CHEMISTRY LETTERS, pp. 421 - 424, 1984.

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

Shunichi FUKUZUMI, Kunio ISHIKAWA, and Toshio TANAKA*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

Alkyl transfer reactions from *cis*-dialkylcobalt(III) complexes, $[R_2Co(bpy)_2]ClO_4$ (R = Me and Et; bpy = 2,2'-bipyridine), to *p*-benzoquinone derivatives in acetonitrile occurred in the presence of $Mg(ClO_4)_2$ which showed a remarkable catalytic effect. Formation of charge-transfer complexes between $[R_2Co(bpy)_2]^+$ and *p*-benzoquinone derivatives is also reported.

There has been considerable interest in the mechanisms of activation of cobalt-alkyl bonds in alkylcobalt(III) complexes which transfer alkyl groups to substrates.$^{1,2)}$ Although the cobalt-alkyl bonds in dialkylcobalt(III) complexes are readily cleaved by various inorganic oxidants such as Hg^{2+},$^{3)}$ Ag^+,$^{4)}$ Zn^{2+},$^{5)}$ and $[IrCl_6]^{2-}$,$^{6)}$ no cleavage of the cobalt-alkyl bonds by organic oxidants has so far been reported.

We wish to report herein the formation of charge-transfer (CT) complexes between *cis*-dialkylcobalt(III) complexes $[R_2Co(bpy)_2]^+$ (R = Me and Et; bpy = 2,2'-bipyridine) and *p*-benzoquinone derivatives, and the occurrence of cleavage of the cobalt-alkyl bonds in $[R_2Co(bpy)_2]^+$ by *p*-benzoquinone derivatives in the presence of Mg^{2+} ion acting as an efficient catalyst.

The *cis*-dialkylcobalt(III) complexes $[R_2Co(bpy)_2]ClO_4$ were prepared according to the literature.$^{7)}$ Mixing of $[R_2Co(bpy)_2]^+$ (1.7×10^{-3} mol dm^{-3}) with *p*-chloranil (0.10 mol dm^{-3}) in *N*,*N*-dimethylformamide (DMF) resulted in an immediate and substantial increase of the absorbance in the electronic spectrum in the long wavelength region (λ > 550 nm). The difference spectrum in Fig. 1 obtained by subtracting the sum of the separate absorbances of $[R_2Co(bpy)_2]^+$ and *p*-chloranil from the absorbance of the admixture shows the presence of a new absorp-

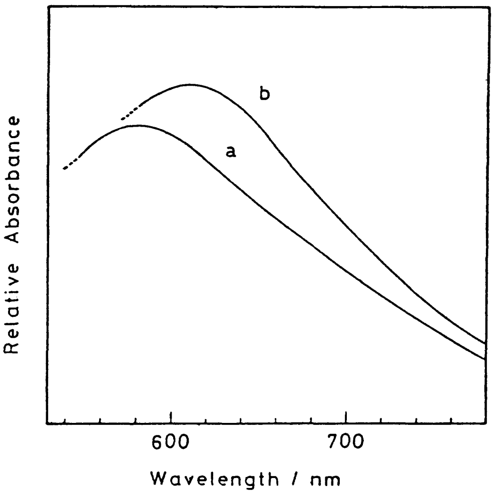

Fig. 1. CT spectra of (a) $[Me_2Co(bpy)_2]^+$-*p*-chloranil and (b) $[Et_2Co(bpy)_2]^+$-*p*-chloranil complexes in DMF.

