53746-36-4; [Fe2(1,1'-binaphthyl)(cp)2](PF6)2, 53849-10-8; Fe2-(chrysene)(cp)2²⁺, 53702-63-9; Fe2(anthracene)(cp)2²⁺, 53702-64-0; Fe2(phenanthrene)(cp)2²⁺, 53702-65-1; Fe(cp)2, 102-54-5; Fe2-(pyrene)(cp)2²⁺, 53746-35-3; Fe2(1,2:4,5-dibenzo-1,4-cyclo-heptadiene)(cp)2²⁺, 53276-64-5; Fe2(biphenylmethane)(cp)2²⁺, 51539-80-1; Fe2(9,10-dihydroanthracene)(cp)2²⁺, 53276-70-3; [Fe2(phenylmesitylene)(cp)2](PF6)2, 53746-33-1; Fe2(β-phenyl-naphthylene)(cp)2²⁺, 53746-34-2; Fe2(p-terphenyl)(cp)2²⁺, 53276-66-7; Fe2(bibenzyl)(cp)2²⁺, 53702-62-8; Fe2(3,3',4,4'-tetra-methylbiphenyl)(cp)2²⁺, 53702-60-6; [Fe2(benzene)2(fulvalene)]-(PF6)2, 53702-59-3.

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Oxidation-State and Electron-Transfer Properties of Mixed-Valence 1,1'-Polyferrocene Ions

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The oxidation state properties of the compounds biferrocene, 1,1'-terferrocene, and 1,1'-quaterferrocene have been investigated using electrochemical techniques. In the polymeric compounds all of the ferrocene groups are oxidizable to ferricenium at distinct potentials. The values of the potentials can be predicted in some cases using ferrocenyl substituent effects. Partial oxidation gives a series of discrete mixed-valence ions. The mixed-valence ions can exist as a series of oxidation state isomers which differ with regard to the site of oxidation. Electron transfer between different oxidation state sites in the polymeric chains is unsymmetric giving energetically nonequivalent isomers. The unsymmetrical nature of electron transfer is reflected in the properties of intervalence-transfer (IT) absorptions in the near-infrared spectra. The existence of energetically equivalent and nonequivalent oxidation state isomers may also influence such properties as the intensities of IT bands, the presence of statistical effects in measured reduction potentials, and rates of intramolecular electron transfer.

Mixed-valence compounds which contain metal ions of the same element in different oxidation states are of considerable current interest.[2-5] Cases in which the different oxidation state sites are held in close proximity either by the properties of a solid-state lattice or by a designed chemical linkage often have unusual physical properties. Commonly, such physical properties are unique to the mixed-valence material and not just the sum of the properties of the separate ions.

Detailed studies on the dimeric systems (NH3)5Ru(pyz)-Ru(NH3)5⁶⁺,⁵⁺,⁴⁺ (pyz is pyrazine)[6-11] and biferrocene,[12,13] (C5H5)Fe(C5H4–C5H4)Fe(C5H5)²⁺,⁺,⁰, have led to a considerable understanding of the extent and consequences of electronic interactions between metals in mixed-valence ions. In more extensively linked systems such as (bipy)2ClRu-(pyz)[Ru(bipy)2pyz]2RuCl(bipy)2¹⁰⁺,⁹⁺,⁸⁺,⁶⁺ (bipy is 2,2'-bipyridine)[14] and (C5H5)Fe(C5H4–C5H4)Fe(C5H4–C5H4)-Fe(C5H5)³⁺,²⁺,⁺,⁰ a series of mixed-valence ions can exist. Because of the possibility of cooperative interactions between more than two sites such mixed-valence systems may have physical properties intermediate between those of the simple dimers and mixed-valence solids. In this paper we report on the oxidation state and electron-transfer properties of the extensively linked 1,1'-polyferrocene compounds
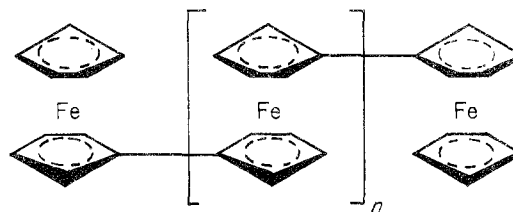
biferrocene (Fc–Fc), $n = 0$
1,1'-terferrocene (Fc–Fc–Fc), $n = 1$
1,1'-quaterferrocene (Fc–Fc–Fc–Fc), $n = 2$

