The Effect of Ion Pairing on the Intervalence Transfer Electronic Absorption
Band of Mixed-Valence Complexes in Solution

Michael D. Lowery   Final Seminar   June 2, 1989

Marcus [1] has shown that the activation barrier for electron transfer in a
self-exchange outer-sphere redox reaction of a metal complex in solution is equal
to $\lambda/4$, where λ is a reorganization energy. λ includes contributions from inner
sphere (λ_{in}) and outer sphere (λ_{out}) reorganizations of the complex. Using a
dielectric continuum model for the solvent contribution λ_{out}, Marcus [1] derived
the following expression

$$\lambda_{out} = \Delta e^2 \left(\frac{1}{2R_A} + \frac{1}{2R_B} - \frac{1}{R_{AB}}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \tag{1}$$

where Δe is the amount of charge transferred, D_{op} and D_s are the optical and
static dielectric constants of the solvent medium, R_A and R_B are the radii of the
coordination spheres about the metal centers, and R_{AB} is the internuclear separa-
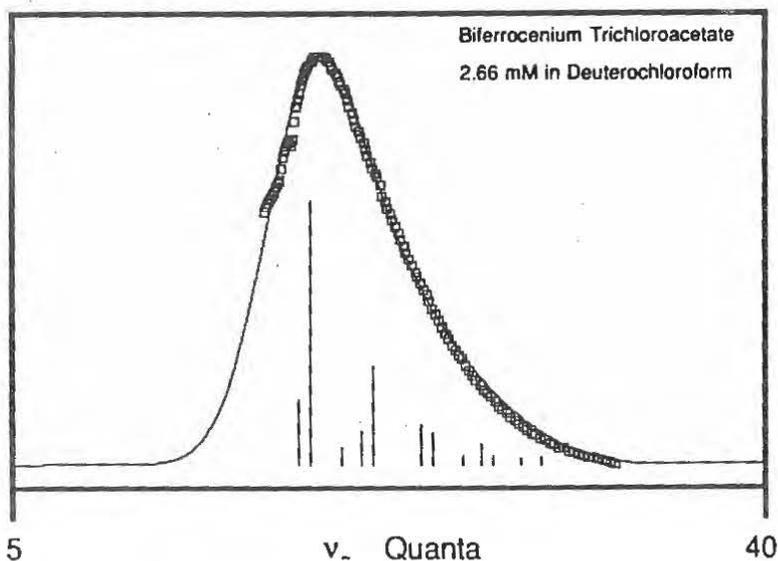tion between the redox sites.

It has been suggested [2] that the intervalence transfer (IT) electronic
absorption band of binuclear mixed-valence complexes [3] can be used to determine
the energetics of electron transfer between the metal ions. The energy of the IT
band maximum (E_{op}) of a given mixed-valence complex examined in a series of sol-
vents is predicted by eqn. (1) to vary linearly with ($1/D_{op} - 1/D_s$), and the inter-
cept of this plot should give λ_{in}. The linear relationship was first reported by
Tom, Creutz, and Taube [4] for the complex $[(NH_3)_5Ru(4,4'\text{-bipyridine})Ru(NH_3)_5]^{5+}$
for which they found $\lambda_{out} = 15.4$ and $\lambda_{in} = 10.0$ kcal/mol. Several other weakly
interacting mixed-valence complexes [5] have been shown to give linear E_{op} versus
($1/D_{op} - 1/D_s$) plots. It is important to note that Powers and Meyer [6] reported
a linear correlation between E_{op} and ($1/D_{op} - 1/D_s$) for the biferrocenium cation.

