Journal of Organometallic Chemistry, 367 (1989) 313–319
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09794

Electron transfer in mixed-valence 1′,6′-bis(triphenylmethyl)biferrocenium triiodide

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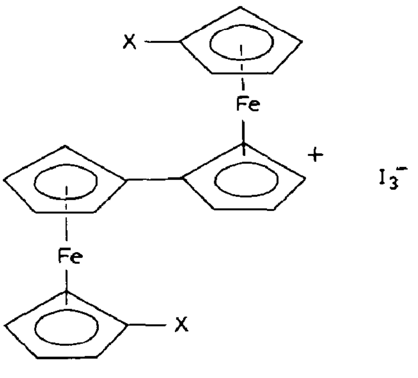
(Received November 11th, 1988)

Abstract

The 1′,6′-bis(triphenylmethyl)biferrocenium triiodide (**6**) was prepared. The intramolecular electron transfer rates in the solid state and in solution have been determined. Compound **6** gives a Mössbauer spectrum which reveals the presence of localized and delocalized species. An investigation of the energy and the line-shape of the intervalence transition band, permitted the calculation of the electron transfer rate in solution.

Introduction

There has been much interest in the electron transfer process in mixed-valence biferrocenium salts **1**–**5** [1–4]. Very recently it was found that the nature of the solid-state environment about a mixed-valence biferrocenium cation can dramati-



1 : X = H
2 : X = C_2H_5
3 : X = C_3H_7
4 : X = C_4H_9
5 : X = $CH_2C_6H_5$
6 : X = $C(C_6H_5)_3$

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0022-328X/89/$03.50

cally affect the intramolecular electron transfer rate [5–7]. Compounds **2**, **3**, **4**, and **5** were reported to have unusually temperature-dependent Mössbauer spectra [4]. At temperatures below 200 K they each show two doublets, one for the Fe^{II} and the other for the Fe^{III} site. In each case an increase in temperature causes the two doublets to move together with no discernible line-broadening, and eventually coalesces into a single "average-valence" doublet at the temperatures 275 for **2**, 245 for **3**, 275 for **4**, and 260 K for **5**. Furthermore, pronounced sample history dependencies of rates of electron transfer have been noted for compounds **1**, **4**, and **5** [4]. For example, a microcrystalline sample of **5** gives a 300 K Mössbauer spectrum which is predominantly that of a valence-localized species (i.e., two doublets). However, a crystalline sample of **5**, grown by allowing hexane to diffuse into a CH_2Cl_2 solution of **5**, gives unique Mössbauer spectrum with one average-valence doublet at 260 K.

Single-crystal X-ray diffraction studies have indicated that compounds **1** [3,4], **3** [8], and **4** [4] all have the *trans* conformation, each is sandwiched between an η^5-cyclopentadienyl ligand and one five-membered ring of the fulvenide ligand. A notable feature in compounds **3** and **4**, is that the alkyl groups are directly above or below the fulvenide ligand. A detailed theoretical model has been presented in order to show the effects of intermolecular interactions on the rate of intramolecular electron transfer [9].

The objective of this paper is to demonstrate the influence of steric factors on intramolecular electron transfer. The results of electrochemical measurements, ^{57}Fe Mössbauer, near-IR, and IR data are presented herein.

Experimental

Solvents were routinely dried by standard procedures and stored under nitrogen.

1-Triphenylmethyl-1′-bromoferrocene. To a mixture of 2.740 g (10.34 mmol) bromoferrocene and 2.911 g triphenylmethanol in 60 ml dry CH_2Cl_2 was added 1.48 g (11.1 mmol) anhydrous $AlCl_3$ at 0 °C under N_2. The reaction mixture was stirred for 10 h at the same temperature and then poured into 150 ml saturated aqueous $Na_2S_2O_3$. The reaction mixture was extracted with CH_2Cl_2 until the dichloromethane extracts became colorless. The extracts were washed successively with saturated aq. $NaHCO_3$ and water, and then dried over Na_2SO_4. The solvent was removed under vacuum. The crude reaction mixture was chromatographed on neutral activity II alumina to give two separate bands. The first band, eluted with hexane, was the recovered bromoferrocene as identified by NMR. The second band, eluted with cyclohexane, was 1-triphenylmethyl-1′-bromoferrocene (2.8 g, 53%). Recrystallization of crude product from hexane-benzene gave orange-yellow crystals. ^1H NMR spectrum (CS_2, δ): 3.60, 3.88, 3.96, and 4.10 (8H, d, Cp ring), 7.12 (15H, s, Ph). Anal. Found: C, 68.35; H, 4.59. $C_{29}H_{23}BrFe$ calcd.: C, 68.67; H, 4.57%.