Experimental Section

Measurements. Visible and very near-infrared spectra were obtained using Cary Model 14 and 17 spectrophotometers. All electrochemical measurements were made at platinum electrodes *vs.* the saturated sodium chloride calomel electrode (ssce) at 24 ± 2° and are uncorrected for junction potentials. In all electrochemical experiments, standard three-electrode operational amplifier circuitry was used as previously described.[15] Values of n, where n is the total number of electrons transferred in exhaustive electrolysis at constant potential, were calculated after measuring the total area under current *vs.* time curves for the complete reaction. Reactions were judged to be complete when the current had fallen below 1% of its initial value.
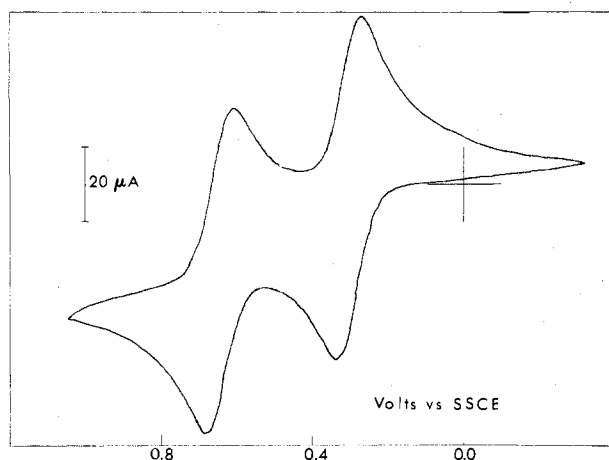
Figure 1. The 200-mV/sec cyclic voltammogram of biferrocene in 1:1 (v/v) CH_2Cl_2-CH_3CN containing 0.1 M TBAH.
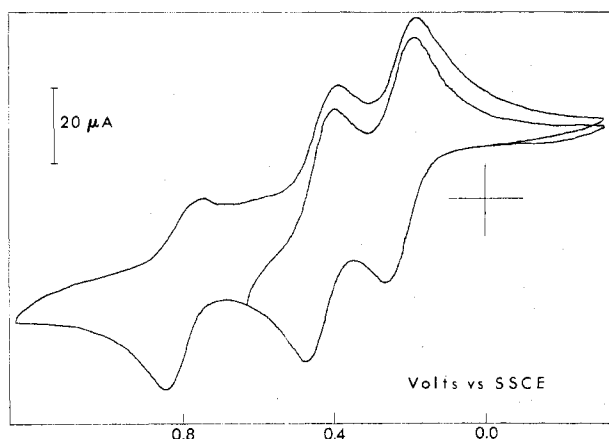

Figure 2. The 200-mV/sec cyclic voltammogram of 1,1'-terferrocene(1+) in 1:1 (v/v) CH_2Cl_2-CH_3CN containing 0.1 M TBAH.

Materials. Tetra-n-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques,[16] recrystallized three times from hot ethanol–water mixtures, and vacuum-dried at 100° for 12 hr. Acetonitrile (MCB "Spectrograde") was dried over Davison 4-Å molecular sieves before use. Dichloromethane (Fisher "Spectranalyzed") was used without further purification. Ferrocene (Aldrich) was purified by sublimation. The compounds biferrocene,[17] 1,1'-terferrocene,[17] and 1,1'-quaterferrocene[17] were prepared by previously reported procedures.

Preparation of Solutions. Because of solubility problems with the neutral and/or oxidized polyferrocene compounds the solvent medium used for electrochemical studies was 1:1 (v/v) dichloromethane–acetonitrile with tetra-n-butylammonium hexafluorophosphate present at 0.1 M as supporting electrolyte. Because of the limited solubility of the neutral compounds, voltammetric measurements were made on solutions of the singly oxidized form of 1,1'-terferrocene and on the doubly oxidized form of 1,1'-quaterferrocene. The oxidized solutions were prepared by controlled-potential oxidation of the sparingly soluble neutral compounds.

Solutions for visible and very near-infrared spectra were prepared in the same manner as were the solutions for electrochemical studies. Spectra of the mixed-valence ions were obtained by removing aliquots from solution. In all cases, spectra were obtained on freshly prepared solutions.

Results[18]

Electrochemistry. In Figures 1 and 2 are shown cyclic voltammograms of the polyferrocene systems biferrocene (Fc-Fc) and 1,1'-terferrocene (Fc-Fc-Fc). As mentioned in the Experimental Section, the cyclic voltammograms were obtained on solutions containing partly oxidized compounds for solubility reasons. For all of the compounds studied the

number of waves observed by cyclic voltammetry was equal to the number of ferrocenyl groups in the polymer unit. In both the voltammetry and cyclic voltammetry experiments the choice of solvent medium—1:1 (v/v) dichloromethane–acetonitrile—was dictated by solubility considerations.

Half-wave potentials for the various polyferrocene compounds as measured by voltammetry or cyclic voltammetry are given in Table I. When possible, the electrochemical reversibility of the reactions was determined from voltammetry experiments by determining the slopes of plots of log [(i_1 − i)/i] vs. E for the oxidations. In cases where adsorption and/or decomposition was evident in stirred-solution voltammograms, reversibility was determined by the peak separations (ΔE_p) and the ratio of the anodic to cathodic peak currents ($i_{p,a}/i_{p,c}$) in cyclic voltammograms. In fact, in rapid scan cyclic voltammetry experiments, ΔE_p was larger than the theoretical value of 59 mV, likely due to uncompensated solution resistance between the reference and working electrodes. Under our experimental conditions the ferrocene–ferricenium couple had ΔE_p = 65mV which was used as the criterion for reversibility. In that the voltammetric or cyclic voltammetric waves are electrochemically reversible, the $E_{1/2}$ values are reduction potentials, except for a usually small correction term involving diffusion coefficients,[19] and refer to reactions like

$$(Fc\text{-}Fc)^{2+} + e \rightarrow (Fc\text{-}Fc)^+$$

$$(Fc\text{-}Fc)^+ + e \rightarrow Fc\text{-}Fc$$
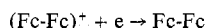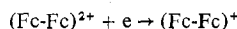
where Fc is an abbreviation for a ferrocenyl unit. In Table I the numbering system used for the $E_{1/2}$ values—(1), (2), (3), (4)—is based on the order of appearance of the waves in the cyclic voltamograms with the wave at lowest potential labeled as (1).