We have employed pressure-induced freezing of solutions of several mixed-
valence complexes to test the applicability of eqn. (1) [7,8]. Upon freezing, the
dielectric constant (D_s) of a liquid decreases by a factor of 2 - 10 depending on
its polarity, and from eqn. (1) it is predicted that pressure-induced freezing of
a solution of a mixed-valence complex should result in a large (2000 - 4000 cm^{-1})
red shift of the IT band maximum. Figure 1 shows representative spectra for
liquid and pressure-frozen solutions of biferrocenium hexafluorophosphate in
nitromethane-d_3. As is evident in the figure, we did not observe the predicted red
shift. The lack of a pronounced red shift upon freezing was also observed for
this complex in a variety of other solvents (nitromethane, nitrobenzene, aceto-
nitrile) and for other cations (biferrocenium triiodide, diferrocenylacetylene
monocation, and $[(bipy)_2ClRu^{II}(pyrazine)Ru^{III}Cl(bipy)_2]^{3+}$ where bipy = bipyridine)
[7,8].
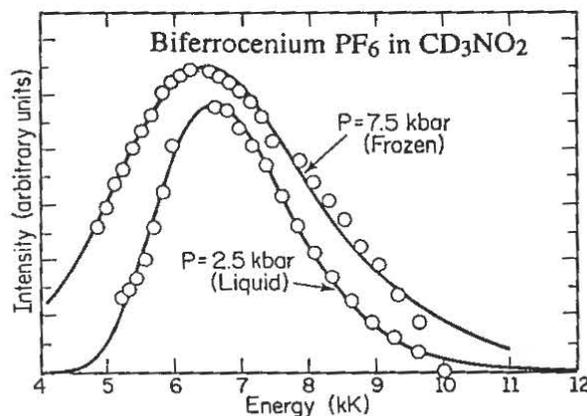
Close examination of the IT band contours from the pressure-induced freezing experiments showed that although the IT band position did not change appreciably upon freezing, the IT band position, full-width at half-maximum (fwhm), and integrated intensity were strongly correlated with the concentration of the mixed-valence complex in solution [7]. The changes in E_{op} with concentration were found to be as large as the changes observed when using a series of differing solvents. We have attributed the change in the IT band parameters with concentration to the formation of ion aggregates in solution [9]. Proof of the formation of ion aggregates in solution was established by observing the nonlinearity of plots of the solution conductivity versus the square root of the metallocene concentration for both biferrocenium triiodide and biferrocenium hexafluorophosphate in nitrobenzene and dichloromethane solutions [9].

To further probe the effect of ion aggregation on the IT band parameters (i.e., peak maximum, fwhm, integrated area), we have fit the IT band contour using the vibronic coupling model proposed by Piepho, Krausz, and Schatz [10] (the PKS model). Figure 2 shows a PKS simulation of an experimental IT band contour. The PKS model consists of three adjustable parameters: (1) ε gauges the degree of electronic coupling between the metal centers, (2) λ is the vibronic coupling parameter, and (3) W gives the zero point energy difference between the two vibronic wells. In all of the systems studied we have found that $|\varepsilon|$ increases, λ remains relatively constant, and W decreases with increasing concentration. A priori we expected that an increased level of ion aggregation would result in an increase in $|\varepsilon|$, not affect λ, and increase W as one of the two potential wells becomes favored. That W was found to decrease with increasing concentration most likely results from the presence of a distribution of cation environments in solution. At low concentrations, an approximately equal distribution of non-aggregated and ion-paired cations exists which results in a broad IT band, but as the concentration of mixed-valence species increases, the distribution tends to favor the aggregated species and the IT band narrows and shifts to higher energies. The simple Marcus, Hush, and PKS theories assume that the IT band parameters arise from one and only one cation site and thus these models are inappropriate when a distribution of environments about the cation is present in solution. Therefore, reliable values of λ_{in} and λ_{out} can be obtained from fitting of the IT band contour only if it can be established that ion aggregates are not present. Accurate estimates for λ_{in} and λ_{out} are best obtained at very low concentration or in solvents of high dielectric constant.

Biferrocenium Trichloroacetate
2.66 mM in Deuterochloroform

5   ν_- Quanta   40

References

1.   (a) Marcus, R. A. J. Chem. Phys. 1956, 24, 966, 979.
     (b) Marcus, R. A. "Special Topics in Electrochemistry", Rock, P. A. Ed.;
         Elsevier: Amsterdam, 1970; p. 180.

