Photoinduced Radical Chain Reactions between Alkylcobalt(III) Complexes and Iodine

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Cobalt–carbon bonds of various alkylcobalt(III) complexes, *cis*-$[CoR_2(bipy)_2]ClO_4$ (R = Me, Et, or $PhCH_2$; bipy = 2,2'-bipyridine), *trans*-$[CoMe_2(L)]$ (L = 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioximate), and $[CoR(Hdmg)_2(py)]$ (R = Me or Et; Hdmg = dimethylglyoximate; py = pyridine), are readily cleaved by iodine in carbon tetrachloride to yield alkyl iodides *via* photoinduced radical chain reactions with large quantum yields (*e.g.* $\Phi = 7.0 \times 10^3$) under low-energy irradiation (λ 517 nm). The rate-determining step in the radical chain reactions is suggested to be electron transfer from alkylcobalt(III) complexes to iodine atoms ($I^\bullet$) which are produced by the photodissociation 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 tetra-alkyltin compounds.

The mechanisms for electrophilic cleavage of cobalt–carbon bonds have been extensively studied in relation to enzymatic cleavage of such bonds.[1–7] In this context, direct photocleavage 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 photochemical cleavage of cobalt–carbon bonds by electrophiles. On the other hand, it has been well established that the photochemical cleavage of tetra-alkyltin compounds (SnR_4) by iodine proceeds *via* photoinduced radical chain reactions,[12] in which the Sn–C bonds are cleaved by electron transfer from SnR_4 to iodine atom produced by the photodissociation 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.* Φ 7.0 × 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 tetra-alkyltin compounds.

Experimental

Materials.—Alkylcobalt(III) complexes, *cis*-$[CoR_2(bipy)_2]ClO_4$ (R = Me, Et, or $PhCH_2$; bipy = 2,2'-bipyridine), *trans*-$[CoMe_2(L)]$ (L = 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioximate), and $[CoR(Hdmg)_2(py)]$ (R = Me or Et; Hdmg = dimethylglyoximate; py = pyridine) were prepared as described previously.[11,15] The purity of the complexes was checked by elemental analysis: *cis*-$[CoMe_2(bipy)_2]ClO_4$ (Found: C, 52.7; H, 4.6; N, 11.1. Calc. for $C_{22}H_{22}ClCoN_4O_4$: C, 52.8; H, 4.4; N, 11.2); *cis*-$[CoEt_2(bipy)_2]ClO_4$ (Found: C, 52.1; H, 5.1; N, 10.0. Calc. for $C_{24}H_{28}ClCoN_4O_4$: C, 52.7; H, 5.2; N, 10.2); *cis*-$[Co(CH_2Ph)_2(bipy)_2]ClO_4$ (Found: C, 62.0; H, 4.6; N, 8.5. Calc. for $C_{34}H_{30}ClCoN_4O_4$: C, 63.0; H, 4.7; N, 8.7); *trans*-$[CoMe_2(L)]$ (Found: C, 47.5; H, 7.7; N, 17.0. Calc. for $C_{13}H_{25}CoN_4O_2$: C, 47.6; H, 7.7; N, 17.1); $[CoMe(Hdmg)_2(py)]$ (Found: C, 43.8; H, 5.8; N, 18.3. Calc. for $C_{14}H_{22}CoN_5O_4$: C, 43.9; H, 5.8; N, 18.3); $[CoEt(Hdmg)_2(py)]$ (Found: C, 45.2; H, 6.0; N, 17.8. Calc. for $C_{15}H_{24}CoN_5O_4$: C, 45.4; H, 6.1; N, 17.6%).