tion band with a broad but distinct maximum centered at λ_{max} = 580 and 610 nm for $[Me_2Co(bpy)_2]^+$ and $[Et_2Co(bpy)_2]^+$, respectively. The broad absorption bands in Fig. 1 are characteristic of intermolecular CT complexes. The intensity of the CT band showed a first-order dependence on each concentration of $[R_2Co(bpy)_2]^+$ and *p*-chloranil, suggesting that the CT bands are due to 1 : 1 complexes formed between $[R_2Co(bpy)_2]^+$ and *p*-chloranil QCl_4 (Eq. 1). The formation constant K

$$[R_2Co(bpy)_2]^+ + QCl_4 \overset{K}{\rightleftharpoons} ([R_2Co(bpy)_2]^+ QCl_4) \qquad (1)$$

and the molar extinction coefficient ε for the $[Et_2Co(bpy)_2]^+$-*p*-chloranil complex in DMF at 298 K have been determined as 1.7 $mol^{-1}\,dm^3$ and 1.0×10^3 $mol^{-1}\,dm^2$, respectively, by a Benesi-Hildebrand plot.[8)] Such small K and ε values are typical for CT complexes of organometallic σ-donor as reported for CT complexes formed between main group alkylmetals and tetracyanoethylene (TCNE).[9)] On the contrary, the large K and ε values (3.9×10^2 $mol^{-1}\,dm^3$ and 1.1×10^5 $mol^{-1}\,dm^2$, respectively) have recently been reported for the CT complex formed between methylcobalamin and TCNE, where the CT band arises from the interaction between corrin π orbitals and TCNE, and thereby the cobalt-alkyl bond is not involved directly in the CT interaction.[10)] Thus, the present case may provide a novel example for the CT complexes of organotransition metals acting as σ-donor.[11)]

When stronger electron acceptors than *p*-chloranil, *i.e.* 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and 2,3-dicyano-*p*-benzoquinone were used instead of *p*-chloranil, the electron transfer from $[R_2Co(bpy)_2]^+$ to the *p*-benzoquinone derivatives occurred in dry acetonitrile (MeCN) and the formation of the radical anions of the corresponding quinones was observed in the visible and ESR spectra (λ_{max} = 585 nm and g = 2.0050, respectively, for both radical anions). On the other hand, the cobalt-alkyl bonds in $[Me_2Co(bpy)_2]^+$ and $[Et_2Co(bpy)_2]^+$ were cleaved by the electron transfer to yield quantitatively ethane and butane, respectively, determined by GLC.

For other *p*-benzoquinone derivatives which are weaker electron acceptors than *p*-chloranil such as *p*-benzoquinone, only the tail of the CT bands was observed in the long wavelength region (λ > 550 nm) owing to the overlap of the blue-shifted CT bands relative to the case of *p*-chloranil with the absorption bands of $[Me_2Co(bpy)_2]^+$ and $[Et_2Co(bpy)_2]^+$ at λ_{max} = 476 and 498 nm, respectively. These CT complexes were stable and no further reaction has occurred in MeCN. When $Mg(ClO_4)_2$ was added to the $[R_2Co(bpy)_2]^+$-*p*-benzoquinone derivative system, however, the reaction of carbanion transfer from $[R_2Co(bpy)_2]^+$ to the *p*-benzoquinone derivative Q occurred, coinciding with the decay of the CT band (Eq. 2).

$$[R_2Co(bpy)_2]^+ + Q \rightleftharpoons ([R_2Co(bpy)_2]^+ Q) \xrightarrow[Mg^{2+}]{} [RCo(bpy)_2]^{2+} + QR^- \qquad (2)$$

After the workup of the reaction mixture with water, *p*-alkoxyphenol QRH was isolated quantitatively. It should be noted that this is the first example of alkyl transfer from dialkylcobalt complexes to organic oxidants. The reaction rates determined by the decay of the absorption bands due to $[R_2Co(bpy)_2]^+$ at a fixed concentration of Mg^{2+} ion in dry MeCN obeyed the second-order kinetics,

