



Correlation of Spectral and Electrochemical Properties of a Series of Ferrocene Derivatives

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Abstract

Charge-transfer-to-solvent (CTTS) bands are observed in the UV/VIS spectra of a series of ferrocene derivatives (ferrocene; 1,1'-dimethyl; 1,2,3,4,5-pentamethyl; 1,2,3,4,1',2',3',4'-octamethyl; and decamethyl) by the addition of increasing amounts of CCl₄ to ethanol solutions. A linear correlation (slope = 8540 cm⁻¹/V) was found between the redox potential and the energy of the CTTS band, consistent with electrochemical and photochemical oxidation by removal of an electron from the same molecular orbital. Inclusion of literature data for ruthenocene and [(η⁵-C₅H₅)Fe(CO)]₄ results in a line with a slope of 8140 cm⁻¹/V, within 1 percent of the wavenumber to electron volt conversion factor. Calculation of association constants (K) shows a slight decrease (1.2 to 0.7 mole fraction⁻¹) as the bulkiness of the cyclopentadienyl ring increases, consistent with either a steric or a repulsive electronic effect. The extinction coefficient of the CTTS absorption was constant at approximately 1700 M⁻¹cm⁻¹.

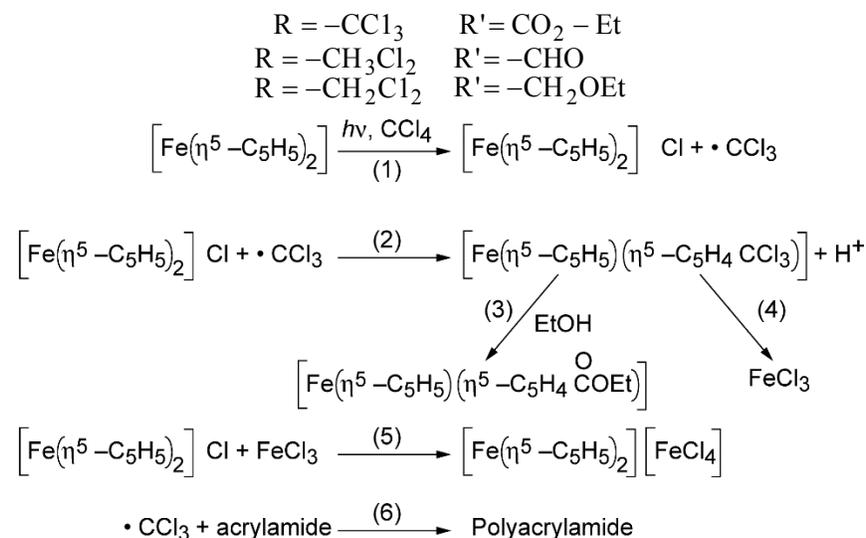
Introduction

Shortly after the synthesis (Ref. 1) and characterization of ferrocene (Refs. 2 and 3), an ultraviolet transition in the presence of halocarbon solvents (i.e., carbon tetrachloride – CCl₄) was observed and characterized (Refs. 4 and 5). The observation of ferrocene oxidation upon photolysis in the ultraviolet led to the conclusion that charge transfer occurred (1) (Ref. 5); the charge-transfer-to-solvent (CTTS) band was also found to be dependent upon the electrochemical potential of the electron acceptor (Ref. 5).



Several studies on ferrocene/halocarbon systems since have shown that photolysis into the CTTS band (Refs. 6 to 12), but not the ferrocene ligand field bands (Refs. 6, 9, and 12) results in photochemistry. In non-polar halocarbon-containing solutions, oxidation (Ref. 5) results in the isolation of ferricenium tetrahaloferrate, [Fe(η⁵-C₅H₅)₂][FeX₄] (Refs. 6 to 9). However, photolysis in ethanol (EtOH)/halocarbon solutions into the CTTS band, yields photosubstitution on the cyclopentadienyl rings, (2) (Refs. 10 to 12).





