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The Optical Absorption Spectra of Ferrocene and Biferrocene Anions Produced in the γ-Ray Irradiation by the Matrix-protection Method

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The absorption spectra of the transient species produced through the one-electron reduction of ferrocene and biferrocene were determined by applying a radiation-chemical method in frozen glass matrices. The spectral shapes were assigned to ferrocene- and biferrocene-anionic species on the basis of the experimental results. In the biferrocene anion, the "intervalence transfer" band was observed at about 2050 nm.

Oxidized ferrocene and biferrocene have been extensively studied by the measurement of their optical-absorption, EPR, and Mössbauer spectra, and much information about their physical and chemical properties has been accumulated.[1–8] On the contrary, nothing is known about the reduced forms of ferrocene and biferrocene, because their syntheses have not yet been completed. The failure of efforts thus far undertaken for the syntheses suggests that the reduced forms are too unstable to be isolated by the usual chemical processes. In the present work, we wish to report on the optical-absorption spectra of the transient species which are observed after a one-electron reduction of ferrocene and biferrocene by applying radiation-chemical reactions to frozen glass solution. The spectra were assigned to the ferrocene and biferrocene anions.

Experimental

All the chemicals used were of the purest grade commercially available. The biferrocene was synthesized by the ordinary method.[9] The 2-methyltetrahydrofuran (MTHF) was purified by distillation over metallic sodium. The distillate was stored in vacuo over a sodium–potassium alloy. The ferrocene was recrystallized before use.

Each ferrocene solution (15 mM) and biferrocene solution (9 mM) in MTHF was sealed in an optical cell with an optical path of 1.5 mm or in an EPR sample tube, and irradiated at 77 K with γ-rays from ^{60}Co; the total doses for the ferrocene and biferrocene MTHF-glass matrix were 215 krad and 420 krad, respectively, for H_2O.

The absorption spectra were measured on a Cary 14 RI, while the EPR measurement was carried out by using a JEOL PF 3AX at 77 K.

Radiation-chemical Method for Preparation of Ion Radicals

Although there seems to be an inveterate prejudice that says radiation-chemical processes are too complicated, it has been demonstrated that the irradiation of a frozen solution in a selected solvent with ionizing rays provides us with an excellent method for the selective preparation of solute cation or anion species.[10,11] The scheme has also been well examined as will be briefly illustrated below.

For the selective preparation of solute anion species in an alcoholic or ethereal glass solution, the processes may be described as follows:

$$e^- + S \longrightarrow S^- \tag{1}$$

$$RH^+ + RH \longrightarrow RH_2^+ + R\cdot, \tag{2}$$

where S and RH denote the solute and a solvent species; e^- and RH^+, the electrons and holes induced by ionizing radiations and S^- and RH_2^+, the solute anion species and protonated holes, respectively. The protonated holes are stable species such as hydronium ions produced in the irradiated water. The reaction of RH^+ with the surrounding solvent molecules (Reaction 2) proceeds so fast that solutes added in a small amount cannot scavenge the holes. The absorption bands of the trapped electrons, which are observed in γ-irradiated glass solutions in the absence of solutes, are replaced by the bands of solute anions when a sufficient amount of solute is added to the glass solution. No absorption band is observed for RH_2^+ and $R\cdot$ in the visible and near-infrared regions.

The selective production of solute cations is also proved by the use of organic halides, RX, such as Freons as solvents:

$$RX^+ + S \longrightarrow S^+ \tag{3}$$

$$e^- + RX \longrightarrow R\cdot + X^-. \tag{4}$$

In Reaction 4, RX works to prevent the solute species from forming a solute-anion species, removing electrons in the system. Those methods described above, which will hereafter be referred to as "matrix protection method," have been successfully applied to the study of radical ions of many organic compounds[10–13] and to the study of the one-electron reduction of several organometallic compounds.[14,15] We have also carefully applied this method to ferrocene and biferrocene in order to prepare their anions.