Iodine was purified by vacuum sublimation three times. Potassium ferrioxalate, $K_3[Fe(C_2O_4)_3]$, 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, shaken with concentrated H_2SO_4 until there was no further colouration, 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 × 10^{-5} mol) was added to an n.m.r. tube containing a CCl_4 solution (0.30 cm^3) of a monoalkylcobalt(III) complex (3.0 × 10^{-5} mol). After the reactant solution in the n.m.r. tube had been mixed and deaerated with a stream of argon, the sample was irradiated with visible light from a Ushio model Ul-501 xenon lamp through a Toshiba glass filter cutting off the light below 460 nm. After completion of the reaction, the products were analyzed by using a Japan Electron Optics JNM-PS-100 ^1H n.m.r. spectrometer (100 MHz) as well as by using a Shimadzu GC-7A gas–liquid chromatograph equipped with a Gaskropak 54 column (2m). In the case of dialkylcobalt(III) complexes, the thermal reactions with iodine occurred slowly in CCl_4.[7] In addition, the solubilities of *cis*-$[CoR_2(bipy)_2]ClO_4$ in CCl_4 were much lower than those of monoalkylcobalt(III) complexes. Thus, as soon as an MeCN solution (5.0 × 10^{-2} cm^3) of a dialkylcobalt(III) complex (2.0 × 10^{-6} mol) was added to a Pyrex tube containing a CCl_4 solution (0.45 cm^3) of I_2 (2.0 × 10^{-6} mol), the sample was irradiated with 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 g.l.c. using a Unibeads 1-S column (1 m).

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 by visible light (λ > 460 nm). After the reaction was complete the absorption spectrum was measured using a Union SM-401 spectrophotometer. The amounts of cobalt(III) complex $[Co(Hdmg)_2(py)]I$ were determined from the absorption band at $\lambda_{max.}$ 450 nm (ε 1.35 × 10^3 dm^3 mol^{-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, ε = 9.03 × 10^2 dm^3 mol^{-1} cm^{-1})[13] under irradiation by monochromatized light (λ = 517

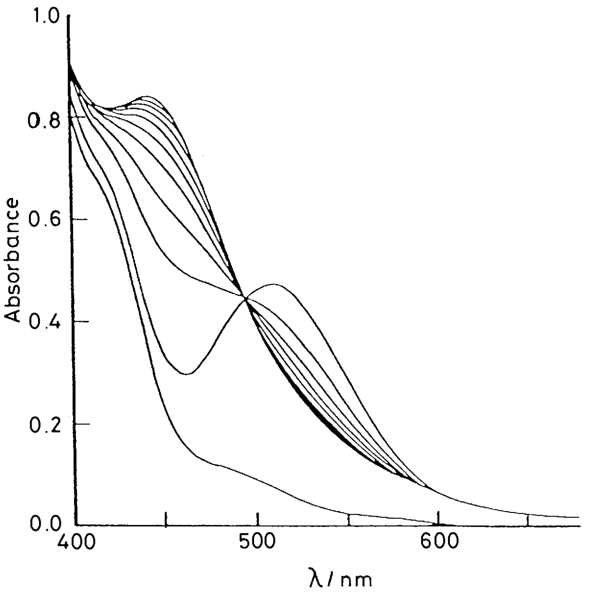


Figure 1. Electronic spectra observed in the photochemical reaction of $[CoMe(Hdmg)_2(py)]$ (8.0×10^{-4} mol dm^{-3}) with iodine (8.0×10^{-4} mol dm^{-3}) in carbon tetrachloride at 298 K under irradiation by monochromatized light (λ 517 nm). The lowest spectrum corresponds to that of $[CoMe(Hdmg)_2(py)]$ in the absence of iodine

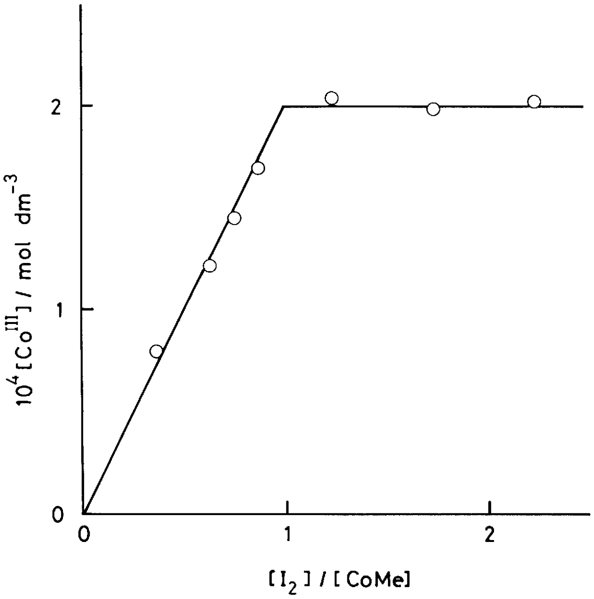


Figure 2. Plot of the concentration of $[Co(Hdmg)_2(py)]I$ formed in the photochemical reaction of $[CoMe(Hdmg)_2(py)]$ with iodine *vs.* the mol ratio of iodine to $[CoMe(Hdmg)_2(py)]$ (2.0×10^{-4} mol dm^{-3}) in carbon tetrachloride at 298 K

nm) from a xenon lamp using a Nikon Model G250 monochromator. The light intensity of the monochromatized light (λ = 350 nm) was determined by using a standard actinometer (potassium ferrioxalate) under conditions where the actinometer absorbed essentially all the incident light.[16] 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. It was varied by changing the slit width of the monochromator.