The results obtained here for biferrocene are consistent with previously reported data.[13,20,21] From cyclic voltammetry (Figure 1) and coulometry (Table I), biferrocene undergoes two electrochemically reversible one-electron oxidations. Oxidation at the first wave giving (Fc-Fc)$^+$ is also chemically reversible. Electrochemically generated solutions of (Fc-Fc)$^+$ are stable in the absence of light and air for at least 1 hr. Oxidation at the second wave gave rise to adsorption of the oxidation product followed by decomposition. Consequently, $E_{1/2}$ values for the second wave were determined by cyclic voltammetry (Figure 1).

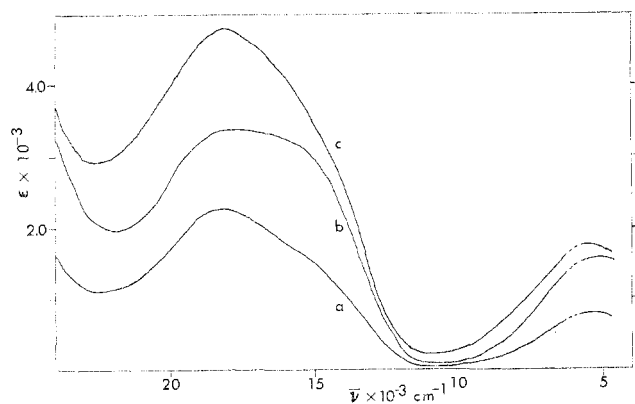The first two oxidations of 1,1'-terferrocene

$$Fc\text{-}Fc\text{-}Fc \xrightarrow{-e^-} (Fc\text{-}Fc\text{-}Fc)^+$$

$$(Fc\text{-}Fc\text{-}Fc)^+ \xrightarrow{-e^-} (Fc\text{-}Fc\text{-}Fc)^{2+}$$
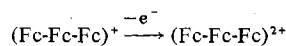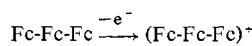
Figure 3. Visible and near-infrared spectra of mixed-valence polyferrocene compounds in 1:1 (v/v) CH_2Cl_2–CH_3CN: (a) biferrocene-(1+), (b) 1,1'-terferrocene(1+), and (c) 1,1'-quaterferrocene(2+).
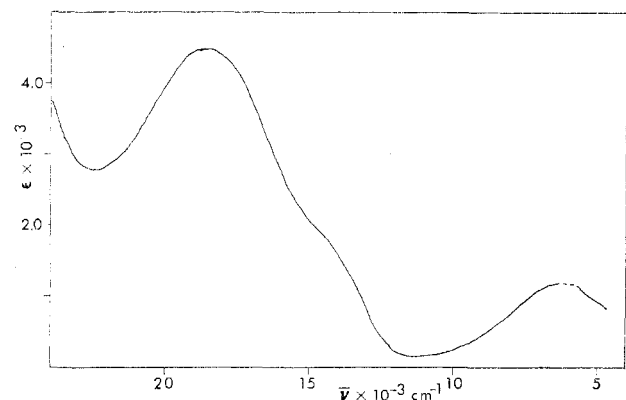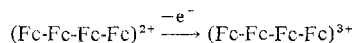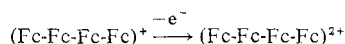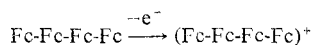

Figure 4. Visible and very near-infrared spectrum of 1,1'-terferrocene(2+) in 1:1 (v/v) CH_2Cl_2-CH_3CN.

and the first three oxidations of 1,1'-quaterferrocene

$$Fc\text{-}Fc\text{-}Fc\text{-}Fc \xrightarrow{-e^-} (Fc\text{-}Fc\text{-}Fc\text{-}Fc)^+$$

$$(Fc\text{-}Fc\text{-}Fc\text{-}Fc)^+ \xrightarrow{-e^-} (Fc\text{-}Fc\text{-}Fc\text{-}Fc)^{2+}$$

$$(Fc\text{-}Fc\text{-}Fc\text{-}Fc)^{2+} \xrightarrow{-e^-} (Fc\text{-}Fc\text{-}Fc\text{-}Fc)^{3+}$$

are electrochemically reversible. Because of adsorption, $E_{1/2}$ values were determined by cyclic voltammetry for the couples involving the more highly oxidized compounds. Adsorption is especially a problem for the third oxidation of 1,1'-terferrocene (Figure 2) and the fourth oxidation of 1,1'-quaterferrocene, and the $E_{1/2}$ values for these waves (Table I) are only estimates from cyclic voltammetry.

The first and second oxidations of 1,1'-terferrocene and 1,1'-quaterferrocene are chemically reversible. Fewer experiments were carried out on 1,1'-quaterferrocene because only a small amount of the compound was available. As with biferrocene, exhaustive electrolysis at potentials sufficient to generate completely oxidized 1,1'-terferrocene ions, (Fc-Fc-Fc)$^{3+}$, or fully or partly oxidized 1,1'-quaterferrocene ions, (Fc-Fc-Fc-Fc)$^{3+}$ and (Fc-Fc-Fc-Fc)$^{4+}$, led to decomposition. The decomposition reactions, which are, in general, considerably slower for the mixed-valence ions, are not surprising in light of the known decomposition chemistry of the ferricenium ion (Fc$^+$).[22]

Visible and Near-Infrared Absorption Spectra. The electronic spectra of the mixed-valence 1,1'-polyferrocene ions (Fc-Fc)$^+$, (Fc-Fc-Fc)$^+$, (Fc-Fc-Fc)$^{2+}$, and (Fc-Fc-Fc-Fc)$^{2+}$ are shown in Figures 3 and 4. The 445–900-nm region is dominated by an intense band which has been assigned to the transition $^2E_{2g}$ → $^2E_{1u}$ for the ferricenium ion. As previously noted for the