Results and Discussion

Prior to applying the method for the one-electron reduction of ferrocene and biferrocene, the absorption spectra of the cationic species produced in γ-ray irradiated frozen solutions of ferrocene and biferrocene in a freon mixture ($CFCl_3$ 1: CF_2BrCF_2Br 1) were determined. Figures 1-a and 1-b show the spectra taken after irradiating frozen freon mixture glass solutions contain-

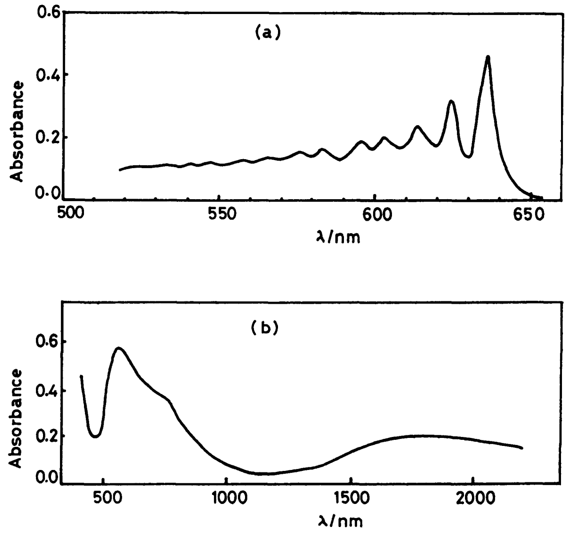

Fig. 1. Absorption spectra of ferrocenium (a) and biferrocene (b) cation obtained by a radiation-chemical method; the total dose for ferrocence (50 mM) and biferrocene (2 mM) Freon-mixture glass solution was 430 krad and 215 krad for H_2O, respectively.

ing ferrocene and biferrocene respectively. The spectral shapes agree well with those of the ferrocenium ions and biferrocene mono-cations prepared by chemical methods.[3,7,8] The dark blue precipitates obtained by warming the solutions to room temperature were determined to be cationic salts.

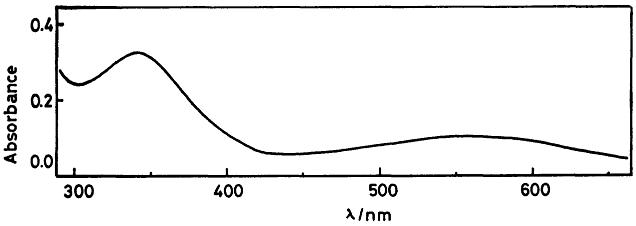

Fig. 2. Absorption spectrum of ferrocene anion taken after photobleaching of residual trapped electrons.

The spectrum taken after the photobleaching of the residual trapped electrons with a filtered light (λ>520 nm) for the γ-ray irradiated MTHF glass solution containing ferrocene is shown in Fig. 2. The two characteristic bands with peaks at 340 and 550 nm in the spectrum can not be found when the solution includes biphenyl (30 mM) as an additional solute before the irradiation, while the bands of biphenyl anions appear clearly. This suggests that the 340- and 500-nm bands are associated with a species resulting from a reaction which competes with the biphenyl-anion formation; *i.e.*, a kind of one-electron reduction process. The results also suggest that the electron affinity of ferrocene should be lower than that of biphenyl previously reported by us.[16] Another experimental result obtained in methanol glass containing ferrocene showed that trapped electrons are not scavenged by ferrocene. In the process of Reaction 1, it is obvious that solutes, S, which a lower electron affinity than the solvent cannot be reduced.