In the case of dialkylcobalt(III) complexes, a 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 [CoR] which has different alkyl groups and a dialkylcobalt(III) complex $[CoR'_2]$ were employed as a standard. Typically, a deaerated CCl_4 solution (1.0 cm^3) containing iodine (5.0×10^{-7} mol) and a large excess of $[CoEt(Hdmg)_2(py)]$ (2.0×10^{-5} mol) was placed in a Pyrex tube which had been flushed with a stream of argon. A deaerated MeCN solution (5.0×10^{-2} cm^3) of *cis*-$[CoMe_2(bipy)_2]ClO_4$ (2.0×10^{-6} mol) was added, and the sample was immediately photolyzed with a xenon lamp through a filter cutting off light below 460 nm. The reaction was completed in a few seconds, judging by the decolouration of iodine. Under such conditions, the contribution from the thermal reactions between dialkylcobalt(III) complexes and iodine can be neglected. The ratio of the quantum yield of *cis*-$[CoMe_2(bipy)_2]ClO_4$ to $[CoEt(Hdmg)_2(py)]$ at the same concentration was determined from the ratio of the products, *i.e.* EtI to MeI by taking account of 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) to dialkylcobalt(III) complexes were varied.

Results

Photochemical Reactions of Alkylcobalt(III) *Complexes with Iodine.*—Irradiation at the absorption band of iodine ($\lambda_{max.}$ = 517 nm) in CCl_4 solution containing a monoalkylcobalt(III) complex $[CoR(Hdmg)_2(py)]$ at 298 K results in a decrease in the absorption band due to I_2, accompanied by an increase in the absorption band due to $[Co(Hdmg)_2(py)]I$ ($\lambda_{max.}$ 450 nm)[7] with an isosbestic point at 498 nm (Figure 1). The alkyl iodide formed in the reaction was identified by ^1H n.m.r. spectroscopy and g.l.c. (see Experimental section). A typical example of the spectral titration is shown in Figure 2, where the concentrations of $[Co(Hdmg)_2(py)]I$ formed in the photochemical reaction are plotted against the mol ratios of iodine to the alkylcobalt(III) complex, revealing the stoicheiometry (1). Any competition

$$[CoR(Hdmg)_2(py)] + I_2 \xrightarrow[CCl_4]{h\nu} [Co(Hdmg)_2(py)]I + RI \quad (1)$$

from the electrophilic cleavage of the monoalkylcobalt(III) complex by I_2 [equation (2)][7] is too slow to be a significant

$$[CoR(Hdmg)_2(py)] + I_2 \xrightarrow[CCl_4]{\text{Heat}} [Co(Hdmg)_2(py)]I + RI \quad (2)$$

complication in a non-polar solvent such as CCl_4 at this temperature. In addition, irradiation by monochromatized light (λ 517 nm) results mainly in 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 (Figure 1), and the quantum yield for the photodissociation of iodine ($\Phi = 0.14$)[18] is known to be much larger than those for the photodissociation of cobalt–carbon bonds of $[CoR(Hdmg)_2(py)]$ ($\Phi = 0.0054$ and 0.0101 for R = Me and Et, respectively).[19]

In the case of dialkylcobalt(III) complexes as well, the quantum yields for the photodissociation of cobalt-carbon bonds {*e.g.* $\Phi = 0.012$ for *cis*-$[CoMe_2(bipy)_2]^+$}[11] are known to be smaller than for the photodissociation of iodine. In the photochemical reactions of dialkylcobalt(III) complexes, *cis*-$[CoR_2(bipy)_2]ClO_4$ (R = Me or Et) and *trans*-$[CoMe_2(L)]$, with iodine minor gaseous products were produced beside the

