield only the homo-coupling product in the case of benzyl bromide or comparable amounts of the homo-coupling and cross-coupling products in the case of allyl bromide. Reaction schemes of the photoredox reactions are discussed based on the ESR measurements to detect the reactive intermediates as well as the quantum yield measurements.

## 5-1 Introduction

Thermal cleavage of metal-carbon bonds of transition-metal alkyls has been studied extensively since it is one of the key steps in transition-metal-catalyzed carbon-carbon bond formation which provides an attractive synthetic use.[1-3] Although some transition-metal alkyls are thermally stable, cleavage of metal-carbon bonds are known to be induced by the redox reactions with organic and inorganic oxidants.[4-9] Photoinduced cleavage of metal-carbon bonds of transition-metal alkyls which are stable thermally is recently attracting growing attention,[10,11] and such reactions of monoalkylcobalt(III) complexes, coenzyme $B_{12}$ models, have been subjected to detailed scrutiny.[12-16] However, very little is known of photoredox reactions of transition-metal alkyls with organic oxidants which are inactive in thermal reactions. Combination of photoactivation of the metal-carbon bonds and the redox reactions with organic oxidants, especially with organic halides, may have potential utility for the formation of carbon-carbon bonds from transition-metal alkyls and organic halides.

In this study,[17] we report the photoinduced cleavage of cobalt-carbon bonds of cis-dialkylcobalt(III) complexes, cis-[$R_2Co(bpy)_2$]$ClO_4$ (R = Me, Et, $PhCH_2$; bpy = 2,2'-bipyridine), as well as the photoredox reactions of cis-[$R_2Co(bpy)_2$]$ClO_4$ with benzyl or allyl bromide, which do not react in the dark, resulting in carbon-carbon bond formation from cis-[$R_2Co(bpy)_2$]-$ClO_4$ and benzyl or allyl bromide. The photoredox reactions of other alkylcobalt(III) complexes with benzyl bromide are also reported. In the present study, we have succeeded in detecting the reactive intermediates by ESR measurements at 77K. These intermediates provide a basis for understanding the reaction mechanism for carbon-carbon bond formation in the photoredox reactions.

## 5-2 Experimental

**Materials.** Alkylcobalt(III) complexes, cis-[$R_2Co(bpy)_2$]-$ClO_4$ (R = Me, Et, $PhCH_2$)[9,18] trans-[$Me_2Co(DpnH)$] (DpnH = 11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1-olate),[19] and [$RCo(DH)_2py$] (R = Me, Et; $(DH)_2$ = bis-(dimethylglyoximato); py = pyridine)[20] were prepared as described previously (see Chapters 1 and 3). Both [$Co(bpy)_3$]-$(ClO_4)_2$ and [$Co(bpy)_3$]$ClO_4$ were prepared by following the literature method.[21] Benzyl and ally bromides obtained from Wako Pure Chemicals were treated with a 5% aqueous $NaHCO_3$ solution and water successively. After the mixture was dried with $MgSO_4$, it was fractionally distilled in the dark under reduced pressure before use. Potassium ferrioxalate used as an actinometer was prepared according to the literature,[22] and purified by recrystallization from hot water. Reagent grade acetonitrile was purified by the standard procedure,[23] followed by redistillation from calcium hydride. Acetonitrile-$d_3$ was stirred with freshly activated Molecular Sieve 4A (Wako Pure Chemicals) and then transferred in vacuum. Other reagents used for the product analyses were obtained commercially.

**Photochemical Reactions of Alkylcobalt(III) Complexes.** Typically, benzyl bromide ($3.1 \times 10^{-5}$ mol) was added to an NMR tube which contained an acetonitrile-$d_3$ (0.5 $cm^3$) solution of cis-[$R_2Co(bpy)_2$]$ClO_4$ ($3.1 \times 10^{-5}$ mol). After the reactant solution in the NMR tube was thoroughly degassed by repeated freeze-pump-thaw cycles, the NMR tube was sealed in vacuum, then, irradiated with visible light from a Ushio Model Ul-501 Xenon lamp through a Toshiba glass filter (O-36) which transmits light of $\lambda > 360$ nm. The photochemical reaction was monitored using a Japan Electron Optics JNM-PS-100 $^1$H NMR spectrometer (100 MHz). After completion of the reaction, the products were analyzed also by GLC. The photodecomposition of cis-$[R_2Co(bpy)_2]ClO_4$ in the absence of benzyl or allyl bromide was also monitored by $^1$H NMR and the gaseous products were analyzed by GLC using a Unibeads 1-S column.

**Quantum-Yield Determinations.** A standard actinometer (potassium ferrioxalate)[22] was used for the quantum-yield determination of the photochemical reactions of cis-$[R_2Co(bpy)_2]ClO_4$ with benzyl and allyl bromides in acetonitrile. Under the conditions of actinometry experiments, both the actinometer and cis-$[R_2Co(bpy)_2]ClO_4$ solutions absorbed essentially all the incident light through a Toshiba C-39A glass filter which transmits light of $350 \text{ nm} < \lambda < 470$ nm. The quantum yields of the photochemical reactions of cis-$[R_2Co(bpy)_2]ClO_4$ with benzyl and allyl bromides were determined from the rate of disappearance of the absorption band due to cis-$[R_2Co(bpy)_2]ClO_4$ in MeCN ($\lambda_{max}$ = 472, 495, 502 nm for R = Me, Et, $PhCH_2$, respectively) under a degassed condition using a Schlenk tube equipped with a sidearm fused to a square quartz cuvette (1 or 10 mm i.d.).

**Electron Spin Resonance Measurements.** Benzyl or allyl bromide was added to a quartz ESR tube which contained an MeCN solution of cis-$[R_2Co(bpy)_2]ClO_4$, and the ESR tube was thoroughly degassed by the repeated freeze-pump-thaw cycles before sealing. The ESR tube was then placed in a transparent Dewar which was maintained at 77 K and irradiated with visible light of $\lambda >$ 360 nm. The ESR measurements were carried out using a JEOL X-band spectrometer (JES-ME-2X). The g-value and the hyperfine splitting constant (hfs) of the ESR spectra were calibrated by using an $Mn^{2+}$ ESR marker. The spin concentration was determined by double integration of the ESR signals using 1,1'-diphenyl-2-picrylhydrazyl (DPPH) as a calibrant ($\pm$20%). The relative spin concentrations measured at various times of irradiation were readily determined to within $\pm$ 5%.

## 5-3 Results and Discussion

**Photodecomposition of cis-$[R_2Co(bpy)_2]ClO_4$.** The cobalt-carbon bond of cis-$[Me_2Co(bpy)_2]ClO_4$ was cleaved homolytically to produce methane and a small amount of ethane upon irradiation with visible light ($\lambda > 360$ nm) as shown by eq 1. In the

$$\text{cis-}[Me_2Co(bpy)_2]^+ \xrightarrow[15h]{h\nu} CH_4 + C_2H_6 \qquad (1)$$

$$1.0 \times 10^{-2}\ M \qquad\qquad 14 : 1$$

photolysis of cis-$[(PhCH_2)_2Co(bpy)_2]ClO_4$, the cobalt-carbon bond was also cleaved homolytically, but the ratio of the coupling product of benzyl radicals (1,2-diphenylethane) to the product derived by the hydrogen abstraction from a solvent (toluene) increased significantly (eq 2), compared with the corresponding

$$\text{cis-}[(PhCH_2)_2Co(bpy)_2]^+ \xrightarrow[50h]{h\nu} PhCH_3 + PhC_2H_4Ph \qquad (2)$$

$$4.5 \times 10^{-2}\ M \qquad\qquad 1 : 1$$

ratio of ethane to methane in the photolysis of cis-$[Me_2Co(bpy)_2]ClO_4$ (eq 1). Since benzyl radical abstracts a hydrogen from a solvent at a much slower rate than methyl radical,[24] the coupling process is much more favorable in the case of cis-$[(PhCH_2)_2Co(bpy)_2]ClO_4$ than $[Me_2Co(bpy)_2]ClO_4$.

When an MeCN solution of cis-$[Et_2Co(bpy)_2]^+$ which has a β hydrogen was irradiated with the visible light, ethane and ethylene were formed with a 2 : 1 ratio as well as a trace amount of butane (eq 3), indicating the involvement of a β-

$$\text{cis-}[Et_2Co(bpy)_2]^+ \xrightarrow[8h]{h\nu} C_2H_6 + C_2H_4 + C_4H_{10} \qquad (3)$$

$$1.0 \times 10^{-2}\ M \qquad\qquad 2 : 1 \qquad \text{trace}$$

elimination pathway to yield ethane and ethylene in a 1 : 1 ratio (eq 4) besides a homolytic pathway to yield mainly ethane with a trace amount of the coupling product of ethyl radicals, *i.e.*, butane. The product ratio of ethane to ethylene remained

$$\text{cis-}[Et_2Co(bpy)_2]^+ \xrightarrow{h\nu} (C_2H_6\text{-cis-}[Et(H)Co(bpy)_2]^+)$$

$$\longrightarrow C_2H_6 + C_2H_4 + [Co(bpy)_2]^+ \qquad (4)$$

approximately constant throughout the irradiation. The involvement of a β-elimination pathway (eq 4) in addition to homolytic pathway was confirmed by the photolysis of <u>cis</u>-$[Et_2Co(bpy)_2]^+$ under an atmospheric pressure of oxygen as shown in Fig. 5-1. Thus, oxygen has essentially no effect on the formation of ethylene, but can trap ethyl radical to yield acetaldehyde as an oxidation product.[12d,25] The operation of a β-elimination pathway from a diethylcobalt(III) complex was reported also in the thermolysis of $[Et_2Co(acac)(PPhMe_2)_2]$ (acac = acetylacetonato).[1f] A cobalt-containing product was detected by monitoring the course of the photolysis in $CD_3CN$ by $^1H$ NMR, and characterized as $[Co(bpy)_3]^+$ by comparing with an authentic sample which was prepared by the reduction of $[Co(bpy)_3]^{2+}$ with $NaBH_4$.[21,26] The bis complex $[Co(bpy)_2]^+$ formed by the photoinduced β-elimination pathway (eq 4) may be converted to the tris complex, since thermodynamic considerations indicate that the tris complex is more stable than the mono- or bis(2,2'-bipyridine)cobalt(I) complexes.[27]

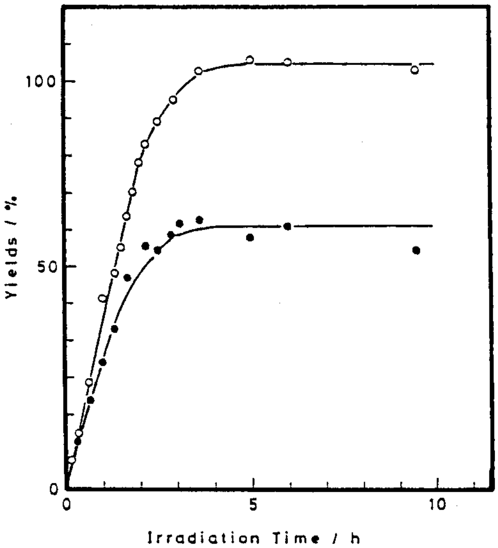


Fig. 5-1. Yields of photodecomposition products of <u>cis</u>-$[Et_2Co(bpy)_2]^+$ ($1.0 \times 10^{-2}$ M) under an atmospheric pressure of oxygen in MeCN based on the cobalt complex plotted against the irradiation time: $CH_3CHO$ (○) and $C_2H_4$ (●).

