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The Temperature Dependence of the Mixed and Intervalence State in Mono-oxidized *trans*-μ-(*as*-Indacene)bis(cyclopentadienyliron)

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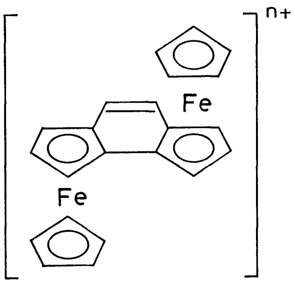
The temperature dependence first observed in the Mössbauer spectrum for mono-oxidized *trans*-μ-(*as*-indacene)bis(cyclopentadienyliron) was interpreted in terms of the increase in the rate of intervalence-electron transfer between two irons with an increase in the temperature. The cyclic voltammetric study of *trans*-μ-(*as*-indacene)bis(cyclopentadienyliron) indicates that the metal-metal interaction in the monocation of the compound is greater than that in the monocation of biferrocene at room temperature.

The so-called "mixed-valence" compounds have been extensively investigated in connection with the increased interest in superconductive materials and biological "mixed-valence" systems.[1-6] The monocation salts of binuclear ferrocenes, in which two kinds of iron atoms, formally Fe(II) and Fe(III), are simultaneously present, have attracted much attention in the field of "mixed-valence" chemistry and have been investigated by using several physico-chemical measurements.[7-19]

As is known by means of Mössbauer spectroscopy, some of the monocation salts of binuclear ferrocenes give two different valence states of irons, corresponding to bi- and trivalent irons, while the others give iron atoms in an intervalent state averaged between these two valence states. In the latter compounds, the "intervalence state" has been interpreted by assuming a thermal-electron transfer between the two iron atoms on a time scale shorter than the life-time of the excited Mössbauer nuclear level, *ca.* 10^{-7} s. There has, however, been no direct experimental proof for this speculative interpretation of the mechanism, because there has been no binuclear ferrocene derivatives' monocation which shows a typical temperature-dependent Mössbauer spectrum from an isolated mixed-valence state to a single averaged valence state.

It is known by means of Mössbauer spectroscopy that the mono-oxidized biferrocenylene(bis(μ-bicyclopentadienyl)-diiron(II)) gives iron atoms in an intervalent state[16,18] and the averaging has been speculated to proceed either through the cyclopentadienyl rings or directly through the overlapped *d*-orbitals of each iron atom. It was recently demonstrated, based on Mössbauer spectroscopic studies of the mono-oxidized salts of acetylene-bridged binuclear ferrocenes, that the π-conjugated system(s) between two ferrocenyl moieties plays an important role in the appearance of the intervalent state.[20,21]

During the process of verifying the role of the π-conjugated system bridged between two ferrocene moieties in the molecule which has a *trans*-conformation with respect to iron atoms, in contrast with biferrocenylene's and [2.2]ferrocenophane-1.13-diyne's monocation, a model compound of biferrocene derivatives with the conformation fixed in the *trans* form, *trans*-μ-(*as*-indacene)bis(cyclopentadienyliron), $(C_{12}H_8)Fe_2(C_5H_5)_2$ (**1**) and its monocation salt, $(C_{12}H_8)Fe_2(C_5H_5)_2{}^+I_3{}^-0.5I_2$ (**2**) were first synthesized.[22] The latter monocation salt (**2**) shows a trapped mixed-valence-type spectrum at 4.2 K and an intervalence-type spectrum at room temperature. The present paper will describe the temperature dependence of the valence state of the salt (**2**) as determined by means of Mössbauer spectroscopy. Cyclic voltammograms of the compound (**1**) will also be reported in order to elucidate the degree of the metal-metal interaction in the monocationic species.



(**1**) n = 0

(**2**) n = 1, $X^- = I_3{}^- 0.5I_2$

Fig. 1. The structure of **1** and **2**.

