

Intervalence Transfer in Mixed-Valence Biferrocene Ions

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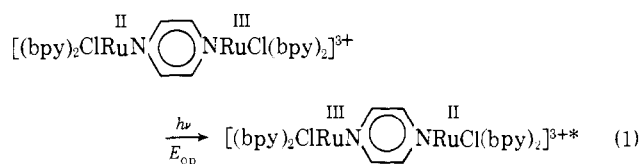
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Abstract: The mixed-valence cations of biferrocene, $(\text{Fc}-\text{Fc})^+$, and biferrocenylacetylene, $(\text{Fc}-\text{C}\equiv\text{C}-\text{Fc})^+$, have been generated in a series of solvents using $[(\text{bpy})_2\text{Ru}(\text{PPh}_3)\text{Cl}](\text{PF}_6)_2$ as an oxidant. The mixed-valence complexes display low-energy (near-infrared) absorption bands which are assigned to intervalence transfer (IT) transitions between isolated Fe(II) and Fe(III) sites. Plots of E_{op} (the energy of the IT band at λ_{max}) vs. $(1/n^2 - 1/D_s)$ where n^2 and D_s are the optical and static dielectric constants of the solvent medium, respectively, have been made and the linear relationship predicted by Hush theory has been found. Using the three ions $(\text{Fc}-\text{Fc})^+$, $(\text{Fc}-\text{C}\equiv\text{C}-\text{Fc})^+$, and $(\text{Fc}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Fc})^+$, the expected linear relationship between E_{op} and $1/d$, where d is the Fe-Fe separation, has also been observed. The results suggest that the mixed-valence ions have localized valence sites and that the observed IT properties are consistent with the Hush treatment for optical electron transfer, although slight deviations may exist because of partial electron delocalization.

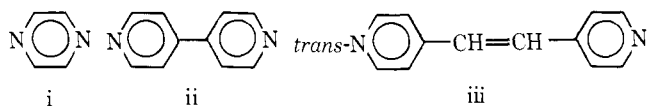
Introduction

The results of previous studies on bis-2,2'-bipyridine and pentaammineruthenium(II)-(III) mixed-valence ions have suggested that a transition from localized to delocalized behavior at the metal sites can result from the effects of relatively subtle changes in molecular structure. In the ion $[(\text{bpy})_2\text{ClRu}(\text{pyr})\text{RuCl}(\text{bpy})_2]^{3+}$ (bpy is 2,2'-bipyridine, pyr is pyrazine) there are discrete Ru(II) and Ru(III) sites,¹⁻³ while in the ions $[(\text{NH}_3)_5\text{RuNCCNRu}(\text{NH}_3)_5]^{5+}$ ⁴ and $[(\text{NH}_3)_5\text{Ru}(\text{pyr})\text{Ru}(\text{NH}_3)_5]^{5+}$ ⁵ there is evidence that the Ru sites are equivalent on the vibrational time scale.

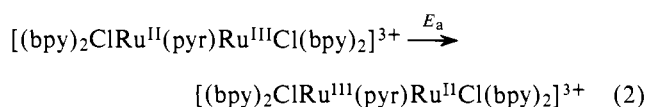
For $[(\text{bpy})_2\text{ClRu}^{\text{II}}(\text{pyr})\text{Ru}^{\text{III}}\text{Cl}(\text{bpy})_2]^{3+}$ and related Ru-bpy mixed-valence ions, intervalence transfer (IT)⁶ bands appear at low energies in the near infrared corresponding to optically induced electron transfer from Ru(II) to Ru(III) as shown in eq 1. The dependence of the IT band energy, E_{op} , on



solvent,^{2,7} and on the internuclear separation between the Ru(II) electron donor and Ru(III) electron acceptor sites,⁸ has been investigated using the ions $[(\text{bpy})_2\text{ClRu}(\text{L})\text{RuCl}(\text{bpy})_2]^{3+}$ (L = i, ii, or iii). The results obtained are consistent



with predictions made by Hush for IT bands,⁶ and reinforce the earlier semiclassical treatments given by Marcus⁹ and Hush¹⁰ for thermal, outer-sphere electron transfer. The results have also demonstrated the connection between optical and related thermal electron transfer processes in mixed-valence dimers (eq 2) suggested by Hush.



The origin of the difference in properties between the pentaammine and Ru-bpy systems may arise in part from greater $d\pi[-\text{Ru}^{\text{II}}(\text{NH}_3)_5] \rightarrow \pi^*(\text{pyr})$ mixing which enhances overlap between the Ru(II) and Ru(III) sites.^{11,12} The C-C bridged, mixed-valence biferrocene ion $[(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4-\text{C}_5\text{H}_4)-\text{Fe}(\text{C}_5\text{H}_5)]^+$, $(\text{Fc}-\text{Fc})^+$, first studied by Cowan and co-workers,¹³⁻¹⁵ is related to the ruthenium complexes in that it

also involves spin-paired d^5-d^6 electron donor and acceptor sites. For $(\text{Fc}-\text{Fc})^+$ a low-energy absorption band appears in the near IR and the results of Mössbauer and ESCA experiments suggest that there are discrete Fc and Fc^+ sites in the mixed-valence ion.¹³⁻²¹ However, $(\text{Fc}-\text{Fc})^+$ is highly favored with respect to disproportionation into $(\text{Fc}-\text{Fc})$ and $(\text{Fc}-\text{Fc})^{2+}$ and this and other lines of evidence suggest that delocalization effects in mixed-valence biferrocene-type ions may be important. As for the mixed-valence ruthenium ions, the extent of delocalization in the biferrocene ions may depend on relatively subtle changes in molecular structure.