**Photoredox Reactions of Alkylcobalt(III) Complexes with Benzyl and Allyl Bromides.** When the photolysis of <u>cis</u>-$[Me_2Co(bpy)_2]^+$ is carried out in the presence of benzyl bromide under a degassed condition, formation of the gaseous products (methane and ethane) observed in the absence of benzyl bromide (eq 1) is suppressed completely. Instead, the coupling product from the benzyl group of benzyl bromide (<u>i.e.</u>, 1,2-diphenylethane) is formed together with methyl bromide (Fig. 5-2). The stoichiometry of the photochemical reaction is given by eq 5,

$$\underline{cis}\text{-}[Me_2Co(bpy)_2]^+ + 3PhCH_2Br \xrightarrow{h\nu} 2MeBr + 3/2PhC_2H_4Ph + [Co(bpy)_2Br]^+ \qquad (5)$$

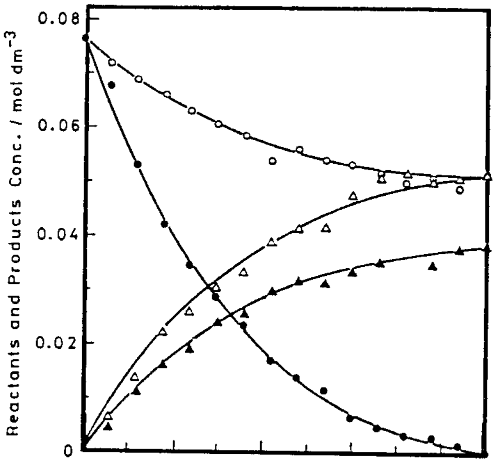


Fig. 5-2. Time course of the photochemical reaction of *cis*-[Me$_2$Co(bpy)$_2$]$^+$ (7.7 x 10$^{-2}$ M) with benzyl bromide (7.7 x 10$^{-2}$ M) under a degassed condition in CD$_3$CN at 298K: *cis*-[Me$_2$Co(bpy)$_2$]$^+$ ( ○ ), PhCH$_2$Br ( ● ), MeBr ( △ ), and PhC$_2$H$_4$Ph ( ▲ ).

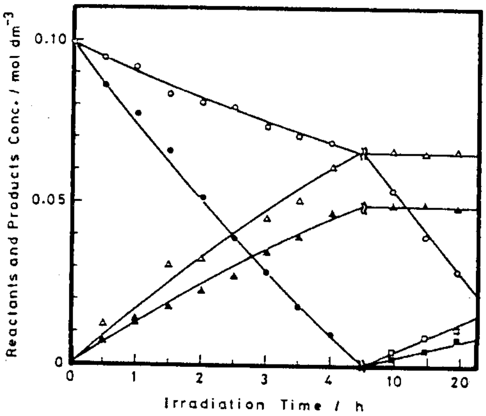


Fig. 5-3. Time course of the photochemical reaction of *cis*-[Et$_2$Co(bpy)$_2$]$^+$ (9.9 x 10$^{-2}$ M) with allyl bromide (9.9 x 10$^{-2}$ M) under a degassed condition in CD$_3$CN containing D$_2$O (0.18 M) at 298 K: *cis*-[Et$_2$Co(bpy)$_2$]$^+$ ( ○ ), C$_3$H$_5$Br ( ● ), EtBr ( △ ), C$_6$H$_{10}$ ( ▲ ), C$_2$H$_6$ ( □ ), and C$_2$H$_4$ ( ■ ).

where one mol of *cis*-[Me$_2$Co(bpy)$_2$]$^+$ reacts with three mols of benzyl bromide.[28] Such a novel stoichiometry was observed also in the photoredox reactions of *cis*-[Me$_2$Co(bpy)$_2$]$^+$ with allyl bromide, where the coupling product from the allyl group of allyl bromide, *i.e.*, 1,5-hexadiene, was formed as well as methyl bromide. Similarly, the photolysis of *cis*-[Et$_2$Co(bpy)$_2$]$^+$ in the presence of allyl bromide proceeds with a 1 : 3 stoichiometry to yield 1,5-hexadiene and ethyl bromide as shown in Fig. 5-3, where it can be seen that after consuming allyl bromide, photodecomposition of *cis*-[Et$_2$Co(bpy)$_2$]$^+$ starts to produce the gaseous products (ethane, ethylene) as observed in the absence of allyl bromide (eq 3). Thus, the presence of benzyl or allyl bromide changes the photoproducts derived from *cis*-[R$_2$Co(bpy)$_2$]$^+$ (R = Me, Et) from the gaseous products (methane, ethane, ethylene, etc) in its absence to the corresponding alkyl bromide in the presence of benzyl or allyl bromide.

In contrast to the above results, when the alkyl group is the same between the reactants, *i.e.*, photolysis of *cis*-[R$_2$Co(bpy)$_2$]$^+$ in the presence of benzyl bromide, the stoichiometry is changed to 1 : 1 as shown in Fig. 5-4, where only the coupling product (1,2-diphenylethane) is produced as a main product (eq 6).

Table 5-1 summarizes the product distributions from the

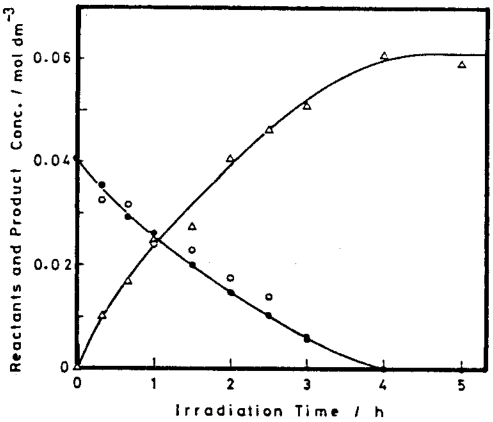


**Fig. 5-4.** Time course of the photochemical reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ ($4.1 \times 10^{-2}$ M) with benzyl bromide ($4.1 \times 10^{-2}$ M) under a degassed condition in $CD_3CN$ at 298K: *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (○), $PhCH_2Br$ (●), and $PhC_2H_4Ph$ (△).

$$\textit{cis}\text{-}[(PhCH_2)_2Co(bpy)_2]^+ + PhCH_2Br \xrightarrow{h\nu} 3/2PhC_2H_4Ph + [Co(bpy)_2Br]^+ \qquad (6)$$

**Table 5-1. Product Distribution in the Photochemical Reactions of Alkylcobalt(III) Complexes with Benzyl and Allyl Bromides under Degassed Conditions in Acetonitrile-$d_3$ at 298 K**

| reaction[a] | | | time, h | product, % based on the cobalt complex |
|---|---|---|---|---|
| *cis*-$[Me_2Co(bpy)_2]^+$ ($7.7 \times 10^{-2}$) | + | $PhCH_2Br$ ($7.7 \times 10^{-2}$) | 45 | $PhC_2H_4Ph$ (49), $PhCH_3$ (1.3), PhEt (3.8) |
| *cis*-$[Et_2Co(bpy)_2]^+$ ($9.9 \times 10^{-2}$) | + | $PhCH_2Br$[b] ($9.9 \times 10^{-2}$) | 24 | $PhC_2H_4Ph$ (48), $PhCH_3$ (0.4), PhPr (3.0) |
| *cis*-$[Me_2Co(bpy)_2]^+$ ($5.9 \times 10^{-2}$) | + | $C_3H_5Br$ ($5.9 \times 10^{-2}$) | 48 | $C_6H_{10}$ (48), $C_3H_6$ (2.2), $C_4H_8$ (4.2) |
| *cis*-$[Et_2Co(bpy)_2]^+$ ($9.9 \times 10^{-2}$) | + | $C_3H_5Br$[b] ($9.9 \times 10^{-2}$) | 24 | $C_6H_{10}$ (49), $C_3H_6$ (1.8), $C_5H_{10}$ (3.8) |
| *cis*-$[(PhCH_2)_2Co(bpy)2]^+$ ($4.1 \times 10^{-2}$) | + | $PhCH_2Br$ ($4.1 \times 10^{-2}$) | 11 | $PhC_2H_4Ph$ (148), $PhCH_3$ (4.0) |
| *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ ($4.1 \times 10^{-2}$) | + | $C_3H_5Br$ ($4.1 \times 10^{-2}$) | 11 | $PhC_2H_4Ph$ (85), $C_6H_{10}$ (36), $PhC_4H_7$ (34) |
| *trans*-$[Me_2Co(DpnH)]$ ($4.0 \times 10^{-2}$) | + | $PhCH_2Br$ ($4.0 \times 10^{-2}$) | 33 | $PhC_2H_4Ph$ (22), $PhCH_3$ (55) |
| $[MeCo(DH)_2py]$ (0.10) | + | $PhCH_2Br$ (0.10) | 71 | $PhCH_3$ (6.4) |
| $[EtCo(DH)_2py]$ (0.10) | + | $PhCH_2Br$ (0.10) | 14 | $PhCH_2$ (33) |

[a] The concentrations of the reactants are shown in the parentheses. [b] In the presence of 0.18 M $D_2O$ (see ref 43).

photochemical reactions of various alkylcobalt(III) complexes with benzyl and allyl bromides including the minor products. In the photoredox reactions of *cis*-$[Me_2Co(bpy)_2]^+$ and *cis*-$[Et_2Co(bpy)_2]^+$ with benzyl and allyl bromides, the coupling products (1,2-diphenylethane and 1,5-hexadiene, respectively) are mainly obtained, and small amounts of cross-coupling products (*e.g.*, ethylbenzene in the case of the reactions of *cis*-$[Me_2Co(bpy)_2]^+$ with benzyl bromide) are formed as well as the products derived from hydrogen abstraction by benzyl and allyl radicals from a solvent (*i.e.*, toluene and propene, respectively). The stoichiometry of these reactions is approximately 1 : 3 as shown by eq 5. In the case of the photoredox reactions of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with benzyl bromide, however, the stoichiometry is 1 : 1 (eq 6) to yield mainly the coupling product (1,2-diphenylethane) together with a small amount of toluene (Table 5-1). When benzyl bromide is replaced by allyl bromide in the reaction with *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, the coupling products (1,2-diphenylethane and 1,5-hexadiene) are formed together with a comparable amount of the cross-coupling product between the benzyl and allyl group, *i.e.*, 4-phenyl-1-butene (Table 5-1). Thus, the photolysis of all the *cis*-dialkylcobalt(III) complexes in the presence of benzyl or allyl bromide results in the formation of carbon-carbon bonds to yield the coupling or cross-coupling products of the benzyl and allyl groups as the main products together with small amounts of products derived from hydrogen abstraction by benzyl or allyl radical from a solvent.

On the other hand, the photolysis of *trans*-$[Me_2Co(DpnH)]$ in the presence of benzyl bromide gives mainly toluene. Thus, carbon-carbon bond formation in the case of *trans*-$[Me_2Co(DpnH)]$ is much less efficient than the case of *cis*-$[R_2Co(bpy)_2]^+$ (Table 5-1). Irradiation of monoalkylcobalt(III) complexes $[RCo(DH)_2py]$ (R = Me, Et) in the presence of benzyl bromide gives only toluene with no appreciable amount of the coupling product, either.

