Photoreaction of Tris(ethylenediamine)cobalt(III) Ion with Bis(2-hydroxyethyl)dithiocarbamate Ion

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Complete ligand replacement of tris(ethylenediamine)cobalt(III)($[Co(en)_3]^{3+}$) by bis(2-hydroxyethyl)-dithiocarbamate ion(htc$^-$) forming $[Co(htc)_3]$ is induced by visible light in aqueous solution. The quantum yield of the reaction depends on the wavelength of the light and on the concentrations of the complex and the ligand. The distinct feature of this photo-induced substitution is that the quantum yield is higher than unity for the solution containing 0.02 mol dm^{-3} $[Co(en)_3]^{3+}$ and 0.13 mol dm^{-3} htc$^-$. The unusually high quantum yield is explained on the basis of a primary photoredox process followed by a chain reaction involving cobalt(II) species as chain carriers. Cobalt(III) complexes of an N_6 donor set such as $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_4(pn)]^{3+}$, $[Co(chxn)_3]^{3+}$, and $[Co(dien)_3]^{3+}$ also undergo similar photo-reaction, where pn, chxn, and dien denote 1,2-propanediamine, 1,2-cyclohexanediamine, and diethylenetriamine, respectively.

It is well known that irradiation on cobalt(III) complexes with light in the d-d band region causes ligand substitutions with quantum yields much lower than those of chromium(III) complexes.[1-4] Among cobalt(III) complexes, $[Co(en)_3]^{3+}$ is known to be quite inert for the irradiation of visible light. Recently, however, Matsubara and Kida found that $[Co(en)_3]^{3+}$ reacts with diethyldithiocarbamate ion(dtc$^-$) in aqueous solution forming solid $[Co(dtc)_3]$ upon irradiation at 550 nm (or even at longer wavelengths).[5] Although they were unsuccessful in determining quantum yield due to the precipitation of the product, they inferred the extremely high quantum yield for this photoreaction. Such a facile replacement of the ligand by the irradiation of light in the d-d band region is unusual for the photochemistry of cobalt(III) complexes. Therefore, the present study was aimed to elucidate the mechanism of this photoreaction by quantitative measurements.

In this study bis(2-hydroxyethyl)dithiocarbamate ion (htc$^-$) was used instead of diethyldithiocarbamate ion. The use of htc$^-$ enabled quantitative measurements of the reaction, because the product, $[Co(htc)_3]$, is fairly soluble in water. The overall reaction is simply expressed as

$$[Co(en)_3]^{3+} + 3htc^- \xrightarrow{h\nu} [Co(htc)_3] + 3en. \qquad (1)$$

Experimental

Materials. $[Co(en)_3]Cl_3 \cdot 3H_2O$,[6] $[Co(NH_3)_6]Cl_3$,[7] $[Co(NH_3)_4(pn)]Cl_3$,[8] $[Co(chxn)_3]Cl_3 \cdot 2H_2O$,[6] $[Co(dien)_2]Cl_3 \cdot 3H_2O$,[9] $[Co(trien)(en)]Br_3$,[10] and $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$[11] were prepared and purified according to the procedures described in the literature. The ligands are abbreviated as: en=ethylenediamine, pn=1,2-propanediamine, chxn=1,2-cycrohexanediamine, dien=diethylenetriamine, trien=triethylenetetraamine. Standard compounds for actinometry, $K[Cr(NH_3)_2(NCS)_4] \cdot H_2O$ and $K_3[Fe(ox)_3] \cdot 3H_2O$ (ox=oxalate ion), were prepared by the procedures described in the literature.[12,13] The crystals were recrystallized in the dark at least three times.

$K(C_2H_4OH)_2NCS_2$: An ethanol solution (100 cm^3) of carbon disulfide (20 g) was slowly added with stirring to a mixture of potassium hydroxide (20 g) and diethanolamine (40 g) in ethanol (300 cm^3). After stirring for 3 h, pale yellow crystals deposited were filtered by suction and dried in air stream. The crude crystals were dissolved in water (70 cm^3), and 300 cm^3 of ethanol was added to this solution. When the solution was cooled in an ice box, colorless crystals were separated out in 4 h. The crystals were recrystallized three times. Since this compound is apt to undergo gradual decomposition at room temperature, it was newly prepared every month and stored in a refrigerator. Found: C, 27.29; H, 4.63; N, 6.53%. Calcd for $C_5H_{10}NO_2S_2K$: C, 27.38; H, 4.60; N, 6.39%.