Scheme 1.—Proposed mechanism for ferrocene photoreaction, from Reference 13.

This apparent discrepancy can be rationalized by a mechanism initiated by charge transfer, proposed by Geoffroy and Wrighton (Ref. 13), accounting for both reactions (Scheme 1). In this mechanism, $\cdot CCl_3$ radical attack of ferricenium (reaction 2) is key. Formation of the postulated intermediate $\{Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4CCl_3)\}$ can then result in the production of $[Fe(\eta^5-C_5H_5)_2]FeX_4$ through reactions 1, 2, 4, and 5 when ethanol is not present (Refs. 6 and 9) or substitution through reactions 1, 2, and 3 in the presence of ethanol (Refs. 10 to 12). Addition of acrylamide prevents reaction 2 via $\cdot CCl_3$ trapping, resulting in formation of $[Fe(\eta^5-C_5H_5)_2]Cl$ (Ref. 9).

There is interest in potential applications of ferrocene-CTTS systems (Ref. 14). For example, investigations of their use in non-silver high resolution imaging (Refs. 15 and 16) or initiators for catalytic hydrogen transfer (Refs. 17 to 19) attempt to exploit the secondary thermal chemistry following charge transfer; quantum yields for ferricenium formation are often greater than one due to the participation of radical reactions (Ref. 9). More recent work has shown that the CTTS transition is also observed in such related systems as ruthenocene (Refs. 20 and 21) and $[(\eta^5-C_5H_5)Fe(CO)]_4$ (Ref. 22). Other potential interest in the CTTS systems relate to electron transfer reactions involving substituted ferrocenes and ferriceniums in both surface-confined (Ref. 23) and solution (Ref. 24) species. Several studies have correlated the energies of the CTTS transition of both ferrocene (Refs. 5 and 9) and $[(\eta^5-C_5H_5)Fe(CO)]_4$ (Ref. 22) with the reduction potential of the electron acceptor halocarbons; we are not aware of any similar correlation of the CTTS energy with the electrochemical properties of the electron donor. In view of the interest in and potential applications of these systems, a study of a series of ferrocene derivatives is warranted. The present study emphasizes the correlation of the redox potential and charge transfer to CCl_4 absorption energy for a series of methyl-substituted cyclopentadienyl ferrocene derivatives.

Experimental Details

UV/VIS spectra were recorded on a Varian Cary 17 spectrophotometer. Cyclic voltammetry was performed with electrochemical equipment manufactured by Princeton Applied Research. Redox potentials ($E_{1/2}$) from cyclic voltammetry were determined versus a saturated calomel electrode (SCE) in 0.1 M tetra n-butylammonium perchlorate (TBAP, Strem Chemicals)/EtOH. All solutions of ferrocenes were prepared under Ar or N₂ using conventional Schlenk line techniques or a Vacuum Atmospheres dry

box, respectively and kept in the dark (Refs. 23 and 24). Absolute EtOH (U.S. Industrial Chemicals) stock solutions of ferrocene derivatives were diluted with the appropriate amount of dry, degassed CCl₄ to produce 1 mM EtOH/CCl₄ solutions. Carbon tetrachloride was distilled over P₂O₅ under N₂ to remove water and sulfur-containing impurities. Ferrocene was purchased from Aldrich and sublimed prior to use; 1,1'-dimethyl ferrocene (Aldrich) was recrystallized from EtOH. Preparation of 1,2,3,4,5-pentamethyl ferrocene (Ref. 23) was accomplished by the reaction of FeCl₂ in THF with one equivalent each of Na(C₅H₅)•1,2-dimethoxyethane (DME) (Ref. 25) and Na[C₅(CH₃)₅] (Refs. 26 and 27). The pentamethyl derivative was isolated by fractional sublimation to give ~60% yield. Preparation of 1,2,3,4,1',2',3',4'-octamethylferrocene was optimized by reaction of anhydrous FeCl₂ in THF with two equivalents of Na[C₅(CH₃)₄H] (Ref. 28) and was purified by sublimation. Decamethylferrocene was purchased (Strem Chemicals) or prepared in an analogous procedure to that for pentamethylferrocene and octamethylferrocene using two equivalents of Na[C₅(CH₃)₅] (Refs. 26 to 28).