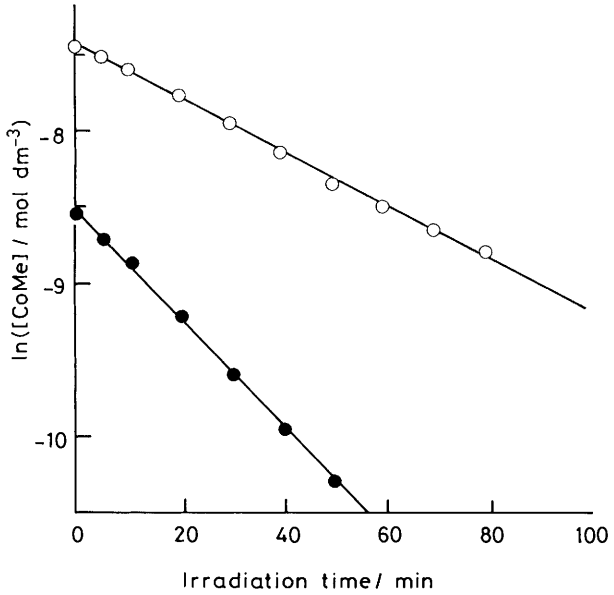


Figure 3. Pseudo-first-order plots for the photochemical reaction of [$CoMe(Hdmg)_2(py)$] with iodine in CCl_4 at 298 K: (○) [complex] = 5.7×10^{-4}, [I_2] = 3.8×10^{-3}; (●) [complex] = 2.0×10^{-4}, [I_2] = 2.0×10^{-3} mol dm^{-3}

Table 1. Product distributions of the photochemical reactions of alkylcobalt(III) complexes (2.0×10^{-6} mol) with I_2 (2.0×10^{-6} mol) in CCl_4 at 298 K

Complex	Yield (%)*
[$CoMe(Hdmg)_2(py)$]	MeI (100)
[$CoEt(Hdmg)_2(py)$]	EtI (100)
cis-[$CoMe_2(bipy)_2$]$^+$	MeI (99), C_2H_6 (0.9), CH_4 (trace)
cis-[$CoEt_2(bipy)_2$]$^+$	EtI (90), C_4H_{10} (10), C_2H_6 (trace)
cis-[$Co(CH_2Ph)_2(bipy)_2$]$^+$	$PhCH_2I$ (100), PhC_2H_4Ph (0)
trans-[$CoMe_2(L)$]	MeI(100),CH_4(0.02),C_2H_6(trace)

* Determined by g.l.c.

Table 2. Quantum yields of the photochemical reactions of alkylcobalt(III) complexes (5.0×10^{-4} mol dm^{-3}) with iodine (5.0×10^{-4} mol dm^{-3}) in carbon tetrachloride at 298 K

Complex	Quantum yield*
[$CoMe(Hdmg)_2(py)$]	2.3×10^2
[$CoEt(Hdmg)_2(py)$]	3.0×10^2
cis-[$CoMe_2(bipy)_2$]$^+$	4.4×10^3
cis-[$Co(CH_2Ph)_2(bipy)_2$]$^+$	1.6×10^3
trans-[$CoMe_2(L)$]	7.0×10^3

* Determined by ferrioxalate actinometry for [$CoR(Hdmg)_2(py)$] under irradiation by monochromatized light (λ 517 nm) with light intensity 1.29×10^{-8} mol dm^{-3} s^{-1} (experimental error within ±5%). The quantum yields of dialkylcobalt(III) complexes relative to [$CoR(Hdmg)_2(py)$] were determined by the competition between these complexes in the photochemical reactions with iodine under irradiation by light of $\lambda > 460$ nm (experimental errors within ±10%).

alkyl iodides as the main products. The yields are listed in Table 1, where the minor gaseous products from *cis*-[$CoR_2(bipy)_2$]ClO_4 are the coupling products of the alkyl groups, *i.e.* ethane and butane for R = Me and Et, respectively. 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 1). On the other hand, *trans*-[$CoMe_2(L)$] yields a small quantity of methane (0.02%) with a trace amount of the coupling product, ethane (Table 1).

