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Notes

Thermochromic Effects in an Asymmetric Mixed-Valence System

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Recently, Walker and Barbara, in collaboration with our lab, reported the first example of time-resolved intervalence electron transfer (ET) based on direct optical intervalence pumping.[1] The reaction examined was

$$(NH_3)_5Ru^{III}\text{–}NC\text{–}Fe^{II}(CN)_5^- \underset{k_{ET}}{\overset{h\nu}{\rightleftarrows}} (NH_3)_5Ru^{II}\text{–}NC\text{–}Fe^{III}(CN)_5^- \quad (1)$$

in H_2O as solvent. Rate measurements via time-resolved (femtosecond) absorbance spectroscopy yielded distinctly nonexponential absorbance recovery kinetics, and therefore a range of values ($k_{ET} = 10^{12}$–10^{13} s^{-1}) rather than a single value for the thermal ET process. One potential source for the nonexponential behavior—a femtosecond coherence artifact—was identified, but could not be fully deconvoluted in the initial study.[1] Subsequent work by Barbara and co-workers has suggested that an additional factor could be a local heating effect, following intervalence transfer and back-electron-transfer.[2] If local heat dispersion occurred on a picosecond timescale and if the ground-state species were thermochromic, then the apparent heating phenomenon would contribute a probe-wavelength-dependent absorption component (artifact) to the observed kinetics.[3] The purpose of this note is to report on the intervalence thermochromism for the ground-state mixed-valence ion and to comment on its origin.

Experimental Section

The mixed-valence compound $[(NH_3)_5Ru\text{–}NC\text{–}Fe(CN)_5]Na$ was prepared[4] and purified[1] as previously described. Variable-temperature visible and near-infrared absorbance measurements were made on an OLIS-modified, CARY 14 spectrophotometer by using an insulated stainless steel cell featuring sapphire windows and a built-in heating element. Additionally, with ethylene glycol as solvent, a liquid-nitrogen-cooled cryostat (Oxford Instruments) was employed. In view of the accompanying electrochemical experiments, optical experiments in water (only) were performed with and without added 0.1 M NaCl. No significant difference was observed. Variable temperature electrochemical measurements were obtained with a glassy carbon working electrode, a platinum counter electrode and an SCE reference by using a nonisothermal cell configuration.[5] The supporting electrolyte was 0.1 M NaCl.

Results and Discussion

At room temperature, in water as solvent, the intervalence absorption maximum (E_{op}) for eq 1 appears at 1.28 eV (965 nm; 10360 cm^{-1}). Figure 1 shows, however, that as the temperature increases, E_{op} decreases. Over the limited temperature range examined, the change is linear, with the temperature dependence given by $dE_{op}/dT = -13.5 \pm 1$ cm^{-1} deg^{-1} (replicate experiments). (Measurements for the analogous $(NH_3)_5Ru\text{–}CN\text{–}Ru(CN)_5^-$ species (single experiment) likewise yielded $dE_{op}/dT = -13$ cm^{-1} deg^{-1}.)

To interpret the temperature effect we turn to the familiar Hush treatment of intervalence energies, where[6,7]

$$E_{op} = \lambda_{vib} + \lambda_s + \Delta E + \Delta E' \quad (2)$$

In eq 2, λ_{vib} and λ_s are vibrational and solvent reorganization energies, ΔE is the vibrationally relaxed initial-state/final-state separation energy, and $\Delta E'$ is an additional term reflecting possible energy contributions due to spin–orbit coupling effects and/or ligand-field asymmetry. (The former is expected to be negligible when the product state contains Fe(III).)

Although the various components of eq 2 are written as internal energies, Marcus and Sutin have convincingly argued that they are better viewed as free energies.[8] If so, then a temperature dependence or entropy contribution to any factor on the right-hand side of the equation should lead directly to an observable temperature dependence for the total intervalence absorption energy.

