Correspondence

Comparison of Observed and Calculated Barriers for Optical Electron Transfer in a Binuclear Ruthenium(II)–Ruthenium(III) Complex

Sir:

In mixed-valence materials[1,2] in which the degree of coupling between the metal centers is moderate, the energy of the intervalence-transfer transition[1,2] may be simply related to the barrier for thermal electron transfer.[3] In Figure 1 this relationship is indicated for the case of a binuclear-bridged metal complex in which the metals and their coordination spheres are identical and the extent of valence delocalization is small ($H_{ab} \ll E_{th}$). The potential energy of the system as a function of nuclear configuration is shown for the idealized system in which the vibrations are harmonic. Thermal electron transfer may occur when nuclear distortions of the solvent and metal coordination spheres result in a situation where the configurations of the two metal centers are energetically equivalent. By contrast, in the process of the optical electron transfer which gives rise to intervalence-transfer absorption, the nuclei are fixed and the transition from one potential energy surface ($\mathrm{M^+}\!\sim\!\mathrm{M}$) to the other ($\mathrm{M}\!\sim\!\mathrm{M^+}$) occurs vertically when $h\nu = E_{op}$. In the limit where valence delocalization is negligible ($H_{ab} \sim 0$) both thermal and optical barriers are straightforward consequences of the Franck–Condon principle and, as is evident from Figure 1, $E_{op} = 4E_{th}$.[3] Thus the spectra of mixed-valence compounds may provide valuable information concerning the process of thermal electron transfer.

As shown in eq 1, both solvation and inner-coordination-

$$E_{op} = E_{in} + E_{out} \tag{1}$$

sphere distortions contribute to the optical barrier to electron transfer.[3] When the M and M$^+$ coordination shells are spherical, the contribution to E_{op} arising from solvent distortion (E_{out}) is given by eq 2, while that due to distortions in the

$$E_{out} = e^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \tag{2}$$

$$E_{in} = \frac{4n}{2}\left(\frac{f_1f_2}{f_1 + f_2}\right)(\Delta r)^2 \tag{3}$$

metal–ligand bonds (E_{in}) is given by eq 3.[3] (Here a_1 and a_2 are the radii of the M and M$^+$ coordination spheres, d is the distance between the metal ions, D_{op} is the solvent optical dielectric constant taken as the square of the solvent refractive index, n is the number of metal–ligand bonds per metal center, Δr is the difference between the M and M$^+$ bond lengths, and f_1 and f_2 are the force constants for these bonds at M and M$^+$, respectively.)

Equation 1 is applicable only when the electronic states of the metal ions are the same in the reactant and product states (i.e., the excited state produced by light absorption is a vibrational, not an electronic, excited state). For many mixed-valence materials, however, more than one intervalence-transfer band may be expected to occur in the near-infrared to ultraviolet region. The number, intensities, and energies of these bands will depend on the detailed electronic structures of M and M$^+$. This may be illustrated by the very simple, hypothetical case in which M and M$^+$ are low-spin Ru(II) and Ru(III) in sites of *genuine* octahedral symmetry. Intervalence transfer as shown in Figure 1 occurs when a Ru(II) t_{2g} electron is transferred to a half-vacant Ru(III) t_{2g} acceptor orbital. In addition, however, much higher energy IT absorption may occur by promotion to an e_g Ru(III) acceptor orbital; here a ligand field excited state of Ru(II) is produced. Both IT bands might be expected to follow the solvent dependence given by eq 2 (i.e., plots of $\bar{\nu}_{max}$ vs. $1/D_{op} - 1/D_s$ should be linear with a slope related to the size of the octahedral units and the intermetal distance). On the other hand, only for the lower energy transition is the intercept (and IT band energy) simply related to the barrier for the thermal electron transfer process; the high-energy band involves formation of an electronically excited state of Ru(II) not likely to be involved in the thermal electron exchange. Obviously, then, some discretion must be used in the interpretation and application of IT band energies.