Results

Table 1 summarizes E_{1/2} and spectral parameters for ferrocene derivatives from this study. Spectroscopic data of ferrocene derivatives includes the CTTS transition (Refs. 4 to 13) and a low energy d-d band (e_{2g}, a_{1g} → e_{1g} transition) (Ref. 29). Figure 1 shows the spectra of 1 mM decamethylferrocene and ferrocene (inset) in EtOH as the concentration of CCl₄ increased to pure CCl₄ for both compounds (e: Fe(η⁵-C₅(CH₃)₅)₂ and inset f: Fe(η⁵-C₅H₅)₂). The addition of CCl₄ results in the growth of an absorption band due to charge transfer from the ferrocenes to CCl₄. Other than the CTTS transition, there is not a sizeable perturbation in the metallocene spectrum upon dissolution in halocarbon solvents (Refs. 5, 9, and 20 to 22). Therefore, the CTTS band maxima were determined by a point-by-point subtraction of the spectra in EtOH from the spectra in pure CCl₄, the electron acceptor. The CTTS maxima of [(η⁵-C₅H₅)Fe(CO)]₄ in the presence of halocarbon donors were determined by instrumental subtraction in an earlier study (Ref. 22).

The CTTS energy is plotted against E_{1/2} for the ferrocenes in Figure 2. The slope of the line, 8540 cm⁻¹/V (R = 0.997, (Ref. 30)), is within 6 percent of a theoretical slope of 8066 cm⁻¹/eV (the wavenumber to electron volt conversion factor). It is apparent that the molecular orbital losing an electron upon electrochemical oxidation is the same as the origin of the CTTS transition. Scheme 2 is a diagram of iron 3d orbital splittings in a ferrocene ligand field (Ref. 31) with ligand field parameters labeled for a D_{5d} point group. The two highest-occupied molecular orbitals (HOMO's) have a_{1g} (d_{z²}) and degenerate e_{2g}

TABLE 1.—E_{1/2} AND SPECTRAL PARAMETERS FOR FERROCENE DERIVATIVES

Derivative	E _{1/2} , V ^a	CTTS maximum ^b		d-d transition ^c		ε _C M ⁻¹ cm ⁻¹	K ^d
		nm	cm ⁻¹	nm	cm ⁻¹		
Ferrocene	+ 0.43	302	33,100	436	22,900	1800	1.2
1,1'-dimethylferrocene	+0.33	310	32,300	431	23,200	1900	1.2
1,2,3,4,5-pentamethyl-ferrocene	+0.18	320	31,300	428	23,400	1600	1.0
1,2,3,4,1',2',3',4'-octa- methylferrocene	+0.05	336	29,800	421	23,700	1400	1.0
Decamethylferrocene	-0.08	347	28,800	418	23,900	1800	0.7

^aIn ethanol (0.1 M TBAP) versus SCE.

^bDetermined by subtracting pure ethanol from pure CCl₄ solution spectra.

^c(e_{2g}, a_{1g} → e_{1g}) transition.

^dIn units of mole fraction⁻¹.