**Quantum Yields.** The quantum yields $\Phi$ for photodecomposition of *cis*-$[R_2Co(bpy)_2]^+$ (R = Me, Et, and $PhCH_2$) were determined in the region of $\lambda_{max}$ of the Co-C charge-transfer (CT) absorption. The magnitude of $\Phi$ observed (Table 5-2), which is similar to that for photodecomposition of alkylcobaloximes,[12e] is typical for charge-transfer induced excitation.[29] The quantum yield of photodecomposition of *cis*-$[Et_2Co(bpy)_2]^+$ is the largest among *cis*-$[R_2Co(bpy)_2]^+$ because of the involvement of a β-elimination step (eq 4) besides a homolytic pathway. The $\Phi$ value is independent of the concentration of *cis*-$[Et_2Co(bpy)_2]^+$ and is affected by neither the presence of oxygen, which is a typical triplet quencher, nor the addition of an excess amount of the ligand 2,2'-bipyridine (Table 5-2). Thus, the photodecomposition may

**Table 5-2. Quantum Yields ($\Phi$) for Photodecomposition of *cis*-$[R_2Co(bpy)_2]^+$ (R = Me, Et, and $PhCH_2$) in MeCN at 298 K[a]**

| *cis*-$[R_2Co(bpy)_2]^+$, M | additive | $\Phi$ |
|---|---|---|
| R = Me | | |
| $1.0 \times 10^{-3}$ | none | 0.012 |
| $1.0 \times 10^{-3}$ | $O_2$[b] | 0.014 |
| R = Et | | |
| $1.0 \times 10^{-3}$ | none | 0.030 |
| $1.0 \times 10^{-3}$ | $O_2$[b] | 0.033 |
| $5.0 \times 10^{-3}$ | none | 0.030 |
| $5.0 \times 10^{-3}$ | $O_2$[b] | 0.030 |
| $1.0 \times 10^{-3}$ | bpy[c] | 0.029 |
| $1.0 \times 10^{-3}$ | $O_2$,[b] bpy[c] | 0.029 |
| R = $PhCH_2$ | | |
| $1.0 \times 10^{-2}$ | none | 0.022 |

[a] Under a degassed condition unless otherwise noted. [b] Under an atmospheric pressure of oxygen. [c] In the presence of $5.0 \times 10^{-2}$ M 2,2'-bipyridine.

be a unimolecular process via the singlet excited state without the dissociation of the 2,2'-bipyridne ligand.

In the presence of benzyl or allyl bromide, the Φ value for the photolysis of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ increases with increasing the concentration of benzyl or allyl bromide, benzyl or allyl bromide completely suppresses the photodealkylation process, i.e., production of ethane and ethylene, which occurs in its absence as shown in Fig. 5-3, the photochemical reactions in the absence and presence of benzyl or allyl bromide are neither independent of each other nor competing process. Thus, the dependence of Φ on the bromide concentration (Fig. 5-5) suggests that a common intermediate produced by the photochemical reaction in the absence and presence of the bromide reacts with the bromide by a bimolecular reaction.

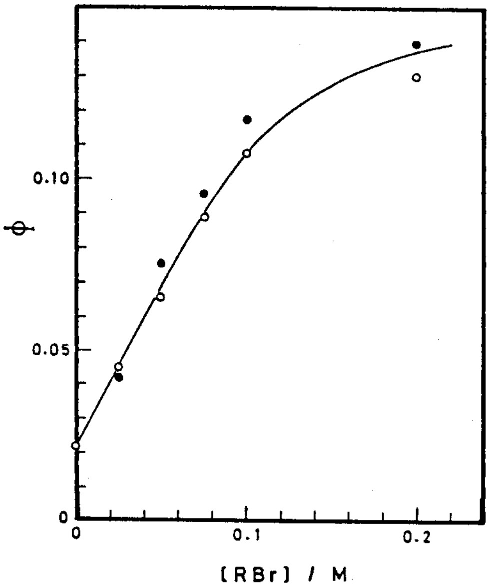


Fig. 5-5. Plots of the quantum yields for photochemical reactions of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ ($1.0 \times 10^{-2}$ M) with RBr [R = $PhCH_2$ (○) and $C_3H_5$ (●)] in the absence of oxygen in MeCN at 298 K vs. the concentration of the bromide.

**Detection of Reactive Intermediates.** In order to detect the reactive intermediates produced in these photochemical reactions, the ESR spectra were measured in the course of photolysis of an MeCN solution of cis-$[R_2Co(bpy)_2]^+$ in the absence and presence of benzyl or allyl bromide at 77 K. In the photolysis of cis-$[R_2Co(bpy)_2]^+$ in the presence of benzyl bromide, the ESR signal due to benzyl radical is observed as shown in Fig. 5-6a, where the computer simulation spectrum of benzyl radical using the ESR parameters reported in the literature[30] ($g = 2.0026$, $a(CH_2) = 1.40$, $a(o\text{-}H) = 0.30$, $a(m\text{-}H) = 0.15$, and $a(p\text{-}H) = 0.32$ mT) with the line width ($\Delta H_{msl} = 0.39$ mT) is indicated by the dotted line, showing a reasonable agreement with the observed spectrum. In the presence of allyl bromide, the ESR spectrum of allyl radical ($g = 2.0026$, $a_1 = 0.41$ for one proton, $a_2 = 1.40$ for two equivalent protons, and $a_2' = 1.48$ mT for other two equivalent protons)[31] with the line width $\Delta H_{msl} = 0.50$ mT is

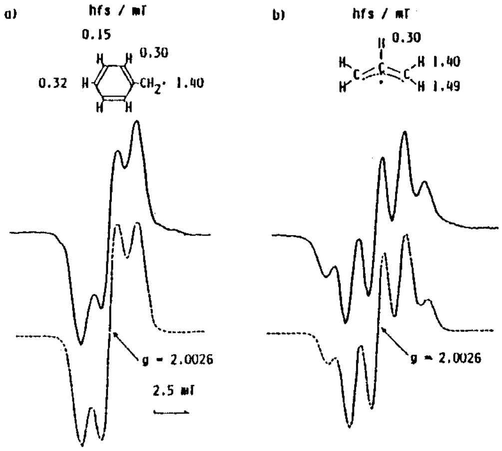


Fig. 5-6. ESR spectra of (a) benzyl and (b) allyl radicals observed in the photolysis of cis-$[Et_2Co(bpy)_2]^+$ ($5.0 \times 10^{-2}$ M) in the presence of benzyl bromide (0.15 M) and allyl bromide (0.30 M), respectively, at 77 K (solvent, MeCN). The broken lines show the computer simulation spectra.

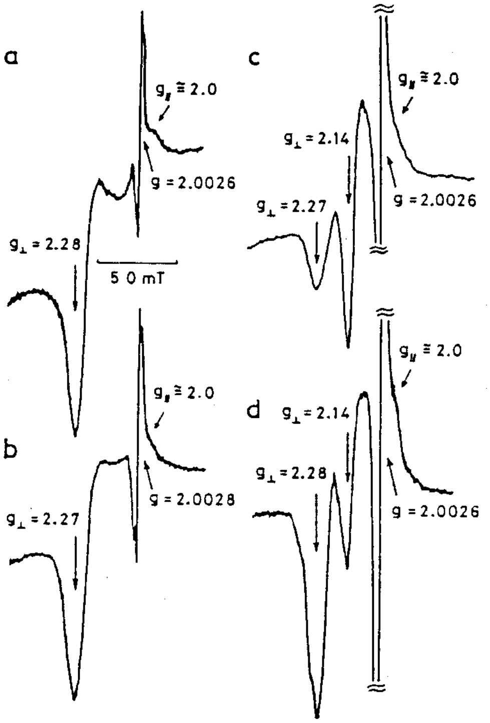


Fig. 5-7. ESR spectra observed in the photolysis of (a) cis-$[(PhCH_2)_2Co(bpy)_2]^+$ ($4.5 \times 10^{-2}$ M) for 8 h, (b) cis-$[Me_2Co(bpy)_2]^+$ ($6.0 \times 10^{-2}$ M) for 10 h, (c) cis-$[Me_2Co(bpy)_2]^+$ ($6.0 \times 10^{-2}$ M) in the presence of benzyl bromide (0.30 M) for 20 h, and (d) cis-$[Me_2Co(bpy)_2]^+$ ($6.0 \times 10^{-2}$ M) in the presence of allyl bromide (0.30 M) for 16 h at 77 K (solvent, MeCN).

observed as shown in Fig. 5-6b.

A cobalt(II) paramagnetic species is also observed in the wide magnetic region. In the photolysis of cis-$[(PhCH_2)_2Co(bpy)_2]^+$, the isotropic signal at $g = 2.0026$ which is attributed to benzyl radical[32] is observed as well as the characteristic signal of a spin doublet possessing axial symmetry at $g_\perp = 2.28$ and $g_\parallel = 2.0$, which is expected for a monobenzylcobalt(II) complex $[PhCH_2Co(bpy)_2]^+$ produced by the homolytic cleavage of the cobalt-carbon bond of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ (Fig. 5-7a). A similar anisotropic signal ($g_\perp = 2.27$ and $g_\parallel = 2.0$) which may be assigned to $[MeCo(bpy)_2]^+$ is also observed in the case of cis-$[Me_2Co(bpy)_2]^+$ (Fig. 5-7b), where the isotropic sharp triplet signal at $g = 2.0028$ with $a(\alpha\text{-H}) = 2.1$ mT can be assigned to $\cdot CH_2CN$ by comparison of the ESR parameters with those in the literature.[33] The $\cdot CH_2CN$ radical may be produced by the hydrogen abstraction by methyl radical from $CH_3CN$, since methyl radical formed initially by the homolytic cleavage of the cobalt-carbon bond of cis-$[Me_2Co(bpy)_2]^+$ is known to be much more reactive than benzyl radical as noted above.[24]

When benzyl bromide is added to an MeCN solution of cis-$[Me_2Co(bpy)_2]^+$, the photolysis at 77 K results in the formation of benzyl radical instead of $\cdot CH_2CN$, and the signal intensity of benzyl radical in the presence of benzyl bromide (Fig. 5-7c) is much stronger than that of $\cdot CH_2CN$ in the absence of benzyl bromide (Fig. 5-7b). In the presence of benzyl bromide, two anisotropic signals are observed at $g_\perp = 2.27$ and 2.14 (Fig. 5-7c); the former is the same as that observed in Fig. 5-7b, being assigned to $[MeCo(bpy)_2]^+$, and the latter may tentatively be assigned to $[Co(bpy)_2Br]^+$. In the cis-$[Me_2Co(bpy)_2]^+$-$C_3H_5Br$ system (Fig. 5-7d) as well, the photolysis results in the formation of allyl radical ($g = 2.0026$)[32] with much stronger intensity than $\cdot CH_2CN$ in the absence of allyl bromide (Fig. 5-7b) as well as $[MeCo(bpy)_2]^+$ ($g_\perp = 2.27$ and $g_\parallel = 2.0$) and $[Co(bpy)_2Br]^+$ ($g_\perp = 2.14$ and $g_\parallel = 2.0$).