1′,6′-Bis(triphenylmethyl)biferrocene (7). A mixture of 1-triphenylmethyl-1′-bromoferrocene (1 g, 2 mmol) and 12 g activated Cu was heated at 120–130 °C for 20 h in a flask under N_2. The mixture was left to cool to room temperature, and was then extracted with CH_2Cl_2 until the dichloromethane extracts appeared colorlesss. The solvent was removed under vacuum and the residue was chromatographed on neutral activity II alumina. The first band, eluted with cyclohexane, was found to be the starting material. Then elution with 2/1 cyclohexane-benzene afforded 1′,6′-

bis(triphenylmethyl)biferrocene (0.48 g, 30%). The crude product can be recrystallized from hexane-benzene, m.p. 168°C. ^{1}H NMR (CS_2, δ): 3.6–4.2 (16H, m, Cp ring), 7.2 (30H, m, ph). Electron-impact mass spectrum, M^+ at m/e 854.

A sample of **6** was prepared by the diffusion procedure previously reported for **4** [4]. Anal. Found: C, 56.12; H, 3.74. $C_{58}H_{46}Fe_2I_3$ calcd.: C, 56.39; H, 3.75%.

Physical methods. The ^{57}Fe Mössbauer measurements were made on a constant-acceleration-type instrument at Academia Sinica. Computer fittings of the ^{57}Fe Mössbauer data to Lorentzian lines were carried out with a modified version of a previously reported program [10]. Velocity calibrations were made by use of a 99.99% pure 10 μm Fe foil. Typical linewidths for all three pairs of iron lines fall in the range 0.28–0.32 mm/s. Isomer shifts are reported with correction for iron foil at 300 K.

^{1}H NMR spectra were recorded with a Bruker MSL 200 spectrometer. Mass spectra were recorded with a VG system, Model TS-250. Near-IR spectra were obtained with a Perkin-Elmer Lambda 9 spectrophotometer in CH_2Cl_2 contained in 1.0 cm quartz cells. Measurements were carried out between 2600 and 900 nm.

Polarographic measurements were carried out with a Princeton Applied Research Model 173 polarograph. Cyclic voltammetry was performed with a stationary Pt electrode, which was cleaned after each run. Runs were duplicated for each sample. The measurements were carried out on 1×10^{-3} *M* CH_3CN solutions containing 0.1 *M* $(n\text{-}C_4H_9)_4NBF_4$ as supporting electrolyte. Degassing with nitrogen prefaced each run. The potentials quoted in this work are relative to a saturated aqueous calomel electrode at 25°C.

Results and discussion

Electrochemical results. The neutral compound (**7**) undergoes two successive reversible one-electron oxidations to yield the mono- and dications (Fig. 1). As shown in Table 1, electrochemical reversibility was demonstrated by the peak-to-peak separation between the resolved reduction and oxidation waves maxima (ΔE_p). The

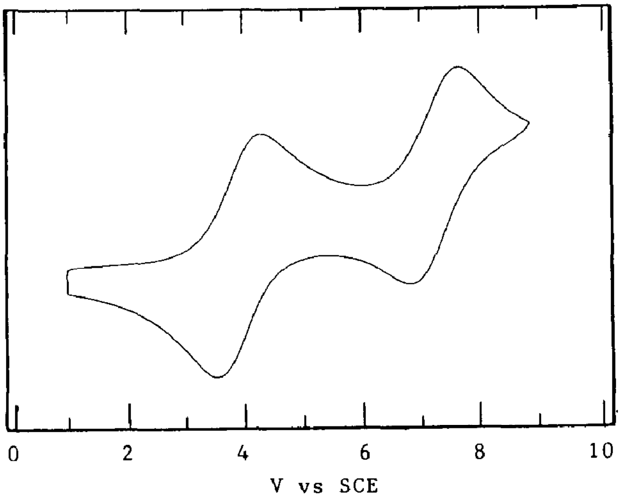

Fig. 1. Cyclic voltammogram for **7** (vs SCE).

Table 1

Polarographic data for various biferrocenes

Compound	$E_{1/2'}$ [a] (V)	$\Delta E_{p'}$ [b] (mV)	$\Delta E_{1/2'}$ [c] (V)	K_{com} [d] ($\times 10^{-5}$)
Ferrocene	0.40	65		
Biferrocene	0.31	70	0.31	1.8
	0.62	75		
1′,6′-Dibutyl-biferrocene	0.26	65	0.32	2.6
	0.58	65		
7	0.39	70	0.32	2.6
	0.71	75		

[a] All half wave potentials are referred to the SCE. [b] Peak-to-peak separation between the resolved reduction and oxidation waves maxima. [c] Peak separation between waves. [d] Comproportionation constant.

half-wave potentials for **7**, as well as those for some other relevant biferrocenes, are given in Table 1.

