The Fundamental Nature of Electron Transfer in Mixed-valence Biferrocenium Salts

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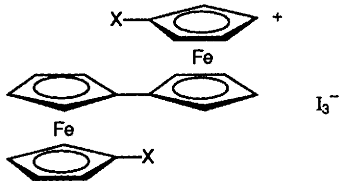
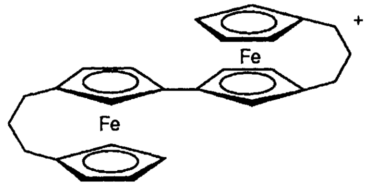
The physical properties of mixed-valence 1′,3 : 1‴,3″-bis(propane-1,3-diyl)-1,1″-biferrocenium tri-iodide clearly indicate that there is a significant influence on the rate of electron transfer as the cyclopentadienyl ring tilts.

Recently, considerable progress has been made in understanding what factors influence the rate of intramolecular electron transfer in the mixed-valence cations (**1**)—(**8**).[1—11] Compounds (**1**)—(**5**) give unusual temperature-dependent Mössbauer spectra.[2—5] At temperatures below 200 K they each show two doublets, one for the Fe^{II} and the other for the Fe^{III} site. Increasing the sample temperature in each case causes the two doublets to move together with no discernible line broadening, eventually to become a single 'average-valence' doublet at temperatures of 365, 275, 245, 275, and 260 K, for (**1**), (**2**), (**3**), (**4**), and (**5**), respectively. It is even more surprising that the cations in (**6**) and (**7**) show only one 'average-valence' doublet in their Mössbauer spectra at 4.2 K.[12] Furthermore, pronounced dependence of rates of electron transfer on sample history has been noted for compounds (**4**) and (**5**).[4] In spite of considerable work in this area, there is still one important question that remains. Does the substituent on the cyclopentadienyl (Cp) ring play a significant role in the electron transfer? To increase our sparse knowledge in this area, we have prepared the mixed-valence cation (**9**) which shows[13] an intervalence transfer band at 5520 cm^{-1} in the solution state. In this communication, we will show that there is a profound effect on the rate of intramolecular electron transfer in mixed-valence biferrocenium cations as the Cp ring tilts.

As shown in Figure 1, the Mössbauer results indicate that compound (**9**) is delocalized on the Mössbauer timescale



(**1**) $X = H$
(**2**) $X = Et$
(**3**) $X = Pr^n$
(**4**) $X = Bu^n$
(**5**) $X = CH_2Ph$
(**6**) $X = I$
(**7**) $X = Br$
(**8**) $X = Cl$



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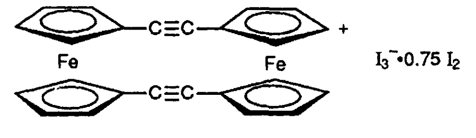

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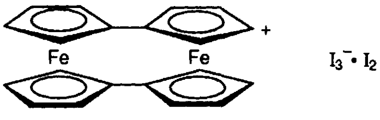

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Table 1. EPR data.[a]

Compound	T/K	$g_{\parallel}$	$g_{\perp}$	Δg[b]
Ferrocenium I_3^-[c]	20	4.35	1.26	3.09
1,1'-Propane-1,3-diylferrocenium I_3^-	300	≈2.0[d]		
	77	3.65	1.86	1.79
1,1'-Propane-1,3-diylferrocenium PF_6^-	300	2.00		
	77	2.00		
	12[e]	3.86	1.81	2.05
(1)[f]	12	3.58	1.72	1.86
(2)[f]	3.3	3.02	2.01 1.89	1.07
(4)[f]	4.2	2.98	1.92	1.06
(5)[f]	4.2	3.42	1.84	1.58
(6)[f]	4.2	2.75	2.01 1.97	0.76
(7)[f]	4.2	2.76	2.01 1.96	0.78
(8)[f]	4.2	3.42	1.84	1.58
(9)	300	2.00		
	77	2.71	1.98	0.73

