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Evidence for a Single-Electron-Transfer Activation in the Cleavage of Cobalt-Carbon Bonds of Alkylcobalt(III) Complexes with Iodine

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Evidence for a single-electron-transfer (SET) activation in the cleavage of cobalt-carbon bonds of alkylcobalt(III) complexes with iodine is shown by the identification of products that could arise only via an SET pathway as well as by the kinetic comparison between the cleavage reaction of alkylcobalt(III) complexes with iodine and the electron-transfer reaction of ferrocene derivatives with iodine in acetonitrile.

Electrophilic cleavage of cobalt-carbon bonds has extensively been studied in relation with enzymatic cleavage of those bonds.[1)] The electrophilic mechanism that had 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 single-electron-transfer (SET) based on the kinetics.[2)] The kinetic studies by themselves, however, are not conclusive for distinguishing between these two mechanisms. On the other hand, identification of products that could arise only via intermediates produced upon an SET pathway may present good evidence for the SET mechanism. We report herein such evidence for the significant contribution of an SET process in the cleavage of Co-C bonds with iodine being a simple electrophile, together with the kinetic comparison between the cleavage reaction of alkylcobalt(III) complexes with iodine and the electron-transfer reaction of ferrocene derivatives with iodine in acetonitrile (MeCN).

The alkylcobalt(III) complexes examined in this study are cis-dialkylcobalt(III) complexes, cis-$[R_2Co(bpy)_2]ClO_4$ (R = Me, Et, and $PhCH_2$; bpy = 2,2'-bipyridine), trans-$[Me_2Co(DpnH)]$ (DpnH = 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-11-ol-1-olate), and monoalkylcobalt(III) complexes, $[RCo(DH)_2Py]$ (R = Me and Et; $(DH)_2$ = bis(dimethylglyoximato); Py = pyridine). Each alkylcobalt(III) complex reacts with iodine in MeCN to yield mainly alkyl iodide and triiodide ion (Eq. 1). The stoichiometry of the reaction, determined

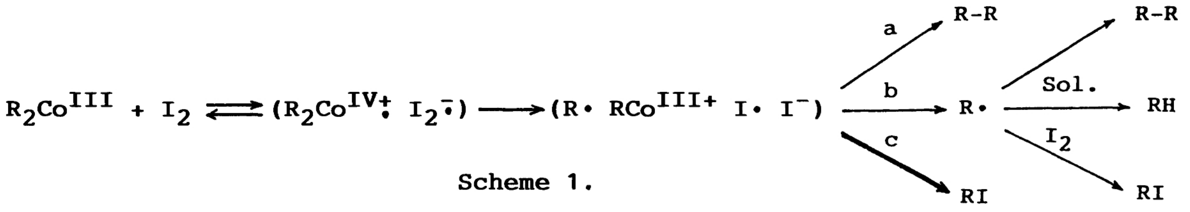
$$RCo^{III} + 2I_2 \longrightarrow RI + Co^{III+} + I_3^- \qquad (1)$$

by the spectroscopic measurments of the concentration of triiodide ion in MeCN with changing the mole ratio of each alkylcobalt(III) complex to iodine, indicates that the Co-C bond of RCo^{III} is cleaved by I_2 to produce Co^{III+}, RI, and I^- which reacts with I_2 to yield I_3^-. The main products other than I_3^- in Eq. 1 were identified from the ^{1}H NMR spectra.