We will consider therefore, each of the component energies: For λ_{vib} it is difficult to envision a significant temperature dependence unless the pertinent vibrational frequencies themselves somehow exhibit a significant temperature dependence, an effect we consider unlikely. For λ_s the temperature dependence can be estimated (perhaps) from dielectric continuum theory by considering the temperature coefficients of both the static (ϵ_s) and optical-frequency (ϵ_{op}) dielectric constants. For water as solvent, the temperature coefficients are small and, to some extent, compensating.[9] For any reasonable estimate of λ_s, the overall temperature dependence ($d\lambda_s/dT$) should be on the order of 0.2 cm^{-1} deg^{-1} or less.[9]

Of the remaining terms, $\Delta E'$ is not obviously temperature dependent, but ΔE is (or could be).[10] Fortunately, ΔE is amenable to direct measurement (or, at least, approximation). For independent redox sites, a straightforward thermodynamic cycle shows that ΔE for eq 1 (forward direction) equals $E_f(Fe) - E_f(Ru)$ where E_f is the formal potential for the M(III) → M(II) electrochemical process. For the cyanide-bridged mixed-valence ion, the sites are not truly independent. Thus the observed formal

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(1) Walker, G. C.; Barbara, P. F.; Doorn, S. K.; Dong, Y.; Hupp, J. T. *J. Phys. Chem.* **1991**, *95*, 5712.

(2) Barbara, P. F. Personal communication (see also ref 3).

(3) An alternative or additional (but related) explanation for transient thermochromism focuses on comparatively slow (picosecond) vibrational relaxation following back-electron-transfer.[2] Evidence for slow relaxation within $(NH_3)_5Ru\text{–}CN\text{–}Ru(CN)_5^-$ has recently been reported by Doorn, Stoutland, Dyer, and Woodruff (*J. Am. Chem. Soc.* **1992**, *114*, 3133) based on transient infrared techniques.

(4) Vogler, A.; Kisslinger, J. *J. Am. Chem. Soc.* **1982**, *104*, 2311.

(5) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131.

(6) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(7) For a review, see: Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(8) (a) Marcus, R. A.; Sutin, N. S. *Comments Inorg. Chem.* **1986**, *5*, 119. (b) Marcus, R. A.; Sutin, N. S. *Biochim. Biophys. Acta* **1985**, *811*, 265. See also: Haim, A. *Comments Inorg. Chem.* **1985**, *4*, 113.

(9) Hush's model[6] (see also: Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1984**, *88*, 1860) predicts

$$d\lambda/dT = \text{constant} \times [(1/\epsilon_{op}^2)(d\epsilon_{op}/dT) - (1/\epsilon_s^2)(d\epsilon_s/dT)]$$

where the constant term is defined by reactant size and shape, distance of charge transfer, and extent of charge transfer. For water as solvent, $\epsilon_{op} = 1.78$, $d\epsilon_{op}/dT = -0.00024$, $\epsilon_s = 78$, $d\epsilon_s/dT = -0.365$ (Sears, P. G.; Holmes, R. R.; Dawson, L. R. *J. Electrochem. Soc.* **1955**, *102*, 145). Estimates for λ_s itself (which effectively defines the constant term) vary depending on assumptions made about both the extent and actual distance of charge transfer. One recent report, however, has suggested that $\lambda_s \approx 2400$ cm^{-1} for reaction 1.[1] This value, together with the variable-temperature dielectric data, yields $d\lambda_s/dT = 0.12$ cm^{-1} deg^{-1}.

(10) ΔE-based thermochromism has also been observed for intervalence absorption in $(NH_3)_5Ru^{III}\text{–}4,4'\text{-bipyridine–}Ru^{II}(bpy)_2Cl^{3+}$ (bpy is 2,2′-bipyridine): Hupp, J. T.; Kober, E. M.; Neyhart, G. A.; Meyer, T. J. *Proceedings of the NATO Advanced Research Workshop on Mixed-Valence Chemistry*; in press.

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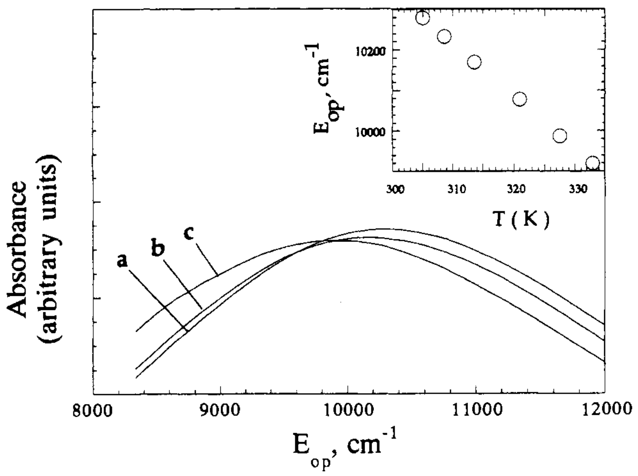


Figure 1. Intervalence absorption spectra for $(NH_3)_5Ru^{III}–NC–Fe^{II}(CN)_5^-$ in water at (a) 31.8, (b) 40.4, and (c) 59.8 °C. Inset: E_{op} versus temperature.

