

Photo-cleavage of Cobalt–Carbon Bonds of Alkylcobalt(III) Complexes by Iodine with Large Quantum Yields

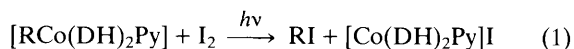
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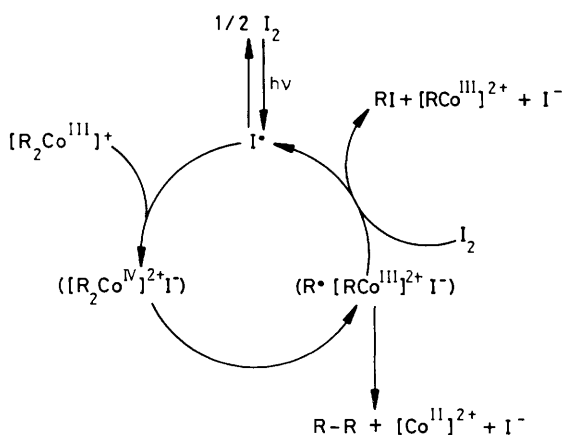
Cobalt–carbon bonds of alkylcobalt(III) complexes are readily cleaved by iodine in carbon tetrachloride to yield alkyl iodides *via* photoinduced electron-transfer radical chain reactions with large quantum yields (*e.g.*, $\Phi = 7.0 \times 10^3$) under low energy irradiation (λ 509 nm).

Electrophilic cleavage of cobalt–carbon bonds has been extensively studied in connection with enzymatic cleavage of the Co–C bonds.^{1,2} The electrophilic mechanism that has been viewed simply as direct displacement of the cobalt atom by the attack of electrophiles at the α -carbon has recently been reconsidered as proceeding *via* electron-transfer in the activation process.^{3–6} On the other hand, little is known of the mechanism of the photochemical cleavage of Co–C bonds by electrophiles, although direct photo-cleavage of cobalt–carbon bonds have been subjected to detailed scrutiny.^{7–9} We wish to report herein the photo-cleavage of the Co–C bonds of the alkylcobalt(III) complexes by iodine under low energy irradiation (λ 509 nm) with large quantum yields. The contribution of the electron transfer pathway in the photochemical reaction will be clarified.

The alkylcobalt(III) complexes examined in this study are the dialkylcobalt(III) complexes, cis -[R₂Co(bpy)₂]⁺ (R = Me, Et, PhCH₂; bpy = 2,2'-bipyridine),⁶ $trans$ -[Me₂Co(DpnH)] (DpnH = 11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-1-olate),⁹ and the monoalkylcobalt(III) complexes, [RCo(DH)₂Py] [R = Me, Et; (DH)₂ = bis(dimethylglyoxymato); Py = Pyridine]. Low energy irradiation of the absorption band of iodine in carbon tetrachloride (λ_{max} 517 nm) containing [RCo(DH)₂Py] results in the cleavage of the Co–C bonds to yield alkyl iodide [equation (1)]. The products were identified by ¹H n.m.r. and electronic

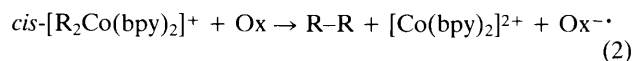


spectra. Little competition from the thermal electrophilic cleavage of the Co–C bonds of [RCo(DH)₂Py] has been observed in this non-polar solvent at 298 K even with a low light intensity through a monochromator (1.29×10^{-8} einstein dm⁻³ s⁻¹). In the case of cis -[R₂Co(bpy)₂]⁺, the photochemical reaction with iodine yields a small amount of the coupling products, *i.e.*, ethane and butane for R = Me and Et,



Scheme 1

respectively, besides alkyl iodide as the main product (Table 1). Such coupling products are known to be produced from cis -[R₂Co^{IV}(bpy)₂]²⁺ upon one-electron oxidation of cis -[R₂Co^{III}(bpy)₂]⁺ by a strong organic or inorganic oxidant Ox [equation (2)].⁶ In the case of $trans$ -[Me₂Co(DpnH)] as well, methane, which is observed in a small quantity for the photochemical reaction with iodine (Table 1), is known to be produced upon the one-electron oxidation.⁴