$[Co(htc)_3]$: An aqueous solution of $[Co(en)_3]Cl_3 \cdot 3H_2O$ (0.6 g in 20 cm^3) was mixed with an aqueous solution of K(htc) (0.5 g in 30 cm^3), and the solution was exposed to room light for three hours. Dark green crystal precipitated was recrystallized from DMF–water (1:1). Found: C, 30.32; H, 5.04; N, 6.84%. Calcd for $C_{15}H_{30}N_3O_6S_6Co$: C, 30.04; H, 5.15; N, 7.01%.

The elementary analyses were carried out at the Kyushu University Elementary Analysis Center.

Apparatus. A tungsten lamp (300 W) was used as a light source. The light beam which passed through a UV filter was monochromatized by an interference filter of transmission maximum at 451 nm ($T_{max}=43\%$, bandwidth at $1/2\,T_{max}=11$ nm). A cell jacket was mounted in a black box which has a window of interference filter. The cell jacket was thermostated at 20±0.1 °C by circulating water with a Taiyo Thermo Unit C-550. Spectroscopic quartz (10 mm) cells were used as reaction vessels. The cells were placed in the jacket at least 30 min before the irradiation so that the solution could reach the temperature of the cell jacket. The wavelength dependence of the photoreaction was studied by irradiating monochromatic lights at 585, 571, 535, 511, 486, and 460 nm with a JASCO Spectroirradiator Model CRM-FA. The irradiator equipped with a 3 kW Xe-lamp gives monochromatic light beams of bandwidth less than 15 nm.

Electronic absorption spectra were measured with a Shimadzu Multipurpose Spectrophotometer Model MPS-5000.

Actinometry. The intensity of 451 nm monochromatic light was measured by the method of Wegner and Adamson (Reineckate actinometry) and by the method of Hatchard and Parker(ferrioxalate actinometry).[12-14] The ratio of the light intensities determined by the different methods was 1.03±0.05, showing the reliability of the measurements. At the actual runs of experiments the intensity of 451 nm light was measured before and after the photoreaction of interest by the ferrioxalate actinometry. For the study of wavelength dependence of the photoreaction, intensity of the monochromatic lights of 585, 571, 535, 511, 486, and 460 nm were determined by the Reineckate actinometry.

Photoreaction. One milliliter of an aqueous solution of $[Co(en)_3]^{3+}$ and 2 cm^3 of an aqueous solution of htc^- were mixed in a quartz cell under dim light. In order to make the error due to the absorption of $[Co(htc)_3]$ formed as small as possible the irradiation time was adjusted for each 451 nm irradiation so that the internal filtration of the light by the absorption of $[Co(htc)_3]$ formed is less than 5% of the total absorption at the end of the irradiation.

Calculation of Quantum Yield. The amount of $[Co(en)_3]^{3+}$ reacted was determined by measuring the concentration of $[Co(htc)_3]$ formed, because no mixed complexes such as $[Co(htc)(en)_2]^{2+}$ and $[Co(htc)_2(en)]^+$ were detected from the observation of the spectra. The concentration of $[Co(htc)_3]$ formed was determined from the difference of absorbance at 630 nm between the solutions before and after irradiation. Thus, the quantum yield at 451 nm was calculated by the equation,

$$\phi = \frac{C_m}{I(1-\tau)t}, \tag{2}$$

where, C_m is the concentration of $[Co(htc)_3]$ (mol dm^{-3}), and I, τ, and t denote the intensity of light(einstein dm^{-3} s^{-1})-(einstein represents 1 mol of light quanta), transmittance of the initial solution, and irradiation time, respectively. In the cases of irradiation in the range 460—585 nm, quantum yield was calculated by using the equation derived by King *et al.*, in which the internal filtration effect was taken into consideration.[15,16)]

Results and Discussion

Absorption spectra of $[Co(en)_3]Cl_3$ and K(htc) are shown in Fig. 1, where quantum yield for the solution containing 0.02 mol dm^{-3} $[Co(en)_3]^{3+}$ and 0.13 mol dm^{-3} htc^- are also plotted in the range 460—585 nm. It is to be noted that very high quantum yields were obtained even at the lower-energy side of the d-d band of $[Co(en)_3]^{3+}$. From this fact it appears that the spin-triplet or -quintet states concern with this photoreaction, although no definite conclusion can be drawn at present.