The biferrocene system can be changed systematically by controlled synthetic modifications. Low-energy absorption bands have been observed for the mixed-valence forms of substituted biferrocenes,²² for biferrocenes like $[(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4\text{C}\equiv\text{CC}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)]^+$ where the metal-metal separation has been extended,²³ and in oligomeric ferrocenes like the 1,1'-terferrocene ions $(\text{Fc}-\text{Fc}-\text{Fc})^+$ and $(\text{Fc}-\text{Fc}-\text{Fc})^{2+}$.²⁴ We report here the results of a study on the properties of the near IR bands for some mixed-valence biferrocene ions. Our intention was to search for possible effects of delocalization and to see if the Hush treatment for IT transitions in terms of solvent effects and the role of the internuclear separation between redox sites is applicable to the biferrocene ions.

Experimental Section

Measurements. Near-infrared, visible, and ultraviolet spectra were measured using Cary Models 14 and 17 and Bausch and Lomb Spectronic 210 spectrophotometers at room temperature. Electrochemical measurements were vs. the saturated sodium chloride calomel electrode (SSCE) at $22 \pm 2^\circ\text{C}$ and are uncorrected for junction potentials. The measurements were made using a PAR Model 173 potentiostat for potential control with a PAR Model 175 universal programmer as a sweep generator for voltammetric experiments.

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques.^{16,25} For electrochemical experiments acetonitrile (MCB Spectrograde) and methylene chloride (Aldrich, spectroanalyzed) were dried over Davidson 4 Å molecular sieves. For near-infrared measurements, solvents were purified over drying agents and vacuum distilled using standard purification techniques.^{26,27}

Deuterated solvents (Stohler Isotope Corporation) used in near-infrared spectral measurements were used as purchased without further purification.

Preparation of Complexes. $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}](\text{PF}_6)$. The preparation and properties of this salt have been described elsewhere.²⁸

$[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$. The Ru(III) salt was prepared from $[(\text{bpy})_2\text{Ru}(\text{PPh}_3)\text{Cl}](\text{PF}_6)$ by first isolating the chloride salt. The chloride salt was precipitated by adding $[\text{N}(\text{n}-\text{C}_4\text{H}_9)_4]\text{Cl}$ to an acetone solution of the PF_6^- salt. The chloride salt was dissolved in 0.1 M HCl and oxidized using a slight excess of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ in 0.1

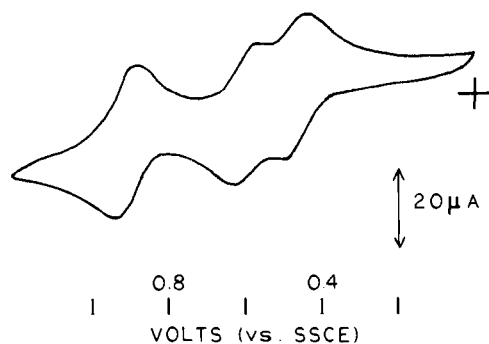


Figure 1. Cyclic voltammogram after mixing $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^{2+}$ ($1.04 \times 10^{-3} \text{ M}$) and $(\text{Fc}-\text{C}\equiv\text{C}-\text{Fc})$ ($1.2 \times 10^{-3} \text{ M}$) in $0.1 \text{ M } [\text{N}(\text{n}-\text{C}_4\text{H}_9)_4](\text{PF}_6)-\text{CH}_3\text{CN}$ (vs. SSCE at $22 \pm 2^\circ \text{C}$).

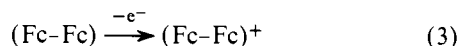
M HCl. Following the oxidation, which occurs immediately upon mixing as shown by the color change from deep red to green, the Ru(III) complex was precipitated as the PF_6^- salt by adding a saturated aqueous solution of ammonium hexafluorophosphate. The Ru(III) salt is slightly light sensitive so the preparation was carried out in the dark. The purity of the isolated salt, $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$, was shown by cyclic voltammetry (the same cyclic voltammogram was obtained as for $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^+$ and the null potential indicated that the wave was a reduction) and by reducing the complex with hydrazine, which gave $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^+$ quantitatively as shown by spectral comparisons. Anal. Calcd for $\text{RuC}_{38}\text{H}_{31}\text{N}_4\text{P}_3\text{ClF}_{12} \cdot \text{H}_2\text{O}$: C, 44.79; H, 3.26; N, 5.50; Cl, 3.48. Found: C, 44.58; H, 2.84; N, 5.29; Cl, 3.55.

Ferrocene Complexes. Biferrocene ($\text{Fc}-\text{Fc}$) and biferrocenylacetylene ($\text{Fc}-\text{C}\equiv\text{C}-\text{Fc}$) were kindly provided by Professor W. F. Little of the Department of Chemistry of The University of North Carolina. Both compounds were purified by column chromatography on alumina using benzene as eluent.

Biferrocene monocation ($\text{Fc}-\text{Fc}^+$) and biferrocenylacetylene monocation ($\text{Fc}-\text{C}\equiv\text{C}-\text{Fc}^+$) were prepared in situ by mixing equimolar amounts of the biferrocene complex with $[(\text{bpy})_2\text{Ru}(\text{PPh}_3)\text{Cl}](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ in the appropriate solvent. In those solvents in which one of the two solids was not completely soluble, the oxidant and reductant were first mixed in CH_2Cl_2 , the CH_2Cl_2 solution was evaporated to dryness, and the appropriate solvent was then added to the solid mixture.