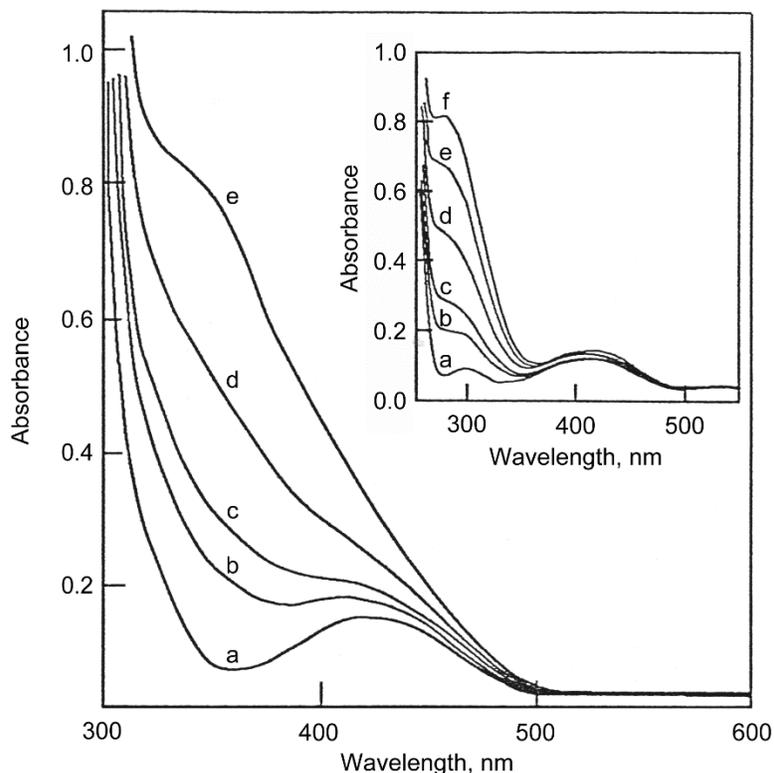


Figure 1.—UV/visible spectra of 1.0×10^{-3} M decamethylferrocene in ethanol with 0, 15, 25, 50, and 100% CCl_4 by volume, (a) – (e), respectively. Inset is 1.0×10^{-3} M ferrocene in ethanol with 0, 15, 25, 50, 75, and 100% CCl_4 by volume, (a) – (f), respectively. Spectra were recorded at 298 K, cell path length is 1 cm.

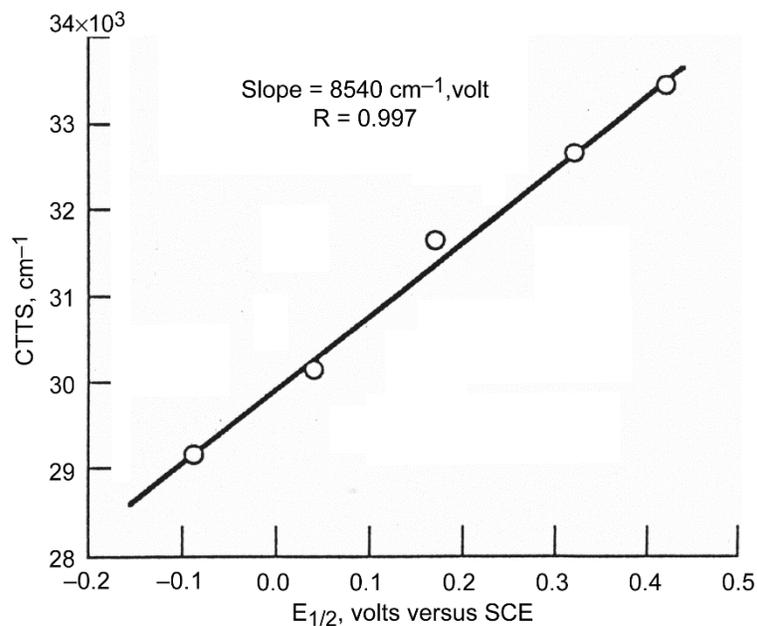
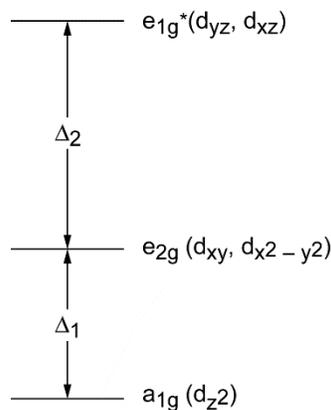


Figure 2.—Least-squares-fit line through a plot of CTTS energies vs. $E_{1/2}$ for a series of ferrocene derivatives. Slope is within six percent of theoretical ($8066 \text{ cm}^{-1}/\text{eV}$) assuming the same molecular orbital for photo- and electrochemical oxidation.