Cobalt(III) complexes of an N_6-donor set such as $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_4(pn)]^{3+}$, $[Co(chxn)_3]^{3+}$, and $[Co(dien)_2]^{3+}$ also undergo similar reactions with htc^- upon irradiation of light in the d-d band region forming $[Co(htc)_3]$. The quantum yields were determined for 451 nm irradiation, and are summarized in Table 1. The table shows that the quantum yields determined are unusually high for cobalt(III) complexes. It is to be noted that the quantum yield for $[Cr(en)_3]^{3+}$ is much less than those of the cobalt(III) complexes (see Table 1). This is the reverse relation to the general rule for the photosubstitution of chromium(III) and cobalt(III) complexes.[1—4)]

In Fig. 2, quantum yields are plotted against the initial concentration of htc^-, the initial concentration of $[Co(en)_3]^{3+}$ being kept at 0.02 mol dm^{-3}. The quantum yield increases with increasing concentration of htc^-, reaching a plateau at higher concentration of htc^-. In Fig. 3, quantum yields are plotted against the initial concentration of $[Co(en)_3]^{3+}$, the initial concentration of htc^- being kept at 0.13 mol dm^{-3}. As seen in the figure, the quantum yield increases almost linearly with the concentration of $[Co(en)_3]^{3+}$ in this range of concentration. These facts may be interpreted on the assumption that the photoreaction

TABLE 1. QUANTUM YIELDS AND CHAIN REACTION PARAMETERS

Complex	ϕ a)	$\pm\delta$ b)	ρ c)
$[Co(NH_3)_6]^{3+}$	2.08	0.12	>10
$[Co(NH_3)_4(pn)]^{3+}$	1.80	0.17	10
$[Co(en)_3]^{3+}$	1.24	0.06	7.8
$[Co(chxn)_3]^{3+}$	1.00	0.05	5.1
$[Co(dien)_2]^{3+}$	0.45	0.02	1.3
$[Co(trien)(en)]^{3+}$	0.04	0.003	1.0
$[Cr(en)_3]^{3+}$	<0.001		1.0

The initial concentrations of the cobalt(III) complexes and htc^- were 0.02 mol dm^{-3} and 0.13 mol dm^{-3}, respectively. a) The quantum yield. b) The maximum error for the quantum yields estimated from repeated (at least three times) experiments. c) The chain reaction parameter, the ratio of the final concentration of $[Co(htc)_3]$ to the initial concentration of $[Co(H_2O)_6]^{2+}$.

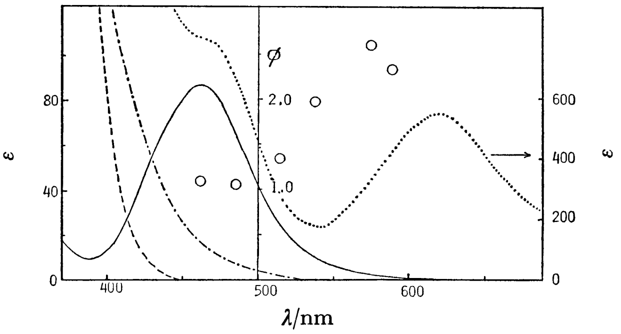

Fig. 1. Absorption spectra and quantum yield.
○: Quantum yield. Absorption spectra; ——: $[Co(en)_3]^{3+}$, — —: htc^-, —·—: difference spectrum of a solution containing htc^- (0.13 mol dm^{-3}) and $[Co(en)_3]^{3+}$ (0.02 mol dm^{-3}), and a solution containing $[Co(en)_3]^{3+}$ (0.02 mol dm^{-3}) extinction coefficient on left scale, ······: $[Co(htc)_3]$.

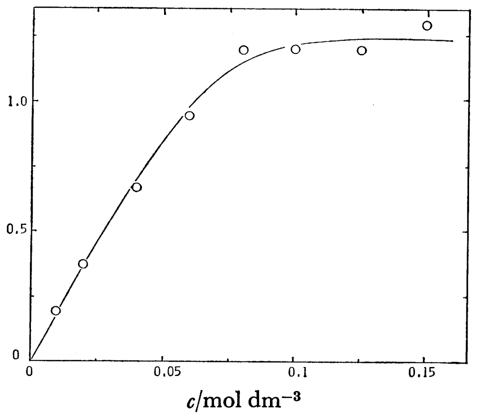

Fig. 2. Quantum yield (at 451 nm) as a function of the initial concentration of htc^-.
Initial concentration of $[Co(en)_3]^{3+}$ was kept at 0.02 mol dm^{-3}.