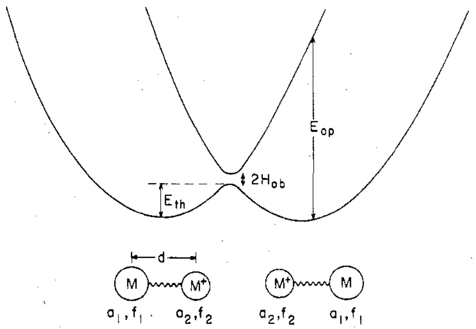

Figure 1. Potential energy as a function of nuclear configuration is shown for the binuclear mixed-valence ions $\mathrm{M}\!\sim\!\mathrm{M^+}$ and $\mathrm{M^+}\!\sim\!\mathrm{M}$. The splitting at the curve intersection ($2H_{AB}$) and the barrier to thermal electron transfer (E_{th}) are shown for the case when M and M$^+$ are equivalent (same metal, same coordination spheres). The process of light absorption when $h\nu = E_{op}$ gives rise to intervalence-transfer absorption.

In the case of $(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5{}^{5+}$, complexities analogous to those described above may be anticipated. For this ion, a band clearly ascribable to intervalence transfer is observed in the near-infrared region.[4] The complex contains low-spin d^6 Ru(II) and low-spin d^5 Ru(III) centers and is thus superficially similar to the hypothetical ion described above. It is, first of all, apparent that the near-infrared transition observed at ~1000 nm cannot involve the formation of a high-energy ligand field ($(\pi d)^5(e_g)^1$) Ru(II) excited state since such a transition must lie at least as high energy as the ligand field bands of $Ru(NH_3)_6{}^{2+}$, etc.—that is, in the visible or ultraviolet region of the spectrum. However, although this particular complication can be eliminated, others arise because of the lower symmetry of the ruthenium coordination sphere. The ruthenium coordination spheres contain one pyridine and five ammonia ligands. Although there is no evidence for any unusual interaction of pyridine with Ru(III) (NH_3 and pyridine appear to be nearly equivalent in their interaction with Ru(III)[5]), the high affinity of $Ru(NH_3)_5{}^{2+}$ for π-acid ligands has been demonstrated from both spectral and thermodynamic studies.[5,6] When $Ru(NH_3)_5{}^{2+}$ interacts with a π acid such as pyridine, the energy of the one πd orbital oriented so that it may overlap the ligand π^* orbital is lowered with respect to the other two orbitals of the set. There is evidence that this splitting may be on the order of 5 kcal mol^{-1} [6,7] and varies according to the nature of the ligand.[7] As a consequence, in such a Ru(II)–Ru(III) mixed-valence ion, two low-energy IT transitions may be envisaged: one results from the transfer

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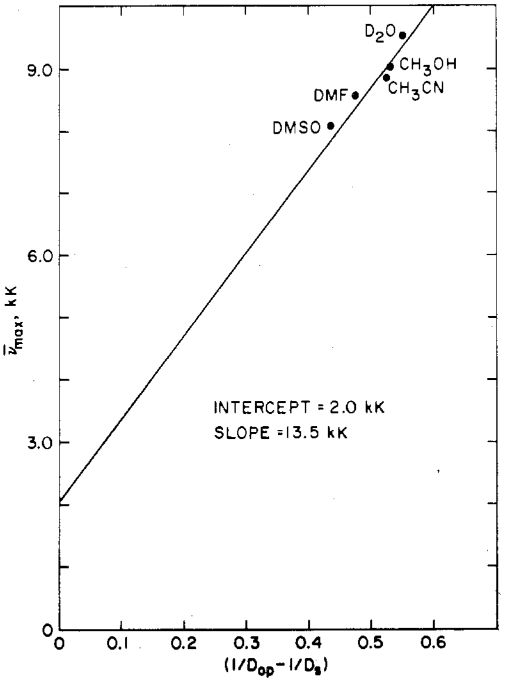

Figure 2. Plot of $\bar{\nu}_{max}$, the frequency of the intervalence-transfer maximum, vs. the solvent parameter $1/D_{op} - 1/D_s$ for $(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5^{5+}$. Data are taken from ref 4.