Scheme 2.—Ligand field splittings for iron 3d orbitals of ferrocene, orbitals labeled for a D_{5d} point group.

($d_{xy}, d_{x^2-y^2}$) symmetry; the lowest-unoccupied molecular orbital (LUMO) has degenerate e_{1g} (d_{xz}, d_{yz}) symmetry. The energy splittings or ligand field transitions (LFT's) are denoted as Δ_1 between the two HOMO's and Δ_2 between the HOMO and LUMO. The absolute energies of the HOMO's (e_{2g}, a_{1g}) actually increase upon ring substitution of electron donating groups, as shown by photoelectron spectroscopy of ferrocene derivatives (Refs. 32 to 40). Because the acceptor (CCl_4) in our study remains the same, this results in a decrease in the energy of the CTTS transition. This is consistent with a study demonstrating a linear correlation between the adiabatic ionization energy and the non-aqueous oxidation potential for a series of substituted ferrocene derivatives (Ref. 40).

Discussion

There is some controversy in the literature (Refs. 37 and 41) as to the exact identity of the HOMO, with proponents for either a_{1g} (Refs. 29, 38, 39, 41, and 42) or e_{2g} (Refs. 32 to 37, 40 and 43). Scheme 2 shows e_{2g} as the HOMO. EPR data is consistent with a 2E_g ($a_{1g}^2 e_{2g}^3$) ground state for a ferricenium ion due to a vacancy in the e_{2g} orbitals (Refs. 44 and 45). Photoelectron spectroscopy by Green et al. on ferrocene and decamethylferrocene implies an e_{2g} HOMO due to intensity variations of He (I) and He(II) spectra correlated with the higher metal character of the a_{1g} orbital (Ref. 36). Intermediate neglect of differential overlap-spectroscopically parameterized (INDO-SP) calculations predict that (transposing into D_{5d} point group designations) a_{1g} is almost pure metal (90% $3d_z^2$, 5% $4s$), but e_{2g} (~15% π) and e_{1g}^* (30% π^*) molecular orbitals have increasingly substantial ligand character (Ref. 43). The INDO-SP calculations also determined that the e_{2g} is 0.5 eV higher in energy than the a_{1g} orbital in accordance with photoelectron spectroscopic data (Refs. 32 to 40).

Interestingly, it has been pointed out that in the case of the isoelectronic sandwich complexes $Cr(\eta^6-C_6H_6)_2$, $Mn(\eta^6-C_6H_6)(\eta^5-C_5H_5)$, and $Fe(\eta^5-C_5H_5)_2$, the increased covalence from benzene π -bonding led to stabilization of the e_{2g} orbital to the point that a_{1g} is the HOMO for the Cr and Mn sandwich compounds (Ref. 33). This same effect was observed by going down through group 8 metallocenes, a_{1g} being the HOMO for $Os(\eta^5-C_5H_4CH_3)_2$ (Ref. 34). However, it does not appear (Ref. 36) that there is a cross-over in the a_{1g} and e_{2g} orbital energies upon permethylation of the cyclopentadienyl rings, consistent with a previous analysis (Ref. 46).