Results

Earlier work on biferrocene-type mixed-valence ions has relied mainly on electrochemical oxidation to produce the mixed-valence ions:



The electrochemical procedure is clumsy because of the necessity of having a supporting electrolyte present and because of the length of time for the electrolyses. The latter is especially a problem given the large number of solvents needed for the solvent dependence studies. We have developed a technique based on homogeneous one-electron oxidation using $[(\text{bpy})_2\text{Ru}(\text{PPh}_3)\text{Cl}](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ as oxidant. For the $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^{2+}/^+$ couple, the formal reduction potential is 0.91 V vs. SSCE in $0.1 \text{ M TBAH}/\text{CH}_3\text{CN}$, and like many other Ru-bpy Ru(III)-(II) couples, the two forms are interrelated by simple one-electron transfer.²⁸ The Ru(III) complex, which was prepared by Ce(IV) oxidation of $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}](\text{PF}_6)$, is stable in the solid state for at least 4 weeks and solutions in pure acetonitrile are stable for at least 4 h.

In Figure 1 is shown a cyclic voltammogram taken after mixing equimolar amounts of $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ and $(\text{Fc}-\text{C}\equiv\text{C}-\text{Fc})$. The absorption spectrum after mixing is consistent with the net reaction

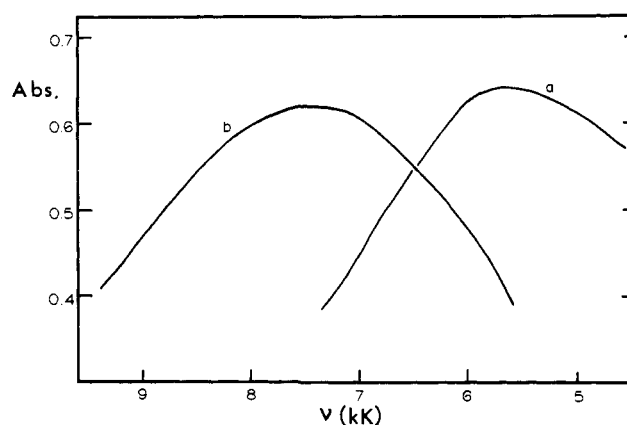
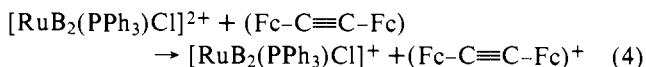


Figure 2. (a) Intervalence transfer band for $(\text{Fc}-\text{Fc})^+$ ($\sim 7.3 \times 10^{-3} \text{ M}$, 0.1 cm path length) in CD_3CN . (b) Intervalence transfer band for $(\text{Fc}-\text{C}\equiv\text{C}-\text{Fc})^+$ ($\leq 2.61 \times 10^{-3} \text{ M}$, 1.0 cm path length) in CH_3CN .

which occurs instantaneously under the conditions used. The cyclic voltammogram in $0.1 \text{ M TBAH}/\text{CH}_3\text{CN}$ has reversible waves at $E_{1/2} (1) = 0.46 \text{ V}$ and $E_{1/2} (2) = 0.60 \text{ V}$ for the $(\text{Fc}-\text{C}\equiv\text{C}-\text{Fc})^{+/0}$ and $(\text{Fc}-\text{C}\equiv\text{C}-\text{Fc})^{2+}/^+$ couples and at $E_{1/2} (3) = 0.91 \text{ V}$ for the $[(\text{bpy})_2\text{Ru}(\text{PPh}_3)\text{Cl}]^{2+}/^+$ couple. The cyclic voltammetry and spectral experiments show that reaction 4 is quantitative as written and that the presence of $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^+$ following oxidation has no effect on the spectral or redox properties of the biferrocene ions. The same general results were obtained after mixing equimolar amounts of $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ and biferrocene in $0.1 \text{ M TBAH}/\text{CH}_2\text{Cl}_2$ showing that oxidation of $(\text{Fc}-\text{Fc})$ by $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^{2+}$ is also quantitative.

Intervalence Transfer Bands. For both $(\text{Fc}-\text{Fc})^+$ and $(\text{Fc}-\text{C}\equiv\text{C}-\text{Fc})^+$ well-defined IT bands were observed in several solvents. Examples for each are shown in Figure 2. In Table I are given variations in E_{op} for the two ions (the IT band energy at λ_{max}) as a function of the dielectric properties of a series of solvents.²⁹ Other properties of the IT bands are also included in Table I. Deuterated solvents were used for $(\text{Fc}-\text{Fc})^+$ where possible because of interferences in the near-IR region from C-H overtone vibrational modes. It was not possible to use dimethylformamide or dimethyl sulfoxide as solvents because they, or an impurity in them, react rapidly with the mixed-valence biferrocene ions.

The data obtained for $(\text{Fc}-\text{Fc})^+$ in CH_2Cl_2 differ slightly from previous results^{13,22,24} where spectra were obtained in solvent mixtures or in the presence of a supporting electrolyte. Formation of $(\text{Fc}-\text{Fc})^+$ by either electrochemical or chemical oxidation using $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^{2+}$ in CH_2Cl_2 gives essentially identical absorption bands, showing that the effect of the added supporting electrolyte at a level of 0.1 M in the electrochemical experiment is slight and the same results are obtained within experimental error. The result also reinforces the point that the $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^+$ ion which is present in dilute amounts following chemical oxidation has no effect on either the spectral or electrochemical properties of the mixed-valence biferrocene ions.