It has been shown that the peak-to-peak separation ($\Delta E_{1/2}$) gives an indication of the interaction between the two Fe sites [11]. A comparison of the $\Delta E_{1/2}$ values for the each member of the biferrocene series indicates that the interaction between the two Fe sites is probably not changing very much throughout the series. If the abbreviation (*3,3*) is used for the dioxidized salt, (*2,3*) for the monooxidized, and (*2,2*) for the neutral compound, then the comproportionation constant (K_{com}) in eq (1) can be calculated from the $\Delta E_{1/2}$ value.

$$(3,3) + (2,2) \overset{K_{com}}{\rightleftharpoons} 2(2,3) \qquad (1)$$

The mixed-valence compound **6** was obtained by chemical oxidation with iodine. The monooxidized cation is stable for several weeks in CH_2Cl_2 solution, when protected from air and moisture, but is stable only for several days in acetone and acetonitrile solutions.

*Physical properties of **6** in the solid state.* The intramolecular electron transfer rate for a mixed-valence compound can be determined by physical methods which can provide the upper or lower limits of the electron transfer rate relative to the timescale of the experiment. In the case of mixed-valence biferrocenes, the Mössbauer and IR spectroscopy have proven useful as an indication of whether a given compound is delocalized or not [4,12]. In the Mössbauer technique, the ferrocenyl groups give spectra characterized by large quadrupole splittings (ΔE_Q) in the range of 2.0–2.5 mm/s, while the spectra of the ferrocenium cations are characterized by a small or vanishing ΔE_Q. Thus, a pattern of two doublets is expected for a mixed-valence compound which is valence-trapped on the Mössbauer time scale. Thus the 300 K Mössbauer spectrum for localized biferrocenium triiodide shows two doublets, one with $\Delta E_Q = 1.907$ mm/s and the other with $\Delta E_Q = 0.385$ mm/s [4]. In the case of delocalized 1′,6′-diiodobiferrocenium triiodide, one average doublet is observed ($\Delta E_Q = 1.340$ mm/s) [5]. IR spectroscopy has indicated that the perpendicular C–H bending band is most diagnostic of the oxidation state [4,5,12]. This band is seen at 815 cm^{-1} for ferrocene and at 851 cm^{-1} for ferrocenium triiodide [13]. Thus a localized mixed-valence biferrocene should exhibit one C–H bending band for the Fe^{II} moiety and one for the Fe^{III} moiety. The mixed-valence

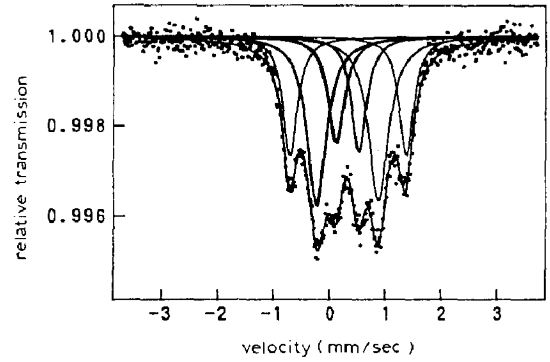

Fig. 2. ^{57}Fe Mössbauer spectrum of **6**.

bis(fulvalene)diiron cation is delocalized because only one band, at 830 cm^{-1}, is observed [14].

The 300 K Mössbauer spectrum for this new mixed-valence compound is illustrated in Fig. 2. The prominent features in this spectrum are two doublets, one with ΔE_Q of 2.073 mm/s and the other with $\Delta E_Q = 0.391$ mm/s. Both doublets have the same area as deduced from a least-squares fitting (Table 2). The spectrum also clearly shows that there is a third doublet with $\Delta E_Q = 1.096$ mm/s. This doublet is associated with a mixed-valence biferrocene having an intramolecular electron-transfer rate greater than $\sim 10^{-7}$ s^{-1}. Mössbauer spectra with both localized and delocalized species were recently reported for microcrystalline samples of **4** and **5**. As with the crystalline samples of **4** and **5**, two doublets are seen to move together as the temperature is increased, and eventually coalesce into a single doublet. This behaviour has not been observed for **6**. It is likely that the bulky substituent in **6** affects the crystal structure. All attempts to grow single crystals failed. The CPK model shows that the bulkiness of the triphenylmethyl group prevents its being located directly above or below the fulvenide ligand, in contrast to compounds **3** [8] and **4** [4].

