

LETTERS

Electron-Transfer Reactions in Water. Contributions from High-Frequency Vibrations?

Joseph T. Hupp and Thomas J. Meyer*

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514

(Received: August 14, 1986; In Final Form: December 23, 1986)

From the solvent dependence of the absorption band energies for metal-to-metal charge-transfer bands in several symmetrical ligand-bridged mixed-valence dimers, water emerges as an anomalous solvent. Explanations based on specific ligand-solvent interactions or the involvement of high-frequency hydroxyl stretching modes are shown to be inconsistent with the available results. The experimental observations can be accommodated, however, by postulating the involvement of relatively high-frequency librational modes known to exist in water. The observation of anomalously high MMCT band energies in water has significant implications for related electron-transfer reactions such as thermally activated self-exchanges.

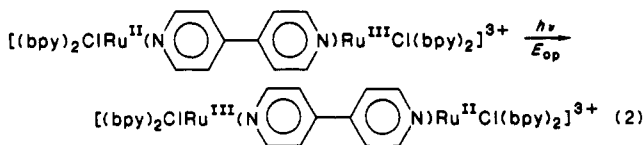
For electron-transfer reactions in polar solvents there is a necessity for the reorientation of solvent dipoles in response to the change in charge distribution associated with the electron-transfer act. Expressions for the resulting "reorganizational energy" (λ_0), which provides a basis for electron trapping at a single chemical site, have been derived by assuming that the solvent can be treated as a dielectric continuum. From the work of Marcus¹ and Hush,² an expression for λ_0 is given in eq 1 for light-induced electron transfer between spherical reactants of radii r_D for the electron donor and r_A for the acceptor which are separated by a distance d . The optical (D_{op}) and static (D_s) dielectric constants of the solvent, and the unit electronic charge (e) also appear in eq 1.

$$\lambda_0 = e^2 \left(\frac{1}{r} - \frac{1}{d} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) \quad (1)$$

$(r_A = r_D = r)$

An experimental approach exists for the direct evaluation of λ_0 via the measurement of metal-to-metal charge-transfer

(MMCT) absorption band energies in symmetrical, ligand-bridged mixed-valence ions.³⁻⁵ A particular example is shown in eq 2



(bpy is 2,2'-bipyridine), where variations in MMCT absorption band energies for a series of polar organic solvents are essentially in quantitative agreement with eq 1 in the form⁶⁻⁸

$$E_{op} = \text{intercept} + \lambda_0 = \text{intercept} + e^2 \left(\frac{1}{r} - \frac{1}{d} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) \quad (3)$$

(3) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, 8, 391. (b) Hush, N. S. *Electrochem. Acta* **1968**, 13, 1005.

(4) (a) Tom, G. M.; Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1974**, 96, 7828. (b) Creutz, C. *Inorg. Chem.* **1978**, 17, 3723.

(5) For reviews see: (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, 30, 1. (b) Meyer, T. J. In *Mixed-Valence Compounds*, Brown, D. B., Ed.; Reidel: Dordrecht, Holland, 1980; pp 75-113.

(1) Marcus, R. A. *J. Chem. Phys.* **1965**, 43, 679.

(2) Hush, N. S. *Trans. Faraday Soc.* **1961**, 57, 557.

TABLE I: Variations in MMCT Band Energies with Solvent at Room Temperature from the Data in Figure 1

dimer	$[\partial E_{op}/\partial(1/D_{op} - 1/D_s)]^a$ cm ⁻¹	intercept, ^{a,b} cm ⁻¹	σ^c cm ⁻¹	λ_0^d , cm ⁻¹	$\lambda_0'^{d,e}$ cm ⁻¹	λ_0'/λ_0
$[(bpy)_2ClRu(BPE)RuCl(bpy)_2]^{3+}$	9.02×10^3	6.24×10^3	210	4.92×10^3	730	0.15
$[(bpy)_2ClRu(4,4'-bpy)RuCl(bpy)_2]^{3+}$	6.8×10^3	6.51×10^3	130	3.71×10^3	770	0.21
$[(bpy)_2ClRu(pz)RuCl(bpy)_2]^{3+}$	3.85×10^3	5.65×10^3	10	2.10×10^3	120	0.06

^a Excluding water or D₂O. ^b Intercepts of the plots of E_{op} vs. $1/D_{op} - 1/D_s$ in Figure 1. ^c Standard deviation in E_{op} for the data in Figure 1 excluding water. The small σ value for the pyrazine-bridged dimer is not statistically meaningful since it is appreciably less than the precision of the individual E_{op} measurements. ^d λ_0 is the value for λ_0 in water taken from the statistically drawn lines in Figure 1 by using $(1/D_{op} - 1/D_s) = 0.546$ and the slopes and intercepts listed above. λ_0' is the amount by which the experimental value of E_{op} lies above the statistical line. ^e In H₂O for the BPE dimer, H₂O or D₂O for the 4,4'-bpy dimer, and D₂O for the pz dimer.