The mode of the Co-C cleavage of dialkylcobalt(IV) complexes upon the one-electron oxidation by strong oxidants (Ox) such as $[Fe(bpy)_3]^{3+}$ and 2,3-dichloro-5,6-dicyano-p-benzoquinone is known to depend on the geometry of the Co-C bonds; two Co-C bonds of cis-$[R_2Co^{IV}(bpy)_2]^{2+}$ are cleaved intramolecularly to yield mainly the coupling product R-R (Eq. 2),[3] while one Co-C bond of trans-$[Me_2Co^{IV}(DpnH)]^{+}$ is cleaved to produce methyl radicals (Eq. 3) which give methane and ethane by the hydrogen abstraction from a solvent and by the coupling reaction of methyl radicals, respectively.[4] In the reactions of cis-$[R_2Co(bpy)_2]^+$ with iodine, only the intramolecular coupling products (ethane and butane for R = Me and Et, respectively) are obtained besides alkyl iodides being the main products, while in the reaction of trans-$[Me_2Co(DpnH)]$ with iodine, methane and ethane derived from methyl radicals are produced, as shown in Table 1. Such product distributions, albeit being small quantities, demonstrate the significant contribution of an SET process in the oxidation of dialkylcobalt(III) complexes R_2Co^{III} with iodine as follows (Scheme 1). Upon the electron transfer from R_2Co^{III} to I_2, the Co-C bond of R_2Co^{IV+} as well as the I-I bond of I_2^{-} may be instantly cleaved to give the radical pair in the cage (Scheme 1). In the case of cis-$[R_2Co(bpy)_2]^+$, an intramolecular coupling of the alkyl groups between R• and RCo^{III+} gives the product R-R (Scheme 1-a), while in the case of trans-$[Me_2Co(DpnH)]$, such an intramolecular coupling process may be disfavored geometrically compared with the case of cis-$[R_2Co(bpy)_2]^+$, and thereby a

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

$$\underline{trans}\text{-}[Me_2Co(DpnH)] + Ox \longrightarrow Me\bullet + [MeCo(DpnH)]^+ + Ox^{-} \qquad (3)$$



Scheme 1.

Table 1. Yields of products (% based on Co), besides alkyl iodide, in the cleavage reactions of dialkylcobalt(III) complexes (4.0 x 10^{-6} mol) with iodine

$[I_2]/[Co]$	cis-$[R_2Co(bpy)_2]^+$ R = Me C_2H_6	cis-$[R_2Co(bpy)_2]^+$ R = Et C_4H_{10}	trans-$[Me_2Co(DpnH)]$ CH_4	trans-$[Me_2Co(DpnH)]$ C_2H_6
1	0.60	3.20	0.34	0.06
2	0.54	3.23	0.47	0.07
3	0.44	2.59	0.37	0.06
4	0.38	2.50	0.35	0.06
6	0.21	2.08	0.22	0.05
10	0.11	1.97	0.07	0.03
20	0.10	1.86	0.06	0.03

free radical (Me•) is escaped from the cage to yield methane and ethane (Scheme 1-b). In each case, the combination reaction between R• and I• in the cage (Scheme 1-c) is expected to be much faster than the other process (Scheme 1-a or 1-b). Thus, alkyl iodide may be formed mainly via the radical pair in the cage (Scheme 1-c). With increasing the mole ratio of I_2 to R_2Co^{III}, the yields of RH and R-R decrease by the quenching of R• by I_2 (Scheme 1-b) as shown in Table 1. At this stage, however, a possibility of the competition between the SET pathway (Scheme 1) and the direct displacement of the cobalt atom by the attack of iodine at the α-carbon cannot be ruled out completely. Thus, we have performed the kinetic comparison between the cleavage reaction of alkylcobalt(III) complexes with iodine and the electron-transfer reaction of ferrocene derivatives with iodine in MeCN at 298 K.

Rates of the cleavage reactions of alkylcobalt(III) complexes with iodine were followed by the rise of the absorbance due to I_3^- (Eq. 1), which showed a first-order dependence on the concentration of each reactant. On the other hand, ferrocene derivatives (Fc) are known to be readily oxidized by various inorganic oxidants via electron-transfer reactions to give ferricenium ions (Fc^+).[5)] The stoichiometry of the reaction (Eq. 4) has been determined