Table II. Electronic Spectra of Mixed-Valence 1,1'-Polyferrocene Compounds[a]

Compd	λ_{max}, nm (ϵ)[b]
Ferricenium$^+$ (Fc$^+$)	615 (208)
Biferrocene$^+$ (Fc-Fc)$^+$	546 (2230), ~680 (1250),[c] 1900 (760)
1,1'-Terferrocene$^+$ (Fc-Fc-Fc)$^+$	556 (3380), ~625 (3200),[c] 1990 (1560)
1,1'-Terferrocene^{2+} (Fc-Fc-Fc)$^{2+}$	540 (4470), ~690 (1800),[c] 1670 (1080)
1,1'-Quaterferrocene^{2+} (Fc-Fc-Fc-Fc)$^{2+}$	550 (4770), ~680 (2800),[c] 1790 (1720)

[a] In 1:1 (v/v) CH_2Cl_2–CH_3CN containing 0.1 M TBAH. [b] Molar extinction coefficients $(M^{-1}\ cm^{-1})$ are given in parentheses. [c] The band is a shoulder and the λ_{max} value is an estimate only.

(Fc-Fc)$^+$ ion,[5] this band in the mixed-valence 1,1'-polyferrocene compounds is broadened relative to ferricenium ion. As discussed in a later section, it is likely that the band is composed of at least two transitions as previously suggested.[5]

Bands similar to the near-infrared absorption previously observed[5] in the (Fc-Fc)$^+$ ion are also observed for the mixed-valence 1,1'-polyferrocene ions (Fc-Fc-Fc)$^+$, (Fc-Fc-Fc)$^{2+}$, and (Fc-Fc-Fc-Fc)$^{2+}$. Cowan and coworkers have assigned the infrared band in (Fc-Fc)$^+$ to an intramolecular intervalence-transfer (IT) absorption.

Spectral data could not be obtained at wavelengths higher than 2150 nm due to the onset of intense solvent absorption. In addition, there is a strong solvent absorption in the region 1630–1760 nm which made quantitative measurements impossible. The spectra in this region were obtained by extrapolation, as indicated in Figures 3 and 4 by the dashed lines.

The mixed-valence polyferrocene ions are not stable in solution for long periods of time. Electrochemically generated solutions of (Fc-Fc-Fc)$^+$, (Fc-Fc-Fc)$^{2+}$ and (Fc-Fc-Fc-Fc)$^{2+}$ are, however, stable for periods long enough (30 min) to obtain visible and very near-infrared spectra (see Table II). Over long periods of time λ_{max} values remain unchanged, but the absorbance of the solutions slowly decreases.

Discussion

Electrochemistry. For the 1,1'-polyferrocene compounds the electrochemical results establish a pattern of oxidation state behavior in which all of the ferrocene units are oxidizable to ferricenium. A series of one-electron waves is observed by cyclic voltammetry corresponding to one wave per ferrocene group. For the more highly oxidized compounds, the electrochemical measurements are complicated by adsorption and/or decomposition.

The pattern of relative $E_{1/2}$ values in Table I can be accounted for by taking into account the known properties of ferrocene compounds, the effect of substituents on the reduction potential of ferrocene, and the effects of ferrocene and ferricenium groups as substituents. In the ferrocene–ferricenium couple (Fc$^{+,0}$), electrons are gained or lost from levels largely nonbonding iron d in character.[5,23] The effect of π-ring substituents on the Fc$^{+,0}$ reduction potential comes mainly from bond polarization (inductive) effects.[24] Electron-donating groups stabilize Fc$^+$, lowering the reduction potential, and electron-withdrawing groups have the opposite effect.

Substituent effects in 1,1'-symmetrical ferrocenes, $(C_5H_4X)Fe(C_5H_4X)$, and in unsymmetrical disubstituted ferrocenes, $(C_5H_4X)Fe(C_5H_4Y)$, have been shown to be additive by reduction potential measurements.[25,26] To a high degree of accuracy the reduction potentials for disubstituted ferrocenes with substituents X and Y can be calculated from the equation

$$E_{calcd} = E_{Fc^{+,0}} + \delta_X + \delta_Y \tag{1}$$

where $E_{Fc^{+,0}}$ is the potential for the Fc$^{+,0}$ couple and δ_X (or

Scheme I

$$\text{Fc-Fc}^+\text{-Fc} + \text{e} \rightarrow \text{Fc-Fc-Fc} \quad (E_{1/2} = 0.22 \text{ V})$$

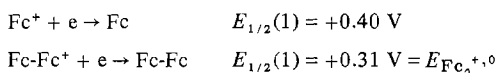$$E_{\text{calcd}} = E_{\text{Fc}^{+,0}} + 2\delta_{\text{Fc}} = 0.22 \text{ V}$$

$$\text{Fc}^+\text{-Fc-Fc}^+\text{-Fc} + \text{e} \rightarrow \text{Fc}^+\text{-Fc-Fc-Fc} \quad (E_{1/2} = 0.36 \text{ V})$$

$$E_{\text{calcd}} = E_{\text{Fc}_3^{2+,+}} + \delta_{\text{Fc}} = 0.35 \text{ V}$$
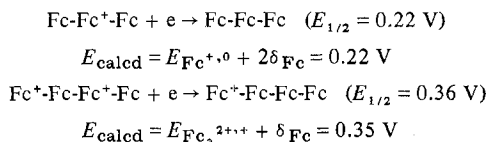
δ_Y) is the difference between the potential for the mono-substituted couple $(C_5H_5)Fe(C_5H_4X)^{+,0}$ [or $(C_5H_5)Fe-(C_5H_4Y)^{+,0}$] and $E_{\text{Fc}^{+,0}}$.