Quantum Yields for the Photochemical Reactions of Alkylcobalt(III) *Complexes with Iodine.*—Quantum yields Φ 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 [$Co(Hdmg)_2(py)$]I ($\lambda_{max.}$ = 450 nm).[7] In the presence of a large excess of iodine the quantum yield increased linearly with an increase in the concentration of alkylcobalt(III) complexes [CoR], equation (3). Thus, the time

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

dependence of the quantum yields is given by equation (4),

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

where the subscript 0 denotes the initial value. Typical linear plots according to equation (4) are shown in Figure 3. On the other hand, the quantum yield depended on the light intensity (I) absorbed by I_2, and the Φ value was proportional to $I^{-\frac{1}{2}}$, equation (5), as reported for the photochemical reactions of

$$\Phi \propto I^{-\frac{1}{2}} \qquad (5)$$

tetra-alkyltin compounds with iodine.[13] The Φ values of [$CoR(Hdmg)_2(py)$] (R = Me or Et) at [$CoR(Hdmg)_2(py)$] = [I_2] = 5.0×10^{-4} mol dm^{-3} with $I = 1.29 \times 10^{-8}$ mol dm^{-3} s^{-1} are listed in Table 2.

In the case of photochemical reactions of dialkylcobalt(III) complexes with iodine, a much higher light intensity than that of 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 Experimental section), see Table 2, where all the Φ values are much larger than unity. The largest quantum yield is 7.0×10^3 for *trans*-[$CoMe_2(L)$]. Such large quantum yields indicate that the photochemical cleavage of the cobalt–carbon bonds is a chain process. The radical chain character is demonstrated by the effect of radical inhibitor. As shown in Figure 4, the addition of isopentyl nitrite, which is known as an efficient radical scavenger of iodine atoms,[13,20] results in a significant decrease in the rate of the photochemical reaction of [$CoMe(Hdmg)_2(py)$] (5.1×10^{-4} mol dm^{-3}) with iodine (6.2×10^{-4} mol dm^{-3}).

Photoinduced Radical Chain Reactions.—We have previously reported that the photoinduced cleavage of Sn–C bonds of tetra-alkyltin compounds (SnR_4) by iodine proceeds *via* radical chain reactions as shown in Scheme 1.[13] As applied to the photochemical reactions of alkylcobalt(III) complexes [CoR], the chain mechanism may be given as shown in Scheme 2. Since the reaction of R$^\bullet$ with I_2 is known to be diffusion-limited,[21] the reaction of [$Co^{III}R$] with I$^\bullet$ 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$^\bullet$) in Scheme 2, the quantum yield is given by equation (6), where Φ_i is the

$$\Phi = k_p[\Phi_i/(k_t I)]^{\frac{1}{2}}[\mathrm{CoR}] \qquad (6)$$

quantum yield for the photodissociation of I_2 as the initiation step, k_p is the propagation rate constant for the reaction of [$Co^{III}R$] with I$^\bullet$, and k_t is the termination rate constant for the bimolecular reaction of I$^\bullet$. According to equation (6), the quantum yield is proportional to [CoR] and $I^{-\frac{1}{2}}$, in agreement with the experimental results as shown in equations (3) and (5),

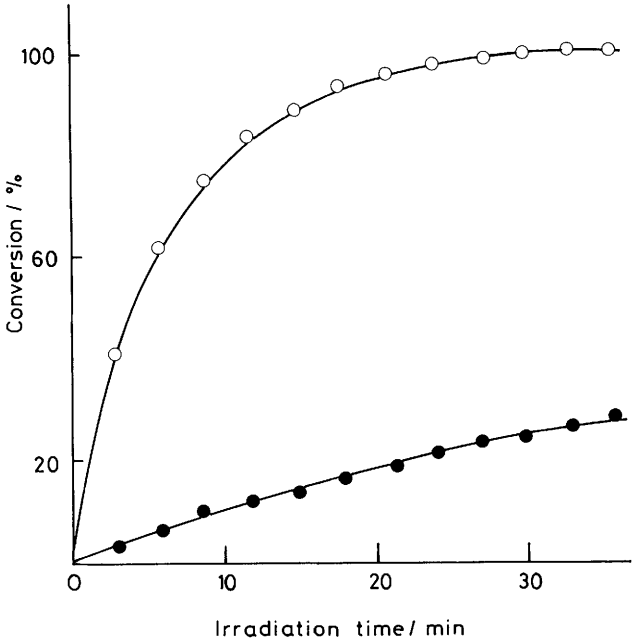
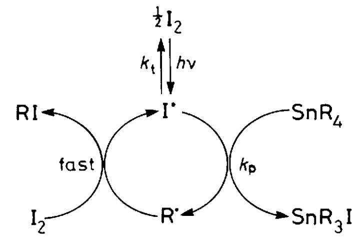
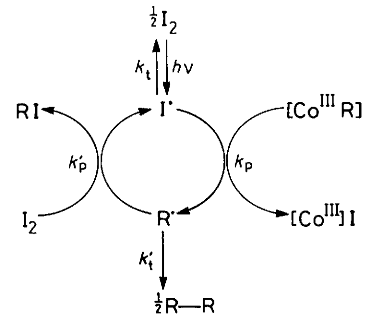