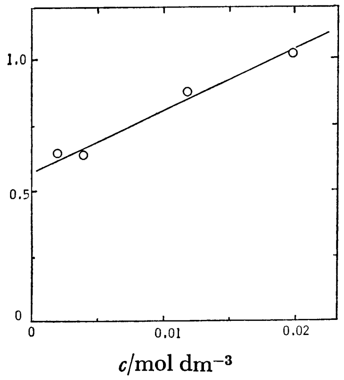

Fig. 3. Quantum yield (at 451 nm, at 15 °C) as a function of the initial concentration of $[\mathrm{Co(en)_3}]^{3+}$. The initial concentration of htc$^-$ was kept at 0.13 mol dm^{-3}.

occurs on the ion-pair $[\mathrm{Co(en)_3}]^{3+}\cdot\mathrm{htc}^-$, *i.e.*, the increase of the concentrations of $[\mathrm{Co(en)_3}]^{3+}$ and htc$^-$ increases the ratio of concentrations, $[\mathrm{Co(en)_3}]^{3+}\cdot\mathrm{htc}^-/[\mathrm{Co(en)_3}]^{3+}$.

The formation of ion-pairs is evidenced by the fact that the absorbance of the solution containing $[\mathrm{Co(en)_3}]^{3+}$ (0.02 mol dm^{-3}) and htc$^-$ (0.13 mol dm^{-3}) is higher than the sum of the absorbances of the solution of $[\mathrm{Co(en)_3}]^{3+}$ (0.02 mol dm^{-3}) and the solution of htc$^-$ (0.13 mol dm^{-3}) in the region <500 nm as shown in Fig. 1. If the above assumption is correct, the quantum yield should be reduced by the addition of the other anions which compete with htc$^-$ in forming ion-pairs with $[\mathrm{Co(en)_3}]^{3+}$. In order to elucidate the effect of anions on the quantum yield, the photoreactions were run in the presence of various anions. The results are illustrated in Fig. 4 and summarized in Table 2, together with the formation constants of the ion-pairs. As seen in Table 2, the presence of the anions considerably reduced the quantum yield, and the effect becomes stronger in the order, $\mathrm{NCS^-} < \mathrm{I^-} < \mathrm{Br^-} < \mathrm{Cl^-} < \mathrm{C_2O_4{}^{2-}}$, which is the same order as that of the ion-pair formation constants. This fact is in good harmony with the above assumption that the photoreaction initiates at the ion-pair $[\mathrm{Co(en)_3}]^{3+}\cdot\mathrm{htc}^-$.

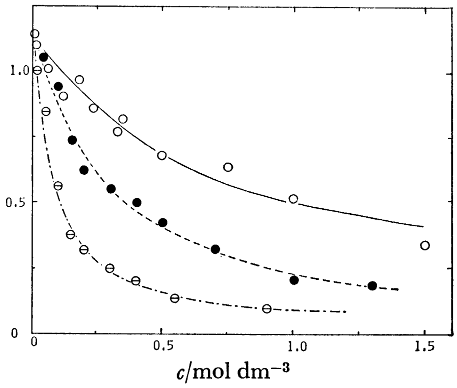

Fig. 4. Effect of anions on the quantum yield (at 451 nm).
○: KCl, ●: $\mathrm{KCH_3CO_2}$, ⊖: $\mathrm{K_2C_2O_4}$.

Table 2. The effect of anions on the quantum yield

Anions[a]	Concn/mol dm^{-3}	$\phi \pm \delta$	log K[b]	Ref.
NCS$^-$	0.33	0.92±0.08	1.34	7
I$^-$	0.33	0.81±0.08	1.46	7
Br$^-$	0.33	0.77±0.06	1.68	7
Cl$^-$	0.33	0.77±0.05	1.72	8
$\mathrm{CH_3COO^-}$	0.30	0.60±0.04	—	
$\mathrm{C_2O_4{}^{2-}}$	0.30	0.25±0.01	3.0	9

a) Potassium salts. b) K is the formation constant of the ion-pair with $[\mathrm{Co(en)_3}]^{3+}$.

Since the quantum yields higher than unity can be rationalized only in terms of a chain reaction induced by the photoreaction, we have assumed that the chain-carriers are produced in the reaction as shown below.

$$[\mathrm{Co(en)_3}]^{3+}\cdot\mathrm{htc}^- \xrightarrow{h\nu} [\mathrm{Co(en)_3{}^*}]^{3+}\cdot\mathrm{htc}^- \longrightarrow [\mathrm{Co(en)_3}]^{2+} + \mathrm{htc}^{\cdot} \tag{3}$$