of an electron in the nonbonding Ru(II) πd set; the other originates from the lower energy (π bonded) Ru(II) πd orbital. Indeed, in a few complexes *metal-to-ligand* charge-transfer transitions originating from both sets have been observed.[8] (In general, however, only the higher energy transition is observed, as the other is of low intensity and is masked by the intense higher energy band.) To a first approximation the two possible IT bands should differ by the splitting of the two sets of πd orbitals induced by the back-bonding ligand. By analogy with the metal-to-ligand charge-transfer transitions, the higher energy band is expected to be the more intense since the interaction of the bonded πd Ru(II) donor orbital with the Ru(III) acceptor orbital is likely to be greater as a consequence of direct d–d or indirect d–ligand–d overlap. Thus it could well be that this higher energy (and more intense) IT transition is that seen in the near-infrared spectrum of $(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5^{5+}$. With these possible complications in mind, some experimental data for this mixed-valence ion will next be considered.

The solvent dependence of the position of the IT band for $(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5^{5+}$, a weakly coupled ruthenium(II)–ruthenium(III) mixed-valence ion, has been reported by Tom, Creutz, and Taube.[4] These data are summarized in Figure 2 in which the frequency of the band maximum is plotted as a function of the solvent parameter $(1/D_{op} - 1/D_s)$. The slope and intercept of the plot are 38.5 kcal mol^{-1} and 5.7 kcal mol^{-1}, respectively. These values will now be compared with the quantities calculated from eq 1–3.

The intercept should contain E_{in} along with any excitation energy involved in forming electronically excited states of the metal ions. No structural data are available for $(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5^{5+}$ so, in evaluating E_{in} and E_{out}, data for mononuclear model systems will be used.[9] Values for Δr may be taken from the structural data obtained by Gress, Creutz, and Quicksall[10] for $[Ru(NH_3)_5pyr](BF_4)_2$ and $[Ru(NH_3)_5pyr](CF_3SO_3)_3$ (pyr = pyrazine). For these ions the average $Ru^{II}–NH_3$ and $Ru^{III}–NH_3$ bond lengths are 2.16 (1) and 2.13 (1) Å, respectively, while the Ru^{II}–pyr and Ru^{III}–pyr bond lengths are 1.99 (1) and 2.08 (1) Å, respectively. Thus $\Delta r_{NH_3} = +0.03$ Å and $\Delta r_{py} = -0.09$ Å. Force constants for the $Ru–NH_3$ bonds are assumed equal and calculated from the A_{1g} symmetric Ru–N stretching frequency at 500 cm^{-1}[11] to be $f_1 = f_2 = 2.5 \times 10^5$ dyn cm^{-1}. For the Ru^{II}–pyr bond f_1 is taken as 2.2×10^5 dyn cm^{-1} from the Raman band observed by Strekas and Spiro[12] at 308 cm^{-1}. For the Ru^{III}–pyr bond f_2 is estimated to be 1.7×10^5 dyn cm^{-1} from typical metal(III)–pyridine stretching frequencies (270 cm^{-1}) recorded by Nakamoto.[13] From eq 3 and the above values the total value of E_{in} is found to be made up equally of contributions from distortions in the ten $Ru–NH_3$ bonds, $E_{in,NH_3} = 1.9$ kcal mol^{-1}, and the two ruthenium–pyridine bonds, $E_{in,py} = 2.1$ kcal mol^{-1}. The value of E_{in} calculated from eq 3 (4.0 kcal mol^{-1}) is thus in rather good agreement with the intercept (5.7 kcal mol^{-1}) obtained from Figure 2, although the fact that the intercept is larger than the calculated E_{in} may indicate that the observed near-infrared band does not correspond to the lowest IT transition of the system.

Table I. Comparison of Observed and Calculated Parameters for Optical Electron Transfer in $(NH_3)_5Ru(4,4\text{-bpy})Ru(NH_3)_5^{5+}$

	calcd	obsd
intercept (E_{in})	4.0 kcal mol^{-1}	5.7 kcal mol^{-1}
slope [$E_{out}/(1/D_{op} - 1/D_s)$]	40.8 kcal mol^{-1}	38.5 kcal mol^{-1}
λ_{max} (D_2O)	1080 nm	1050 nm