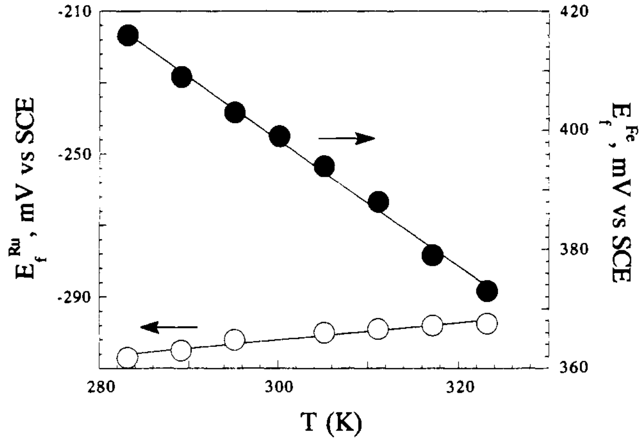


Figure 2. E_f versus temperature (nonisothermal cell configuration) for $Fe^{III/II}$ (eq 3) and $Ru^{III/II}$ (eq 4) in aqueous 0.1 M NaCl.

potentials could contain additional contributions from electrostatics, redox-variable back-bonding, and, perhaps, electronic mixing effects.[11] Nevertheless, for our purposes E_f measurements may be sufficient for assessing at least the temperature dependence of ΔE, if not its absolute value. (This is obviously true, of course, if the various additional contributions to E_f[11] are immune to temperature effects.)

In any case, Figure 2 shows the measured temperature dependences of E_f for the iron and ruthenium redox sites (eqs 3 and 4). Yee et al. have shown that temperature coefficients for

$$(NH_3)_5Ru^{III}–NC–Fe^{III}(CN)_5^0 + e^- \rightarrow (NH_3)_5Ru^{III}–NC–Fe^{II}(CN)_5^- + e^- \quad (3)$$

$$(NH_3)_5Ru^{III}–NC–Fe^{II}(CN)_5^- + e^- \rightarrow (NH_3)_5Ru^{II}–NC–Fe^{II}(CN)_5^{2-} \quad (4)$$

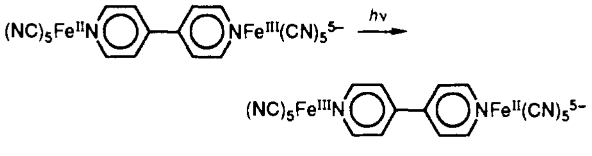
individual E_f's can likely be identified with good accuracy (ca. 1–2 e.u.) with true half-reaction entropies ($\Delta S_{rc}^\circ = \bar{S}_{red}^\circ - \bar{S}_{ox}^\circ$), provided that nonisothermal measurement techniques are employed.[5,12] On this basis we find $\Delta S_{rc}^\circ(Ru^{III/II}) = +3 \pm 3$ eu (+1 cm^{-1} deg^{-1}) and $\Delta S_{rc}^\circ(Fe^{III/II}) = -23 \pm 1.4$ eu (−8 cm^{-1} deg^{-1}).

Table I. Temperature Dependence of Intervalence Absorption Maximum for $(NH_3)_5Ru–NC–Fe(CN)_5^-$

solvent	E_{op}(300 K), cm^{-1}	dE_{op}/dT, cm^{-1} deg^{-1}	temp range, K
water	10360	−13.5	303–333
ethylene glycol	9150	−19	265–334
glycerol	9650	−18	303–333
formamide	8450	−15	304–334

These values may be compared with literature values[5,13,14] of +10 eu for $Ru(NH_3)_5Cl^{2+/+}$ and −42 eu for $Fe(CN)_6^{3-/4-}$ or, perhaps more appropriately, −23 eu for the $Fe(CN)_6^{3-/4-}$ ion paired to La^{3+}.[15] Detailed interpretations of reaction entropies for transition-metal redox couples have been offered previously.[16] It is perhaps sufficient to note here simply that the present findings are qualitatively consistent with previously established charge effects. It does appear, however, that proximity of an oppositely charged reactant or product leads, for both half-reactions, to a significant diminution in the absolute entropy change.