The quantum yields (ϕ) for the photochemical reaction of [RCo(DH)₂Py] with iodine were determined spectroscopically by using ferrioxalate actinometry under irradiation of monochromatized light (509 nm),¹⁰ since direct irradiation results in the instant completion of the reaction. Thus, all manipulations were effected in the dark. It has been confirmed that the monitoring light in the spectroscopic measurements has a negligible effect on the photochemical reaction rate. In the case of cis -[R₂Co(bpy)₂]⁺, however, a much higher light intensity was required to avoid the contribution from the thermal electrophilic cleavage of the Co–C bonds. Thus, the quantum yields of dialkylcobalt(III) complexes were determined by the competition method, comparing the reactivities relative to [RCo(DH)₂Py] under direct irradiation from a xenon lamp through a filter cutting off below 460 nm. The quantum yields thus determined are listed in Table 2, together with the one-electron oxidation potentials E_{ox}^0 of the alkylcobalt(III) complexes.^{5,6,11} The ϕ value increases with the negative shift in the E_{ox}^0 value as the one-electron oxidation of alkylcobalt(III) complexes becomes energetically more favourable. In the case of $trans$ -[Me₂Co(DpnH)], the quantum yield is as large as 7.0×10^3 . Such large quantum yields indicate the photochemical cleavage of the Co–C bonds to be a chain process. The radical chain character is confirmed by the effect of a radical inhibitor; the ϕ value was significantly decreased in the presence of isoamyl nitrite which is known to be an effective quencher of iodine atoms.¹² In the presence of a large excess of iodine, the ϕ value was proportional to the concentration of alkylcobalt(III) complexes [RCo^{III}] when the time dependence of ϕ is given by equation (3), where subscript 0 denotes the initial value. Thus, the rate-determining step for the radical chain reaction may involve the reaction of alkylcobalt(III) complexes with iodine atom.

Table 1. Photochemical reactions of dialkylcobalt(III) complexes (2.0×10^{-6} mol) with I₂ (2.0×10^{-6} mol) in CCl₄ (6.0 cm³).

Dialkylcobalt(III) complex	Yield (%) ^a
cis -[Me ₂ Co(bpy) ₂] ⁺	MeI (99) C ₂ H ₆ (0.9) CH ₄ (trace)
cis -[Et ₂ Co(bpy) ₂] ⁺	EtI (90) C ₄ H ₁₀ (10) C ₂ H ₆ (trace)
$trans$ -[Me ₂ Co(DpnH)]	MeI (100) CH ₄ (0.02) C ₂ H ₆ (trace)

^a 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 CCl $_4$, and the one-electron oxidation potentials of alkylcobalt(III) complexes in MeCN.

Alkylcobalt(III) complex	E_{ox}^0 ^a	Quantum yield ^b
[MeCo(DH) $_2$ Py]	0.88	2.3×10^2
[EtCo(DH) $_2$ Py]	0.82	3.0×10^2
<i>cis</i> -[(PhCH $_2$) $_2$ Co(bpy) $_2$] ⁺	0.66	1.6×10^3
<i>cis</i> -[Me $_2$ Co(bpy) $_2$] ⁺	0.63	4.4×10^3
<i>trans</i> -[Me $_2$ Co(DpnH)]	0.53	7.0×10^3

^a Vs. standard calomel electrode (S.C.E.) (refs. 5, 6, and 11). Determined by ferrioxalate actinometry for [RCo(DH) $_2$ Py] under irradiation of light (λ 509 nm) with the light intensity of 1.29×10^{-8} einstein dm $^{-3}$ s $^{-1}$. 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 their photochemical reactions with iodine under irradiation of light (λ > 460 nm).

$$\ln[\text{RCo}^{\text{III}}]/[\text{RCo}^{\text{III}}]_0 = \ln(\phi/\phi_0) = -k_{\text{obs}}t \quad (3)$$

Based on the above results, a radical chain mechanism for the photochemical reactions of dialkylcobalt(III) complexes with iodine is shown in Scheme 1, where the chain carrier is the iodine atom. Since photodissociation of molecular iodine is known to proceed with a quantum yield of 0.14,¹² the maximum chain length under the conditions in Table 2 ($\phi = 7.0 \times 10^3$) is obtained as 5.1×10^4 . The electron affinity E_A of iodine atom is reported to be much larger than that of molecular iodine; $E_A(\text{I}^\cdot) - E_A(\text{I}_2) = 138$ kJ mol $^{-1}$.¹³ Thus, the electron transfer from the alkylcobalt(III) complex to iodine atom may readily occur to produce the alkylcobalt(IV) complex which is known to yield alkyl radicals by the facile cleavage of the Co–C bond (Scheme 1).¹⁴ The first-order dependence of ϕ on the concentration of alkylcobalt(III) complexes indicates that the electron-transfer process is the rate-determining chain propagation step. The subsequent

reaction of alkyl radical with molecular iodine to yield alkyl iodide, accompanied by regeneration of iodine atom, is known to be diffusion controlled.¹² In the case of *cis*-[R $_2$ Co(bpy) $_2$]⁺, the coupling product of the alkyl ligands of *cis*-[R $_2$ Co^{IV}(bpy) $_2$]²⁺ upon one-electron oxidation of *cis*-[R $_2$ Co^{III}(bpy) $_2$]⁺ by iodine atom (Table 2) may be obtained in competition with the quenching of the alkyl radical by molecular iodine to yield alkyl iodide (Scheme 1).

Received, 19th September 1988; Com. 8/03559H

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