In the calculation of the outer-sphere contribution to E_{op} the two "halves" $(Ru(NH_3)_5NC_5–)$ of the binuclear molecule are approximated by spheres of a mean radius $\bar{a}$ calculated from $\bar{a} = [a_{NH_3}a_{NH_3}(a_{NH_3} + a_{py})/2]^{1/3}$.[14] Here a_{NH_3} is the radius of the $(NH_3)_5RuNC_5–$ moiety along the $NH_3–Ru–NH_3$ axes (3.5 Å). In calculating the "radius" along the NH_3–Ru–py axis the averaged quantity $(a_{NH_3} + a_{py})/2$ (5.25 Å) is used. The value of $\bar{a}$ thus calculated is 4.0 Å while d is 8 Å. This treatment yields the value 22.4 kcal mol^{-1} for E_{out} in D_2O and a calculated slope for Figure 2 of 40.8 kcal mol^{-1} (observed 38.5 kcal mol^{-1}). Evidently this simple model in which the binuclear ion is treated as a pair of spheres of mean radius is quite successful in calculating the solvent dependence of the IT band. Interestingly, this model gives much better agreement with experiment than an alternative model[15] in which the binuclear ion is treated as an ellipsoid. The value of E_{out} in D_2O calculated from the latter model is 137 kcal mol^{-1}. The observed and calculated values for the solvent dependence of the intervalence charge-transfer absorption band for $(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5^{5+}$ are summarized in Table I. Clearly excellent agreement is obtained for the slope of the plot (calculated 40.8, observed 38.5 kcal mol^{-1}). Agreement for the intercept—although poorer (calculated 4.0, observed 5.7 kcal mol^{-1})—is acceptable. The discrepancies in slope and intercept are in opposite directions and cancel to some extent in E_{op}; thus the agreement between the calculated and observed position of the band in D_2O is better than that in either of the contributory parameters.

For $(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5^{5+}$ the reasonably good agreement obtained for the intercept and the calculated values of E_{in} may be taken to indicate that the ambiguities introduced by the low electronic symmetry of the ion do not preclude useful applications of the simple model. On the other hand, data reported by Meyer and co-workers for mixed-valence ions containing the moiety $Ru(2,2'\text{-bpy})_2Cl–$ attached to another ruthenium center through L = pyrazine, 4,4'-bipyridine, or *trans*-1,2-bis(bipyridyl)ethylene[16,17] indicate that quantities in addition to E_{in} must be contained in the solvent-independent contribution to the IT band energy for these ions. For the symmetrical $(Ru(2,2'\text{-bpy})_2Cl)_2L^{3+}$ ions the solvent-independent terms range from 15.5 to 17.2 kcal mol^{-1}. No bond length data are available for these ions, but it is known that for the closely related $Fe(2,2'\text{-bpy})_3^{2+}$ and $Fe(2,2'\text{-bpy})_3^{3+}$ ions (and by analogy for $Ru(2,2'\text{-bpy})_3^{2+/3+}$) $\Delta r = 0.00$ Å.[18,19] If typical force constants of 2×10^5 dyn cm^{-1} for all of the metal–ligand bonds in the $[Ru(2,2'\text{-bpy})_2Cl]_2L^{3+}$ species are assumed, average Δr values of nearly 0.1 Å/bond are required to account for the magnitude of the observed intercepts. Such large distortions do not appear compatible with the data for the $Fe(2,2'\text{-bpy})_3{}^{2+/3+}$ complexes. As suggested earlier, electronic factors introduced by the low symmetry of these mixed-valence ions may be responsible for contributions to the intercept. In any case, it is clear that the intercepts may conceal many complicating factors.