The possibility of the protonation of the anions may be excluded, because the spectrum shown in Fig. 2 is not in accordance with that of the cyclopentadiene anions observed by Shida,[17] although cyclopentadiene anions, $C_5H_6^-$, would be formed if protonation occurred. A dissociative electron attachment, like Reaction 4, was observed for solutes of certain organic halides.[10] Recent studies have revealed that cobalt(III) coordination compounds can undergo a one-electron reduction in the γ-ray irradiation of a MTHF glass solution at 77 K to form their anions, which they decompose on warming.[14,15] EPR studies of γ-ray irradiated tetraphenylporphyrinatocobalt(III) chloride in MTHF at 77 K indicate that the cobalt ions and chloride ions remain at a distance close enough to interact with each other in a transient species.[15] This suggests that MTHF glass is very effective for protecting the dissociation of any fragments at 77 K. In conclusion, therefore, the spectrum shown in Fig. 2 may be safely assigned to ferrocene anions. The disappearance of the spectra on warming the glass solution indicates that ferrocene anions are too unstable to be isolated at higher temperatures. The assignment is also verified by the resemblance of the observed spectrum of cobaltocene,[18] an isoelectronic analogue to the ferrocene anion. The band around 550 nm is attributable to the transition of an electron from a doubly occupied e_{2g} or a_{1g} orbital to the half-occupied e_{1g} orbital, by analogy to cobaltocene. EPR measurements taken for the same species with the absorption bands at 340 and 550 nm showed the g-values, g_x and g_z, to be 1.52 and 1.66 respectively. These values are close to those ($1.65<g_x<1.85$ and $g_z=1.685$) reported for cobaltocene doped in ferrocene at 4.2 K.[18]

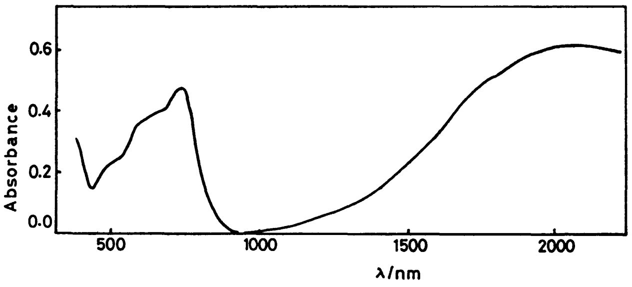

Fig. 3. Absorption spectrum of biferrocene anion taken after photobleaching of residual trapped electrons.

Figure 3 demonstrates the spectrum of a γ-ray-irradiated MTHF glass solution containing biferrocene, measured after photobleaching the residual trapped electrons with a filtered light (λ>520 nm). The spectrum consists of the visible bands (500—800 nm) and a near-infrared band with a peak at *ca.* 2050 nm. All those bands decay when the solution is warmed, and may be attributed to a single species. The spectrum can be assigned to biferrocene mono-anions, on the basis of the radiation-chemical studies described in the consideration of the ferrocene anions.

The visible bands are attributable to the ferrocene-anion moiety in the biferrocene mono-anion because of its similarity to the 550-nm broad band in Fig. 2. (No transition occurs above 550 nm for ferrocene and biferrocene.[3,8]) The near-infrared band at 2050 nm that was not observed in the ferrocene anion is quite similar to the 1900-nm band of the biferrocene mono-cation found in Fig. 1-b, which has been known as the "intervalence transfer" band.[7,8] It seems, therefore, reasonable to ascribe the 2050-nm band to the "intervalence transfer" between $[\mathrm{Fc(I)Fc(II)}]^- \rightarrow [\mathrm{Fc(II)Fc(I)}]^-$, where Fc(I) and Fc(II) denote the ferrocene anion and the ferrocene moiety respectively. The near-infrared band has a shoulder at about 1700 nm, as is found in Fig. 3.

The results of the work on the ferrocene and biferrocene anions show that the reduced organometallic compounds can be prepared by applying the matrix-protection method in a MTHF glass solution. The observation of the absorption spectra on the reduced species will provide us with valuable information about the physical and chemical properties of the species too unstable to be isolated, such as the intriguing character of mixed-valence species.

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