From $E_{1/2}(1)$ values, biferrocene is more easily oxidized than ferrocene itself; *i.e.*

$$\text{Fc}^+ + \text{e} \rightarrow \text{Fc} \qquad E_{1/2}(1) = +0.40 \text{ V}$$

$$\text{Fc-Fc}^+ + \text{e} \rightarrow \text{Fc-Fc} \qquad E_{1/2}(1) = +0.31 \text{ V} = E_{\text{Fc}_2^{+,0}}$$

As a substituent, the ferrocenyl group clearly acts as a net electron donor both here and in its effects on the pK_a values of substituted benzoic acids.[27] A substituent effect can be calculated for the ferrocenyl group (δ_{Fc}) as for other substituents by

$$\delta_{\text{Fc}} = E_{\text{Fc}_2}^{+,0} - E_{\text{Fc}^{+,0}} = -0.09 \text{ V}$$

The calculated substituent effect includes a statistical factor of 2. The equilibrium $\text{Fc-Fc}^+ + \text{e} = \text{Fc-Fc}$, where e represents the reference electrode half-reaction, will be favored by a factor of 2 over the equilibrium $\text{Fc}^+ + \text{e} = \text{Fc}$, since there are two energetically equivalent ways of forming $(\text{Fc-Fc})^+$, as $\text{Fc}^+\text{-Fc}$ or Fc-Fc^+.[28,29] The effect is small, $(RT/nF) \ln 2 = 0.018$ V, and nearly within experimental error (± 0.01 V). The effect will largely be neglected, both here and later in the discussion.

In the mixed-valence 1,1'-terferrocene and 1,1'-quater-ferrocene ions, $(\text{Fc-Fc-Fc})^+$, $(\text{Fc-Fc-Fc-Fc})^{2+}$, etc., it is reasonable to assume that the polymeric chains contain weakly interacting but discrete Fe(II) and Fe(III) sites. The ions have intervalence-transfer (IT) bands in the near-infrared spectra (Table II) with energies and intensities similar to those of the band found at 1900 nm for $(\text{Fc-Fc})^+$. It has been concluded that in $(\text{Fc-Fc})^+$ there are discrete Fe(II) and Fe(III) sites and that electronic delocalization between the two sites is relatively small.[5]

If electron delocalization effects are small and/or simply additive, the effects of adjacent ferrocenyl groups as substituents should also be additive. As for other substituents, reduction potentials should be calculable using equations like (1). As shown in Scheme I potentials can be calculated which are in good agreement with experimental $E_{1/2}$ values.[30]

Oxidation State Isomerism. For the 1,1'-polyferrocene compounds there are chemically different sites (Fc- and -Fc-) in the polymeric units. Upon oxidation to the mixed-valence ions, more than one oxidation state isomer can exist. The isomers differ with regard to the site(s) of oxidation and, therefore, may differ in free energy. For example, the ion $(\text{Fc-Fc-Fc})^+$ can exist as one of two energetically equivalent isomers, $\text{Fc}^+\text{-Fc-Fc}$ and Fc-Fc-Fc^+, or as the energetically nonequivalent isomer $\text{Fc-Fc}^+\text{-Fc}$. For $(\text{Fc-Fc-Fc})^+$ the distribution between the various isomers will depend on the free energy difference(s) between them.

The existence of isomers like $\text{Fc-Fc}^+\text{-Fc}$ and $\text{Fc}^+\text{-Fc-Fc}$ is an example of *oxidation state isomerism*[31] in which the isomers differ with regard to the site of oxidation.

In certain cases it is possible to estimate the free energy difference between isomers. The $E_{1/2}$ value for the couple $(\text{Fc-Fc-Fc-Fc})^{+,0}$ which reflects the potentials of two reactions
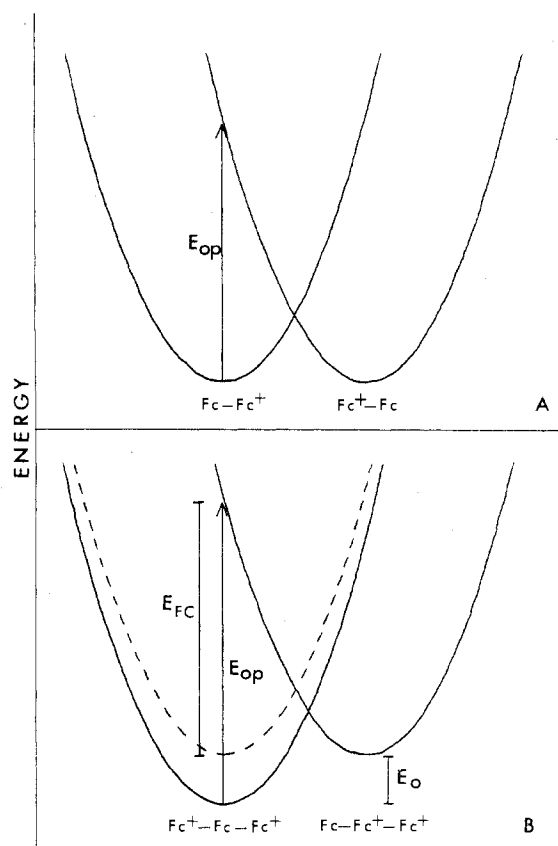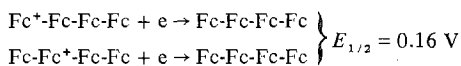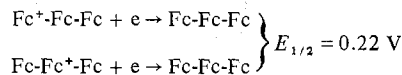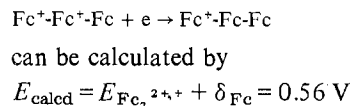
$$\left.\begin{array}{l}\text{Fc}^+\text{-Fc-Fc-Fc} + \text{e} \rightarrow \text{Fc-Fc-Fc-Fc} \\ \text{Fc-Fc}^+\text{-Fc-Fc} + \text{e} \rightarrow \text{Fc-Fc-Fc-Fc}\end{array}\right\} E_{1/2} = 0.16 \text{ V}$$