Experimental

Materials. *trans*-μ-(*as*-Indacene)bis(cyclopentadienyliron) (**1**) was prepared by the reaction of iron(II) chloride with a mixture of lithium cyclopentadienide and dilithium *as*-indacenide prepared by the reaction of dihydro-*as*-indacene with *n*-butyllithium. To a solution of tetrahydrofuran containing 0.62 g (4 mmol) of dihydro-*as*-indacene and cooled to −70 °C, 2.64 g (40 mmol) of cyclopentadiene was added. 32 ml of solution of 1.5 M *n*-butyllithium in hexane was added in drops over a period of 15 min. The mixture was allowed to stand for about 15 min until the temperature rose to room temperature. After the mixture had then been left for another 10 min, it was poured, at room temperature, into a suspension of iron(II) chloride prepared immediately before use. After the mixture had been allowed to stand for 30 min under stirring, the solvent was evaporated off and the residues were extracted with hexane. The extract was rapidly separated from ferrocene by column chromatography on alumina. **1** was thus obtained in the form of reddish needles in a yield of 3%. Mp 210—211 °C. Found: C, 66.79; H. 4.73%. Calcd for $C_{22}H_{18}Fe_2$: C, 67.05; H, 4.60%.

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TABLE 1. HALF-WAVE POTENTIALS FOR *trans*-μ-(*as*-INDACENE)-BIS(CYCLOPENTADIENYLIRON) (**1**) AND RELATED COMPOUNDS IN A CH_3CN SOLUTION CONTAINING 0.1 M *n*-Bu_4NClO_4

Compound	$E_{1/2}(1)$[a]	$E_{1/2}(2)$[a]	$\Delta E_{1/2}$[b]
trans-μ-(*as*-Indacene)-bis(cyclopentadienyliron)	0.29	0.70	0.41
Biferrocene	0.36	0.68	0.32
1′,1‴-Diacetylbiferrocene	0.62	0.92	0.30
1′,1‴-Diethylbiferrocene	0.28	0.63	0.35
2,2″-Dimethylbiferrocene[c]	0.37	0.63	0.26

a) Volts *vs.* Ag/AgCl electrode at 250 mm/s. b) $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$. c) Cited from Ref. 15, where CV was determined in CH_3CN containing Et_4NClO_4 (0.1 M) in volts *vs.* SCE at 100 mm/s.

The monocation salt, $(C_{12}H_8)Fe_2(C_5H_5)_2{}^+I_3{}^-$ $0.5I_2$ (**2**), was prepared through the oxidation of **1** in benzene with iodine. Found: C, 29.23; H, 2.23%. Calcd for $C_{22}H_{18}Fe_2I_4$: C, 29.31; H, 2.06%.

Biferrocene derivatives,[23-26] polyethylferrocenes,[27] and aminoferrocene[38] were prepared according to the methods previously reported in the literature.

Measurements. The ^{57}Fe Mössbauer measurements were carried out by using a ^{57}Co(Pt) source moving in a constant acceleration mode. The isomer shifts are determined relative to metallic iron foil. The experimental errors of the isomer shifts and quadrupole splittings are ±0.05 mm/s for Compound **2** and ±0.02 mm/s for the other compounds.

Cyclic voltammograms of biferrocene, 1′,1‴-diacetyl- and 1′,1‴-diethylbiferrocene, and Compound **1** were obtained using a Hokuto Denki HB-107A function generator and a Hokuto Denki HA-201 potentiostat combined with a standard three-electrode configuration. The working electrode, a platinum button (Beckman), and the reference, an Ag/AgCl electrode, were connected *via* a salt bridge containing *n*-Bu_4NClO_4 (0.1 M) in CH_3CN. The half-wave potentials given in Table 1 were calculated from the peak potentials.

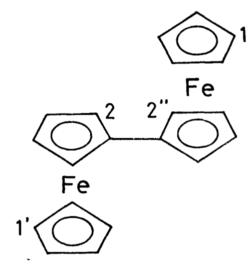

Fig. 2. The number of positions of substituents in the biferrocenes.