The intercept of a plot of E_{op} vs. $1/D_{op} - 1/D_s$ includes contributions from intramolecular vibrational trapping and multiple MMCT transitions arising from the low symmetry and spin-orbit coupling at Ru(III).⁹

As an alternative to the two-sphere model, ellipsoidal cavity models have been developed which account for solvent effects in terms of the change in electronic distribution within a regular ellipse enclosing both the electron donor and acceptor.¹⁰⁻¹³ Both approaches assume a dielectric continuum for the solvent and are only approximations of the actual geometries involved. For the dimer in eq 2 either model provides a basis for accounting for solvent effects although the ellipsoidal model is less revealing physically and requires a somewhat arbitrary assumption regarding molecular dimensions. As noted below, eq 1 provides a quantitative basis for accounting for solvent effects in the dimer based on known molecular dimensions.

Dielectric continuum theories of solvent trapping appear to provide an adequate basis for including the contribution of low-frequency (1–10 cm⁻¹) solvent librational modes which are responsible for solvent dipole reorientations, at least in the absence of specific solvent effects such as H bonding. However, in hydroxylic solvents and, in particular, in water a broad range of molecular and collective modes exists, from the low-frequency librational modes to high-frequency $\nu(OH)$ vibrations at ~ 3400 cm⁻¹. Largely on the basis of the appearance of nonnegligible k_{H_2O}/k_{D_2O} kinetic isotope effects, it has been suggested that contributions to the activation barrier for the $Fe(H_2O)_6^{3+/2+}$ self-exchange may exist from high-frequency $\nu(OH)$ modes of the bound solvent as well as from low-frequency librations,¹⁴ and in nonradiative decay of the metal-to-ligand charge-transfer (MLCT) excited state of $Ru(bpy)_3^{2+}$, from $\nu(OH)$ modes in the surrounding solvent.^{15,16} In general, contributions to electron transfer or nonradiative decay exist for any molecular motion of the system for which there is a change in equilibrium normal coordinate or vibrational frequency between the initial and final states.

In polar organic solvents, the dimer in eq 2 has provided a quantitative basis for verifying the predictions of dielectric continuum theory. Consequently, its MMCT transition provides an experimental probe for investigating possible solvent-based contributions to electron transfer in water which may exist in addition to low-frequency librational modes. In order to pursue the point, we have extended the earlier solvent-dependence studies. The results that were obtained here and earlier for the dimers

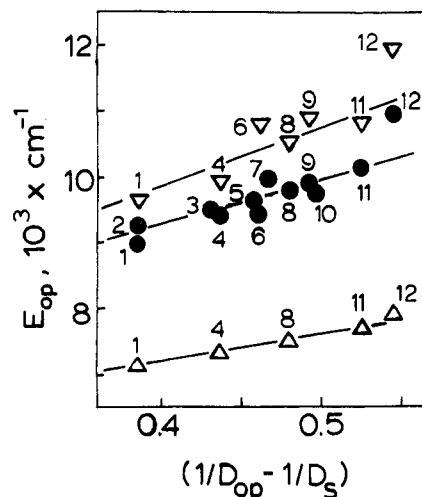
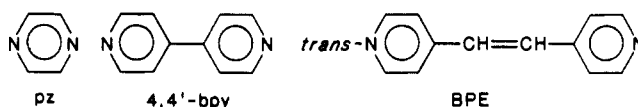


Figure 1. MMCT band energies for $[(bpy)_2ClRu(L)RuCl(bpy)_2]^{3+}$ plotted against $(1/D_{op} - 1/D_s)$. Lines represent statistical best fits (Table I) excluding H₂O and D₂O. Key to bridging ligand: ∇ = BPE, $\bullet$ = 4,4'-bpy, Δ = pz. Key to solvents: 1, nitrobenzene; 2, benzonitrile; 3, 1-methyl-2-pyrrolidinone; 4, dimethyl sulfoxide; 5, dimethylacetamide; 6, dimethylformamide; 7, formamide; 8, propylene carbonate; 9, acetone; 10, nitromethane; 11, acetonitrile; 12, water. All except 2, 3, 5, 7, 10, and 12 for L = 4,4'-bpy are from ref 6. Average uncertainties in E_{op} values are ± 150 (BPE), ± 70 (4,4'-bpy), and ± 70 cm⁻¹ (pz).