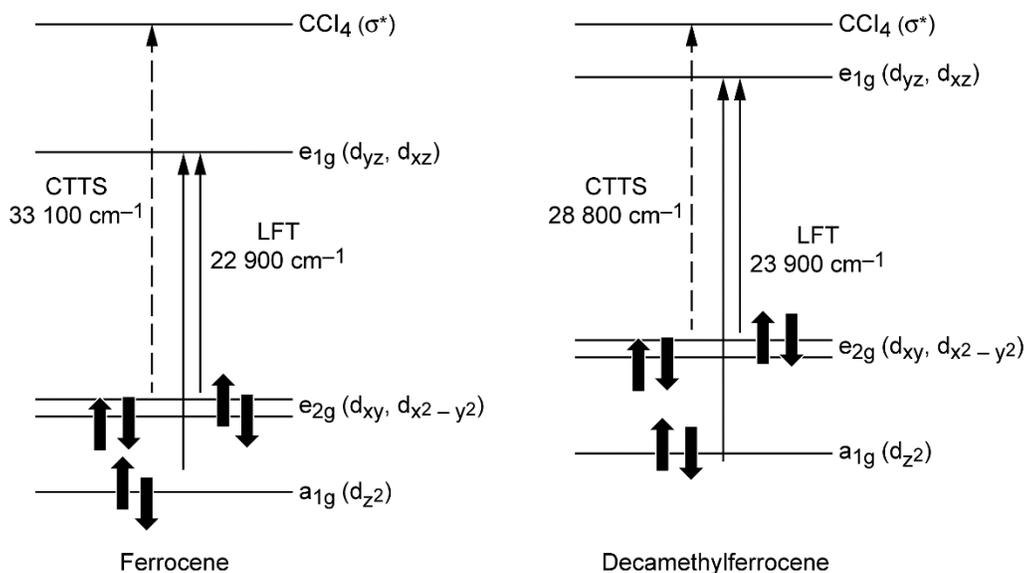


Figure 3.—Comparison of frontier orbitals of ferrocene and decamethylferrocene consistent with spectral parameters in Table 1 and prior literature (Refs. 37 and 43).

Table 1 shows an increase in d-d band energy upon methyl substitution of the cyclopentadienyl ring(s). The ligand field band ($e_{2g}, a_{1g} \rightarrow e_{1g}^*$) describes the relative energies of the molecular orbitals of the ferrocenes. The increase in Δ_2 is due to the destabilization of the antibonding (d_{xz}, d_{yz}) metal orbitals upon interaction with the more electron-rich cyclopentadienyl rings. This trend agrees with earlier calculations of Δ_1 and Δ_2 from electronic absorption (Ref. 47) and photoelectron data (Ref. 36) for $\text{Fe}(\text{C}_5(\text{CH}_3)_5)$. Figure 3 compares frontier orbitals for CTTS and LFT electronic absorptions; these are labeled to coincide with our data and are consistent with literature analyses (Refs. 29, 37, 43, and 47).

It is appropriate at this point to reiterate the caution of Zerner et al. (Ref. 43) that UV-visible (Refs. 29 and 47) and ionization (Refs. 32 to 40) “*spectra measured differences in states not orbital energies. Ionization and electronic excitation (to an excited state of the neutral) can be two very different processes*” (Ref. 43). Since one-electron descriptions of the electronic structure of ferrocenes appear to be somewhat inadequate, unambiguous spectroscopic determination of the HOMO may be difficult if not impossible. However, as we are mainly focused on correlating two different processes (electrochemical oxidation vs. spectral charge transfer by removal or promotion of an electron from the same molecular orbital), the exact identity of the HOMO (a_{1g} vs. e_{2g}) is not of primary concern.