No hyperfine structure of $[RCo(bpy)_2]^+$ and $[Co(bpy)_2Br]^+$ due to the cobalt nuclear spin ($I = 7/2$) is observed in Fig. 5-7, probably because paramagnetic centers are not diluted as reported in the case of isothiocyanate complex of cobalt(II) with the tridentate ligand N-(2-(diphenylphosphino)ethyl)-N',N'-diethylethylenediamine $[Co(NCS)_2(nnp)]$[34] as well as $[Co(NCS)(dpe)_2]ClO_4$ where dpe is 1,2-bis(diphenylphosphino)ethane,[35] which is known as a five-coordinate cobalt(II) complex with a square pyramidal structure. No superhyperfine structure due to the alkyl group of $[RCo(bpy)_2]^+$ is observed, either, suggesting that little or no unpaired electron density is located on the alkyl group. In fact, the greater $g_\perp$ value than the $g_\parallel$ value indicates that the unpaired electron is mainly located in the $d_{z^2}$ orbital of cobalt(II) in a low-spin $d^7$ configuration.[35,36] Thus, the structure of $[RCo(bpy)_2]^+$ may be better described as $[R^- \text{-} Co^{II}(bpy)_2]^+$ in which the Co-R bond is almost dissociated to produced the carbanion ligand as the case of the reduced benzyl(pyridine)cobaloxime which has been reported to dissociate into the benzyl anion and (pyridine)cobaloxime.[37,38]

The spin concentrations of both benzyl radical and monoalkylcobalt(II) complex produced by the photolysis of cis-$[R_2Co(bpy)_2]^+$ in the presence of benzyl bromide at 77 K increase linearly with the irradiation time, and the concentration of benzyl radical is approximately the same as that of the monoalkylcobalt(II) complex as shown in Fig. 5-8 in the case of R = Et. Thus, both the benzyl radical and $[RCo(bpy)_2]^+$ may be formed at the same time by the initial photochemical step (eq 7). All the ESR signals in Fig. 5-7 disappeared instantly when the samples were warmed up to room temperature, followed by the measurement at 77 K, indicating that the paramagnetic species observed in Fig. 5-7 (benzyl or allyl radical, $[RCo(bpy)_2]^+$, and $[Co(bpy)_2Br]^+$) are reactive intermediates involved in the subsequent thermal reactions. On the disappearance of the ESR

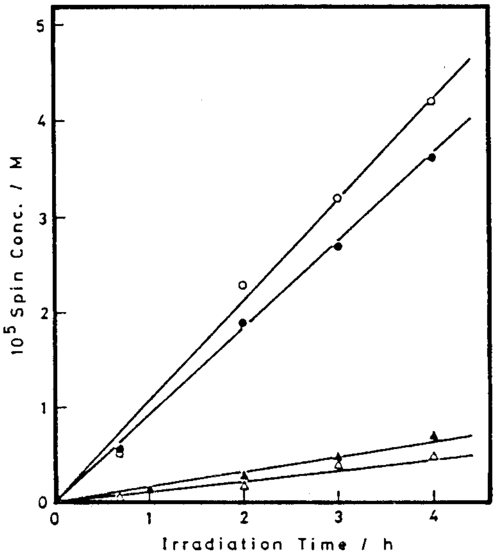


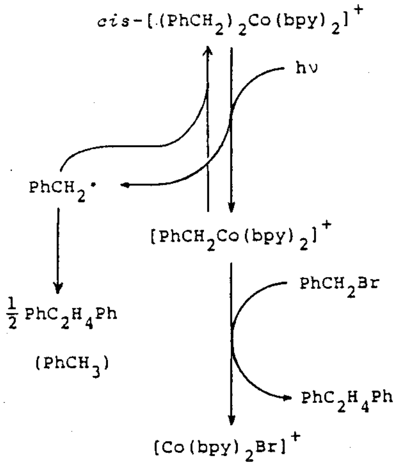
Fig. 5-8. Plots of the spin concentrations of the paramagnetic species formed by the photolysis of <u>cis</u>-$[R_2Co(bpy)_2]^+$ ($6.0 \times 10^{-2}$ M) in the presence of benzyl bromide (0.18 M) <u>vs.</u> the irradiation time at 77 K: $PhCH_2\cdot$ (○), $[RCo(bpy)_2]^+$ (●), and $[Co(bpy)_2Br]^+$ (△) for R = Et, and $PhCH_2\cdot$ (▲) for R = Me.

$$\underline{\text{cis}}\text{-}[R_2Co(bpy)_2]^+ + PhCH_2Br \xrightarrow{h\nu} PhCH_2\cdot + [RCo(bpy)_2]^+ + RBr \qquad (7)$$

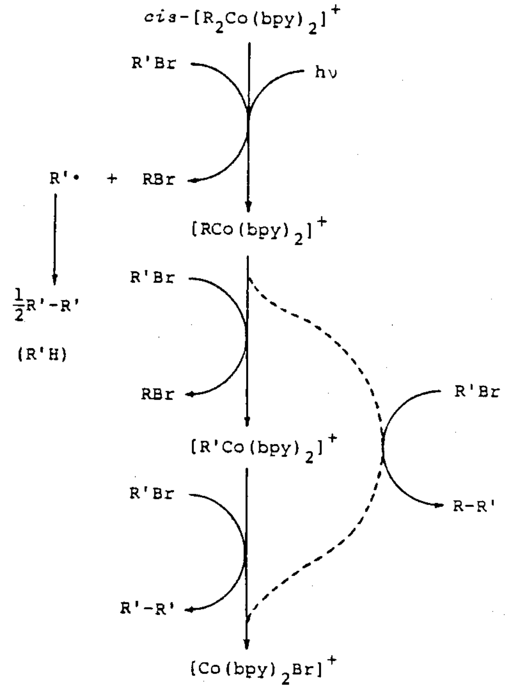
signals due to five coordinate cobalt(II) species in Fig. 5-7, an eight line spectrum which is identical with that of $[Co(bpy)_3]^{2+}$ reported in the literature[39] was observed. Thus, $[Co(bpy)_3]^{2+}$ is the final product from <u>cis</u>-$[R_2Co(bpy)_2]^+$ in the photochemical reaction with benzyl or allyl bromide as confirmed by the $^1H$ NMR measurement,[28] suggesting that $[Co(bpy)_2Br]^+$ observed in Fig. 5-7c or 7d, which may be the initial product (eq 5), is converted to $[Co(bpy)_3]^{2+}$ being the most stable form among the mono-, bis-, and tris(2,2'-bipyridine)cobalt(II) complexes.[29]

**Reaction Schemes.** Based on the above results, the reaction mechanisms for the photoredox reactions of <u>cis</u>-$[R_2Co(bpy)_2]^+$ with benzyl and allyl bromides may be given by Schemes 5-1, 5-2, 5-3. In the photoredox reactions of <u>cis</u>-$[(PhCH_2)_2Co(bpy)_2]^+$ with benzyl bromide (Scheme 5-1), which is the simplest case, excitation of <u>cis</u>-$[R_2Co(bpy)_2]^+$ leads to the homolytic cleavage of the cobalt-carbon bond to produce benzyl radical and mono-

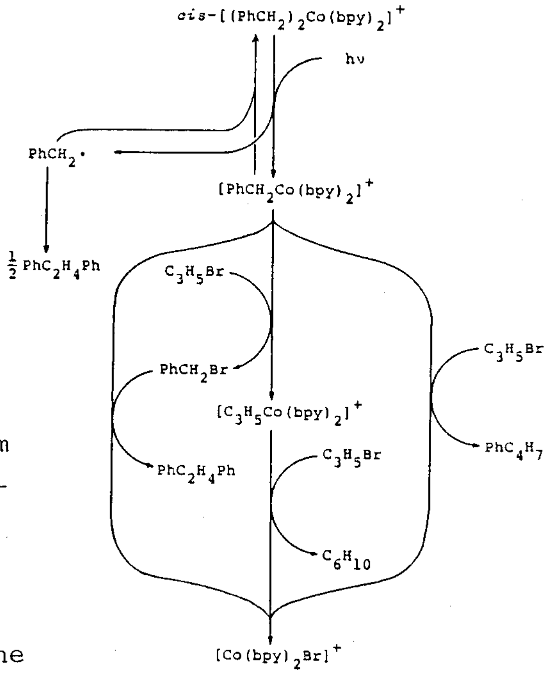
Scheme 5-1



Scheme 5-2



Scheme 5-3



benzyl cobalt(II) complex $[PhCH_2Co(bpy)_2]^+$ as confirmed by the ESR measurement (Fig. 5-7a). In the absence of benzyl bromide, the quantum efficiency is much lowered by the facile recombination of benzyl radical with $[PhCH_2Co(bpy)_2]^+$. In the presence of benzyl bromide, however, $[PhCH_2Co(bpy)_2]^+$ in which the benzyl group is considered as the benzyl anion as discussed above may undergo the facile coupling reaction with benzyl bromide to yield 1,2-diphenylethane and $[Co(bpy)_2Br]^+$. Thus, the quantum yield is increased by the presence of benzyl bromide to prevent the recombination between $[PhCH_2Co(bpy)_2]^+$ and benzyl radical, approaching the limited Φ value with increasing the bromide concentration (Fig. 5-5).[40] When the reciprocal of the increase in the Φ value in the presence of benzyl or allyl bromide, i.e., $(\Phi - \Phi_0)^{-1}$ where $\Phi_0$ is the quantum yield in the absence of benzyl or allyl bromide, was plotted against $[PhCH_2Br]^{-1}$ or $[C_3H_5Br]^{-1}$ by using the data in Fig. 5-5, each plot gave a straight line with approximately the same intercept,[41] from which the quantum yield for the photocleavage of the Co-C bond of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ without the back reaction can be evaluated as 0.3 ± 0.1. On the other hand, benzyl radicals also give 1,2-diphenylethane by the coupling reaction together with a small amount of toluene by the hydrogen abstraction from a solvent (Table 5-1). According to Scheme 5-1, the stoichiometry of the photoredox reaction is 1 : 1 (eq 6).

When the alkyl groups between the reactants (cis-$[R_2Co(bpy)_2]^+$ and R'Br) are different, the reaction scheme becomes more complicated (Scheme 5-2). Excitation of cis-$[R_2Co(bpy)_2]^+$ (R = Me, Et) also leads to the homolytic cleavage of the cobalt-carbon bond to produce $[RCo(bpy)_2]^+$ and alkyl radical (Fig. 5-7b).[42] In the presence of R'Br (R' = $PhCH_2$, $C_3H_5$), the alkyl radical (Me•, Et•) may be converted to the more stable radical ($PhCH_2$•, $C_3H_5$•) by the reaction with R'Br as observed by the ESR spectra (Fig. 5-6, 5-7c, 5-7d). Thus, the photochemical reaction of cis-$[R_2Co(bpy)_2]^+$ with R'Br produces R'•, $[RCo(bpy)_2]^+$ and RBr (eq 7).[43] The benzyl and allyl radicals give mainly the coupling products (1,2-diphenylethane and 1,5-hexadiene, respectively) together with small amounts of byproducts derived from the hydrogen abstraction from a solvent (toluene and propene, respectively) as shown in Table 5-2. The carbanion ligand in $[RCo(bpy)_2]^+$ may react readily with R'Br to produce the more stable carbanion ligand, and $[R'Co(bpy)_2]^+$ thus formed may undergo the coupling reaction with R'Br to yield R'-R' and $[Co(bpy)_2Br]^+$. $[RCo(bpy)_2Br]^+$ may also participate in a cross coupling reaction with R'Br, which is shown by the broken line in Scheme 5-2, yielding R-R' as a minor byproduct (ethylbenzene, propylbenzene, 1-butene, and 1-pentene for the cis-$[Me_2Co(bpy)_2]^+$-$PhCH_2Br$, cis-$[Et_2Co(bpy)_2]^+$-$PhCH_2Br$, cis-$[Me_2Co(bpy)_2]^+$-$C_3H_5Br$, and cis-$[Et_2Co(bpy)_2]^+$-$C_3H_5Br$ systems, respectively). According to Scheme 5-2, the stoichiometry of the photoredox reaction of cis-$[R_2Co(bpy)_2]^+$ with R'Br is 1 : 3 (eq 5), in contrast with the case in Scheme 5-1.

The photoredox reaction of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ with allyl bromide (Scheme 5-3) is the most complicated case, where the photocleavage reaction occurs to give $[PhCH_2Co(bpy)_2]^+$, which can undergo the exchange, coupling, and cross-coupling reactions with comparable rates, because of similar stabilities between the benzyl and allyl anions to yield 1,2-diphenylethane and 1,5-hexadiene as the homo-coupling products as well as 4-phenyl-1-butene as the cross-coupling product (Table 5-2). According to Scheme 5-3, the stoichiometry is 1 : 1 as the case of Scheme 5-1.

In conclusion, the photocleavage of the cobalt-carbon bond of cis-dialkylcobalt(III) complexes produces monoalkylcobalt(II) complexes as reactive intermediates in which the alkyl group has carbanion character, inducing the facile reduction of benzyl and allyl bromides to yield coupling and cross coupling products depending on the stabilities of the carbanion ligands.