$[(bpy)_2ClRu^{II}(L)Ru^{III}Cl(bpy)_2]^{3+}$ (L = pyrazine (pz), 4,4'-bipyridine (4,4'-bpy), and *trans*-1,2-bis(pyridyl)ethylene (BPE))



are shown in Figure 1 and the slopes and intercepts of the statistically best fit lines to the data are given in Table I.

For the dimers where L = 4,4'-bpy or BPE the slopes, $[\partial E_{op}/\partial(1/D_{op} - 1/D_s)]$, of the best fit lines to the solvent dependence data in Figure 1, excluding H₂O or D₂O, are within 9% of those calculated from eq 1 by using $r = 6.5$ Å and $d = 11.1$ or 13.2 Å, respectively. Equation 1 is not adequate for the pyrazine-bridged dimer. It is derived by assuming nonpenetrating spheres, $d \geq 2r$. For L = pz, $d = 6.9$ Å, and the solvent dependences are more adequately treated by the ellipsoidal cavity model.¹³

It is apparent from the solvent dependence data for the 4,4'-bpy and BPE dimers that MMCT band energies in H₂O or D₂O occur at energies which are higher to a statistically significant degree than could be calculated from eq 3, or taken from the best-fit line for the nonaqueous solvents in Figure 1. Unfortunately, we were unable to obtain reliable data in other hydroxylic solvents such as methanol and ethanol because of a lack of solubility. In Table I are given values of λ_0 in H₂O or D₂O calculated from the statistically drawn lines in Figure 1 by using $1/D_{op} - 1/D_s = 0.546$. Also listed are values for λ_0' which is the amount by which the experimental value of E_{op} lies above the statistical line. λ_0' , which is a measure of the extent of deviation from dielectric continuum theory, appears to track λ_0 suggesting that, like λ_0 , it is a function of the dipole length (d) of the transition. By inference λ_0' arises

- (6) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289.
- (7) Powers, M. J.; Salmon, D. J.; Callahan, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 6731.
- (8) Sullivan, B. P.; Curtis, J. C.; Kober, E. M.; Meyer, T. J. *Nouv. J. Chem.* **1980**, *4*, 643.
- (9) (a) Kober, E. M.; Goldsby, K. A.; Narayana, D. N. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4303. (b) Neyhart, G. A.; Westmoreland, D.; Meyer, T. J., manuscript in preparation.
- (10) Cannon, R. D. *Chem. Phys. Lett.* **1977**, *49*, 299.
- (11) Kharkats, Yu. I. *Elektrokhimiya* **1976**, *15*, 1251.
- (12) German, E. D. *Chem. Phys. Lett.* **1979**, *64*, 305.
- (13) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657.
- (14) Guarr, T.; Buhks, E.; McLendon, G. *J. Am. Chem. Soc.* **1983**, *105*, 3763.
- (15) VanHouten, J.; Watts, R. J. *Inorg. Chem.* **1978**, *17*, 3381.
- (16) (a) Caspar, J. V.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *Chem. Phys. Lett.* **1982**, *91*, 91. (b) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J., manuscript in preparation.

from a response in the surrounding medium to the change in charge distribution which accompanies the optical electron transfer.

The origin of λ_0' appears not to be from specific solvent effects arising, for example, from interactions of H_2O or D_2O with the bound Cl^- ions. In the dimers $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{bipyrimidine})\text{Os}^{\text{III}}(\text{bpy})_2]^{5+}$ and $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$, where there are no chloro ligands, E_{op} varies as $1/D_{\text{op}} - 1/D_s$ with D_2O as a high-energy anomaly.¹⁷ In addition, if the origin of λ_0 were in specific interactions with the chloro group, a correlation of E_{op} with a solvent acidity function such as Gutmann's acceptor number might have been expected.¹⁸ In fact, water is quite distinct when compared with other solvents of high acceptor number.