Figure 5. Potential energy–configurational coordinate diagrams: (a) the symmetrical case for the biferrocenium ion $(\text{Fc-Fc})^+$ showing the transition $\text{Fc-Fc}^+ + h\nu \rightarrow (\text{Fc}^+\text{-Fc})^*$; (b) an unsymmetrical case, $(\text{Fc-Fc-Fc})^{2+}$, showing the transition $\text{Fc}^+\text{-Fc-Fc}^+ + h\nu \rightarrow (\text{Fc}^+\text{-Fc}^+\text{-Fc})^*$.

is lower by 0.06 V than is $E_{1/2}$ for the couple $(\text{Fc-Fc-Fc})^{+,0}$

$$\left.\begin{array}{l}\text{Fc}^+\text{-Fc-Fc} + \text{e} \rightarrow \text{Fc-Fc-Fc} \\ \text{Fc-Fc}^+\text{-Fc} + \text{e} \rightarrow \text{Fc-Fc-Fc}\end{array}\right\} E_{1/2} = 0.22 \text{ V}$$

The difference in $E_{1/2}$ values (-0.06 V) is a measure of the effect of a nonadjacent ferrocenyl group.[32] Since the effect of a nonadjacent ferrocenyl group is nearly the same as the effect of an adjacent group (-0.09 V), free energy differences between isomers like $\text{Fc}^+\text{-Fc-Fc}$ and $\text{Fc-Fc}^+\text{-Fc}$ and between isomers like $\text{Fc}^+\text{-Fc-Fc-Fc}$ and $\text{Fc-Fc}^+\text{-Fc-Fc}$ should be small.

The potential for the reaction

$$\text{Fc}^+\text{-Fc}^+\text{-Fc} + \text{e} \rightarrow \text{Fc}^+\text{-Fc-Fc}$$

can be calculated by

$$E_{\text{calcd}} = E_{\text{Fc}_2^{2+,+}} + \delta_{\text{Fc}} = 0.56 \text{ V}$$

Since $E_{1/2}$ for the couple $(\text{Fc-Fc-Fc})^{2+,+}$ is significantly lower (0.44 V), the experimental value must refer, mainly, to the reaction

$$\text{Fc}^+\text{-Fc-Fc}^+ + \text{e} \rightarrow \text{Fc}^+\text{-Fc-Fc} \quad (E_{1/2} = 0.44 \text{ V})$$
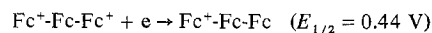
By combining the half-reactions, it is possible to estimate the free energy difference between the isomers

$$\text{Fc}^+\text{-Fc-Fc}^+ \rightarrow \text{Fc}^+\text{-Fc}^+\text{-Fc}$$

$$(\Delta E = -0.12 \text{ V}; \Delta G = 2.8 \text{ kcal/mol}) \tag{2}$$
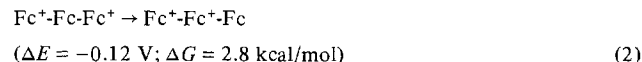
Intervalence-Transfer Absorption. The band at λ_{max} 1900 nm for Fc-Fc^+ has been assigned to an intervalence-transfer (IT) transition[5]
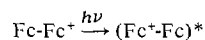
$$\text{Fc-Fc}^+ \xrightarrow{h\nu} (\text{Fc}^+\text{-Fc})^*$$

In the transition, light-induced electron transfer occurs giving

Table III. Intervalence-Transfer Bands for Mixed-Valence
1,1'-Polyferrocene Ions[a]

Transition	λ_{max}		
	cm^{-1}	nm	ϵ
Fc$^+$-Fc $\xrightarrow{h\nu}$ (Fc-Fc$^+$)*	5260	1900	760
Fc-Fc$^+$-Fc $\xrightarrow{h\nu}$ (Fc$^+$-Fc-Fc)*	5020	1990	1560
Fc$^+$-Fc-Fc$^+$ $\xrightarrow{h\nu}$ (Fc$^+$-Fc$^+$-Fc)*	5990	1670	1080
Fc$^+$-Fc-Fc$^+$-Fc $\xrightarrow{h\nu}$ (Fc$^+$-Fc$^+$-Fc-Fc)*	5590	1790	1720

[a] In 1:1 (v/v) CH$_2$Cl$_2$-CH$_3$CN-0.1 *M* in (*n*-Bu)$_4$NPF$_6$.

a vibrationally excited state of the product ion (Fc$^+$-Fc)* (Figure 5). The product ion is formed in a vibrationally excited state because nuclear motion is much slower than electron motion (Franck–Condon principle). Light-induced electron transfer gives -Fc with the inner coordination sphere and solvation sphere arrangement of -Fc$^+$ and -Fc$^+$ with the inner coordination sphere and solvation sphere arrangement of -Fc.