In Table I are also given values of $\Delta\bar{\nu}_{1/2}$ (the bandwidth at half-height) and ϵ_{max} where those values were obtainable. They are consistent with earlier results.^{13,22,24} For the IT bands, plots of absorbance vs. $\bar{\nu}$ for both $(\text{Fc}-\text{Fc})^+$ and $(\text{Fc}-\text{C}\equiv\text{C}-\text{Fc})^+$ in all solvents showed that the bands were essentially Gaussian in shape.⁶ Only the high-energy half-heights were available owing to low-energy tailing of the IT bands into regions of high background solvent absorption. As a consequence, we were unable to use the procedure recommended by Hush for obtaining $\Delta\bar{\nu}_{1/2}$.⁶ The values reported were obtained by measuring the band half-width on the high-energy side of $\bar{\nu}_{\text{max}}$,

Table I. Properties of the Intervalence Transfer Bands for (Fc-Fc)⁺ and (Fc-C≡C-Fc)⁺

Ion	Solvent	$1/n^2 - 1/D_s^a$	λ_{\max} , nm ^b	$\bar{\nu}_{\max}$, μm^{-1} ^b	ϵ_{\max} ^c	$\Delta\bar{\nu}_{1/2}(\text{obsd})^d$	$\Delta\bar{\nu}_{1/2}(\text{calcd})^d$
(Fc-Fc) ⁺	Acetone- <i>d</i> ₆	0.496	1776	0.564		0.416	0.361
	Acetonitrile- <i>d</i> ₃	0.528	1760	0.568		0.390	0.362
	Methylene- <i>d</i> ₂ chloride	0.382	2000	0.500	919	0.370	0.340
	Nitrobenzene- <i>d</i> ₅	0.388	1920	0.523	723	0.374	0.348
	Nitromethane	0.489	1830	0.545	759	0.402	0.355
	Propylene carbonate	0.481	1795	0.557	650	0.412	0.359
(Fc-C≡C-Fc) ⁺	Acetone	0.496	1320	0.756		0.572	0.418
	Acetonitrile	0.526	1340	0.747		0.546	0.415
	Benzonitrile	0.388	1578	0.634		0.510	0.383
	Methylene chloride	0.380	1620	0.618	487	0.520	0.378
	Nitrobenzene	0.384	1582	0.632	514	0.476	0.382
	Nitromethane	0.489	1385	0.722		0.498	0.408
	Propylene carbonate	0.481	1355	0.738		0.524	0.413

^a n^2 , the square of the refractive index, is the optical dielectric constant of the solvent and D_s is the static dielectric constant. ^b λ_{\max} is the wavelength of maximum absorbance for the IT band. $\bar{\nu}_{\max} = E_{\text{op}}$ is the energy of the band at λ_{\max} . ^c ϵ is the molar extinction coefficient at λ_{\max} in $\text{M}^{-1} \text{cm}^{-1}$. ^d $\Delta\bar{\nu}_{1/2}(\text{obsd})$ is the observed bandwidth at half-height; $\Delta\bar{\nu}_{1/2}(\text{calcd})$ was calculated using eq 5 in the text; in μm^{-1} .

where the absorbance was half that at the absorbance maximum, and doubling it. The calculated values of $\Delta\bar{\nu}_{1/2}$ given in Table I were obtained using eq 5, which has been derived by Hush for IT transitions in the high-temperature limit. In eq 5, $\bar{\nu}_{\max}$ is the energy of the IT band at λ_{\max} ,

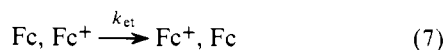
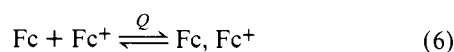
$$\bar{\nu}_{\max} = (\Delta\bar{\nu}_{1/2})^2 / 2.31 \quad (5)$$

In Figure 3 are shown plots of E_{op} vs. $(1/n^2 - 1/D_s)$ for the two ions studied. For (Fc-Fc)⁺, the best-fit straight line gives a slope of $0.412 \mu\text{m}^{-1}$ and a y intercept of $0.35 \mu\text{m}^{-1}$. The correlation coefficient, r , from a linear least-squares program used to fit the line, was 0.94. For (Fc-C≡C-Fc)⁺ the slope was $0.96 \mu\text{m}^{-1}$; y intercept, $0.26 \mu\text{m}^{-1}$; and r , 0.98.

Discussion

Nature of the Near-IR bands. As shown by our experimental data and by the data reported earlier,^{13,22,23} (Fc-Fc)⁺ and (Fc-C≡C-Fc)⁺ have well-defined near-IR absorption bands. For (Fc-C≡C-Fc)⁺, the band half-widths, $\Delta\bar{\nu}_{1/2}$, are consistent with Hush theory in that they are larger than $\Delta\bar{\nu}_{1/2}(\text{calcd})$, which is to be expected given the assumptions involved in the derivation of eq 5. The ratio $\Delta\bar{\nu}_{1/2}(\text{obsd})/\Delta\bar{\nu}_{1/2}(\text{calcd})$ in the various solvents has the average value 1.1 for (Fc-Fc)⁺ and 1.3 for (Fc-C≡C-Fc)⁺ and these values are similar to results obtained for the mixed-valence Ru-bpy ions [(bpy)₂ClRu(L)RuCl(bpy)₂]³⁺ (L = 4,4'-bipyridine or *trans*-1,2-bis(4-pyridyl)ethylene) where ratios average 1.2.³⁹