On this assumption, the reaction rate must be affected by the presence of an oxidizing agent, *e.g.*, $\mathrm{O_2}$. In fact, the formation of $[\mathrm{Co(htc)_3}]$ was considerably decreased in the reaction under $\mathrm{O_2}$ stream as compared with the case under $\mathrm{N_2}$ stream, (1/30 at the optimum condition so far examined). In the product of a long time irradiation pale yellow solid was detected. It was revealed to be solid sulfur, because it melted at 118 °C and showed no peaks in the IR spectrum.[20] Thus, it is likely that the radical htc$^{\cdot}$ which had been formed in the reaction 3 was removed from the reaction system forming –S–S– bonds finally yielding $\mathrm{S_8}$. Since $[\mathrm{Co(en)_3}]^{2+}$ is labile, it readily undergoes the ligand substitution reaction in the solution containing excess of htc$^-$.

$$[\mathrm{Co(en)_3}]^{2+} + 3\mathrm{htc}^- \longrightarrow [\mathrm{Co(htc)_3}]^- + 3\mathrm{en} \tag{4}$$

This reaction may be followed by the reaction,

$$[\mathrm{Co(en)_3}]^{3+} + [\mathrm{Co(htc)_3}]^- \longrightarrow [\mathrm{Co(en)_3}]^{2+} + [\mathrm{Co(htc)_3}]. \tag{5}$$

Thus, the net reaction of 4 and 5 is

$$[\mathrm{Co(en)_3}]^{3+} + 3\mathrm{htc}^- \longrightarrow [\mathrm{Co(htc)_3}] + 3\mathrm{en}, \tag{6}$$

where $[\mathrm{Co(en)_3}]^{2+}$ acted as a chain-carrier of the reaction 4 and 5.

In order to examine the validity of the above assumption we have added a small amount of aqueous cobalt(II) chloride to a solution containing $[\mathrm{Co(en)_3}]^{3+}$ (0.02 mol dm^{-3}) and htc$^-$ (0.13 mol dm^{-3}) in the dark. The reaction proceeded readily in the dark forming $[\mathrm{Co(htc)_3}]^{3+}$. In order to describe the effect of $[\mathrm{Co(H_2O)_6}]^{2+}$ on the reaction 6, we defined a parameter $\rho =$ the final amount of $[\mathrm{Co(htc)_3}]$/the amount of $[\mathrm{Co(H_2O)_6}]^{2+}$ added. In Table 1 quantum yield(ϕ) and ρ for various cobalt(III) complexes of the $[\mathrm{CoN_6}]^{3+}$ type are summarized. As seen in the table, ρ is generally larger than unity, except for $[\mathrm{Co(dien)_2}]^{3+}$ and $[\mathrm{Co(trien)(en)}]^{3+}$, clearly indicating that the chain reaction took place. Table 1 also shows that the increasing order of the quantum yield is exactly in accord with that of ρ. Thus, it is clear that the unusually high quantum yield and the complete replacement of ligands is due to the chain reaction initiated at the photoredox process 3 and the labile cobalt(II) species $[\mathrm{Co(en)_3}]^{2+}$ which undergoes complete ligand replacement in the presence of excess htc^- (reaction 4).

On the basis of the above discussion, we propose the total reaction mechanism as follows:

$$\begin{aligned}&[\mathrm{Co(en)_3}]^{3+} + \mathrm{htc}^- \longrightarrow [\mathrm{Co(en)_3}]^{3+}\cdot\mathrm{htc}^- && \text{ion-pair formation}\end{aligned}$$

$$\left.\begin{aligned}&[\mathrm{Co(en_3}]^{3+}\cdot\mathrm{htc}^- \xrightarrow{h\nu} [\mathrm{Co(en)_3{*}}]^{3+}\cdot\mathrm{htc}^-\\ &\longrightarrow [\mathrm{Co(en)_3}]^{2+} + \mathrm{htc}\cdot\end{aligned}\right\}\ \text{photoredox reaction}$$

$$\left.\begin{aligned}&[\mathrm{Co(en)_3}]^{2+} + 3\mathrm{htc}^- \longrightarrow [\mathrm{Co(htc)_3}]^- + 3\mathrm{en}\\ &[\mathrm{Co(htc)_3}]^- + [\mathrm{Co(en)_3}]^{3+} \longrightarrow [\mathrm{Co(htc)_3}] + [\mathrm{Co(en)_3}]^{2+}\end{aligned}\right\}\ \text{chain reaction}$$

$$\left.\begin{aligned}&[\mathrm{Co(htc)_3}]^- \xrightarrow{\mathrm{O_2}} [\mathrm{Co(htc)_3}]\\ &[\mathrm{Co(en)_3}]^{2+} \xrightarrow{\mathrm{O_2}} [\mathrm{Co(en)_3}]^{3+}\\ &\mathrm{htc}\cdot \longrightarrow \dashrightarrow \mathrm{S_8}\end{aligned}\right\}\ \text{chain-stopping reactions}$$

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