Figure 4. Effect of isopentyl nitrite on the photochemical reaction of $[CoMe(Hdmg)_2(py)]$ (5.1×10^{-4} mol dm^{-3}) with iodine (6.2×10^{-4} mol dm^{-3}) in carbon tetrachloride at 298 K under irradiation by monochromatized light (λ 517 nm): (○) no nitrite; (●) 7.4×10^{-3} mol dm^{-3} nitrite



Scheme 1.



Scheme 2.

respectively. Since Φ_i and k_t are known (0.14[18] and 7.2×10^9 dm^3 mol^{-1} s^{-1},[22] respectively) the propagation rate constants k_p can be evaluated from the values of Φ, Φ_i, k_t, I, and [CoR] using equation (6). The k_p values thus determined are listed in Table 3, together with the reported k_p values for tetra-alkyltin compounds,[13] and the one-electron oxidation potentials E^0_{ox} of the alkylcobalt(III)[7,15,23] and tetra-alkyltin compounds.[24,25]

Table 3. Rate constants k_p for the reactions of alkylcobalt(III) and tetra-alkyltin compounds with iodine atoms in CCl_4 at 298 K and the one-electron oxidation potentials E^0_{ox} *vs.* saturated calomel electrode (s.c.e.) of the alkylmetal complexes in MeCN

Alkylmetal	E^0_{ox}/ V	$k_p{}^a$/ dm^3 mol^{-1} s^{-1}
(1) *trans*-$[CoMe_2(L)]$	0.53^b	3.6×10^8
(2) *cis*-$[CoMe_2(bipy)_2]^+$	0.63^c	2.3×10^8
(3) *cis*-$[Co(CH_2Ph)_2(bipy)_2]^+$	0.60^c	8.2×10^7
(4) $[CoEt(Hdmg)_2(py)]$	0.82^c	1.5×10^7
(5) $[CoMe(Hdmg)_2(py)]$	0.88^c	1.2×10^7
(6) $SnBu_4$	1.04^d	2.7×10^6
(7) $SnPr_4$	1.08^d	2.6×10^6
(8) $SnEt_4$	1.12^d	2.7×10^6
(9) $SnMe_4$	1.56^d	5.3×10^4

[a] The k_p values of alkylcobalt(III) complexes were determined from equation (6), and those of tetra-alkyltin compounds were taken from ref. 13. [b] Ref. 23. [c] Refs. 7 and 15. [d] Refs. 24 and 25.

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 [CoR] with iodine atoms (I•), would be the single-step abstraction of R from [CoR] by I•. In such a case, the smaller the cobalt–alkyl bond dissociation energy (D_{Co-R}), the larger will be the k_p value. However, the k_p value of *cis*-$[Co(Ch_2Ph)_2(bipy)_2]^+$ is the smallest among the dialkylcobalt(III) complexes (Table 3), while the D_{Co-R} value (22 kcal mol^{-1}, *ca.* 92 kJ mol^{-1}) is known to be the smallest.[26] Thus, it seems appropriate to consider a multi-step rather than a single-step mechanism for the reactions of [CoR] with I•.

In this context, it has already been established that the reactions of SnR_4 with I•, which are designated as bimolecular homolytic substitutions (S_H2) of SnR_4 by I•,[12] proceed *via* electron transfer from SnR_4 to I• [equation (7)].[13] The

$$SnR_4 + I^\bullet \longrightarrow (SnR_4{}^{\bullet+}\ I^-) \longrightarrow R^\bullet + SnR_3I \quad (7)$$

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

$$SnR_nR'_{4-n}{}^{\bullet+} \longrightarrow R^\bullet + SnR_{n-1}R'_{4-n}{}^+ \quad (8)$$

$$SnR_nR'_{4-n}{}^{\bullet+} \longrightarrow R'^\bullet + SnR_nR'_{3-n}{}^+ \quad (9)$$

Scheme 3.

