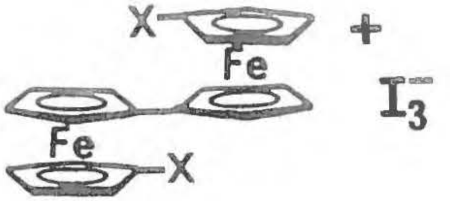
The Effect of the Solid-State Environment on Intramolecular Electron-Transfer Rates in Mixed-Valence Complexes

Teng-Yuan Dong　　Final Seminar　　December 17, 1985

The fundamental nature of electron transfer in mixed-valence biferrocenium salts is studied [1]. Various substituents and counterions are employed in order to understand the factors which control electron transfer in the solid state between the two iron ions in mixed-valence biferrocenes. The preparation and characterization of several new series of mixed-valence biferrocenes (1-8), as well as interesting observations on all of the complexes, are described. The rate of thermal electron transfer for a mixed-valence complex in the solid state is characterized by variable-temperature ^{57}Fe Mössbauer, EPR, and IR measurements [2,3].



1: X = -H

2: X = $-CH_2CH_3$

3: X = $-CH_2CH_2CH_3$

4: X = $-CH_2CH_2CH_2CH_3$

5: X = $-CH_2-$ 

6: X = -I

7: X = -Br

8: X = -Cl

A detailed and interesting picture of what controls the electron transfer between the two iron ions in the mixed-valence 1',6'-disubstituted biferrocene cation is emerging. The x-ray structures of 4 [4], 6 [5], and 8 [5] have been determined. The two iron ions are on opposite sides of a planar fulvenide ligand. Compound 8 transfers electrons slower than the Mössbauer time scale at 340 K [5]. On the other hand, 6 and 7 transfer electrons faster than the Mössbauer time scale not only at 298 K, but also all the way down to 4.2 K [4]. Finally, mixed-valence complexes 4 and 5 each show one Fe^{II} and one Fe^{III} doublet in Mössbauer spectra measured below 200 K. As the temperature of these compounds is increased above 200 K the two doublets change to become eventually a single average doublet in the range of 250-275 K. The magnitude of the electronic interaction of the d-manifolds on the two iron ions in a given cation is probably not very different from one cation to another in the 1',6'-disubstituted mixed-valence biferrocenes. Furthermore, the vibronic coupling is also probably not changing very much throughout the series. From an examination of all the data it has become clear that it is the environment about each cation in these solids that is determining whether or not intramolecular electron transfer occurs.

For 6 the x-ray structure shows that the I_3^- anions are symmetrically disposed relative to the two halves of the cation. In this case it is possible to transfer an electron back and forth between the two iron ions (Fe••Fe = 5.1 Å) at a rate in the range of 10^{10}-10^{12} sec^{-1} (i.e., faster than EPR, but slower than IR time scale). The x-ray structure of 8 shows the I_3^- anions are positioned closer to one iron ion of a neighboring cation than the other. This asymmetric environment about a cation dramatically affects the rate at which charge can be pulled back and forth in the cation of 8. The transfer rate for 8 is less than 10^7 sec^{-1} at 340 K (via the Mössbauer spectrum).

It is our suggestion that the temperature dependence observed in the Mössbauer spectra for a good crystalline sample of diethyl-, dipropyl-, dibutyl-, and dibenzylbiferrocenium triiodide salts results from a phase transition involving motion of the I_3^- anion and perhaps the substituents on the cation. At low temperature the I_3^- ion and biferrocenium cation are fixed in position. As the sample temperature is increased the phase transition temperature is reached and each I_3^- ion begins to move between two or more positions in the lattice. This transformation could well lead to a dramatic increase in the rate of intramolecular electron transfer. There are actually two possibilities for the movement of the I_3^- anions. As stated above, it is possible that the I_3^- anions move as a unit in the solid. However, it is more probable that the I_3^- anions are interconverting between two configurations, one which can be described in a limiting form as $I_A^- \cdot\cdot I_B\text{-}I_C$ and the other one as $I_A\text{-}I_B \cdot\cdot I_C^-$. That is, in each configuration one I-I bond is shorter than the other one in each I_3^- anion.

The anion dependence of electron transfer rate for the biferrocenium [6] and dihalobiferrocenium [7] cations and endothermic peaks seen in heat capacity [8] and DSC data for biferrocenium triiodide further support the presence of phase transitions. A qualitative model is developed [6] to explain the effect of the anion replacement. The importance of the cation-anion interactions, as well as the intrinsic charge-oscillation barrier heights in the mixed-valence cations and anions, is discussed relative to the phase transition that are believed to be present in these compounds.

References

1. Hendrickson, D. N.; Oh, S. M.; Dong, T.-Y.; Kambara, T.; Cohn, M. J.; Moore, M. F., Comments in Inorg. Chem., in press.

2. Morrison, W. H., Jr.; Hendrickson, D. N. Inorg. Chem. **1975**, 14, 2331.

3. Kramer, J. A.; Hendrickson, D. N. Inorg. Chem. **1980**, 19, 3330.

4. Dong, T.-Y.; Hendrickson, D. N.; Iwai, K.; Cohn, M. J.; Geib, S. J.; Rheingold, A. L.; Sano, H.; Motoyama, I.; Nakashima, S. J. Am. Chem. Soc., in press.

5. Dong, T.-Y.; Hendrickson, D. N.; Pierpont, C. G.; Moore, M. F. J. Am. Chem. Soc., in press.

6. Dong, T.-Y.; Kambara, T.; Hendrickson, D. N., submitted to J. Am. Chem. Soc..

7. Dong, T.-Y.; Hendrickson, D. N., in preparation.

8. Sorai, M.; Dong, T.-Y.; Cohn, M. J.; Hendrickson, D. N., unpublished results.