

Electron Transfer in Mixed-Valence Binuclear Ferrocenes

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Final Seminar

February 12, 1985

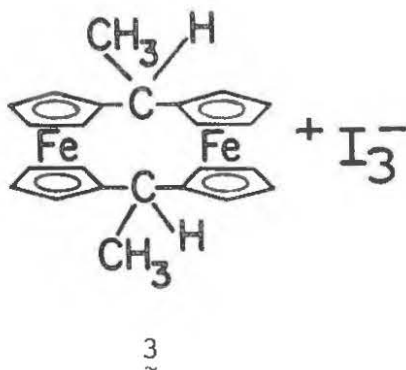
The study of mixed-valence ferrocene complexes could lead to a better understanding of the factors which control the rate of thermal electron transfer in oxidation-reduction, electrochemical, and biological reactions [1].

The mixed-valence monocation of bis(fulvalene)diiron (1) has been fully characterized by a variety of physical techniques [2-4].



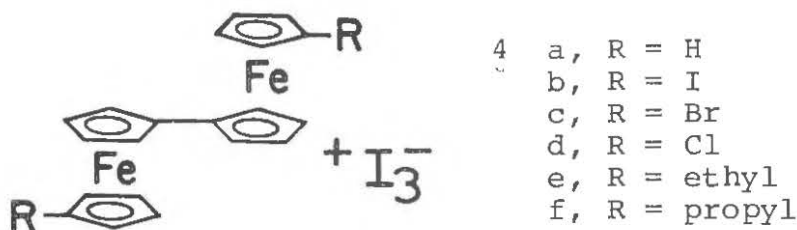
The rate of intramolecular thermal electron transfer in this monocation is faster than the ⁵⁷Fe Mössbauer and EPR time scales. Hence there is no barrier to electron transfer in this complex. A study was undertaken to determine directly if there is any change in the electron transfer rate resultant upon substitution of a single acetyl group in the 3-position of 1. The acetyl substituent acts as an electron withdrawing group, increasing the oxidation potential of the ferrocenyl unit to which it is attached. This could serve to localize the odd electron of the mixed-valence cation on the unsubstituted half of the molecule. ⁵⁷Fe Mössbauer data, EPR data, and IR data collected on the triiodide salt of 2 indicate that this mixed-valence cation has a delocalized ground state.

The preparation and characterization of the mixed-valence triiodide salt of 1,12-dimethyl[1.1]-ferrocenophane (3) has been reported [3,5].



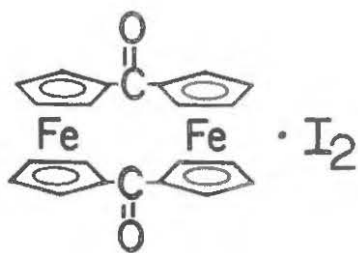
^{57}Fe Mössbauer spectra collected on **3** exhibit both Fe(II) and Fe(III) absorptions. The appearance of an additional quadrupole-split doublet ($\Delta E_Q = 1.85$ mm/sec) in the ^{57}Fe Mössbauer spectra of **3** led to speculation that a separate conformer within the crystal lattice had a delocalized ground state. The single-crystal X-ray structure of **3** was obtained. Only one unique cation is observed for this molecule within the unit cell. Distinguishable Fe(II) and Fe(III) sites in the crystal structure of **3** are consistent with a trapped valence description for this mixed-valence salt. The dioxidized $(\text{I}_3^-)_2 \cdot \text{I}_2$ salt of **3** was prepared and characterized. A small exchange interaction is seen to develop between the two $S = \frac{1}{2}$ ions in this dication.

The mixed-valence biferrocenium cation (**4a**) has been shown to be localized on both the ^{57}Fe Mössbauer and EPR time scales [3,6,7].



The triiodide salts of 1,6-diiodobiferrocenium (**4b**) and 1,6-dibromobiferrocenium (**4c**) have delocalized ground states as gauged by ^{57}Fe Mössbauer spectroscopy [3,8]. The triiodide salt of the chlorosubstituted cation (**4d**) is valence localized [8]. Substitution of alkyl groups onto the biferrocenium framework yields mixed-valence compounds which exhibit a temperature dependence of the rate of thermal electron transfer [9]. Compounds **4e** and **4f** are both localized on the ^{57}Fe Mössbauer time scale below 100 K. At room temperature both of these compounds appear to be delocalized with one average valence quadrupole-split doublet observed in their Mössbauer spectra. An interesting feature of the Mössbauer spectra collected on **4e** and **4f** is the complete absence of line broadening of the Mössbauer signals in going from low temperatures to high temperatures. Variable-temperature EPR and IR spectra were collected for **4e** in an effort to understand the anomalous Mössbauer behavior. A model is proposed which accounts for the lack of line broadening observed in these systems.

Considerable interest has been generated recently in understanding the unusual electronic and magnetic properties associated with quasi-one-dimensional charge-transfer salts [10]. Slow crystallization of 1,12-dione[1.1]ferrocenophane from hot CHCl_3 solutions in the presence of a twentyfold excess of iodine leads to the formation of lustrous golden crystals of empirical formula $[(\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}(\text{CO})_2\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2] \cdot \text{I}_2$ (**5**).



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Iodine containing materials are particularly amenable to characterization by Raman spectroscopy [11,12]. A resonance Raman spectrum collected for a solid sample of **5** indicates the iodine present in this salt to be of the form $(I_3^-) \cdot I_2$. This result suggests that **5** is best formulated as $[(\eta^5-C_5H_4)_2Fe(CO)_2Fe(\eta^5-C_5H_4)_2]_5^{2+} (I_3^-)_2 \cdot (I_2)_2$. Magnetic susceptibility measurements and ^{57}Fe Mössbauer spectra collected on **5** are consistent with the proposed partial oxidation of this complex. The rate of thermal electron transfer in **5** is less than the ^{57}Fe Mössbauer and EPR time scales.

References

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