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approximately the same as that in the presence of oxygen (Fig. 5-2)

(26) All the complexed ligand signals in $[Co(bpy)_3]^+$ appeared as broad singlets in the $^1H$ NMR spectrum; $\delta$ referenced to an internal standard $Me_4Si$: 39(5,5'-H), 44(3,3'-H), 62(4,4'-H), and 108 ppm (6,6'-H).

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benzyl or allyl bromide; when the concentration of benzyl or allyl bromide was increased from 7.7 x $10^{-2}$ to 0.24 M, the initial rate monitored by $^1$H NMR in $CD_3CN$ as shown in Fig. 5-2 was not changed appreciably.

(41) In the plots of $(\Phi - \Phi_0)^{-1}$ vs. $[PhCH_2Br]^{-1}$ and $[C_3H_5Br]^{-1}$ (the correlation coefficients are 0.98 and 0.99, respectively), the datum at the lowest concentration of benzyl or allyl bromide in Fig. 5-5 was excluded since the experimental error in the $(\Phi - \Phi_0)^{-1}$ value is the largest.

(42) In the case of cis-$[Et_2Co(bpy)_2]^+$ which has a β-hydrogen, a β-elimination pathway is also involved in the photocleavage of the cobalt-carbon bond (eq 4).

(43) In the photochemical steps in eq 7, the β-elimination pathway may also give the same species as the homolytic pathway by the facile reaction with R'Br in the presence of water, since the β-elimination pathway may be regarded as β-hydrogen transfer between the geminate radical pair following the homolytic cleavage of the cobalt-carbon bond; see: Tsou, T.; Loots, M.; Halpern, J. J. Am. Chem. Soc. **1982**, 104, 623. However, the detailed mechanism is not clear at present.

# Chapter 6 REDOX REACTIONS OF cis-DIALKYLCOBALT(III) COMPLEXES WITH BENZYL AND ALLYL BROMIDES, INDUCED BY THERMAL CLEAVAGE OF THE COBALT-CARBON BOND

The thermal cleavage of the cobalt-carbon bond of cis-dialkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]^+$ (R = Me, Et, $PhCH_2$; bpy = 2,2'-bipyridine), was enhanced by the presence of benzyl and allyl bromide, inducing the C-C bond formation to yield mainly 1,2-diphenylethane and 1,5-hexadiene, respectively. In the cis-$[(PhCH_2)_2Co(bpy)_2]^+$-allyl bromide system, a comparable amount of the cross-coupling product (4-phenyl-1-butene) was obtained together with the homo-coupling products (1,2-diphenylethane and 1,5-hexadiene). The enhancement of the thermal cleavage of the cobalt-carbon bond of cis-$[R_2Co(bpy)_2]^+$ by the reactions with benzyl and allyl bromides is caused by the high reactivity of the carbanion ligand of $[RCo(bpy)_2]^+$ produced by the homolytic cleavage of the cobalt-carbon bond of cis-$[R_2Co(bpy)_2]^+$, which undergoes the exchange, coupling, and cross-coupling reactions with benzyl and allyl groups of the bromides. Based on the kinetics and the activation parameters, the cobalt-carbon bond dissociation enthalpy of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ has been estimated to be 92 kJ $mol^{-1}$.

## 6-1 Introduction

The mechanisms of thermal decomposition of organo-transition-metals[1,2] as well as the bond dissociation energies of the metal-carbon bonds[3] have been subjects of much interest, since the application of transition-metal reagents to organic, organometallic, and biochemical synthesis, stoichiometric or catalytic, requires the cleavage of metal-carbon bonds. Significant attention has been devoted to mono-organocobalt complexes, which relate to the naturally occurring coenzyme, vitamin $B_{12}$.[4-8] Although cobalt-carbon bonds of many mono- and di-organocobalt(III) complexes are thermally stable at moderate temperatures, the cleavage of cobalt-carbon bonds is known to be enhanced significantly by redox reactions with organic and inorganic oxidants.[9-13] The cleavage of cobalt-carbon bonds of di-organocobalt(III) complexes, which has been much less studied than mono-organocobalt(III) complexes, is of particular interest, since the cleavage of the cobalt-carbon bond may produce coordinately unsaturated mono-organocobalt(II) complexes which may be much more reactive than di-organocobalt complexes.[14,15]

We have previously reported that the photocleavage of cobalt-carbon bonds of cis-dialkylcobalt(III)complexes, cis-$[R_2Co(bpy)_2]^+$ (R = Me, Et, $PhCH_2$; bpy = 2,2'-bipyridine), induces C-C bond formation via the redox reactions with benzyl and ally bromides to yield 1,2-diphenylethane and 1,5-hexadiene, respectively, as the main products.[16] In this study, we report that the thermal cleavage of the cobalt-carbon bond of cis-$[R_2Co(bpy)_2]^+$ also induces the C-C bond formation in redox reactions with benzyl and allyl bromides. The present study provides a nice opportunity to compare the thermal and photochemical redox reactions of cis-dialkylcobalt(III) complexes with organic halides, revealing both the common and the different aspects in mechanisms between the thermal and photochemical redox reactions.

## 6-2 Experimental

**Materials.** cis-Dialkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]^+$ (R = Me, Et, $PhCH_2$), were prepared as described previously (see Chapters 1 and 3).[16,17] Both $[Co(bpy)_3](ClO_4)_2$ and $[Co(bpy)_3]ClO_4$ were prepared by following the literature method.[18] Benzyl or allyl bromide obtained from Wako Pure Chemicals was washed with a 5% aqueous $NaHCO_3$ solution and water successively. After the solution was dried with $MgSO_4$, it was fractionally distilled in the dark under reduced pressure before use. Reagent grade acetonitrile was purified by the standard procedure,[19] followed by redistillation from calcium hydride. Acetonitrile-$d_3$ was stirred with freshly activated Molecular Sieve 4A (wako Pure Chemicals) and then transferred in vacuum. Other reagents used for the product analyses were obtained commercially.

**Analytical Procedure.** Thermal decomposition of cis-$[R_2Co(bpy)_2]^+$ was carried out in a pyrex tube (8 mm i.d.) which contained an MeCN solution (0.5 $cm^3$) of cis-$[R_2Co(bpy)_2]^+$ ($1.0 \times 10^{-2}$ M). The solution in the tube was thoroughly degassed by the repeated freeze-pump-thaw cycles before sealing. The top of sealed tube was covered with a reflux condenser and the bottom containing the solution was immersed in an oil bath which was thermostated at 353 K. After the reaction for 52 h, an atmospheric pressure of nitrogen was introduced to the tube, and the gaseous products were analyzed by GLC using a Unibeads 1S column.

The redox reactions of cis-$[R_2Co(bpy)_2]^+$ with benzyl and allyl bromides were monitored using a Japan Electron Optics JNM-PS-100 $^1H$ NMR spectrometer (100 MHz). Typically, cis-$[R_2Co(bpy)_2]^+$ ($5.0 \times 10^{-2}$ mol) and benzyl bromide ($5.0 \times 10^{-2}$ mol) was added to an NMR tube which contained 0.5 $cm^3$ $CD_3CN$. After the solution was degassed, the sealed NMR tube with a reflux condenser was immersed in an oil bath at 353 K. The NMR spectra were measured periodically at 298 K and the products were identified by comparing the spectra with those of authentic samples. The conversion of cis-$[R_2Co(bpy)_2]^+$ to $[Co(bpy)_3]^{2+}$ was confirmed by the appearance of the down field signals of the 2,2'-bipyridine ligand.[18] The organic products were analyzed by GLC using an OV-17 column.

**Kinetic Measurements.** Kinetic data were obtained by using a Union SM-401 spectrophotometer equipped with thermostated cell holders. Reaction rates were determined by the disappearance of the absorption band due to cis-$[R_2Co(bpy)_2]^+$ in MeCN ($\lambda_{max}$ = 472, 495, 502 nm for R = Me, Et, $PhCH_2$, respectively) under degassed conditions using a Schlenk tube equipped with a side-arm fused to a square cuvette (1 or 10 mm i.d.). All the data followed pseudo-first-order kinetics, from which rate constants were determined by least-squares curve fitting using an NEC 9801VM microcomputer.

## 6-3 Results and Discussion

**Thermal Decomposition of cis-$[R_2Co(bpy)_2]^+$.** cis-Dialkylcobalt(III) complexes are stable in MeCN at 298 K. When the temperature was raised to 353 K, cis-$[R_2Co(bpy)_2]^+$ decomposed slowly to undergo the dealkylation reaction. The product distributions are shown in Table 6-1, together with the data of the corresponding photodecomposition[16] for comparison. The product distributions between thermal and photodecomposition of cis-$[R_2Co(bpy)_2]^+$ are similar to each other, except for the ratio of the coupling products of the alkyl groups. For example, both the thermolysis and photolysis of cis-$[Me_2Co(bpy)_2]^+$ give methane and ethane, but the mol ratio of ethane to

**Table 6-1.** Product Distributions of Thermal and Photochemical Decomposition of *cis*-$[R_2Co(bpy)_2]^+$ under Degassed Conditions in Acetonitrile

| *cis*-$[R_2Co(bpy)_2]^+$ | Reaction | Time | Conversion | Product distribution |
|---|---|---|---|---|
| | | h | % | % |
| R=Me[a)] | $\Delta^{c)}$ | 52 | 22 | $CH_4$(66), $C_2H_6$(34) |
| | $h\nu^{d)}$ | 15 | 91 | $CH_4$(91), $C_2H_6$(9) |
| R=Et[a)] | $\Delta^{c)}$ | 52 | 79 | $C_2H_6$(67), $C_2H_4$(24), $C_4H_{10}$(9) |
| | $h\nu^{d)}$ | 15 | 76 | $C_2H_6$(73), $C_2H_4$(27), $C_4H_{10}$(trace) |
| R=$PhCH_2$[b)] | $\Delta^{c)}$ | 5 | 57 | $PhCH_3$(94), $PhC_2H_4Ph$(6), |
| | $h\nu^{d)}$ | 50 | 43 | $PhCH_3$(47), $PhC_2H_4Ph$(51) |

a) $1.0\times10^{-2}$ mol dm$^{-3}$. b) $4.5\times10^{-2}$ mol dm$^{-3}$. c) Thermolysis at 353 K. d) Photolysis was carried out under irradiation with visible light from a Xenon lamp through a Toshiba glass filter (O-36) which transmits light of $\lambda>360$ nm at 298 K (Ref. 16).

methane in the thermolysis at 353 K (34/66) is significantly larger than that in the photolysis at 298 K (9/91). In the case of cis-$[Et_2Co(bpy)_2]^+$ as well, an appreciable amount of the coupling product (butane) is obtained only in the thermolysis (Table 6-1). On the other hands, thermolysis of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ gives a smaller amount of the coupling product (1,2-diphenylethane) than the photolysis (Table 6-1).