2.   Hush, N. S. Prog. Inorg. Chem. 1976, 8, 391.

3.   For recent reviews of mixed-valence complexes see:
     (a) Day, P. Intl. Rev. Phys. Chem. 1981, 1, 149.
     (b) Brown, D. B., Ed. Mixed-Valence Compounds, Theory and Applications in
         Chemistry, Physics, Geology and Biology; Reidel: Dordrecht, 1980.
     (c) Creutz, C. Inorg. Chem. 1983, 30 1.
     (d) Richardson, D. E.; Taube, H. Coord. Chem. Rev. 1984, 60, 107.
     (e) Zuckerman, J. J., Ed. Inorganic Reactions and Methods Volume 15,
         Electron-Transfer and Electrochemical Reactions. Photochemical and Other
         Energized Reactions, VCH Publishers: Deerfield Beach, Florida, 1986.

4.   Tom, G. M.; Creutz, C.; Taube, H. J. Am. Chem. Soc. 1974, 96, 7827.

5.   (a) Callahan, R. W.; Brown, G. M.; Meyer, T. J. Inorg. Chem. 1975, 14, 1443.
     (b) Powers, M. J.; Callahan, R. W.; Salmon, D. J.; Meyer, T. J. Inorg. Chem.
         1976, 15, 1457.
     (c) Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. J. Am. Chem.
         Soc. 1977, 99, 1064.
     (d) Powers, M. J.; Salmon, D. J.; Callahan, R. W.; Meyer, T. J. J. Am. Chem.
         Soc. 1976, 98, 6731.
     (e) Meyer, T. J. Acc. Chem. Res. 1978, 11, 94.
     (f) Krentzien, H.; Taube, H. J. Am. Chem. Soc. 1976, 98, 6379.
     (g) Taube, H. Ann. N. Y. Acad. Sci. 1978, 313, 481.
     (h) Cannon, R. D. Adv. Inorg. Chem. Radiochem. 1978, 21, 179.
     (i) Powers, M. J.; Meyer, T. J. Inorg. Chem. 1978, 17, 1785.
     (j) Felix, F.; Ludi, A. Inorg. Chem. 1978, 17, 1782.
     (k) Creutz, C. Inorg. Chem. 1978, 17, 3723.
     (l) Meyer, T. J. in ref. 3(b), page 75.
     (m) Powers, M. J.; Meyer, T. J. J. Am. Chem. Soc. 1980, 102, 1289.
     (n) Sullivan, B. P.; Curtis, J. C.; Kober, E. M.; Meyer, T. J. Nouv. J. Chim.
         1980, 4, 643.
     (o) Dowling, N.; Henry, P. M.; Lewis, N. A.; Taube, H. Inorg. Chem. 1981, 20,
         2345.
     (p) Krentzien, H.; Taube, H. Inorg. Chem. 1982, 21, 4001.
     (q) Amer, S. I.; Dasgupta, T. P.; Henry, P. M. Inorg. Chem. 1983, 22, 1970.
     (r) Kober, E. M.; Goldsby, K. A.; Narayana, D. N. S.; Meyer, T. J. J. Am.
         Chem. Soc. 1983, 105, 4303.
     (s) Bignozzi, C. A.; Roffia, S.; Scandola, F. J. Am. Chem. Soc. 1985, 107,
         1644.
     (t) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. Inorg. Chem. 1983, 22, 224.

6.   Powers, M. J.; Meyer, T. J. J. Am. Chem. Soc. 1978, 100, 4393.

7.   Hammack, W. S.; Drickamer, H. G.; Lowery, M. D.; Hendrickson, D. N. Chem.
     Phys. Lett. 1986, 132(3), 231-235.

8. Hammack, W. S.; Drickamer, H. G.; Lowery, M. D.; Hendrickson, D. N. *Inorg. Chem.* **1988**, *27*, 1307-1308.

9. Lowery, M. D.; Hammack, W. S.; Drickamer, H. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 8019-8024.

10. Wong, K. Y.; Schatz, P. N. *Prog. Inorg. Chem.* **1981**, *28*, 369, and references therein.