The cleavage mode of the Co–C bonds of dialkylcobalt(III) complexes upon one-electron oxidation has also been established as follows.[7] The one-electron oxidation of *cis*-$[CoR_2(bipy)_2]ClO_4$ (R = Me or Et) with $[Fe(bipy)_3]^{3+}$ 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 $[Fe(bipy)_3]^{3+}$ is known to produce $PhCH_2O_2^\bullet$ instead of the coupling product, PhC_2H_4Ph.[7,28] Such effects of oxygen on the one-electron oxidation of *cis*-$[CoR_2(bipy)_2]^+$ are well explained by Scheme 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 oxi-

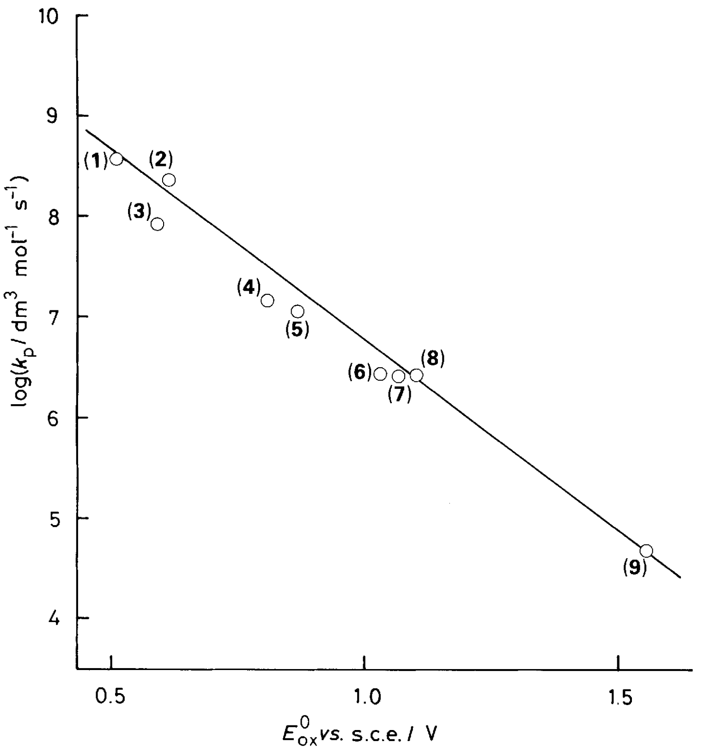
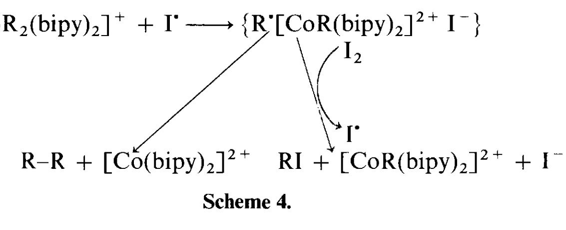


Figure 5. Plot of logarithm of the rate constant k_p for the reactions of alkylcobalt(III) and tetra-alkyltin compounds with iodine atoms in CCl_4 at 298 K *vs.* the one-electron oxidation potentials E^0_{ox} of the alkylmetal complexes in MeCN. The numbers refer to the alkylmetal complexes in Table 3

dation of *cis*-$[CoR_2(bipy)_2]^+$ (R = Me or Et) results in the cleavage of one cobalt–carbon bond, followed by the reation of the resulting alkyl radical with $[CoR(bipy)_2]^{2+}$ 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 is stable enough to be trapped by oxygen to give $PhCH_2O_2^{\bullet}$ which is further oxidized to yield the final product, benzaldehyde.[7,28] Such a difference in the stability of the radicals produced by oxidative cleavage of 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*-$[CoR_2(bipy)_2]^+$ with I_2 (Table 1) as shown in Scheme 4. In the case of R = Me and Et, the facile coupling reactions of $R^{\bullet}$ with $[CoR(bipy)_2]^{2+}$ can compete well with the trapping of $R^{\bullet}$ by I_2, yielding the observed coupling products R–R (Table 1). In the case of R = $PhCH_2$, the benzyl radical being more stable than $Me^{\bullet}$ or $Et^{\bullet}$ may readily be trapped by I_2 before the reaction with $[Co(CH_2Ph)(bipy)_2]^{2+}$, as observed in the one-electron oxidation in the presence of oxygen (Scheme 3). This may be the reason why no coupling product has been detected in the case of *cis*-$[Co(CH_2Ph)_2(bipy)_2]^+$ (Table 1).