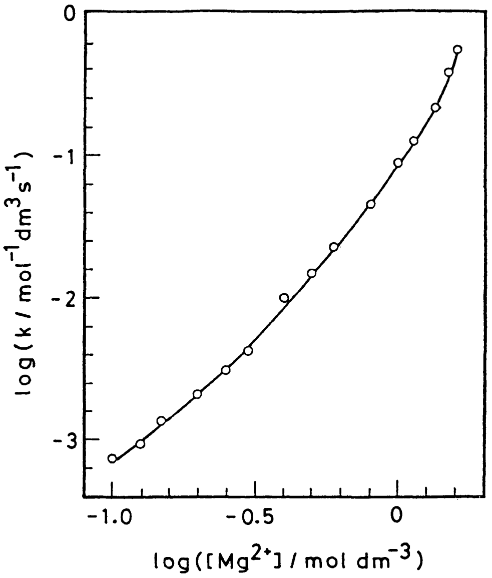

Fig. 2. A plot of log k *vs.* log [Mg^{2+}] for the reaction of $[Et_2Co(bpy)_2]^+$ (5.14×10^{-4} mol dm^{-3}) with *p*-benzoquinone (more than 10 fold excess of $[Et_2Co(bpy)_2]^+$) in the presence of various concentrations of Mg^{2+} ion in MeCN at 298 K.

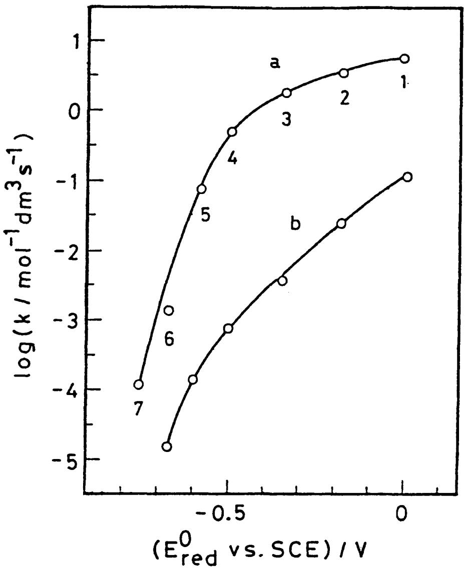

Fig. 3. Logarithms of the rate constants k for the reactions of $[Et_2Co(bpy)_2]^+$ with various *p*-benzoquinone derivatives in the presence of (a) 1.6 mol dm^{-3} and (b) 0.10 mol dm^{-3} Mg^{2+} ion in MeCN plotted against the reduction potentials E^0_{red} of *p*-benzoquinone derivatives; 1) *p*-chloranil, 2) 2,6-dichloro-*p*-benzoquinone, 3) chloro-*p*-benzoquinone, 4) *p*-benzoquinone, 5) methyl-*p*-benzoquinone, 6) 2,6-dimethyl-*p*-benzoquinone, 7) trimethyl-*p*-benzoquinone.

showing a first-order dependence on each reactant. The second-order rate constant k increases sharply with increasing the Mg^{2+} concentration as shown in Fig. 2, where the log k value for the reaction of $[Et_2Co(bpy)_2]^+$ with *p*-benzoquinone is plotted against log [Mg^{2+}] as a typical example. Such a remarkable catalytic effect of Mg^{2+} ion is not due to the change of the ionic strength since almost no reaction has occurred between $[Et_2Co(bpy)_2]^+$ and *p*-benzoquinone in the presence of 1.0 mol dm^{-3} $NaClO_4$ or *n*-Bu_4NClO_4. The slope in Fig. 2 varies from 2 in the lower Mg^{2+} concentrations to 4 in the higher concentrations, suggesting that two or more Mg^{2+} ions are involved in the alkyl transfer reaction (Eq. 2).

