Photochemical Generation of μ-Amido-μ-peroxo-bis[bis(ethylenediamine)-cobalt(III)] Complex from the Corresponding μ-Hyperoxo Complex in Neutral Aqueous Solution

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Synopsis. A μ-amido-μ-hyperoxo complex, $[(en)_2Co(NH_2,O_2^-)Co(en)_2]^{4+}$, was found to generate the corresponding μ-peroxo complex, together with mononuclear cobalt(III) complexes upon irradiation with near-ultraviolet light in a neutral aqueous solution. The result is different from that obtained in an acidic aqueous solution, in which the products are $[Co(NH_3)(en)_2(H_2O)]^{3+}$ and Co_{aq}^{2+}. The photochemical reaction mechanisms are discussed.

The photosensitivity of the μ-hyperoxo-bis[pentaamminecobalt(III)] complex, $[(NH_3)_5Co(O_2^-)Co(NH_3)_5]^{5+}$, first observed by Sykes,[1] has been investigated by Barnes, et al.,[2] and by Valentine and Valentine.[3-5] The μ-hyperoxo cobalt(III) complexes are photosensitive, and photodecomposition occurs upon irradiation with near-ultraviolet light (i.e. light with wavelengths longer than 300 nm).

Photochemical reactions of μ-amido-μ-hyperoxo-bis[bis(ethylenediamine)cobalt(III)] complex, $[(en)_2Co(NH_2,O_2^-)Co(en)_2]^{4+}$, in acidic aqueous solutions were studied by Valentine and Valentine,[4] who established the stoichiometry of the reactions as follows:

$$[(en)_2Co(NH_2,O_2^-)Co(en)_2]^{4+} \xrightarrow[H^+,\ H_2O]{h\nu(>300\,nm)} cis\text{-}[Co(NH_3)(en)_2(H_2O)]^{3+} + O_2 + Co^{2+} + 2enH_2^{2+} \quad (1)$$

We have studied the photochemistry of the same complex in a neutral aqueous solution, and found that the corresponding μ-peroxo cobalt(III) complex is formed together with mononuclear cobalt(III) complexes, which is different from the result obtained in an acidic aqueous solution.

Experimental

$[(en)_2Co(NH_2,O_2^-)Co(en)_2](ClO_4)_4$ and $[(en)_2Co(NH_2,O_2^{2-})Co(en)_2](NO_3)_3\cdot 2.5H_2O$ were obtained by methods described in the literature,[4,6] and recrystallized. The deaerations of the solutions used for photolysis were carried out by bubbling with pure nitrogen. A sample solution containing the μ-amido-μ-hyperoxo complex was irradiated continuously in a 1-cm quartz cell using a high-pressure mercury lamp, UM-102 (100 W), or an ultrahigh-pressure mercury lamp, USH-500D (500 W) (Ushio Electric Co.), at room temperature. Monochromatic light (313, 365, and 436 nm) was obtained by a combination of solution and glass filters. The absorption spectra were recorded on a Shimadzu MPS-2000 spectrophotometer.

For investigating the reaction products, about 20 ml of the solution in a fused silica cell was irradiated with light. The number of components of the photochemical decomposition products and their identities were determined by spectrophotometric analyses of the photolyzed solutions and by ion-exchange chromatography on a cation-exchange resin (CM-Sephadex C-25 in the sodium form). A portion of the irradiated solution was passed through a cation-exchange column. The absorbed band was eluted with 1.2 mol dm^{-3} sodium perchlorate solution. The first group eluted consisted of two mononuclear complexes which could not be separated from each other for the acid-base equilibria in a neutral aqueous solution as described later. After removing mononuclear complexes, μ-peroxo and μ-hyperoxo complexes were successively eluted in this order. Another portion of the irradiated solution was passed through a column for the separation of two mononuclear complexes. The absorbed band was eluted with a 0.01 mol dm^{-3} sodium hydroxide solution containing 0.3 mol dm^{-3} sodium perchlorate. The first two bands corresponded to mononuclear complexes, *cis*-$[Co(OH)_2(en)_2]^+$ and *cis*-$[Co(OH)(NH_3)(en)_2]^{2+}$. The μ-peroxo complex was identified by comparing the absorption spectrum with that of an authentic sample synthesized by a method described in the literature.[6] The mononuclear products were identified spectrophotometrically.[7,8] Oxygen was determined by gas chromatography.