Scheme 4.

The one-electron oxidation of *trans*-$[CoMe_2(L)]$ is also known to result in the cleavage of one cobalt–one carbon bond to give a methyl radical [equation (10)].[23,29] In this case, the

$$trans\text{-}[CoMe_2(L)] \xrightarrow{-e} Me^{\bullet} + [CoMe(L)]^+ \quad (10)$$

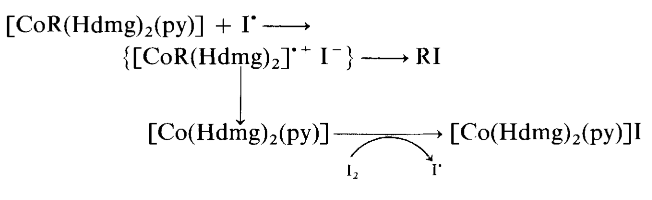
reaction of this methyl radical with another cobalt–methyl bond is disfavoured, compared with the case of *cis*-$[CoR_2(bipy)_2]^+$, because of the *trans* configuration, and thereby the methyl radical diffuses out of the cage.[23,29] Thus, electron transfer from *trans*-$[CoMe_2(L)]$ with $I^{\bullet}$ may produce free methyl radical, followed by the reaction of I_2 to yield methyl iodide, accompanied by the regeneration of $I^{\bullet}$. Such involvement of free methyl radicals in radical chain reactions may be responsible for the detection of a small quantity of methane (Table 1), formed by the hydrogen abstraction from the solvent by the methyl radical.[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 2. However, the chain length, which is designated by Φ/Φ_i ($\Phi_i = 0.14$),[18] is as large as 3.1×10^4 for *cis*-$[CoMe_2(bipy)_2]^+$ under the experimental conditions in Table 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 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 equation (11), instead of (6). Clearly,

$$\Phi = k'_p[\Phi_i/(k'_t I)]^{\frac{1}{2}}[I_2] \quad (11)$$

equation (11) is not in accord with the experimental results in Figure 3. Thus, it can be concluded that the minor gaseous products in Table 1 are formed *via* dialkylcobalt(IV) complexes (Scheme 4).

In the case of monoalkylcobalt(III) complexes, $[CoR(Hdmg)_2(py)]$,[30] one-electron oxidation is known to produce rather stable monoalkylcobalt(IV) complexes, $[CoR(Hdmg)_2(py)]^+$, in which the Co–C bond is cleaved by a nucleophile such as I^-.[31,32] Thus, the reaction of $[CoR(Hdmg)_2(py)]$ with $I^{\bullet}$ may proceed as shown in Scheme 5, where cleavage of the Co–C bond may occur by nucleophilic attack of I^- towards the alkylcobalt(IV) complexes to yield RI and $[Co(Hdmg)_2(py)]$; the latter cobalt(II) complex may reduce I_2 to yield $[Co(Hdmg)_2(py)]I$ 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 $[CoR(Hdmg)_2(py)]$ (Table 1).



Scheme 5.

As discussed above, the photoinduced cleavage of the Co–C bonds by iodine consists of radical chain reactions in which the S_H2 reaction of the alkylcobalt(III) complex with $I^{\bullet}$ is the rate-determining step and is suggested to proceed *via* 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 tetra-alkyltin compounds.[13] The propagation rate constants k_p for electron transfer from alkylcobalt(III) complexes to iodine atom are correlated well with those of tetra-alkyltin compounds as shown in Figure 5, where the log k_p values increases linearly with a negative shift in the one-electron oxidation potentials E^0_{ox} of the alkylcobalt(III) and tetra-alkyltin compounds in MeCN when electron transfer becomes energetically more favourable. Although the energetics of electron transfer from alkylmetal complexes to iodine atoms in CCl_4 and the structures of the resulting ion-pair intermediates are not known at present, such a linear correlation indicates a coincidence of reaction mechanism, *i.e.* photoinduced electron-transfer radical chain, where the ease of the one-electron oxidation determines the reactivities of the alkylmetal complexes.

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