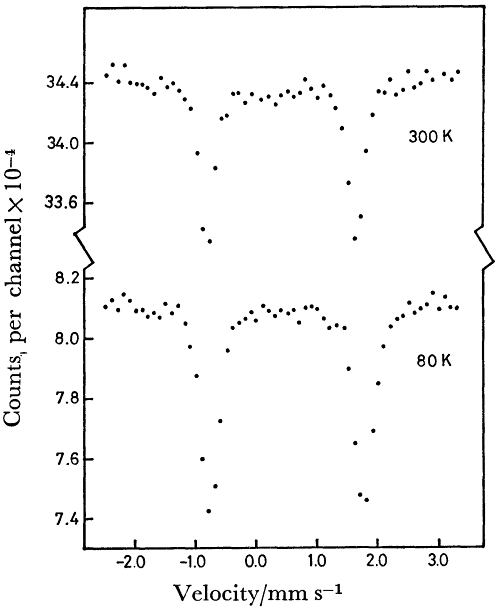

Fig. 3. Mössbauer spectra of $(C_{12}H_8)Fe_2(C_5H_5)_2$ (**1**) at 80 and 300 K.

Results and Discussion

The half-wave potentials obtained by means of cyclic voltammetry for Compound **1** and related compounds are summarized in Table 1. The number of positions of substituents in biferrocenes shown in Table 1 are illustrated in Fig. 2. In the cyclic voltammograms of the compounds in CH_3CN solutions containing 0.1 M *n*-Bu_4NClO_4, two steps of the one-electron oxidation were observed. It is known that the difference in the half-wave potentials ($\Delta E_{1/2}$) can be used as the measure of the metal-metal interaction in a mono-oxidized binuclear ferrocene.[14] The larger value of $\Delta E_{1/2}$ in **1** (0.41 V) compared to that in biferrocene (0.32 V) suggests that the metal-metal interaction in the monocation of **1** is greater than that in the monocation of biferrocene. The $\Delta E_{1/2}$ of **1** is also somewhat greater than those of the substituted biferrocenes listed in Table 1, indicating that the large $\Delta E_{1/2}$ of **1** should be ascribed to the *trans*-conformation of the ferrocenyl moieties of **1** rather than to a simple substituent's effect of the fused ring in **1**. The values of $\Delta E_{1/2}$ reported for other substituted biferrocenes by LeVanda *et al.* are also lower than that of **1**,[15] although their experimental conditions were a little different from those of the present studies. The small $\Delta E_{1/2}$ (0.26 V) found on 2,2″-dimethylbiferrocene[15] may be ascribed to the incomplete *trans*-conformation caused by the steric hindrance attributable to substituted rings. The results obtained for the compounds listed in Table 1 suggest that the two ferrocenyl moieties are twisted from a coplanar conformation with respect to the two combined cyclopentadienyl rings, except for **1**.

The Mössbauer parameters of Compound **1** and **2** are summarized in Table 2, with the data of biferrocene shown also for comparison. The neutral species (**1**) gives biferrocene-like spectral parameters, as may be seen in Fig. 3, although the quadrupole splitting (qs) is rather greater than that of biferrocene. This is similar to the relation between the qs of cyclopentadienyl(indenyl)iron(II) or bis(indenyl)iron(II) and that of biferrocene.[28,29] As may be seen in Table 3, it is found in the present studies that some ferrocene derivatives with electron-donating substituents give larger values of qs than that of ferrocene; that is, such a substituent increases the qs of ferrocene. On the other hand, it has been reported that the electron-attracting substituents decrease the qs of ferrocene.[30] Thus, the large qs of **1** is ascribable to the electron-donating effect of the fused ring in **1** to the ferrocenyl

Table 2. Mössbauer data for *trans*-μ-(*as*-indacene)-bis(cyclopentadienyliron) $(C_{12}H_8)Fe_2(C_5H_5)_2$ (**1**), its monocation salt, $(C_{12}H_8)Fe_2(C_5H_5)_2{}^+I_3{}^-$ $0.5I_2$ (**2**), and biferrocene