Results and Discussion

The absorption spectrum of $[(en)_2Co(NH_2,O_2^-)Co(en)_2]^{4+}$ in an aqueous solution has two peaks (466 and 686 nm) in visible region. The electronic structure was studied by Lever and Gray.[9] The absorption spectral changes are shown in Fig. 1 for irradiation of the deaerated aqueous solution at the $O_2^-\rightarrow Co(III)$ charge-transfer band (351 nm). The absorption at 466 and 686 nm decreased with an increase in the irradiation time. Valentine and Valentine[4] proposed Eq. 1 in order to account for the photodecomposition reaction by determining the photolyzed products chromatographically. We can suggest that more

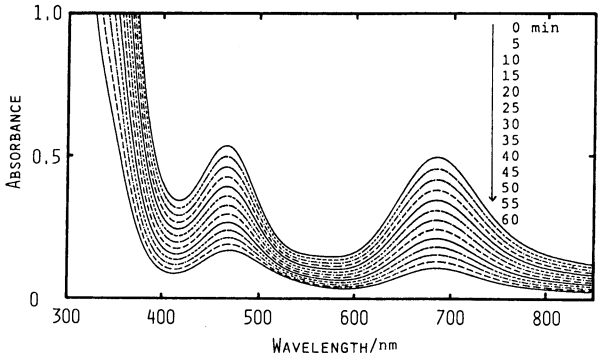

Fig. 1. Absorption spectral changes of 1.00×10^{-3} mol dm^{-3} $[(en)_2Co(NH_2,O_2^-)Co(en)]^{4+}$ in deaerated aqueous solution of 0.1 mol dm^{-3} $HClO_4$ upon irradiation at 365 nm light.

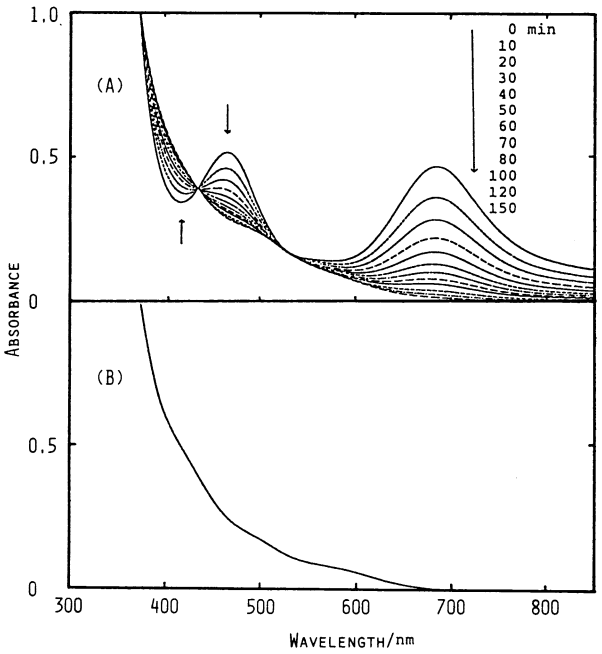

Fig. 2. UV and visible absorption spectra.
A: Absorption spectrtal changes of 1.00×10^{-3} mol dm^{-3} $[(en)_2Co(NH_2, O_2^-)Co(en)_2]^{4+}$ upon irradiation of the neutral deaerated solution at 365 nm light.
B: Absorption spectrum of 5.00×10^{-4} mol dm^{-3} $[(en)_2Co(NH_2, O_2^{2-})Co(en)_2]^{3+}$ in neutral aqueous solution.

detailed photodecomposition reactions in aqueous solutions are as follows. In the excited state that can be formulated as $*[(en)_2Co(III)(NH_2,O_2^0)Co(II)(en)_2]^{4+}$, the oxygen molecule should be released by a kinetically labile Co(II) species (Eq. 2), which then undergoes a very rapid aquation leading to the Co_{aq}^{2+} (Eq. 3) in an acidic aqueous solution. Since

$$[(en)_2Co(NH_2, O_2^-)Co(en)_2]^{4+} \xrightarrow{h\nu} *[(en)_2Co(NH_2, O_2^0)Co(en)_2]^{4+} \xrightarrow{H_2O} cis\text{-}[Co(OH)(NH_3)(en)_2]^{2+} + cis\text{-}[Co(en)_2(H_2O)_2]^{2+} + O_2 \quad (2)$$

$$cis\text{-}[Co(en)_2(H_2O)_2]^{2+} \xrightarrow{H^+} Co^{2+} + 2enH_2^{2+} + 2H_2O \quad (3)$$

the ligand dissociation reaction in Co(II)–polyamine complexes becomes slower as the pH is increased,[10,11] it appears that $[Co(en)_2(H_2O)_2]^{2+}$ reacts with μ-hyperoxo complex before the dissociation in neutral solution as stated below.