The energies of the optical transitions can be estimated from the rate of ferrocene-ferrocenium self-exchange



in CD₃CN for which $E_a = 5 \pm 1$ kcal/mol.³⁰ Q (eq 6) can be estimated from the Fuoss equation³¹⁻³³ where d is the internuclear separation between reactants. However,

$$Q = (2.524 \times 10^{-3})d^3 \exp\left[\frac{-9.03Z_1Z_2}{dRT}\right] \quad (8)$$

the product of ionic charges is 0 for the ferrocene-ferrocenium self-exchange. The preexponential term in eq 8 is an entropic term and to a first approximation E_a then refers solely to the activation requirements for electron transfer within the association complex (eq 7). Using molecular radii of 3.9 Å for Fc

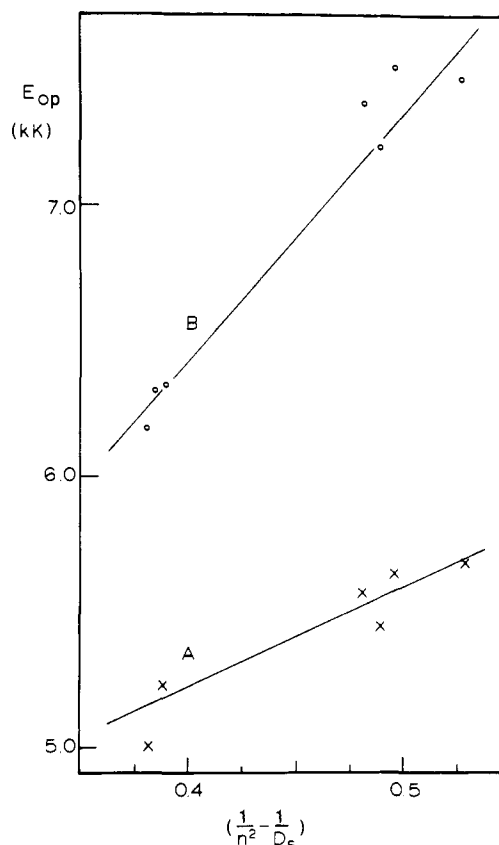
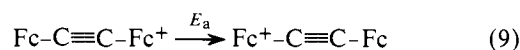


Figure 3. Plot of E_{op} vs. $(1/n^2 - 1/D_s)$ for (Fc-Fc)⁺ (A) and (Fc-C≡C-Fc)⁺ (B).

and Fc^+ ,³⁴



the internuclear distance for electron transfer in the Fc,Fc⁺ ion pair (eq 7) is 7.8 Å, which is close to the Fe-Fe distance in Fc-C≡C-Fc⁺ in the *trans* configuration (7.3 Å; see Figure 4).³⁴ Using E_a from the self-exchange experiment as the energy of activation for intramolecular electron transfer in (Fc-C≡C-Fc)⁺ (eq 9) gives $E_a \sim 5$ kcal/mol and from the equation,

$$E_a \leq E_{\text{op}}/4 \quad (10)$$

which follows from Hush's work if delocalization is small, E_{op}

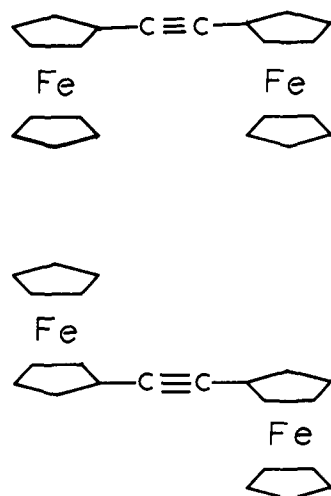


Figure 4. Cis and trans configurations for bis(ferrocenyl)acetylene.

Table II. λ_i and Slopes from the Variation of E_{op} with $(1/n^2 - 1/D_s)$ in Figure 3

Ion	$\lambda_i, \mu\text{m}^{-1}$	$d, \text{\AA}$	Slope (obsd), μm^{-1}	Slope (calcd), μm^{-1}
Fc-Fc ⁺	0.353	5.0 ^a	0.412	0.654 ^a
Fc-C≡C-Fc ⁺				
cis	0.281	6.5	0.908	1.190
trans	0.281	7.3	0.908	1.385

^a Assuming the trans configuration for $[(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4-\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)]^+$.

(calcd) $\sim 4E_a \sim 20 \pm 4$ kcal/mol. The value estimated from the self-exchange data is in good agreement with the observed value of 21.6 kcal/mol in acetonitrile. In fact, the evidence cited here and later is consistent with earlier suggestions^{13,15,22-24} that the near-IR bands have as their origin IT transitions between localized Fc and Fc⁺ sites.