Such product distributions between the thermolysis and photolysis may be explained by Scheme 6-1, where both the

**Scheme 6-1**

$$\begin{tikzcd} & & R^{\bullet} \\ \underline{cis}\text{-}[R_2Co(bpy)_2]^+ \arrow[r, "\Delta \text{ or } h\nu"] & (R^{\bullet}\ [RCo(bpy)_2^{+}]) \arrow[ur, "a"] \arrow[r, "b"] \arrow[dr, "c"] & R\text{-}R \\ & & RH + R(\text{-}H) \end{tikzcd}$$

thermolysis and photolysis of cis-$[R_2Co(bpy)_2]^+$ results in the homolytic cleavage of the cobalt-carbon bond to produce a geminate radical pair ($R^{\bullet}$ $[RCo(bpy)_2]^+$) which undergoes (a) free radical reactions out of the cage to yield RH and R-R, (b) a coupling reaction in the cage to yield R-R, or (c) a β-hydrogen transfer in the cage to give RH and R(-H) with a 1 : 1 ratio when the alkyl group contains a β hydrogen. Such a homolytic cleavage of the Co-C bond in the photolysis of cis-$[R_2Co(bpy)_2]^+$ has been confirmed by the detection of alkyl radicals in the ESR measurements at 77 K.[16] In the case of R = Me or Et, the alkyl radical formed in the geminate radical pair may be reactive enough to undergo the coupling reaction in the cage at a high temperature (e.g., 353 K) to yield more coupling product R-R than the case of photolysis at 298 K. On the other hand, the activation barrier of hydrogen abstraction by benzyl radical from a solvent is known to be higher than that of bimolecular coupling reaction of benzyl radicals,[20] Thus, in the case of cis-$[(PhCH_2)_2Co(bpy)_2]^+$, the former becomes a major process in the thermolysis at 353 K to yield mainly toluene (Table 6-1). Although the stepwise homolytic processes (Scheme 6-1) appear to account for the product distribution in both the thermal and photochemical decomposition of cis-$[R_2Co(bpy)_2]^+$ in the absence and presence of benzyl or allyl bromide as discussed later in more detail, the present conclusion that the coupling R-R and olefin R(-H) products arise via the homolytic cleavage of the cobalt-carbon bond must be accepted with reservation, since the concerted processes for the reductive coupling and β-elimination pathways are difficult to distinguish from the stepwise, homolytic processes.[21-24]

**Redox Reactions of cis-$[R_2Co(bpy)_2]^+$ with Benzyl and Allyl Bromides.** When the thermal decomposition of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ is carried out in the presence of benzyl bromide at 353 K, the rate is enhanced significantly as shown in Fig. 6-1, where the reaction is completed in 20 min. In addition, the product distribution is changed drastically from toluene as a main product in the absence of benzyl bromide to 1,2-diphenylethane in the presence of benzyl bromide (Fig. 6-1). The approximate stoichiometry of the reaction is given by eq 1, which is the same as the corresponding photochemical reaction.[16]

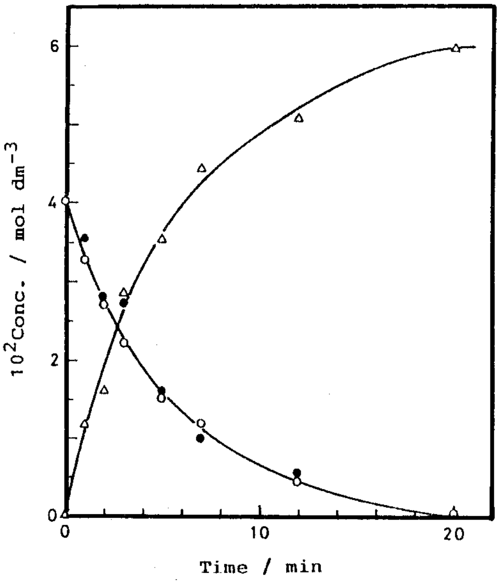


Fig. 6-1. Time course of the thermal reaction of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ (4.0 x $10^{-2}$ M) with benzyl bromide (4.0 x $10^{-2}$ M) under a degassed condition in $CD_3CN$ at 353 K; cis-$[(PhCH_2)_2Co(bpy)_2]^+$ (○), $PhCH_2Br$ (●), and $PhC_2H_4Ph$ (△).

$$\text{cis-}[(PhCH_2)_2Co(bpy)_2]^+ + PhCH_2Br \xrightarrow{\Delta} PhC_2H_4Ph + [Co(bpy)_2Br]^+ \qquad (1)$$

Thermolysis rate of cis-$[Me_2Co(bpy)_2]^+$ is also enhanced by the presence of benzyl bromide, although the rate is much slower than that of cis-$[(PhCH_2)_2Co(bpy)_2]^+$, as shown in Fig. 6-2. The presence of benzyl bromide suppresses completely the formation of methane observed in the absence of benzyl bromide (Table 6-1), instead methyl bromide is formed as well as 1,2-diphenylethane as a main product, while the ethane formation is not suppressed completely (Fig. 6-2). The apparent stoichiometry of the reaction between cis-$[Me_2Co(bpy)_2]^+$ and benzyl bromide is 1 : 2.3. Such a stoichiometry in Fig. 6-2 may be explained by considering the occurrence of two different reactions; one is the same as the corresponding photochemical reaction (eq 2),[16] where cis-$[Me_2Co(bpy)_2]^+$ reacts with three equivalent amounts of benzyl bromide to yield 1,2-diphenylethane and methyl bromide, and the other is the reaction with a 1 : 1 stoichiometry to yield ethane (eq 3), where benzyl bromide may be reduced by $[Co(bpy)_2]^+$ following the coupling reaction in the cage (Scheme 6-1b).

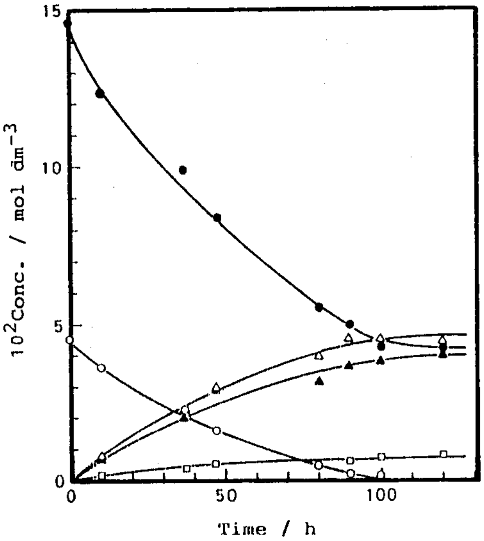


Fig. 6-2. Time course of the thermal reaction of cis-$[Me_2Co(bpy)_2]^+$ ($4.5 \times 10^{-2}$ M) with benzyl bromide ($1.46 \times 10^{-1}$ M) under a degassed condition in $CD_3CN$ at 353 K; cis-$[Me_2Co(bpy)_2]^+$ (○), $PhCH_2Br$ (●), MeBr (△), $PhCH_2H_4Ph$ (▲), and $C_2H_6$ (□).

$$\text{cis-}[Me_2Co(bpy)_2]^+ + 3PhCH_2Br \longrightarrow PhC_2H_4Ph + 2MeBr + [Co(bpy)_2Br]^+ \quad (2)$$

$$\text{cis-}[Me_2Co(bpy)_2]^+ + PhCH_2Br \longrightarrow PhC_2H_4Ph + C_2H_6 + [Co(bpy)_2Br]^+ \quad (3)$$

The occurrence of two different reactions (eqs 2 and 3) can also account for the product distribution in the thermolysis of cis-$[Et_2Co(bpy)_2]^+$ in the presence of benzyl bromide (Fig. 6-3), where one mol of cis-$[Et_2Co(bpy)_2]^+$ reacts with 1.4 mol of benzyl bromide to yield 1,2-diphenylethane, ethyl bromide, and butane with small amounts of toluene and ethylene.

Similar results are obtained in the thermolysis of cis-$[R_2Co(bpy)_2]^+$ in the presence of allyl bromide. Table 6-2 summarizes the product distribution including the minor products. In the reactions of cis-$[Me_2Co(bpy)_2]^+$ and cis-[$Et_2$Co-

$(bpy)_2]^+$ with benzyl and allyl bromides, the coupling products of the organic groups of the bromides (1,2-diphenylethane and 1,5-hexadiene, respectively) are obtained, and small amounts of cross-coupling products between the alkyl group of cis-$[R_2Co(bpy)_2]^+$ and the organic group of the bromides (e.g., ethylbenzene in the cis-$[Me_2Co(bpy)_2]^+$-benzyl bromide system) are formed as well as the products derived from hydrogen abstraction by benzyl and allyl radicals from a solvent (i.e., toluene and propene, respectively). The stoichiometry of these reactions is between 1 and 3 on the degree of the contribution of two different reactions (eqs. 2 and 3). In the case of the reactions of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ with benzyl bromide, however, the stoichiometry is 1 : 1 (eq 1) to yield mainly the homo-coupling product (1,2-diphenylethane) together with a small amount of toluene. When benzyl bromide is replaced by allyl bromide in the reaction with cis-$[(PhCH_2)_2Co(bpy)_2]^+$, the cross-coupling product between benzyl and allyl group, i.e., 4-phenyl-1-butene are formed together with the homo-coupling products (1,2-diphenylethane and 1,5-hexadiene) as shown in Table 6-2. Thus, the thermolysis of all the cis-

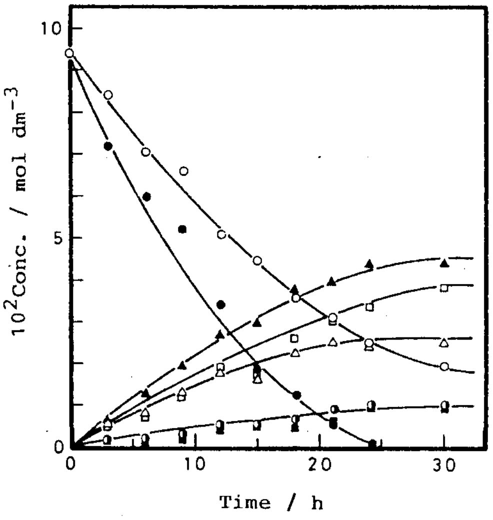


**Fig. 6-3.** Time course of the thermal reaction of cis-$[Et_2Co(bpy)_2]^+$ ($9.4 \times 10^{-2}$ M) with benzyl bromide ($9.4 \times 10^{-2}$ M) under a degassed condition in $CD_3CN$ at 353 K; cis-$[Et_2Co(bpy)_2]^+$ (○), $PhCH_2Br$ (●), EtBr (△), $PhC_2H_4Ph$ (▲), $C_4H_{10}$ (□), $C_2H_4$ (■), and $PhCH_3$ (◑).

**Table 6-2.** Product Yields in the Thermal Reactions of *cis*-$[R_2Co(bpy)_2]^+$ with Benzyl and Allyl Bromides under Degassed Conditions in Acetonitrile at 353 K

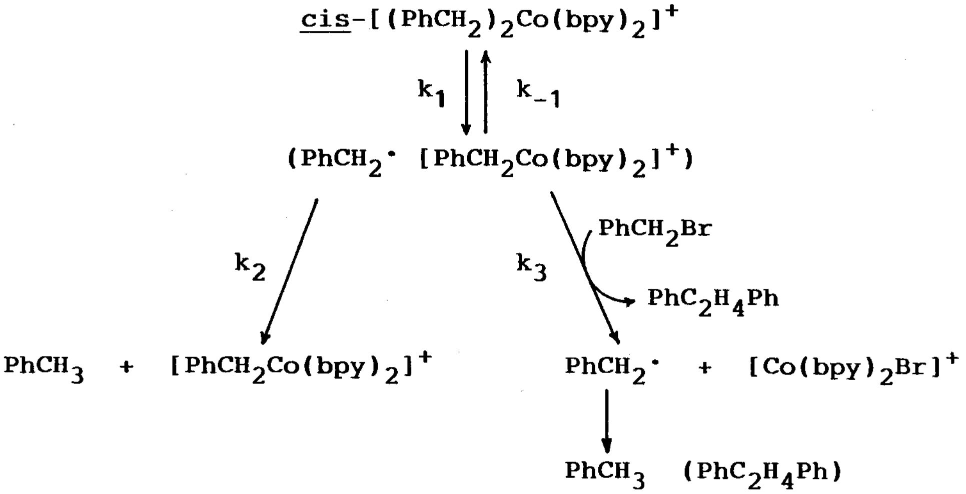
| *cis*-$[R_2Co(bpy)_2]^{+\,a)}$ | $R'Br^{a)}$ | Time<br>h | Product<br>%$^{b)}$ |
|---|---|---|---|
| R=Me ($4.5\times10^{-2}$) | R'=$PhCH_2$ ($1.46\times10^{-1}$) | 103 | $PhC_2H_4Ph$(49), $PhCH_3$(1.0), $C_2H_6$(33), MeBr(98) |
| R=Et ($9.6\times10^{-2}$) | R'=$PhCH_2$ ($9.6\times10^{-2}$) | 54 | $PhC_2H_4Ph$(48), $PhCH_3$(2.1), $C_4H_{10}$(38), $C_2H_4$(10), EtBr(23) |
| R=Me ($7.1\times10^{-2}$) | R'=$C_3H_5$ ($7.1\times10^{-2}$) | 100 | $C_6H_{10}$(48), $C_3H_6$(3.3), $C_4H_8$(2.2), $C_2H_6$(32), MeBr(98) |
| R=Et ($9.5\times10^{-2}$) | R'=$C_3H_5$ ($9.5\times10^{-2}$) | 30 | $C_6H_{10}$(49), $C_3H_6$(1.8), $C_5H_{10}$(2.2), $C_4H_{10}$(37), $C_2H_4$(10), EtBr(22) |
| R=$PhCH_2$ ($4.0\times10^{-2}$) | R'=$PhCH_2$ ($4.0\times10^{-2}$) | 0.5 | $PhC_2H_4Ph$(147), $PhCH_3$(5.4) |
| R=$PhCH_2$ ($4.0\times10^{-2}$) | R'=$C_3H_5$ ($4.0\times10^{-2}$) | 0.5 | $PhC_2H_4Ph$(86), $C_6H_{10}$(35), $PhC_4H_7$(17), $PhCH_3$(12), $C_3H_6$(4.3) |

a) The concentrations of the reactants in parentheses. b) Based on the cobalt complex.