It is evident that the spectral properties of mixed-valence ions are proving of value in assessing some of the parameters for thermal electron-transfer reactions. The solvent dependence expected from eq 2 has been found for several systems[4,18,19] and lends support to the solvent model for thermal reactions. In a different kind of application of the spectral data, Taube and co-workers have used the intensities of IT transitions in mixed-valence diruthenium complexes as a criterion for adiabaticity of intramolecular electron transfer in ruthenium(II)–cobalt(III) complexes.[20] For the ion $(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5{}^{5+}$ both the observed solvent-dependent and -independent behaviors of the IT band are in good agreement with theory. The calculated values $E_{in} = 4.0$ kcal mol^{-1} and $E_{out} = 22.4$ kcal mol^{-1} (in D_2O) lead to $E_{op} = 26.4$ kcal mol^{-1} (in D_2O). Thus the calculated value of E_{th} is 6.8 kcal mol^{-1} in D_2O. From E_{th} a first-order rate constant for intramolecular electron transfer (k_{th}) within this mixed-valence ion in D_2O at 25 °C is calculated to be 1.1×10^8 s^{-1}. This value should probably be regarded as a low estimate since the thermal barrier may be lowered if $H_{ab} \neq 0$ (see Figure 1) or it may be lowered by other factors (for example see ref 21). Experiments designed to determine k_{th} directly in this and related ions are presently in progress.[22]

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Electron Transfer between Cobalt(I) and Cobalt(III) in Vitamin B_{12}[1a]

Sir:

The rate of electron transfer between the Co(I) and Co(III) derivatives of vitamin B_{12} (B_{12s} and B_{12a}, respectively) has recently been determined by two different groups. Although conditions appeared comparable, the use of quite different experimental techniques led to distinctly different rate constants for the reaction

$$(Co^I)^- + (Co^{III})^+ \rightarrow 2Co^{II} \quad (1)$$

Kaufmann and Espenson[2] used chemical production of B_{12s} and stopped-flow kinetics to evaluate second-order rate constants on the order of 10^4 dm^3 mol^{-1} s^{-1}. The values varied with pH according to[3]

$$-d[B_{12s}]/dt = k[B_{12s}][B_{12b}] \quad (2)$$

$$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} = 5.8 \times 10^3 + 70.7/[OH^-] \quad (3)$$
$$(25\ °C, \mu = 0.1\ M)$$

Alternatively, B_{12s} was generated by pulse radiolysis[4] using reactions 4–5. These studies were carried out in buffer

$$e_{aq}^- + CO_2 \rightarrow CO_2^{-}\cdot \quad (4a)$$

$$CO_2^{-}\cdot + (Co^{II}) \rightarrow CO_2 + (Co^I)^- \quad (4b)$$

$$\dot{O}H \text{ (or } \dot{H}) + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O \text{ (or } H_2) \quad (5a)$$

$$(CH_3)_2\dot{C}OH + (Co^{II}) \rightarrow (CH_3)_2CO + H^+ + (Co^I)^- \quad (5b)$$

solutions (5.8 < pH < 11.0) *saturated with CO_2*. They reported a pH-independent reaction with a rate constant 3.2×10^7 dm^3 mol^{-1} s^{-1}.

To resolve this discrepancy, we have carried out pulse radiolysis experiments under a variety of conditions. We first confirmed[5] by spectroscopic detection the production of B_{12s} in solutions of B_{12r} (2×10^{-5} M) in the following combinations: (1) by e_{aq}^- and $(CH_3)_2\dot{C}OH$ in He-saturated solutions containing 0.1 M 2-propanol, (2) by e_{aq}^- and $CO_2^{-}\cdot$ in He-saturated solutions containing 0.1 M sodium formate, (3) by $CO_2^{-}\cdot$ in CO_2-saturated solutions containing 0.1 M sodium formate, and (4) by $CO_2^{-}\cdot$ and $(CH_3)_2\dot{C}OH$ in CO_2-saturated solutions containing 0.1 M 2-propanol. In solutions containing formate, reaction 6 replaces reaction 5a.

$$\dot{O}H \text{ (or } \dot{H}) + HCO_2^- \rightarrow CO_2^{-}\cdot + H_2O \text{ (or } H_2) \quad (6)$$

A second set of pulse radiolysis experiments consisted of pulsing a mixture of B_{12r} and B_{12a} containing 0.1 M 2-propanol (formate solutions of B_{12a} developed yellow coloration on standing and thus were not used in the kinetic experiments). The former is preferentially reduced to B_{12s},[5] following which the electron-transfer reaction of interest (eq 1) occurs. The pulse is such that about 3×10^{-6} M B_{12s} is formed in the presence of excess B_{12a} at pH 4–12. Many solutions were free of buffers to avoid possible complications from side reactions,

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