Solvent Dependence. As shown in Figure 3, E_{op} for the IT bands varies linearly with $(1/n^2 - 1/D_s)$ where n^2 and D_s are the optical and static dielectric constants of the solvent involved. From the treatment given by Hush for the localized valence case,⁶ E_{op} is given by eq 11 in terms of the inner- and outer-sphere reorganizational parameters λ_i and λ_o .

$$E_{op} = \lambda = \lambda_i + \lambda_o \quad (11)$$

λ_o has been treated using a dielectric continuum model for the solvent which gives

$$\lambda_o = (me)^2 (1/2a_1 + 1/2a_2 - 1/d)(1/n^2 - 1/D_s) \quad (12)$$

where m is the number of electrons transferred, e is the unit electron charge, a_1 and a_2 are the molecular radii of the redox sites, and d is the internuclear separation. From eq 11 and 12, the intercept of a plot of E_{op} vs. $(1/n^2 - 1/D_s)$ gives an estimate for λ_i and the slope the quantity $(me)^2 (1/2a_1 - 1/2a_2 - 1/d)$. In Table II are given values of λ_i for the two ions from the plots of E_{op} vs. $(1/n^2 - 1/D_s)$ and calculated and observed values of the slopes of the lines. The trans configuration has been assumed for Fc-Fc⁺.³⁴

The calculated slopes in Table II are consistently greater than the observed slopes, which is in contrast to the $[(\text{bpy})_2\text{ClRu}(\text{L})\text{RuCl}(\text{bpy})_2]^{3+}$ dimers,³⁹ where good agreement between calculated and observed slopes was found for L = ii and iii. There are several possible origins for the larger than predicted slopes for the ferrocene dimers;

1. The calculations are sensitive to the values chosen for a_1 , a_2 and d . If $a_1 = a_2$ were taken as 4.21 \AA rather than 3.9 \AA ,

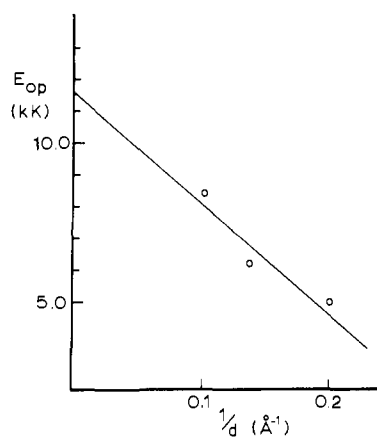


Figure 5. Plot of E_{op} vs. $1/d$ for (Fc-Fc)⁺, (Fc-C≡C-Fc)⁺, and (Fc-(C≡C)₂Fc)⁺.^{23b} Values of d used were for the trans configurations in all cases. The Fe-Fe separation in (Fc-(C≡C)₂-Fc)⁺ was calculated using known dimensions for bisferrocene and appropriate C-C distances.

the calculated and observed slopes for Fc-Fc⁺ would be the same. If the actual configuration were cis or somewhere between cis and trans, the calculated values of the slope would also be lower.

2. The simple dielectric continuum model used for λ_o can only be an approximation. It fails to account for the dielectric properties of the organic bonding system which connects the metal sites and incorporates the distance dependence between sites in an overly simple way.³⁹

3. In eq 12, me represents the amount of charge transferred in the optical transition. If there is a significant ground-state delocalization, m will not be 1 because delocalization amounts to partial charge transfer which can have a sizable effect since it enters as the square, $(me)^2$. If the deviation between calculated and observed slopes were due solely to delocalization, m for Fc-Fc⁺ would be 0.81, suggesting that as an upper limit, electron delocalization from the Fc site to the Fc⁺ site has led to the fractional valences (Fc^{2.19}-Fc^{+2.81})⁺ in the ground state.

Distance Dependence. Equations 11 and 12 can be rearranged to give eq 13, which predicts that for a series of ions

$$E_{op} = \left[\lambda_i + (me)^2 \left(\frac{1}{a_1} - \frac{1}{d} \right) - \left(\frac{1}{n^2} - \frac{1}{D_s} \right) \right] - \frac{me^2}{d} \left(\frac{1}{n^2} - \frac{1}{D_s} \right) \quad (13)$$

having the same $a_1 = a_2$ in a single solvent, E_{op} should vary as $-1/d$. The distance dependence occurs only in the outer-sphere term since if delocalization is small, the electron donor and acceptor sites should behave as uncoupled oscillators. In one view, the $1/d$ term is a correction for the fact that outer-sphere solvent molecules are shared between the two redox sites.^{6,9,10}

Although no detailed data are available, E_{op} for the mixed-valence ion (Fc-(C≡C)₂-Fc)⁺ in 0.1 M $[\text{N}(\text{n-C}_4\text{H}_9)_4](\text{BF}_4)\text{-CH}_2\text{Cl}_2$ has been reported.^{23b} A plot of E_{op} vs. $1/d$ for the three ions (Fc-Fc)⁺, (Fc-C≡C-Fc)⁺, and (Fc-C≡C-C≡C-Fc)⁺ in dichloromethane is shown in Figure 5. As found earlier for the ions $[(\text{bpy})_2\text{ClRu}(\text{L})\text{RuCl}(\text{bpy})_2]^{3+}$,^{8,39} a nearly linear decrease in E_{op} with $1/d$ is observed. As for the Ru-bpy ions, the experimental slope ($-3.30 \mu\text{m}^{-1} \text{\AA}^{-1}$) is smaller than the calculated value of $-4.41 \mu\text{m}^{-1} \text{\AA}^{-1}$ but this is not surprising given the oversimplified nature of the model and an empirical correction will be developed in a later paper.³⁹ Assuming for λ_i an average of the values for (Fc-Fc)⁺ and (Fc-C≡C-Fc)⁺ in Table II gives $\lambda_i = 0.317 \mu\text{m}^{-1}$ and using that value gives a calculated y intercept of 1.48

μm^{-1} compared to the experimental value of $1.14 \mu\text{m}^{-1}$.