The mixed-valence polyferrocene ions also have IT bands in the near-infrared spectra (Table III). For some of the ions, λ_{max} values are shifted significantly from λ_{max} for Fc-Fc$^+$. The shifts can be accounted for if it is realized that the reactants and products of light-induced electron transfer are not symmetric. In some cases the electron-transfer products are energetically unfavorable oxidation state isomers, *e.g.*
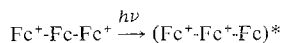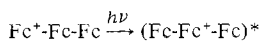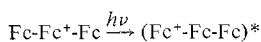
$$Fc^+\text{-}Fc\text{-}Fc^+ \xrightarrow{h\nu} (Fc^+\text{-}Fc^+\text{-}Fc)*$$

As described by Hush,[4] the energy for such a transition (E_{op}) will equal the sum of the Franck–Condon energy (E_{FC}) and the difference in energy (E_0) between the equilibrium vibrational states of Fc$^+$-Fc-Fc$^+$ and Fc$^+$-Fc$^+$-Fc, $E_{op} = E_{FC} + E_0$. For the IT transition

$$\bar{\nu}_{op} = \bar{\nu}_{FC} + \bar{\nu}_0 \tag{3}$$

where $\bar{\nu}$ is the transition frequency in wave numbers. The relationship is shown diagrammatically in Figure 5B. Figures 5A and 5B are potential energy–configurational coordinate diagrams used by Hush in describing IT transitions.

For the case of Fc$^+$-Fc-Fc$^+$ it is possible to estimate both E_{FC} and E_0 and so to calculate E_{op}. In a previous section an estimate was made for the difference in free energy between the oxidation state isomers of (Fc-Fc-Fc)$^{2+}$ (eq 2). The transition E values, E_{op}, E_{FC}, and E_0, are internal energies. If ΔS is small for eq 2, then $\Delta G \approx E_0$ and $E_0 \approx 2.8$ kcal/mol ($\bar{\nu}_0 = 980$ cm^{-1}). E_{FC} can be estimated using the IT band for Fc-Fc$^+$. If the potential energy surfaces for the mixed-valence polyferrocene ions are not greatly distorted from the case for Fc-Fc$^+$, E_{FC} should be nearly the same giving $\bar{\nu}_{FC} = 5263$ cm^{-1}. The calculated value for $\bar{\nu}_{op}$ (6.2×10^3 cm^{-1}) using eq 3 is in reasonable agreement with $\bar{\nu}_{max}$ (6.0×10^3 cm^{-1}) for the IT band of Fc$^+$-Fc-Fc$^+$, especially considering the assumptions used in the calculation.

For the ion (Fc-Fc-Fc)$^+$ the reactants and products of light-induced electron transfer are nearly equivalent energetically

$$Fc\text{-}Fc^+\text{-}Fc \xrightarrow{h\nu} (Fc^+\text{-}Fc\text{-}Fc)*$$

$$Fc^+\text{-}Fc\text{-}Fc \xrightarrow{h\nu} (Fc\text{-}Fc^+\text{-}Fc)*$$

The energy difference (E_0) between isomers is small since (Fc-Fc$^+$-Fc) is favored slightly (~0.03 V) by ferrocenyl substituent effects and (Fc$^+$-Fc-Fc) by a statistical factor of 2 (0.018 V). Since $E_0 \approx 0$, $E_{op} \approx E_{FC}$. If E_{FC} is nearly the same for both (Fc-Fc-Fc)$^+$ and Fc-Fc$^+$, the IT λ_{max} values should also be nearly the same, which they are, 1900 *vs.* 1990 nm. The similarity in IT λ_{max} values supports the assumption

made earlier that E_{FC} values were similar for Fc-Fc$^+$ and for the polyferrocene mixed-valence ions.

The IT molar extinction coefficients for the mixed-valence 1,1'-polyferrocene ions are considerably greater than for Fc-Fc$^+$ (Table III). Unfortunately, we have been unable to determine oscillator strengths for the IT bands. The intensity enhancements for the mixed-valence polyferrocene ions can be explained by the existence of equivalent transitions. For example, for the ion (Fc-Fc-Fc)$^{2+}$ two equivalent IT transitions can occur, *i.e.*

$$Fc^+\text{-}Fc\text{-}Fc^+ \rightarrow (Fc^+\text{-}Fc^+\text{-}Fc)*$$

$$Fc^+\text{-}Fc\text{-}Fc^+ \rightarrow (Fc\text{-}Fc^+\text{-}Fc^+)*$$
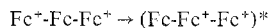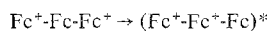
If delocalization were extensive, IT excitation would not be localized to a given Fc$^+$-Fc- pair—the IT transitions would interact giving rise to delocalized exciton states. The mixed-valence 1,1'-polyferrocene ions are apparently not significantly delocalized as evidenced by the presence of discrete Fe(II) and Fe(III) oxidation state sites in (Fc-Fc)$^+$. Interactions between the IT transitions are apparently weak and the transition intensities therefore additive[4] which explains the simple intensity enhancements observed.