The appropriate electrochemical quantity for comparison to dE_{op}/dT is ΔS_{rc}°(Fe) − ΔS_{rc}°(Ru). The observed value for the latter (−9.2 ± 1.5 cm^{-1} deg^{-1}) compares reasonably well with the intervalence absorption experiment, supporting our contention that the thermochromic effect originates with the ΔE term. As a further test, however, we carried out a control experiment, based on the following symmetrical reaction:[17]



(5)

For eq 5, E_{op} will clearly depend on λ_{vib}, λ_s, and $\Delta E'$, but not on ΔE (which is necessarily zero). Our expectation then, is that intervalence thermochromism will be negligible. The experimental observation is dE_{op}/dT = +0.1 ± 0.6 cm^{-1} deg^{-1}.

Returning to the original motivation for the study, the observed thermochromism clearly supports the local-heating interpretation of Barbara and co-workers.[2] For reaction 1, because transient absorbance measurements[1] were made on the high-energy side of the intervalence band (probe energy = 12 600 cm^{-1}) and because dE_{op}/dT is negative, a transient thermochromic bleaching and recovery would be expected. It is worth noting, however, that observation on the low energy side should lead to a sign reversal (i.e. a transient absorbance *increase*, followed by slower decay kinetics).

A second point is that ΔE for intervalence absorption (forward ET) is, after sign change, identically the thermodynamic driving force for the back ET process. The present experiments clearly demonstrate that the driving force is temperature dependent and that it is greatest (i.e. ΔG is most negative) when the temperature is lowest. If back-electron-transfer occurs in the "normal" free energy regime ($-\Delta G < \lambda$) and if low-frequency vibrational modes contribute significantly to the Franck–Condon barrier, then temperature-induced changes in ΔG should strongly affect the observable ET kinetics. On the other hand, if the reaction is strongly inverted ($-\Delta G \gg \lambda$) or if the barrier is largely comprised

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(11) See, for example: Sutton, D.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

(12) Strictly speaking, measurements of $(dE_f/dT)_{ni}$ could also contain a contribution from a temperature-dependent redox enthalpy. A reviewer has suggested specifically that temperature dependent ligand(CN)/solvent H-bonding effects (enthalpic) could contribute to our apparent ΔS_{rc}° measurements. Presumably the enthalpic effect, if it exists, could be detected via an appropriate calorimetric measurement. We note, however, that "special" H-bonding explanations have not proven necessary for the rationalization of ΔS_{rc}° measurements[16] (although such effects are clearly important in determining overall formal potentials).

(13) Hanania, G. I. H.; Irvine, D. H.; Eaton, W. A.; George, P. *J. Phys. Chem.* **1967**, *71*, 2022.

(14) Reaction entropy data do not exist for the desired monomeric cyanoruthenium pentaammine entity.

(15) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1984**, *23*, 256.

(16) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1984**, *23*, 3639.

(17) Reaction 5 was examined without added electrolyte because of known complications attributable to ion pairing (Blackbourn, R. L., Ph.D. Dissertation, Northwestern University, 1991).

of high frequency (i.e. frozen) modes,[18] then variations in ΔG with temperature should be of comparatively little kinetic consequence.

Variable-temperature kinetics studies are currently underway to examine these and related points.[19] The solvents of choice are formamide, glycerol, and ethylene glycol. We conclude our report, therefore, with a summary of ground-state thermochromic results for $(NH_3)_5Ru-NC-Fe(CN)_5^-$ in these solvents; data are given in Table I.[20]

Acknowledgment. We thank Dr. Dahv Kliner and Prof. Paul Barbara for informative discussions regarding transient thermochromism and for communicating unpublished ET kinetics results. We also thank Dr. Stephen Doorn (Los Alamos) for a copy of the manuscript cited in ref 3. We gratefully acknowledge the Office of Energy Research, Division of Chemical Sciences, U.S. Department of Energy, (Grant No. DE-FG 02-87ER13808) for support of this research. J.T.H. acknowledges support as an Alfred P. Sloan Fellow (1990–1992) and as a Dreyfus Teacher–Scholar (1991–1996).

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(18) Franck–Condon barrier assessments,[1] based on a time-dependent Raman scattering analysis, indicate that displacement of both low- and high-frequency vibrational modes occurs upon electron transfer.

(19) Kliner, D.; Tominaga, K.; Barbara, P. F. Work in progress.

(20) *N*-Methylformamide was also examined. Unfortunately, solubility problems severely diminished the quality of the absorption data. Nevertheless, reaction 1 clearly does exhibit a negative thermochromic effect in this solvent; the apparent value of dE_{op}/dT is (with considerable uncertainty) -19 cm^{-1} deg^{-1} (data obtained with liquid-nitrogen cryostat). $E_{op}(300\ K)$ is ~8250 cm^{-1}.