If we assume that dielectric continuum theory properly incorporates the low-frequency librational contributions to electron transfer in water, there are at least two reasonable origins for λ_0 . The first is in the $\nu(\text{OH})$ stretching mode at $\sim 3400\text{ cm}^{-1}$. However, the magnitude of the quantum spacing for the mode is comparable to the MMCT band width at half-maximum ($\sim 5000\text{ cm}^{-1}$ at room temperature). Therefore, if contributions from $\nu(\text{OH})$ to the spectral profile were important, they would appear as distinct shoulders on the high-energy side of the absorption manifold arising from the transitions $v = 0 \rightarrow v' = 0$, $v = 0 \rightarrow v' = 1$, etc., rather than as a shift in the band maximum.¹⁹ Also the energies of the shoulders (relative to E_{op}) should decrease by ~ 1.4 with the exchange of D for H in the solvent. Experimentally, the high-energy shoulder is absent and we observe no isotope effect in E_{op} for $\text{L} = 4,4'\text{-bpy}$. (Admittedly, a significant isotope effect could exist but escape detection due to experimental error; for the comparison between H_2O and D_2O the overall uncertainty in the measured value of E_{op} is $\sim 200\text{ cm}^{-1}$.)

A second possibility exists based on the results of Raman spectral studies of H_2O and D_2O .²⁰ From the Raman results three

broad bands appear in the range $250\text{--}800\text{ cm}^{-1}$ which have been assigned to restricted rotational motions (librations) of individual water molecules but within five-membered clusters. If, as might be expected given their librational character, these modes respond to changes in charge distribution within the dimers, they could be the origin of λ_0' . Spectrally, the quantum spacings for the high-frequency librational modes are small compared to the MMCT band width. Their contribution to both the band width and band energy would be additive, e.g.

$$E_{\text{op}} - \text{intercept} = \lambda_0 + \lambda_0' \quad (4)$$

and relatively insensitive to the exchange of deuterium for hydrogen. If the origin of λ_0' is in high-frequency librations, then the average electron-vibrational (librational) coupling constant for these modes is $S \sim 1.2$ for the $4,4'\text{-bpy}$ and BPE dimers and $S \sim 0.2$ for $\text{L} = \text{pyrazine}$ as calculated from $S = \lambda_0'/\hbar\omega(\text{H}_2\text{O})$. S is related to the reduced mass (M), angular frequency (ω), and change in librator displacement (ΔQ_e) by $S = 1/2(M\omega/\hbar) \cdot (\Delta Q_e)^2$.¹⁹ When an average value of $\hbar\omega(\text{H}_2\text{O}) = 600\text{ cm}^{-1}$ is taken for the three librational contributions at 450 , 550 , and 775 cm^{-1} ,²⁰ the magnitudes of the values of S suggest that librational effects on E_{op} are chiefly from $v = 0 \rightarrow v' = 0$ and $v = 0 \rightarrow v' = 1$ transitions.

Regardless of the details of its origin, the appearance of the factor λ_0' in the MMCT experiments has some important general implications for electron-transfer processes in water. For example, for a self-exchange reaction the contribution from solvent to the activation energy is given by $\lambda_0/4$. Using eq 1, $\lambda_0/4$ for hexaaqua metal(III)/(II) self-exchanges like $\text{Fe}(\text{H}_2\text{O})_6^{3+/2+}$ has been calculated to be about 7 kcal mol^{-1} .²¹ If the ratio of $(\lambda_0'/\lambda_0) \sim 0.2$ from the optical experiments is carried over to the self-exchange reactions, an additional contribution of 1.4 kcal mol^{-1} would exist in the energy of activation for the hexaaqua self-exchanges (and for other small-molecule reactions) in H_2O . An increase of this magnitude in E_a would decrease the rate of self-exchange by a factor of ~ 10 compared to an equivalent non-hydroxylic solvent where only low-frequency librational modes contribute to solvent trapping.

Acknowledgment. Acknowledgment is made to the Army Research Office under grant DAAG29-85K-0121 for support of this research.

(17) For $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{bpm})\text{Os}^{\text{III}}(\text{bpy})_2]^{5+}$ the MMCT band maximum in water is significantly obscured by the tail of a metal-to-ligand charge-transfer transition at higher energy. Resolution of E_{op} by spectral subtraction based on the corresponding $\text{Ru}(\text{II})\text{--Os}(\text{II})$ dimer suggests that λ_0 is in the range $200\text{--}600\text{ cm}^{-1}$. (Hupp, J. T., unpublished results.) For $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$, $\lambda_0'/\lambda_0 \sim 0.12$, although additional complications appear to exist. (Hupp, J. T.; Meyer, T. J. *Inorg. Chem.*, in press).

(18) See, for example: Marcus, Y.; Pross, E.; Hormadaj, J. J. *Phys. Chem.* **1980**, *84*, 2708.

(19) Ballhausen, C. J. *Molecular Electronic Structures of Transition Metal Complexes*; McGraw-Hill: New York, 1979.

(20) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: London, 1969; pp 242–245.

(21) See, for example: Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.