For the ferricenium ion, Fc$^+$, the blue color arises from an absorption band at λ_{max} 617 nm. The band has been assigned to a ligand (e$_{1u}$) → metal (e$_{2g}$(3d)) transition.[35,36] In Fc-Fc$^+$ the 617-nm band is broadened and λ_{max} occurs at higher energy. It has been suggested by Cowan, *et al.*,[5] that the 600-nm band in Fc-Fc$^+$ is composed of two transitions: the normal, localized -Fc$^+$ transition, Fc-Fc$^+$(e$_{1u}$) → Fc-Fc$^+$(e$_{2g}$), and at higher energy an excited-state IT transition, Fc-Fc$^+$(e$_{1u}$) → (Fc$^+$(e$_{2g}$)-Fc)*. In some cases distinct shoulders are observed in the 550–700-nm region for the mixed-valence 1,1'-polyferrocene ions (Figures 3 and 4). However, the interpretation given by Cowan, *et al.*, for the splitting of the 600-nm band does not account satisfactorily for the quantitative details of the absorption bands (Table II). For example, if the lower energy component of the band arises from a -Fc$^+$ transition, the band intensities should be roughly proportional to the number of -Fc$^+$ groups. In comparing the molar extinction coefficients of the low-energy shoulders for (Fc-Fc-Fc)$^+$ and (Fc-Fc-Fc)$^{2+}$ this is clearly not the case: for (Fc-Fc-Fc)$^+$, ϵ is 3200 (at 625 nm) while for (Fc-Fc-Fc)$^{2+}$ ϵ is 1800 (at 690 nm). In fact, recent work indicates that the two bands arise from separate ligand to metal transitions from the cyclopentadienyl and bridging fulvalene ligands.[37]

Electron-Transfer Properties. In mixed-valence compounds it is possible to estimate the activation energy for thermal electron transfer between the different oxidation state sites
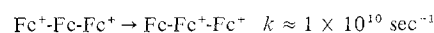
$$Fc\text{-}Fc^+ \rightarrow Fc^+\text{-}Fc \quad (E_{th})$$
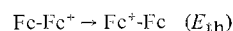
In theory the relationship between the energy of the optical IT transition E_{op} and E_{th} is[4,7]

$$E_{op} \geqslant 4E_{th} \tag{4}$$

The rate of thermal electron transfer (k_{th}) for a reaction can be estimated using reaction rate theory, $k_{th} = (kT/h) \exp(-\Delta H^\ddagger/RT + \Delta S^\ddagger/R)$, and eq 4. If the entropy of activation is assumed to be 0

$$k_{th} \approx (kT/h) \exp[-(E_{op}/4 - RT)/RT] \tag{5}$$

since $E_{op}/4 \approx E_{th} = \Delta H^\ddagger + RT$. Equation 5 allows estimates to be made for intramolecular electron-transfer processes like

$$Fc^+\text{-}Fc \rightarrow Fc\text{-}Fc^+ \quad k \approx 3 \times 10^{10} \text{ sec}^{-1}$$

$$Fc^+\text{-}Fc\text{-}Fc^+ \rightarrow Fc\text{-}Fc^+\text{-}Fc^+ \quad k \approx 1 \times 10^{10} \text{ sec}^{-1}$$

The absolute values for k calculated in this way are, at best, rough estimates. However, the calculations for Fc$^+$-Fc and Fc$^+$-Fc-Fc$^+$ are based on spectral data obtained in the same medium under the same conditions.

The calculated k values should be meaningful when compared with each other, even if they are not meaningful in the absolute sense. From the calculated values for k, the rate of electron hopping between ferrocenyl and ferricenium groups is slower in Fc^+-Fc-Fc^+ than in Fc^+-Fc mainly because of the energetically different chemical sites in Fc^+-Fc-Fc^+. The rate differences involved are small, but worth noting, since they indicate that in ligand-bridged complexes where there are weak metal–metal interactions, rates of intramolecular electron transfer can be varied systematically by changing the chemical environments of the constituent ions.

Registry No. Fc, 102-54-5; Fc-Fc, 1287-38-3; Fc-Fc-Fc, 1273-59-2; Fc-Fc-Fc-Fc, 1299-15-6; (Fc)$^+$, 12125-80-3; (Fc-Fc)$^+$, 51263-10-6; (Fc-Fc-Fc)$^+$, 53730-59-9; (Fc-Fc-Fc)$^{2+}$, 53730-60-2; (Fc-Fc-Fc-Fc)$^{2+}$, 53730-61-3.

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Localized Scrambling of Carbonyl Ligands in Compounds with Metal-to-Metal Bonds

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We report the results of ^{13}C nmr investigations of (acenaphthylene)Fe$_2$(CO)$_5$ (**1**) and (cycloheptatriene)Fe$_2$(CO)$_6$ (**2**). In **1**, which has Fe(CO)$_2$ and Fe(CO)$_3$ groups connected by an Fe–Fe bond, the CO groups of Fe(CO)$_3$ scramble among themselves but do not exchange with those on the Fe(CO)$_2$ group, thus proving that the localized process is important in compounds with Fe(CO)$_3$–Fe type groups. In **2** scrambling also occurs, and, because of the very long Fe–Fe distance (2.87 Å), which would destabilize a bridged intermediate, it is believed that this system provides another example of localized scrambling within an (allyl)Fe(CO)$_3$–Fe type unit.

Introduction

It is now well established that in many binuclear,[1-9] trinuclear,[2,10] and tetranuclear[11-13] metal carbonyl compounds, carbonyl groups are scrambled by processes which involve their passage from one metal atom to another. In these processes they pass from bridging to terminal positions, and *vice versa*. It has also been shown that in some mononuclear organocarbonyl species which have nonequivalent CO groups within M(CO)$_3$ sets, rapid site exchange occurs by some process which is indistinguishable from and may well be the same in actuality