Compound	Temperature K	δa) mm s^{-1}	ΔE_Q mm s^{-1}
$(C_{12}H_8)Fe_2(C_5H_5)_2$ (**1**)	300	0.46	2.37
	80	0.55	2.42
$(C_{12}H_8)Fe_2(C_5H_5)_2{}^+$ $I_3{}^-0.5I_2$ (**2**)	300	0.35	0.86
	200	0.48b)	0.76b)
		ca. 0.5c)	*ca.* 2.1c)
	100	0.44b)	0.56b)
		0.49c)	2.25c)
	4.2	0.58	0.29
		0.65	2.30
Biferrocene	298	0.45	2.30
		0.45d)	2.30d)
	78	0.55	2.34
		0.52d)	2.36d)

a) The isomer-shift data are reported with respect to metallic iron foil. b) Apparent inner doublet. c) Apparent outer doublet. d) See G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, **38**, 2106 (1963).

Table 3. Mössbauer data for ferrocene and its derivatives at 78 K

Compound	δa mm s^{-1}	ΔE_Q mm s^{-1}
Ferroceneb)	0.52	2.39
Aminoferrocene	0.55	2.43
Diethylferrocene	0.52	2.42
Tetraethylferrocene	0.53	2.44
Hexaethylferrocene	0.53	2.47
Octaethylferrocene	0.54	2.48
Decaethylferrocene	0.52	2.48
Decamethylferrocene	0.53	2.50

a) The isomer-shift data are reported with respect to metallic iron foil. b) This value agrees well with the value reported in Ref. 30.

moieties.

The Mössbauer spectra of the monocation salt (**2**) were determined at 4.2, 100, 200, and 300 K. As is shown in Fig. 4, the shape of the spectrum of **2** greatly depends upon the temperature. The spectrum at 4.2 K consists of inner and outer doublets in nearly a 1:1 ratio; these doublets are ascribed to the ferrocenium-type and ferrocene-type irons (Fe(III) and Fe(II)) in **2** respectively. This is a typical trapped-valence type spectrum. On the other hand, only a single quadrupole doublet with a large half-line width (hlw) is observed in the spectrum at 300 K. The spectra at 100 and 200 K apparently consist of an intense "inner doublet" and a weak "outer doublet."

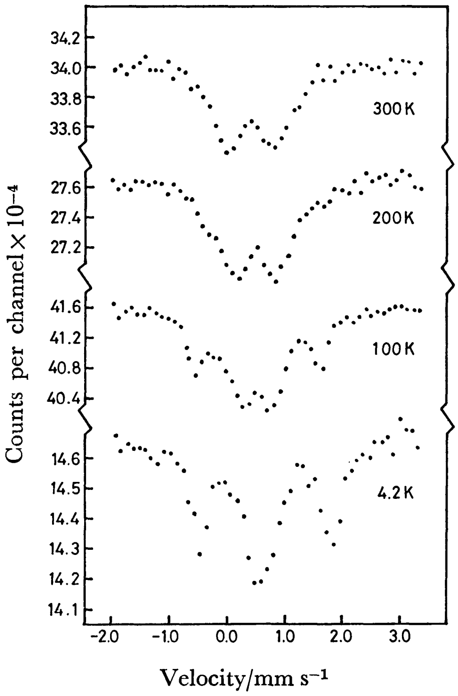

Fig. 4. Mössbauer spectra of $(C_{12}H_8)Fe_2(C_5H_5)_2{}^+$-$I_3{}^-$ $0.5I_2$ (**2**) at 4.2, 100, 200, and 300 K.

It is obvious that the results obtained for **2** cannot be interpreted essentially in terms of trapped-valence states with different spectral areas which are simply temperature-dependent. First of all, we cannot explain why the qs of the "inner doublet" increases considerably as the temperature increases (0.57 mm/s in qs from 4.2 to 300 K), despite the fact that qs slightly decreases as the temperature increases in most cases. Secondly, the anomalously large hlw of the "inner doublet" at higher temperatures cannot be explained either, because the hlw of ^{57}Fe absorption in most mono-oxidized binuclear ferrocenes has been reported to be in the range from *ca.* 0.3 to 0.4 mm/s, while the hlw of the "inner doublet" at 300 K is as large as 0.65 mm/s. Thirdly, such an extreme difference between the spectral areas in each component can only be explained by assuming a greatly different dependence in recoil-free fractions between the outer ferrocene-like and inner ferrocenium-like components, although a nearly equal recoil-free fraction for the two irons is to be expected from the point of view of the importance of the intermolecular interaction on the recoil-free fraction.[31)]