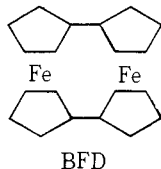
The results of the solvent and distance dependence experiments reinforce the view that the near-IR bands in the mixed-valence biferrocene ions have their origin in IT transitions between valence-localized Fc and Fc^+ sites. The results further confirm the theoretical treatment given by Hush for IT transitions. They also strongly reinforce the experimental and theoretical connections between IT processes and thermal electron transfer both for outer-sphere and inner-sphere reactions where delocalization between redox sites is not extensive.

Delocalization in Mixed-Valence Biferrocene Ions. The conclusion that there are localized valence sites in $(\text{Fc}-\text{Fc})^+$ is supported by earlier physical measurements in the solid state including ESCA,⁴⁰ Mossbauer,^{13,16,17} and magnetic susceptibility.^{19,20} There may be partial delocalization in $(\text{Fc}-\text{Fc})^+$ as evidenced by the magnitude of the value of α^2 for the IT band, and perhaps by the smaller than calculated value for the slope in the plot of E_{op} vs. $(1/n^2 - 1/D_s)$.

The origin of valence trapping lies in the vibrational changes which occur in the inner and outer coordination spheres upon oxidation of Fc to Fc^+ . The vibrational trapping energy corresponds to the thermal activation barrier to electron transfer between Fc and Fc^+ .

Electronic orbital overlap between the Fc and Fc^+ sites leads to electronic delocalization. If delocalization is appreciable the "oxidation states" and coordination spheres at the two sites respond and become more nearly alike. The loss in vibrational trapping energy would be compensated for by the gain in electronic resonance energy.^{6c} If overlap is sufficient, the electronic resonance energy will overcome the trapping barrier^{6c} and the metal sites become equivalent on the vibrational time scale.

For the mixed-valence biferrocene ions, relatively slight changes in the coordination environments may be sufficient to cause the transition from trapped to delocalized ground states. For a biferrocenium system the energy needed to make the sites equivalent is essentially the activation energy for electron transfer between localized sites. From the IT results and the results of the Fc/ Fc^+ self-exchange experiment, E_a is small (~ 5 kcal/mol). In fact, there is good experimental evidence^{17,41} and a supporting theoretical treatment⁴² for delocalized iron sites in the closely related mixed-valence form of bis(fulvalene)diiron, $(\text{BFD})^+$. A band appears for $(\text{BFD})^+$



in the near IR^{14,17} (1500 nm in CH_3CN) but the band is narrow ($\Delta\bar{\nu}_{1/2} = 0.325 \mu\text{m}^{-1}$), and given the Fe-Fe separation, is much higher in energy than would be predicted from the plot in Figure 5. We find that E_{op} for the band is also relatively insensitive to changes in solvent. λ_{max} values for the two extreme cases of solvents in Table I (extreme in terms of $1/n^2 - 1/D_s$) are at 1510 (CH_3CN) and 1560 nm (CH_2Cl_2). The near-IR band which appears in BFD^+ is also more complex than the Gaussian appearing IT bands of $\text{Fc}-\text{Fc}^+$ and $\text{Fc}-\text{C}\equiv\text{C}-\text{Fc}^+$. There is clear evidence that the absorption band is a composite band with components at $\sim\lambda_{\text{max}}$ 1510 nm and at $\sim 1220 \text{ nm}$ in CH_3CN and clearly the band widths at half-height for the separate components are considerably less than $0.325 \mu\text{m}^{-1}$.

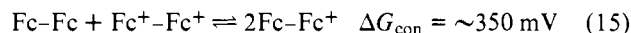
There is a close relationship between the mixed-valence biferrocene and dimeric ruthenium ions. The Ru sites in $[(\text{NH}_3)_5\text{Ru}(\text{pyr})\text{Ru}(\text{NH}_3)_5]^{3+}$ appear to be delocalized on the vibrational time scale, and its near-IR band is noticeably

narrow and does not respond to changes in solvent.⁵ There is some delocalization in $[(\text{bpy})_2\text{ClRu}(\text{pyr})\text{RuCl}(\text{bpy})_2]^{3+}$ and in $\text{Fc}-\text{Fc}^+$ but the extent of delocalization is insufficient to affect the Hush treatment noticeably. The values of α^2 , which are an approximate measure of the extent of delocalization of the optical electron in the ground state, are 2.4×10^{-3} for $\text{Fc}-\text{C}\equiv\text{C}-\text{Fc}^+$, $\sim 9 \times 10^{-3}$ for $\text{Fc}-\text{Fc}^+$, and 2×10^{-3} for $[(\text{bpy})_2\text{ClRu}(\text{pyr})\text{RuCl}(\text{bpy})_2]^{3+}$. The α^2 values were calculated from the IT bands, using eq 14 where d is the metal-metal separation.^{6a}

$$\alpha^2 = \frac{(4.2 \times 10^{-4})\epsilon_{\text{max}}\Delta\bar{\nu}_{1/2}}{\bar{\nu}_{\text{max}}d^2} \quad (14)$$

There may be a difference between the iron and ruthenium systems in the nature of the orbital interaction between redox sites. In the ruthenium complexes, $d\pi(\text{Ru})-\pi^*(\text{pyz})$ mixing can "carry" Ru(II) character across the ligand bridge to Ru(III). In the biferrocene complexes, the $\pi(\text{C}_5\text{H}_5)$ levels are near the $d\pi(\text{Fe})$ levels, and the predominant mechanism for orbital overlap may be through $\pi(\text{C}_5\text{H}_5)-d\pi(\text{Fe(III)})$ mixing with electron hole delocalization to the Fe(II) site.