$$2Fc + 3I_2 \longrightarrow 2Fc^+ + 2I_3^- \qquad (4)$$

from the spectroscopic measurements of the concentration of Fc^+ with changing the mole ratio of Fc to I_2. Such a stoichiometry indicates that the electron-transfer reaction from Fc to I_2, being the rate-determining step, gives Fc^+ and $I_2^{\cdot -}$, the latter of which is known to dissociate to produce I• and I^-,[6)] ($Fc + I_2 \rightarrow Fc^+ + I\cdot + I^-$), followed by the fast electron-transfer reaction from Fc to I• ($Fc + I\cdot \rightarrow Fc^+ + I^-$), and the iodide ion reacts with iodine to yield triiodide ion, as the case of the reactions of alkylcobalt(III) complexes with iodine (Eq. 1). Rates of the electron-transfer reactions from Fc to I_2 were followed by the rise of the absorbance due to

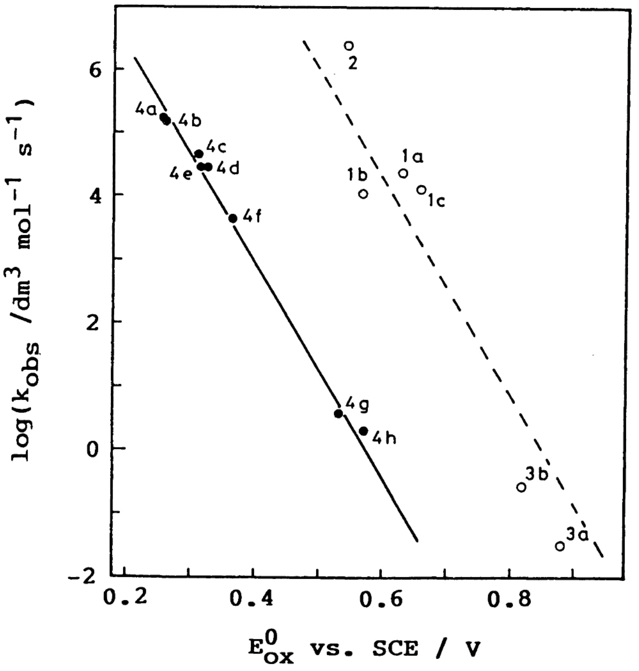


Fig. 1. Plots of log k_{obs} vs. the one-electron oxidation potentials E^0_{ox} of alkylcobalt(III) complexes (○) and ferrocene derivatives (●) for the reactions with iodine in MeCN at 298 K; **1** cis-$[R_2Co(bpy)_2]^+$: (a) R = Me, (b) R = Et, (c) R = $PhCH_2$, **2** trans-$[Me_2Co(DpnH)]$, **3** $[RCo(DH)_2Py]$: (a) R = Me, (b) R = Et, **4** ferrocene derivatives: (a) 1,1'-di-n-butyl-, (b) 1,1'-dimethyl-, (c) n-butyl-, (d) n-amyl-, (e) t-amyl-, (f) ferrocene, (g) 1,1'-dicarboxy-, (h) benzoyl-.

Fc^+, which also showed a first-order dependence on the concentration of each reactant.

The logarithms of the observed second-order rate constants (log k_{obs}) for both the cleavage reactions of alkylcobalt(III) complexes with iodine (Eq. 1) and electron-transfer reactions of ferrocene derivatives with iodine (Eq. 4) are plotted against the one-electron oxidation potentials E^0_{ox} of alkylcobalt(III) complexes[7)] and ferrocene derivatives,[7)] respectively, as shown in Fig. 1. Both the log k_{obs} values decrease linearly as the E^0_{ox} values are shifted in the positive direction, with the slope of -17, which corresponds to -2.3RT/F, as observed generally for endothermic electron-transfer reactions.[8)] Such a parallel dependence of log k_{obs} on E^0_{ox} between the cleavage reaction of alkylcobalt(III) complexes with iodine and electron-transfer reaction of ferrocene derivatives with iodine (Fig. 1), together with the identification of products that could arise only via dialkylcobalt(**IV**) complexes (Table 1) presents evidence for involvement of the SET mechanism at least in part in the cleavage reactions of alkylcobalt(III) complexes with iodine (Scheme 1).

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