dialkylcobalt(III) complexes in the presence of benzyl or allyl bromide results in the C-C bond formation to yield the homo- or cross-coupling products of benzyl and allyl groups as the main products together with small amounts of products derived from hydrogen abstraction by benzyl or allyl radical from a solvent.

**Kinetics and Mechanism.** The rate of thermal decomposition of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ at 353 K is the fastest among *cis*-$[R_2Co(bpy)_2]^+$, and decreases in the order R = $PhCH_2$ > Et > Me. The detailed kinetic study has been limited to the thermolysis of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, since only *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ decomposed at measurable rates at relatively low temperatures (*e.g.*, 323 K). The decomposition rates of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ in both the absence and presence of benzyl bromide obeyed the pseudo-first-order kinetics, and the observed rate constant was increased significantly by the presence of benzyl bromide. Such enhancement of the rate by the presence of benzyl bromide may be explained by Scheme 6-2, where the

**Scheme 6-2**



cleavage of the cobalt-carbon bond ($k_1$ in Scheme 6-2) occurs to give a geminate radical pair ($PhCH_2^\bullet$ $[PhCH_2Co(bpy)_2]^+$). In the absence of benzyl bromide, the overall decomposition rate may be much lowered owing to the facile recombination of benzyl radical with $[PhCH_2Co(bpy)_2]^+$ in the cage ($k_{-1}$).[24] The recombination between free benzyl radical and $[PhCH_2Co(bpy)_2]^+$, which are escaped from the cage, may be neglected compared with the recombination of the geminate radical pair in Scheme 6-2, since the former unimolecular process may be much faster than the latter bimolecular process. Applying the steady-state approximation to the intermediate ($PhCH_2^{\cdot}$ $[PhCH_2Co(bpy)_2]^+$) in Scheme 6-2, the observed rate constant $k_0$ in the absence of benzyl bromide is expressed by eq 4, where $k_2$ is the rate constant for hydrogen

$$k_0 = k_1k_2/(k_{-1} + k_2) \tag{4}$$

abstraction by benzyl radical from a solvent to yield toluene. Since the recombination process ($k_{-1}$) may be highly exothermic, $k_{-1}$ may be much larger than $k_2$; $k_{-1} \gg k_2$, when eq 4 is reduced to eq 5.

$$k_0 = k_1k_2/k_{-1} \tag{5}$$

The benzyl group of $[PhCH_2Co(bpy)_2]^+$ produced by the homolytic cleavage of the cobalt-carbon bond of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ is regarded as the benzyl anion ligand on the basis of the ESR spectrum of $[PhCH_2Co(bpy)_2]^+$ observed in the photolysis of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ at 77 K.[15,16] Thus, in the presence of benzyl bromide, the benzyl anion ligand of $[PhCH_2Co(bpy)_2]^+$ may undergo the facile coupling reaction with benzyl bromide ($k_3$) to yield 1,2-diphenylethane as the case of the photoredox reaction of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ with benzyl bromide.[16] Then, the observed rate constant $k_{obs}$ in the presence of benzyl bromide may be given by eq 6. Under the

$$k_{obs} = \frac{k_1(k_2 + k_3[PhCH_2Br])}{k_{-1} + k_2 + k_3[PhCH_2Br]} \tag{6}$$

condition that $k_{-1} \gg k_2$, from eqs 5 and 6 is derived eq 7.

$$\frac{1}{k_{obs} - k_0} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_3[PhCH_2Br]} \tag{7}$$

The validity of eq 7 is confirmed by the linear plots between $(k_{obs} - k_0)^{-1}$ and $[PhCH_2Br]^{-1}$ at various temperatures as shown in Fig. 6-4. The rate constant $k_1$ and $k_3k_1/k_{-1}$ at 323 are obtained as $7.7 \times 10^{-4}$ $s^{-1}$ and $1.1 \times 10^{-2}$ $M^{-1}$ $s^{-1}$, respectively. The rate constant $k_{-1}$ for the cage recombination of an alkyl radical and cob(II)alamin has been reported to be $1.39 \times 10^9$ $s^{-1}$.[5b] By using this value, the rate constant $k_3$ for the redox reaction of $[PhCH_2Co(bpy)_2]^+$ with benzyl bromide is estimated as

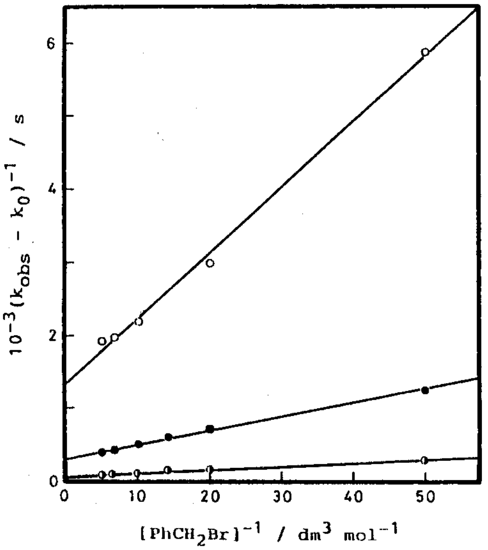


Fig. 6-4. Plots of $(k_{obs} - k_0)^{-1}$ vs. $[PhCH_2Br]^{-1}$ for the thermal reaction of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ ($1.1 \times 10^{-2}$ M) with benzyl bromide in MeCN at 323 (○), 338 (●), and 353 K (◑); see eq 7.

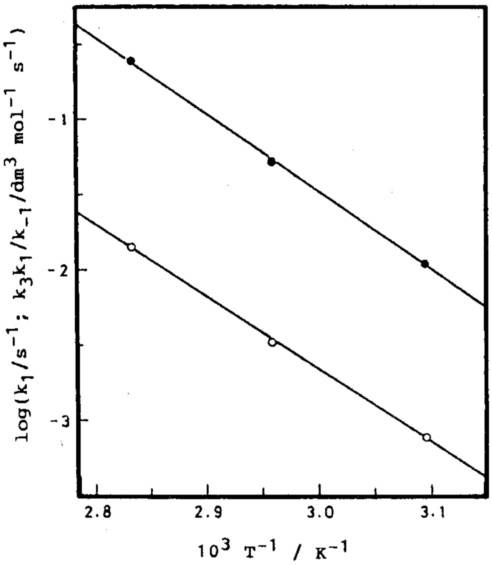
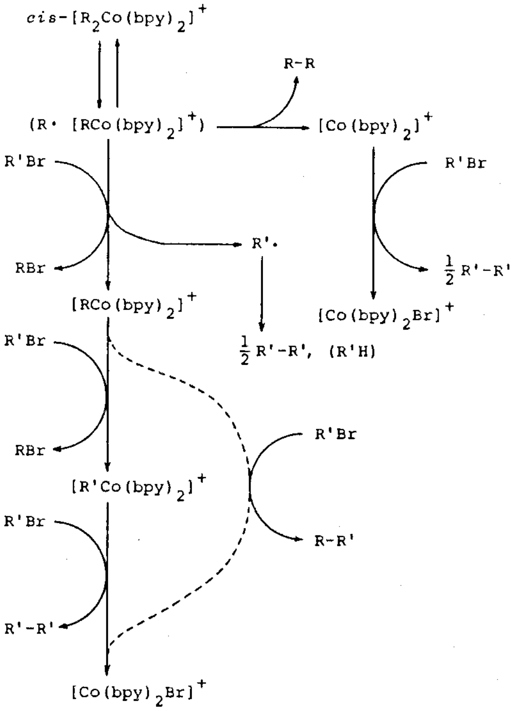


Fig. 6-5. Arrhenius plots of $k_1$ (○) and $k_3k_1/k_{-1}$ (●) for the thermal reaction of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ with benzyl bromide in MeCN.

$2.0 \times 10^{10}$ $M^{-1}$ $s^{-1}$, which is identical with the diffusion rate constant in MeCN.[25] Arrhenius plots of both $k_1$ and $k_3k_1/k_{-1}$ give good straight lines with similar slopes to each other (Fig. 6-5), from which the values of $\Delta H_1^‡$ and $\Delta H_3^‡ + \Delta H_1$ are obtained as 92 ± 4 and 96 ± 4 kJ $mol^{-1}$, respectively.

Thus, the cobalt-carbon bond dissociation enthalpy $\Delta H_1$ is estimated as 92 ± 4 kJ $mol^{-1}$ by assuming that $\Delta H_{-1}^‡ = 0$, which is a reasonable approximation for the highly exothermic radical recombination process.[5,6,24] The $\Delta H_1$ value obtained here is similar to those of many organocobalt(III) complexes reported in the literatures.[3a,5,6] The $\Delta H_3^‡$ value may also be estimated as 4 ± 4 kJ $mol^{-1}$ from the values of $\Delta H_1$ and $\Delta H_3^‡ + \Delta H_1$. Such a small $\Delta H_3^‡$ value is compatible with the rate constant $k_3$ being diffusion controlled as described above. The facile reaction of $[PhCH_2Co(bpy)_2]^+$ with benzyl bromide may be responsible for the efficient C-C bond formation from cis-$[R_2Co(bpy)_2]^+$ and benzyl bromide, induced by the thermal cleavage of the cobalt-carbon bond. A cobalt-containing product $[Co(bpy)_2Br]^+$, which may be the initial product by the reaction of $[PhCH_2Co(bpy)_2]^+$ with benzyl bromide as confirmed by the ESR spectrum in the photolysis of the cis-$[R_2Co(bpy)_2]^+$-benzyl bromide system at 77 K,[16] is converted to $[Co(bpy)_3]^{2+}$ being the most stable form among the mono-, bis-, and tris(2,2'-bipyridine)cobalt(II) complexes (see Experimental).[26] On the other hand, benzyl radicals produced by the homolytic cleavage of the cobalt-carbon bond of cis-$[R_2Co(bpy)_2]^+$ give 1,2-diphenylethane and a small amount of toluene (Table 6-2).[27] According to Scheme 6-2, the stoichiometry of the thermal reaction of cis-$[R_2Co(bpy)_2]^+$ with benzyl bromide is 1 : 1, agreeing with the observation in Fig. 6-1 (eq 2).