Further analysis of the spectral data was according to the classic work of Mulliken for charge transfer complexes (Refs. 48 to 50) employed by numerous workers for aromatic and halogen-containing systems (Refs. 48 and 51 to 55) and specifically applied to metallocene CTTS systems (Refs. 5, 9, 20 and 21). The calculation of both the association constant and the complex extinction coefficient (see Table 1) relies upon a transformation of the Benesi-Hildebrand equation (3) (Ref. 50) for an equilibrium process with an association constant (K) defined in equation (4) (Refs. 5, 9, 20 and 21).

$$\frac{1}{\epsilon - \epsilon_{\text{Fc}}} = \frac{1}{K(\epsilon_{\text{c}} - \epsilon_{\text{Fc}})} \cdot \frac{1}{[\text{A}]} + \frac{1}{\epsilon_{\text{c}} - \epsilon_{\text{Fc}}} \quad (3)$$



Equation (3) is derived using the association constant, K , the absorbance of the CTTS system, as defined in (5) and the fact that ferrocene is associated and nonassociated in solution (6) (Refs. 5 and 52);

$$\varepsilon(\text{Fc})_{\text{Total}} = \varepsilon_{\text{Fc}}(\text{Fc}) + \varepsilon_{\text{c}}(\text{Fc} \bullet \text{A}) \quad (5)$$

$$(\text{Fc})_{\text{Total}} = (\text{Fc})(1 + K[\text{A}]) \quad (6)$$

concentrations are given as $(\text{Fc} \bullet \text{A})$ and (Fc) , respectively. The symbol ε is the apparent molar extinction coefficient of the entire ferrocene system; ε_{Fc} and ε_{c} are the extinction coefficients of (nonassociated) ferrocene and the associated ferrocene or charge transfer complex, respectively. The term ‘ $[\text{A}]$ ’ represents the mole fraction of the acceptor molecule, CCl_4 . As noted previously, this analysis is relevant for either a thermodynamically stable charge transfer complex or a “contact charge transfer” (Refs. 5 and 9) where K would be better defined as a probability factor (Refs. 5, 9, 21 and 30). The resultant quantities K and ε_{c} were determined by plotting $(\varepsilon - \varepsilon_{\text{Fc}})^{-1}$ and $[\text{A}]^{-1}$ and using the values obtained for the slope and y intercept. The value of K obtained for ferrocene is 20% lower than K (1.5 ± 0.2 mol. fraction⁻¹) determined by Traverso and Scandola (Ref. 9).

The decrease in the association constant, K , is consistent with either increased steric hindrance as methyl substituents are added or an electronic effect due to increased repulsion of non-bonding in electrons on CCl_4 by the added electron-density on the higher methyl-substituted cyclopentadienyl rings. The association constant between CCl_4 and ruthenocene is 1.8 mol fraction⁻¹; the increased covalence relative to ferrocene implies a higher association due to the reduced repulsion of CCl_4 . This result argues for an electronic effect. A related study on ion-pair $(\text{Fc}^+\text{I}_3^-)$ formation between ferrocenes and I_2 in benzene argues for both alternatives (Ref. 56). In this work, a linear correlation was found between the equilibrium constant, K , and the reducing power of the ferrocene. A higher K for the less hindered ferrocene with the same reduction potential (e.g. 1,1'-dimethyl, 3314; 1,1'-diisopropyl, 1482) argues for a steric effect (Ref. 56). A glaring exception in this study was that K for phenylferrocene was lower by a factor of four than 1,1'-diphenylferrocene even though both had the same reduction potential, 0.03 V higher than ferrocene; this result supports an electronic effect due to the enhanced electron withdrawal of two phenyl rings and the consequent reduced repulsion of I_2 . Our results do not rule out either effect; this is most likely a repulsive electronic effect enhanced by steric factors. The intensity of the CTTS band, ε_{c} , remains constant at $\sim 1700 \text{ M}^{-1}\text{cm}^{-1}$ in our study. The ε_{c} determined for the ferrocenes per cyclopentadienyl ring approximates that of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ ($\varepsilon_{\text{c}} = 4000 \text{ M}^{-1}\text{cm}^{-1}$ for the tetramer, (Ref. 22)) and ruthenocene with CCl_4 in two different studies: 1500 (Ref. 20) and 2100 (Ref. 21) $\text{M}^{-1}\text{cm}^{-1}$. The opposing effects of reduced association constants and increased probability for charge transfer with more powerful, bulkier reductants result in very similar ε_{c} 's for the ferrocenes.