Room-temperature IR spectra of **6** and **7** (KBr pellets) were also recorded. The C–H bending mode of the cyclopentadienyl groups for the unoxidized biferrocene (**7**) is at 816 cm^{-1}. Two bands at 817 and 858 cm^{-1} are observed for the mixed-valence compound **6**. If the band at 858 cm^{-1} can be assigned to the C–H bending mode associated with the Fe^{III} moiety, then **6** is localized on the IR time scale.

Table 2

^{57}Fe Mössbauer least-squares fitting parameters for **6** at 300 K

ΔE_Q [a] (mm/s)	δ [b] (mm/s)	Γ [c] (mm/s)	Area ratio (%)
2.073	0.439	0.310, 0.311	25.60
1.096	0.442	0.417, 0.432	48.78
0.391	0.435	0.348, 0.322	25.60

[a] Quadrupole splitting. [b] Isomer shift. [c] Full width at half-height taken from the least-squares fitting. The width for the line at more negative velocity is listed first for each doublet.

*Physical properties of **6** in solution.* Electronic absorption spectroscopy, and in particular the energy and line-shape of the intervalence transition (IT) band in the near-IR region are useful for determining the photo-induced electron transfer rate of a given mixed-valence compound. Cowan and co-workers have recently applied the PKS model to mixed-valence ions of biferrocene and bis(fulvalene)diiron in solution [15].

In common with most mixed-valence complexes, the mixed-valence compound **6** has a near-IR transition at 2200 nm which is not present for the neutral or dioxidized ion. The bandwidth ($\Delta\nu_{1/2}$, $\epsilon = 570\ M^{-1}\ \mathrm{cm}^{-1}$ in CH_2Cl_2) at half height is 5% broader than that expected on the basis of the equation derived by Hush [16] ($\Delta\nu_{1/2} = 3.41$ kK compared to a calculated value of 3.24 kK). A broader band will usually be observed for a class-II mixed-valence compound [17]. The intensity of the IT band is dependent on the degree of interaction of the donor and acceptor sites in the ground state. The values of the interaction parameter (α^2) and the electron transfer rate constant (K_{et}) can be estimated from eqs (2) and (3), respectively.

$$\alpha^2 \simeq (4.24 \times 10^{-4})\Delta\nu_{1/2}\epsilon_{\mathrm{max}}/\bar{\nu}r^2 \tag{2}$$

$$K_{\mathrm{et}} = (2\pi/\hbar)V_{\mathrm{ab}}{}^2(\pi/K_{\mathrm{B}}T\bar{\nu})^{1/2}\exp(-\bar{\nu}/4K_{\mathrm{B}}T) \tag{3}$$

$$V_{\mathrm{ab}} = \left(4.24 \times 10^{-4}\epsilon_{\mathrm{max}}\Delta\nu_{1/2}\bar{\nu}/r^2\right)^{1/2} \tag{4}$$

In equations (2), (3), and (4) the term ϵ_{max} is the extinction coefficient, r is the donor–acceptor distance, α is the mixing coefficient, $\Delta\nu_{1/2}$ is the bandwidth, and $\bar{\nu}$ is the frequency. The average value of 5.1 Å in compounds **1** [4], **3** [8], and **4** [4] is used as donor–acceptor distance. Thus, $\alpha^2 = 0.007$ and $K_{\mathrm{et}} = 1.34 \times 10^{12}$.

Conclusions

Mössbauer spectra indicating the presence of both delocalized and localized species have been observed for a microcrystalline sample of **6**. This type of observation was observed for **4** and **5** [4a]. Furthermore, the presence of a cooperative phase transition in the series of mixed-valence biferrocenes has been established from heat capacity studies [18]. The microcrystalline form of **6** could have a high concentration of defects which can make a cooperative phase transition very gradual. If this is correct, then it is clear why both the localized and the delocalized species can been seen in the Mössbauer spectrum.

The energy and the line-shape of the IT band clearly indicate that the intramolecular electron-transfer rate of **6** in solution is greater than that of **6** in the solid state. In the past it has generally been assumed that the rate of intramolecular electron transfer in the solid state is similar to that in solution. The effect of the environment about the mixed-valence cation on the solid-state electron transfer rate has been described [4]. In solution, the manner in which the mixed-valence cation is solvated also influences the rate of intramolecular electron transfer. If ion pairing is present, the anion must move rapidly so as not to limit the rate of intramolecular electron transfer. For **6** in solution, we believe that the solvent molecules solvating the mixed-valence cation can adjust rapidly so that the electron transfer rate is not limited.

Acknowledgement

We are grateful for the support from the National Science Council (NSC-77-0208-M001-01).

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