**Scheme 6-3**



When the alkyl groups of the reactants (cis-$[R_2Co(bpy)_2]^+$ and R'Br) are different, the reaction scheme becomes more complicated as shown in Scheme 6-3, where the thermolysis of cis-$[R_2Co(bpy)_2]^+$ (R = Me and Et) also leads to the homolytic cleavage of the cobalt-carbon bond to produce the geminate radical pair (R• $[RCo(bpy)_2]^+$). In the presence of R'Br (R' = $PhCH_2$ and $C_3H_5$), the alkyl radical (Me• and Et•) may be converted to the more stable radical ($PhCH_2$• and $C_3H_5$•) by the reaction with R'Br as confirmed by the ESR spectrum in the photolysis of the cis-$[R_2Co(bpy)_2]^+$-R'Br system at 77 K.[16] The benzyl and allyl radicals give the homo-coupling products (1,2-diphenylethane and 1,5-hexadiene, respectively) with small amounts of by-products derived from the hydrogen abstraction from a solvent (toluene and propene, respectively) as shown in Table 6-2. The carbanion ligand in $[RCo(bpy)_2]^+$ may react readily with R'Br to produce the more stable carbanion ligand, and $[R'Co(bpy)_2]^+$ thus formed by the exchange reaction may undergo the homo-coupling reaction with R'Br to yield R'-R' and $[Co(bpy)_2Br]^+$, while $[RCo(bpy)_2]^+$ may proceed also to the cross-coupling reaction with R'Br, which is shown by the broken line in Scheme 6-3, yielding R-R' as a minor product in Table 6-2 (ethylbenzene, propylbenzene, 1-butene, and 1-pentene for the cis-$[Me_2Co(bpy)_2]^+$-$PhCH_2Br$, cis-$[Et_2Co(bpy)_2]^+$-$PhCH_2Br$, cis-

$[Me_2Co(bpy)_2]^+$-$C_3H_5Br$, and *cis*-$[Et_2Co(bpy)_2]^+$-$C_3H_5Br$ systems, respectively). In this case, the stoichiometry of the reaction of *cis*-$[R_2Co(bpy)_2]^+$ with R'Br is 1 : 3 (eq 2), in contrast with the case in Scheme 6-2.

On the other hand, a coupling reaction in the geminate radical pair produced by the homolytic cleavage of the cobalt-carbon bond of *cis*-$[R_2Co(bpy)_2]^+$ may occur in the case of R = Me and Et to yield R-R and $[Co(bpy)_2]^+$ (Scheme 6-1b).[28] A β hydrogen transfer in the geminate radical pair may also occur in the case of R = Et which has a β hydrogen to yield ethane and ethylene as well as $[Co(bpy)_2]^+$ (Scheme 6-1c). In the presence of R'Br, such processes are suppressed by the facile reaction of $[RCo(bpy)_2]^+$ in the geminate radical pair with R'Br, but the reductive coupling process is not suppressed completely to yield R-R as well as $[Co(bpy)_2]^+$ which may readily reduce R'Br to give R'-R' (Scheme 6-3). Although the reaction mechanism for the reduction of R'Br by $[Co(bpy)_2]^+$ is less clear than that for the reduction of R'Br by $[RCo(bpy)_2]^+$, a likely pathway may be proposed as shown by eqs 8-10, since the facile reduction of

$$[Co(bpy)_2]^+ + R'Br \longrightarrow [Co(bpy)_2Br]^+ + R'\cdot \tag{8}$$

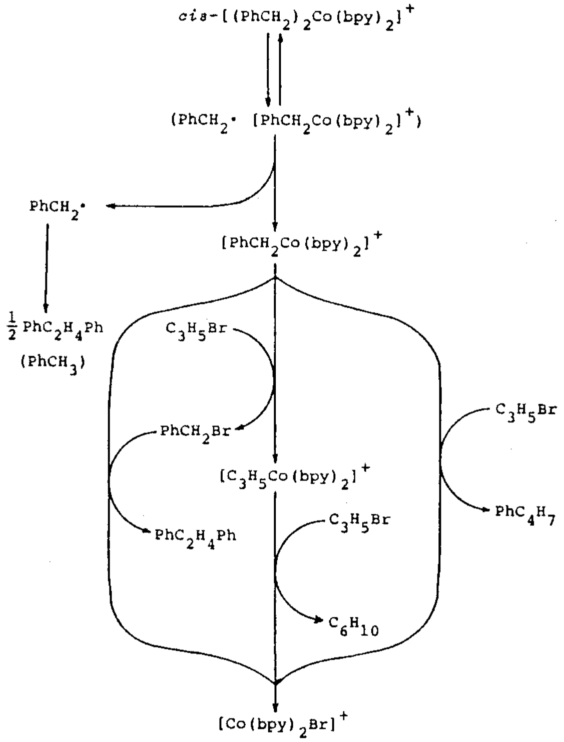
$$R'\cdot + [Co(bpy)_2Br]^+ \longrightarrow [R'Co(bpy)_2Br]^+ \tag{9}$$

$$R'\cdot + [R'Co(bpy)_2Br]^+ \longrightarrow R'\text{-}R' + [Co(bpy)_2Br]^+ \tag{10}$$

alkyl halides by Co(I) complexes is known to occur to yield alkyl radicals and Co(II) complexes eq 8,[29] and the coupling reaction of alkyl radicals may be enhanced in the presence of $[Co(bpy)_2Br]^+$ by the fast recombination with alkyl radicals (eq 9),[5,6,24] followed by the bimolecular homolytic displacement reactions (eq 10).[23,30] In this case, the stoichiometry is 1 : 1 (eq 3). Thus, these two different processes (eqs 2, 3) in Scheme 6-3 can account for the observed stoichiometry as well as the product distribution in the reaction with R'Br (Fig. 6-2, 6-3, and Table 6-2).

Although the thermal reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with allyl bromide (Scheme 6-4) is the most complicated case, the reaction scheme is identical with that for the corresponding photochemical reaction reported in the previous paper,[16] except that the thermal cleavage of the cobalt-carbon bond occurs instead of the photocleavage. The monobenzylcobalt(II) complex $[PhCH_2Co(bpy)_2]^+$ produced by the thermal cleavage of the cobalt-carbon bond of cis-$[(PhCH_2)_2Co(bpy)_2]^+$ can undergo the exchange, homocoupling, and cross-coupling reactions with comparable rates, because of similar stabilities between benzyl and allyl anions, yielding 1,2-diphenylethane and 1,5-hexadine as the homocoupling products as well as 4-phenyl-1-butene as the cross-coupling product (Table 6-2). The benzyl radicals which are also produced by the thermal cleavage of the cobalt-carbon bond give 1,2-diphenylethane and toluene by the bimolecular coupling reaction and the hydrogen abstraction from a solvent, respectively (Table 6-2).[27,31]

**Scheme 6-4**



In conclusion, the present study has demonstrated that monoalkylcobalt(II) complexes produced by the thermal cleavage of the cobalt-carbon bond of cis-dialkylcobalt(III) complexes are highly reactive in the reduction of benzyl and allyl bromides, undergoing the C-C bond formation to yield the homo- and cross-coupling products depending on the stability of the carbanion ligand. In addition to this process which is essentially the same as employed in the corresponding photoredox reaction, the reductive elimination process, where the pair of cobalt-carbon bonds of cis-$[R_2Co(bpy)_2]^+$ is cleaved thermally, is also involved in the reduction of benzyl and allyl bromides.

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(22) For a β-elimination pathway through a rate-determining homolysis, see: refs 3a, 5a and 23.

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(27) The coupling reaction of benzyl radicals to yield 1,2-diphenylethane may be enhanced by the presence of $[Co(bpy)_2Br]^+$ (see eqs 9, 10), which can account for the smaller yield of toluene in the presence of benzyl bromide (Table 6-2) than that in its absence (Table 6-1).

(28) A cobalt-containing product was identified as $[Co(bpy)_3]^+$ by comparing the NMR spectrum in the course of the thermolysis of *cis*-$[Et_2Co(bpy)_2]^+$ in $CD_3CN$ at 353 K with that of the authentic sample prepared by the reduction of $[Co(bpy)_3]^{2+}$ with $NaBH_4$ (see ref 18). The bis complex $[Co(bpy)_2]^+$ formed initially may be converted to the tris complex being the most stable form (ref 26).

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(31) Some benzyl radicals may be converted to allyl radicals by the reaction with allyl bromide as the case in Scheme 6-3, yielding 1,5-hexadiene and a small amount of propene (Table 6-2).

## CONCLUDING REMARKS

This thesis has reported mechanisms of both stoichiometric and catalytic cleavage of cobalt-carbon bonds with various oxidants and the associated carbon-carbon bond formation reactions, focusing on the redox reactivitis of dialkylcobalt(III) complexes.

The results and findings in this work are summarized as follows.

1. cis-Dialkylcobalt(III) complexes are readily oxidized by various one-electron oxidants such as tetracyanoethylene to produce cis-dialkylcobalt(IV) complexes, in which the facile cleavage of cobalt-carbon bond occurs. Alkyl radicals formed by the homolytic cleavage of cobalt-carbon bond of cis-dialkylcobalt(IV) complexes react with the remaining alkyl ligand in the cage to produce the coupling products of alkyl ligands in the absence of a radical scavenger.

2. cis-Dialkylcobalt(III) complexes show no reactivity towards dioxygen in acetonitrile. In the presence of catalytic amounts of redox coenzyme analogues, however, cis-dialkylcobalt(III) complexes are readily oxidized by dioxygen to yield both oxygenated and oxidative coupling products of alkyl ligands depending on the difference in alkyl ligands.

3. Electrophilic cleavage of cobalt-carbon bonds of various alkylcobalt(III) complexes with iodine in acetonitrile is shown to occur via electron-transfer from alkylcobalt(III) complexes to iodine.

4. Cobalt-carbon bonds of alkylcobalt(III) complexes are cleaved by the photochemical reactions with iodine in $CCl_4$. The radical chain mechanism and the contribution of electron transfer processes in the chain propagation steps are discussed.

5. Photocleavage of cobalt-carbon bonds of cis-dialkylcobalt(III) complexes induces the selective C-C bond formation from benzyl and allyl bromide to yield 1,2-diphenylethane and

1,5-hexadiene, respectively. The monoalkylcobalt(III) complexes formed by the photocleavage reactions are responsible for the selective reduction of benzyl and allyl bromides.

**6.** The thermal cleavage of cobalt-carbon bonds of *cis*-$[R_2Co(bpy)_2]^+$ also induces the selective C-C bonds formation from benzyl and allyl bromides to yield the coupling products of alkyl groups.

In each case, dialkylcobalt(III) complexes have much higher reactivities than monoalkylcobalt(III) complexes. Such high reactivities of *cis*-dialkylcobalt(III) complexes in both the stoichiometric and catalytic oxidation by various oxidants are ascribed to the stronger reducing abilities of *cis*-dialkylcobalt(III) complexes as compared with monoalkylcobalt(III) complexes. Formation of the coupling products of alkyl ligands upon the one-electron oxidation is characteristic of *cis*-dialkylcobalt(III) complexes.

As far as the homolytic cleavage in the absence of substrate is concerned, no significant difference is observed between monoalkylcobalt(III) and dialkylcobalt(III) complexes. In the presence of reducible substrates such as alkyl bromide, however, dialkylcobalt(III) complexes show much higher reactivity as compared with monoalkylcobalt(III) complexes, since monoalkylcobalt(II) complexes formed by thermal and photochemical homolytic cleavage of one cobalt-carbon bond of dialkylcobalt(III) complexes act as strong reductants.

Further developments of new redox reactions may be stimulated by utilizing the unique reactivities of dialkylcobalt(III) complexes described in this thesis.

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