When the μ-amido-μ-hyperoxo complex was irradiated with light at 365 nm in a neutral aqueous solution, the absorption changes were different from those obtained in acidic aqueous solutions, as shown in Fig. 2A. The intensity of the absorption in the 432—850 nm range decreased with an isosbestic point at 432 nm. The absorbance at 686 nm disappeared after 150 min irradiation with a high-pressure mercury lamp under our experimental conditions. The spectrum in Fig. 2A changed with the irradiation time and approached a final form, which was very similar to the spectrum of the corresponding μ-peroxo complex (Fig. 2B). Similar results were obtained for 313 and 436 nm irradiation. Such an attainment of the limiting spectrum is due to the inertness of the resulting μ-peroxo complex, compared to the photosensitive μ-hyperoxo complex, upon irradiation in the range of the wavelength examined. The decomposition reaction was independent of the presence or absence of dissolved oxygen.

The number of components and their identities were determined by spectrophotometric analyses of photolyzed solutions and by ion-exchange chromatography. It was found that μ-amido-μ-peroxo complex and two kinds of mononuclear complexes could be generated in neutral solutions. The photodecomposition of μ-hyperoxo complex is also accompanied by the generation of oxygen. Accordingly, we concluded that Eq. 4 describes the stoichiometry for the photochemical decomposition of μ-amido-μ-hyperoxo complex in a neutral aqueous solution.

$$2[(en)_2Co(NH_2, O_2^-)Co(en)_2]^{4+} + 3H_2O \xrightarrow{h\nu} [(en)_2Co(NH_2, O_2^{2-})Co(en)_2]^{3+} + cis\text{-}[Co(OH)(NH_3)(en)_2]^{2+} + cis\text{-}[Co(OH)(en)_2(H_2O)]^{2+} + O_2 + H^+ \quad (4)$$

The resulting mononuclear hydroxo complexes in Eq. 4 are in equilibria with aqua complexes, *cis*-$[Co(NH_3)(en)_2(H_2O)]^{3+}$ and *cis*-$[Co(en)_2(H_2O)_2]^{3+}$, whose acid ionization constants are pK=6.05 (25 °C) and pK=6.06 (25 °C), respectively.[8,12]

The absorption near 500 nm of the final spectrum in Fig. 2A is a little larger than that in Fig. 2B, which is due to a contribution of the mononuclear complexes formed together with a μ-peroxo complex. The contribution is very small for the small molar extinction coefficient of the mononuclear cobalt(III) complexes, compared with that of the μ-peroxo complex.

We believe that in neutral aqueous solution the *cis*-$[Co(en)_2(H_2O)_2]^{2+}$, formed by the photodecomposition of the μ-hyperoxo complex (Eq. 2), reacts with the remaining μ-hyperoxo complex to give *cis*-$[Co(OH)(en)_2(H_2O)]^{2+}$ and μ-peroxo complex:

$$cis\text{-}[Co(en)_2(H_2O)_2]^{2+} + [(en)_2Co(NH_2, O_2^-)Co(en)_2]^{4+} \longrightarrow cis\text{-}[Co(OH)(en)_2(H_2O)]^{2+} + [(en)_2Co(NH_2, O_2^{2-})Co(en)_2]^{3+} + H^+ \quad (5)$$

The rate of the dissociation of en from $[Co(en)_2(H_2O)_2]^{2+}$ is slower in a neutral solution than in an acidic solution.[10,11] Therefore, it appears that the reaction shown by Eq. 5 occurs before the decomposition of $[Co(en)_2(H_2O)_2]^{2+}$ to $[Co(en)(H_2O)_4]^{2+}$ or Co_{aq}^{2+}.

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