One puzzling feature is the stability of $\text{Fc}-\text{Fc}^+$ with regard to $\text{Fc}-\text{Fc}$ and Fc^+-Fc^+ as shown by the comproportionation equilibrium



The mixed-valence ion is favored slightly by electrostatic factors;² yet $\Delta G_{\text{con}} = \sim 350 \text{ mV}$ for $\text{Fc}-\text{Fc}^+$, 140 mV for $\text{Fc}-\text{C}\equiv\text{C}-\text{Fc}^+$ (both in $0.1 \text{ M TBAH } 1:1-\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$). However, as pointed out by Taube,¹² ΔG_{con} depends on the properties of $\text{Fc}-\text{Fc}$ and Fc^+-Fc^+ as well as on the properties of $\text{Fc}-\text{Fc}^+$. ΔG_{con} is not necessarily a direct measure of the effects of electronic delocalization between the electron donor and acceptor sites.

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Intramolecular Electron Transfer in the N-Hydroxyethylethylenediaminetriacetatovanadium(II,IV) Binuclear Ion

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Abstract: The cross reaction of V(heedta)⁻ (II) and VO(heedta)⁻ (IV) forming a detectable (II,IV) precursor complex has been studied as a function of pH and temperature. At 298 K, $\mu = 0.20$, the following kinetic parameters have been measured: k_1 (II + IV outer-sphere electron transfer) = $(2.7 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$; k_2 ((II,IV) formation) = $(4.0 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$; k_{-2} ((II,IV) dissociation) = $2.0 \pm 2.0 \text{ s}^{-1}$; k_3 ((II,IV) intramolecular electron transfer) = $25.5 \pm 0.2 \text{ s}^{-1}$; $K_4 k_5$ ((II,IV) H⁺ intramolecular electron transfer) = $(1.22 \pm 0.14) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$; k_6 (IV + (II,IV) outer-sphere electron transfer) = $(9.30 \pm 1.58) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$; k_7 (II + (II,IV) outer-sphere electron transfer) = $(4.61 \pm 0.79) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$; $\log K_2$ (association constant for formation of (II,IV) from II + IV) = 4.30 ± 0.30 . Temperature-dependent studies of the k_2 , k_3 , and $K_4 k_5$ paths reveal $\Delta H_2^\ddagger = 6.1 \pm 1.0 \text{ kcal/mol}$, $\Delta S_2^\ddagger = -17 \pm 3 \text{ eu}$; $\Delta H_3^\ddagger = 7.97 \pm 0.36 \text{ kcal/mol}$, $\Delta S_3^\ddagger = -25.4 \pm 1.2 \text{ eu}$; $\Delta H_{4,5}^\ddagger = -7.04 \pm 4.79 \text{ kcal/mol}$, $\Delta S_{4,5}^\ddagger = -49.7 \pm 16.1 \text{ eu}$. The V(heedta)⁻/VO(Cydt)²⁻ cross-reaction parameters comparable to ΔH_3^\ddagger and ΔS_3^\ddagger are $6.27 \pm 0.44 \text{ kcal/mol}$ and $-30.4 \pm 1.5 \text{ eu}$, respectively. The large negative ΔS_3^\ddagger value is discussed in terms of coordination rearrangements ($\Delta S_{\text{CR}}^\ddagger$) which limit intramolecular electron transfer. The reaction of Cr(heedta)⁻/VO(heedta)⁻ is found to be competitive with stopped-flow mixing and predominantly outer-sphere.

Introduction

Intramolecular electron transfer has been observed for the V(II,IV) binuclear complex formed from the inner-sphere component of the cross reaction of VO(heedta)⁻ and V(heedta)⁻ (heedta³⁻ = N-hydroxyethylethylenediaminetriacetate).¹ The V(III,III) binuclear ion, (heedta)-VOV(heedta)²⁻, is the product of the electron transfer step. This species has been studied for its monomerization and formation reactions and its solution properties.² The V(III,III) complex is similar to the oxo-bridged (heedta)FeOFe(heedta)²⁻ complex studied by Walling and Gray,^{3,4} Wilkins⁵ and Martell.⁶

The intramolecular electron transfer process within the V(II,IV)(heedta) binuclear complex is unusually slow by comparison with other inner-sphere systems.¹ A number of reports concerning intramolecular electron transfer within binuclear ions have appeared since the first report of Isied and Taube.^{1,7-12} In general the reactant metal centers of the precursor complexes have been separated by means of bifunctional

conjugated ligands. The only cases where electron transfer within a binuclear complex has been slow enough to allow detection of a precursor complex having the oxidant and reductant centers separated by a single atomic distance are the VO(heedta)⁻/V(heedta)⁻ cross reaction of our laboratory and Lane's report of the mercaptide bridged Cu(I)-Co(III) intermediate in the reduction of [Co(en)₂SCH₂CO₂]⁺.¹² Electron transfer to Co(III) is often affected by the spin-state change in forming Co(II).^{13a} The activation enthalpy in Lane's system is in agreement with a change in spin state as being rate determining.¹⁴ Spin-state changes cannot affect the VO(heedta)⁻/V(heedta)⁻ system.² The explanation for the slow intramolecular electron transfer step must be found in a different phenomenon. Taube has inferred that entropy of activation which has been measured for many labile reactant pairs is dominated by the entropy costs to bring charged reactants together in solution in order to form the precursor complex.¹⁵ His conclusion is based on the intramolecular electron transfer within (NH₃)₅CoLRu(NH₃)₄(H₂O)⁵⁺ complexes (L = li-