We have previously reported a similar catalytic effect of Mg^{2+} ion on the hydride transfer reactions from an NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH) to *p*-benzoquinone derivative Q in MeCN (Eq. 3),

$$\mathrm{BNAH} + \mathrm{Q} \rightleftharpoons [\mathrm{BNAH\ Q}] \xrightarrow[\mathrm{Mg}^{2+}]{} \mathrm{BNA}^+ + \mathrm{QH}^- \qquad (3)$$

where the CT complex formed between BNAH and Q is an intermediate for the hydride transfer from BNAH to Q and two or more Mg^{2+} ions interact with Q to activate the substrate Q.[12] Thus, the role of Mg^{2+} ion in the carbanion transfer from

$[R_2Co(bpy)_2]^+$ to Q (Eq. 2) may be similar to that in the hydride transfer from BNAH to Q (Eq. 3).

The k values for the reactions of $[Et_2Co(bpy)_2]^+$ with various *p*-benzoquinone derivatives Q in the presence of 1.6 and 0.10 mol dm^{-3} Mg^{2+} ion decrease as the electron acceptor ability of Q decreases, *i.e.* with negative shifts of the reduction potential of Q[13] as shown in Fig. 3. Moreover, the rate constant k for the reaction of $[Et_2Co(bpy)_2]^+$ with each *p*-benzoquinone derivative was about 2×10^2 times larger than that of $[Me_2Co(bpy)_2]^+$, in accordance with the donor ability of the alkylcobalt(III) complex; $[Et_2Co(bpy)_2]^+ > [Me_2Co(bpy)_2]^+$. Thus, the electron-donor-acceptor interaction between $[R_2Co(bpy)_2]^+$ and Q may play an important role in the activation of the cobalt-alkyl bonds where the role of Mg^{2+} ion (a hard acid) is considered as enhancing the acceptor ability of Q. The study on the detailed mechanism of the reactions of $[R_2Co(bpy)_2]^+$ with Q catalyzed by various hard acids and the relation to the electron transfer reactions from $[R_2Co(bpy)_2]^+$ to electron acceptors is now under progress.

References

1) M. W. Witman and J. H. Weber, *Inorg. Chim. Acta*, 23, 263 (1977) and references therein.
2) J. K. Kochi, "Organometallic Mechanisms and Catalysis," Academic Press, New York (1978), Chap. 16 and references therein.
3) J. H. Espenson, H. L. Fritz, R. A. Heckman, and C. Nicolini, *Inorg. Chem.*, 15, 906 (1976).
4) G. Costa, G. Mestroni, and C. Cocevar, *J. Chem. Soc., D*, 1971, 706.
5) J. H. Dimmit and J. H. Weber, *Inorg. Chem.*, 21, 700 (1982); M. W. Witman and J. H. Weber, *ibid.*, 15, 2375 (1976); M. W. Witman and J. H. Weber, *ibid.*, 16, 2512 (1977).
6) W. H. Tamblyn, R. J. Klingler, W. S. Hwang, and J. K. Kochi, *J. Am. Chem. Soc.*, 103, 3161 (1981).
7) G. Mestroni, A. Camus, and E. Mestroni, *J. Organomet. Chem.*, 24, 775 (1970).
8) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 71, 2703 (1949); R. S. Mulliken and W. B. Person, "Molecular Complexes, a Lecture and Reprint Volume," Wiley-Interscience, New York (1969).
9) S. Fukuzumi, K. Mochida, and J. K. Kochi, *J. Am. Chem. Soc.*, 101, 5961 (1979); S. Fukuzumi and J. K. Kochi, *ibid.*, 102, 2141, 7290 (1980).
10) Y.-T. Fanchiang, *J. Chem. Soc., Chem. Commun.*, 1982, 1369.
11) For π complexes of organotransition metals, see: T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, 93, 3350, 3360 (1971).
12) S. Fukuzumi, N. Nishizawa, and T. Tanaka, *Chem. Lett.*, 1983, 1755.
13) D. H. Evans, "Encyclopedia of Electrochemistry of the Elements, Organic Section," ed by A. J. Bard and H. Lund, Marcel Dekker, New York (1978), Chap. XII-1 and references therein.

(Received January 11, 1984)