On the other hand, the Mössbauer spectroscopic behaviour of some "mixed-valence" compounds (*e.g.*, Fe_3O_4,[32)] $Fe_3(CH_3COO)_6\cdot O\cdot 5H_2O$,[33)] and Eu_3S_4[34)]) has already been interpreted successfully in terms of an electron-hopping model. The temperature dependence of the Mössbauer spectra of the salt (**2**) was examined by applying this model to clarify the rate of thermal electron-transfer between two irons.

The shapes of the spectra of 100 and 200 K can well be described as the consequences of an increased electron-transfer rate with the increased temperature, which makes the qs values of the ferrocene-like and ferrocenium-like components closer to each other, causing the line to broaden on each component, while the rate of the electron-transfer is much smaller than *ca.* 10^7 s^{-1} at 4.2 K. The line components of the two types of iron atoms virtually merge into a single resonance line at 300 K at a transfer rate larger than *ca.* $10^7\ s^{-1}$. The broadened line shape of the spectrum at 300 K can be explained in terms of the remaining relaxation effects caused by electron-hopping. The qs value at this temperature is slightly smaller than the average of the qs values of the two doublets at 4.2 K. This inconsistency can probably be ascribed to the simplicity of the model, since essentially no temperature-dependence is assumed for the basic electronic configurations of the pure ferrocene-like and ferrocenium-like components.

The general formula given by Wickman for the relaxation Mössbauer spectrum[35] has been applied to the explanation of the electron-hopping mechanism in Eu_3S_4 by Berkooz *et al.*[34] Both the relations derived from Wickman's formula of the transfer-rate with the peak positions and the half-line width of the spectral line component,[36] were used in the present study for the estimation of the electron-transfer rate in **2**, based on the assumption that the transfer rate at 4.2 K is much less than *ca.* $10^7\ s^{-1}$. In the calculation of the transfer rate, it is also assumed that the magnetic quantum number (m_I) of the excited Mössbauer nucleus does not change during the relaxation processes, *i.e.*, the relaxation between ferrocene-like and ferrocenium-like iron atoms occurs independently in each transition, $m_I = \pm 1/2 \rightarrow \pm 1/2$ and $m_I = \pm 1/2 \rightarrow \pm 3/2$, in Compound **2**.

The sign of the electric-field gradient (efg) of the ferrocenium-like component, like that of the ferrocene-like component in **2**, is assumed to be positive, because the ferrocenium-like component in biferrocene monocation salt is known to have a positive sign of efg.[19]

The electron-transfer rates, κ, were estimated to be $1.4 \times 10^7\ s^{-1}$ and $2.0 \times 10^8\ s^{-1}$ at 100 K and 300 K respectively. The values of the transfer rate derived from each transition coincide with each other within the range of experimental error.

The activation energy, E_p, of the electron-hopping in **2** was evaluated to be roughly 1 kcal mol^{-1} (0.04 eV) by using the following equation, as in the case of Eu_3S_4;[34]

$$\kappa = \kappa_0 \exp(-E_p/kT).$$

The rate of the intermolecular electron transfer was determined at various temperatures in the NMR studies between ferrocene and ferrocenium ions in solutions of acetonitrile and of methanol.[37] The E_p value for the intermolecular electron-transfer was estimated to be 5 kcal mol^{-1} in acetonitrile and 3 kcal mol^{-1}. The lower value of E_p estimated in the present work may be ascribed to the smaller intramolecular Fe–Fe distance of the salt (*ca.* 5.0 Å) than that of the ferrocene-ferrocenium association complex (*ca.* 7.8 Å) and also the intramolecular π-conjugated system in **2**.

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