[a] EPR spectra were recorded for microcrystalline samples. [b] g-Tensor anisotropy, $\Delta g = g_{\parallel} - g_{\perp}$. [c] S. E. Anderson and R. Rai, *Chem. Phys.*, 1973, **2**, 216. [d] There is some uncertainty in this number as a result of broad spectral features. [e] Ref. 17. [f] Ref. 12.

above 77 K. Only a single 'average-valence' doublet is seen from 77 to 300 K. The value of the quadrupole splitting (ΔE_Q 1.6140 mm s^{-1}) at 77 K could indicate that there is a strong electronic coupling between the d-manifolds on the two iron ions in (**9**). This does not happen for (**1**)—(**8**) (ΔE_Q 1.2 mm s^{-1}),[2—5,12] but it does occur in the dibridged delocalized mixed-valence cations (**10**) and (**11**). Both compounds exhibit one quadrupole-split doublet. In the case of (**10**) ΔE_Q was reported to be 1.519(5) mm s^{-1} at 300 K.[14–16] The value of ΔE_Q at 300 K for (**11**) is even larger [1.719(3) mm s^{-1}].[5,16]

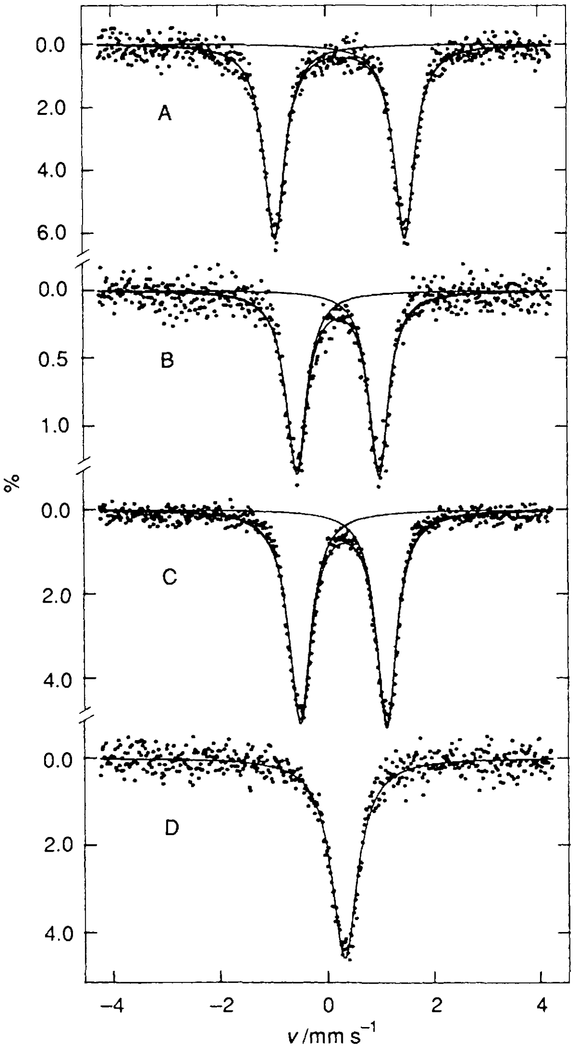

Figure 1. ^{57}Fe Mössbauer spectra for (A) neutral 1',3 : 1''',3''-bis(propane-1,3-diyl)-1,1''-biferrocene, (B) (**9**) at 300 K, (C) (**9**) at 77 K, and (D) 1,1'-propane-1,3-diylferrocenium tri-iodide.