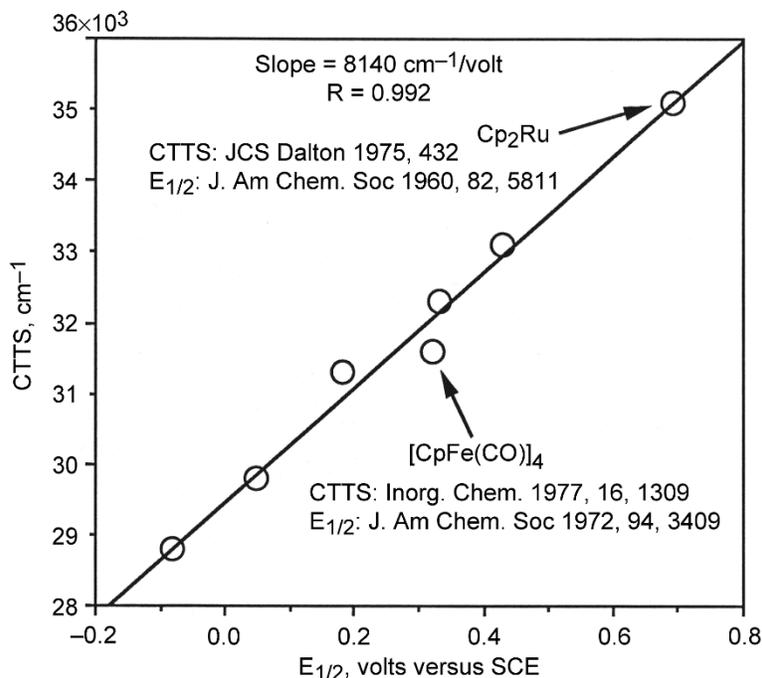


Figure 4.—Least-squares-fit line through a plot of CTTS energies vs. $E_{1/2}$ for a series of ferrocene derivatives and related compounds. Two extra points are included from literature data (see Refs. 20, 22, 59, and 60 for relevant data from each compound). Slope is within one percent of conversion factor ($8066 \text{ cm}^{-1}/\text{eV}$) assuming the same molecular orbital for photo- and electrochemical oxidation.

Concluding Remarks

The CTTS maxima of several metallocenes are related to the redox potentials. As noted previously (Ref. 57), nickelocene is easier to oxidize than ferrocene and has a lower energy CTTS transition (CTTS = 312 nm) (Refs. 57 and 58). This correlation holds for both ruthenocene (CTTS = 285 nm) (Refs. 20 and 21) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_4]$ (CTTS = 316 nm) (Ref. 22), having a higher and lower redox potentials than ferrocene, respectively. In fact, re-plotting our results and including data from ruthenocene (Refs. 20, 21, and 59) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_4]$ (Refs. 22 and 60) produces a line with a slope within 1 percent of the conversion factor ($8140 \text{ cm}^{-1}/\text{V}$), in agreement with theory for CTTS in these systems (see Figure 4). This is consistent with electrochemical and photochemical oxidation by removal of an electron from the same molecular orbital.

The CTTS excited state may also be viewed as intermediate between ionization and a neutral electronic excitation (Refs. 13 and 26). A variation of $E_{1/2}$ for the halocarbon affects the CTTS energy (Refs. 5, 9, and 22) in a similar manner to a change in metal-to-ligand-charge-transfer energy by a change in ligand π^* for a series of analogous compounds (Ref. 13). Finally, variation of the originating orbital of a metallocene affects the CTTS transition energy in the same manner as what would be predicted during ionization (Refs. 32 to 40).

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