X-band EPR spectra were run at 77 and 300 K for (**9**). An 'axial'-type spectrum was observed at 77 K. The g values extracted from all these spectra are collected in Table 1, together with some g values for related compounds. It has been found that the value of g-tensor anisotropy (Δg) is considerably reduced for a mixed-valence biferrocenium cation. This is a reflection of considerably reduced orbital angular momentum in the ground state which results from admixture of the $S = 0$ Fe^{II} description into the ground state. From Table 1, the Δg values for (**9**) is 0.73 which is even smaller than that for the delocalized mixed-valence cations (**6**) and (**7**). A comparison of the Δg value of 1,1'-propane-1,3-diylferrocenium with that of ferrocenium suggests that the cation (**9**) would experience a greater low-symmetry crystal field than the biferrocenium cation. This could be the origin of the reduced Δg value. Additional evidence that the low-symmetry crystal field has an important impact on the EPR spectra is available from the room temperature EPR spectra. In the case of 1,1'-propane-1,3-diylferrocenium and (**9**), EPR signals can be readily seen at room temperature. On the other hand, EPR signals for the other species in Table 1 are visible at low temperatures but cannot be seen at tempertures above 200

K. For the monoferrocenium species, 1,1′-propane-1,3-diylferrocenium cation is the first compound to show EPR signals at room temperature.

The electronic ground state of ferrocene is a singlet, $^1A_{1g}$ ($e_{2g}{}^4a_{1g}{}^2$), where the one-electron molecular orbitals are predominantly d orbital in character: a_{1g} (d_z) and e_{2g} ($d_{x^2-y^2}$, d_{xy}).[17] As indicated by magnetic susceptibility[18] and EPR[19—21] measurements, the electronic ground state of ferrocenium is a doublet, $^2E_{2g}$ ($a_{1g}{}^2e_{2g}{}^3$). In 1,1′-propane-1,3-diylferrocenium and (**9**), the Cp rings are tilted from the parallel geometry for ferrocene. Lauher and Hoffmann[22] have derived the fragment orbitals for a bent $(Cp)_2M$ unit from the parallel geometry. Bending back the Cp rings splits the e_{2g} set into orbitals of a_1 ($d_{x^2-y^2}$) and b_2 (d_{xy}) symmetry. The a_{1g} orbitals rise rapidly in energy as the Cp rings are bent back. In this case, some metal $x^2 - y^2$ character from a_1 mixes into a_1 which was a_{1g} so that the torus of z^2 becomes hybridized away from the Cp rings. In the case of 1,1′-propane-1,3-diylferrocenium cation, it has also been reported that there is an increased ($d_{x^2-y^2}$, d_{xy}) ring overlap as the rings tilt. The greater the admixture the greater the probability for unpaired electron density on the a_{1g}. Under these circumstances the iron ions lose some degree of their Fe^{III} character, and this results in an increase in ΔE_Q because each iron ion is closer to Fe^{II} in its properties. This is what we observe for compound (**9**). Furthermore, the splitting of e_{2g} orbitals could be the origin of the EPR signals which can be seen at room temperature.

It is also necessary to discuss why the substituent on the Cp ring plays a significant role in the electron transfer for (**1**)—(**8**). We suggest that the Cp rings in the cations (**1**)—(**8**) are tilted by substituents on the rings and the e_{2g} metal orbitals are now bonding more with the tilted rings. The tilt angles in each ferrocenyl unit for 1,1′-propane-1,3-diylferrocenium cation,[23] (**1**),[4] (**2**),[24] (**3**),[25] and (**6**)[12] are 13.7, 0.3, 4.7, 6.6, and 15.6°, respectively. The transition temperatures from localized to delocalized states on the Mössbauer timescale for (**1**), (**2**), and (**3**) are 365, 275, and 245 K, respectively.[4] Furthermore, compounds (**6**)[12] and (**9**) are even delocalized at 4.2 and 77 K, respectively. Therefore, there is a correlation between the tilt angle and the rate of electron transfer: the larger the tilt angle, the faster the electron transfer. The impact of ring tilt could explain why the physical properties of mixed-valence cations (**4**) and (**5**) depend on the history of the sample.[4] In the case of microcrystalline samples, the possibility of various kinds of conformational arrangements in the longer alkyl substituents induces different kinds of tilt angles. Characterization of the electronic interactions in these mixed-valence systems by MO calculations and investigation of the counterion effects are underway.

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