

dependence on this ratio, but it is probable that, if it falls much below three, the conductivity will be low. In fact, if it is two, it is very unlikely that the material will be a solid electrolyte.

Interactions between cations on nearest-neighbor tetrahedral sites must be strong and repulsive because the intersite distances are too short to allow such sites to be simultaneously occupied. The "squeezing" of the  $\text{Ag}^+$  ions on passing through a shared triangular face from one polyhedron to another probably determines the activation enthalpy of motion.<sup>5</sup> This is also a very complicated matter for a crystal with crystallographically nonequivalent saddle points, because the activation enthalpies of motion through the different "windows" must also be different. Therefore, even when directional  $\sigma$  vs.  $T$  measurements are made, the

activation enthalpies derived therefrom are directional averages.

According to Armstrong et al.<sup>40</sup> the stability of the  $\text{Ag}^+$  and  $\text{Cu}^+$  ions in both four- and three-coordination and their monovalency are responsible for their being the mobile ion in most good solid electrolytes.

Additional discussion of these points will be found in papers already referenced and also in ref 41 and 42.

*This work was supported in part by National Science Foundation Grant DMR No. 72-03271-A01.*

(40) R. D. Armstrong, R. S. Bulmer, and T. Dickinson, *J. Solid State Chem.*, **8**, 219 (1973).

(41) S. Geller in "Fast Ion Transport in Solids", W. Van Gool, Ed., North-Holland, Amsterdam, 1973, pp 607-616.

(42) S. Geller in "Superionic Conductors", G. D. Mahan and W. L. Roth, Ed., Plenum Press, New York, N.Y., 1976, pp 171-181.

## Optical and Thermal Electron Transfer in Metal Complexes

THOMAS J. MEYER<sup>1</sup>

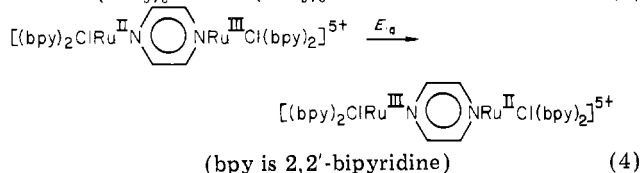
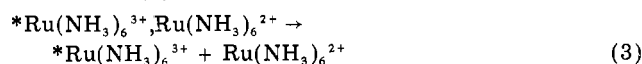
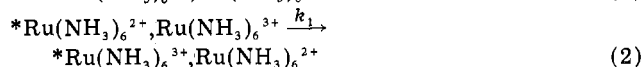
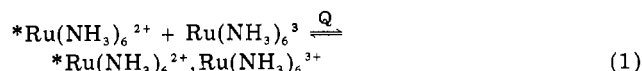
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*Received March 9, 1977*

There are many cases of transition-metal complexes which retain the same basic structure in different oxidation states. In ions like  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  the gross structures are the same, but the detailed structures are different. Metal-ligand bond strengths and distances usually vary somewhat with oxidation state, and outer-sphere solvation energies and solvent structure vary with ion charge. Simple electron-transfer processes are often facile for such ions because no bonds need be broken, but a sizeable activation barrier to electron transfer can still exist. The barrier arises from the influence of oxidation-state changes on the coordination spheres around the ions.

A reaction coordinate diagram for electron transfer is shown in Figure 1A. The diagram describes the activation barrier for electron transfer within an ion pair of the reactants (eq 2) for an outer-sphere self-exchange reaction (e.g., eq 1-3).<sup>2</sup> It applies equally well to inner-sphere electron transfer in a symmetrical mixed-valence ion like that shown in eq 4, where delocalization is slight.<sup>3</sup> For both reactions, the overall free energy change is 0.

In Figure 1A the curve (2,3) refers to the case where the exchanging electron is localized on one side. It represents a plane drawn through a multidimensional, energy-coordinate surface along a coordinate which is sensitive to changes in oxidation state at both Ru(II) and Ru(III), perhaps the two Ru-Cl distances in re-



action 4. With regard to the center of the molecule, there are two possible ways of finding the dimer, with Ru(II) on one side or on the other. Curves (2,3) and (3,2) are then identical but displaced along P because the spatial coordinates of the vibrational modes that we are following are different for the two possibilities. Orbital overlap between the electron donor and acceptor sites leads to the splitting in the surface crossing region in Figure 1A and to ground-state electron delocalization from Ru(II) to Ru(III).

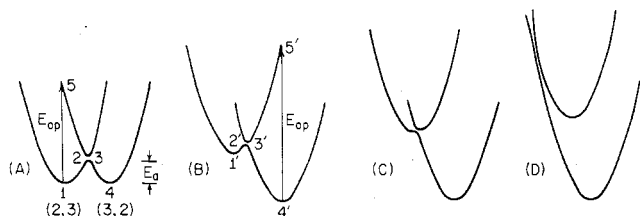
Electron transfer can occur by thermal activation and surface crossing,  $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$  in Figure 1A. Absorption of heat from the surroundings leads to changes in nuclear configurations at the Ru(II) and Ru(III) sites until they are identical at points 2 and 3. Within the limits of the uncertainty principle, the energies at 2 and 3 are also the same, and the only difference between

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(1) Written in part while on sabbatical leave at the Department of Inorganic Chemistry, The University of Sydney.

(2) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

(3) (a) R. W. Callahan, F. R. Keene, T. J. Meyer, and D. J. Salmon, *J. Am. Chem. Soc.*, **99**, 1064 (1977); (b) R. W. Callahan and T. J. Meyer, *Chem. Phys. Lett.*, **39**, 82 (1976).



**Figure 1.** Reaction coordinate diagrams for electron transfer. (A)  $\Delta G^\circ = 0$ ; (B)  $\Delta G^\circ$  negative; (C) diffusion-controlled limit,  $-\Delta G^\circ_{R'} = \lambda$ ; (D) abnormal free-energy region,  $-\Delta G^\circ_{R'} > \lambda$ .

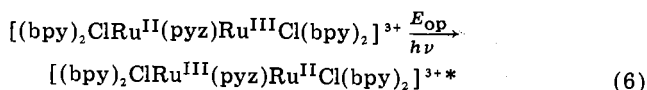
reactants and products is the position of the exchanging electron.

In the absence of quantum effects involving nuclear motion, the rate constant for electron transfer is given by eq 5.<sup>4,5</sup> The thermal activation barrier has been

$$k = \nu_{et} \exp(-E_a/RT) \quad (5)$$

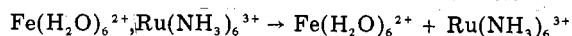
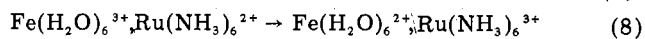
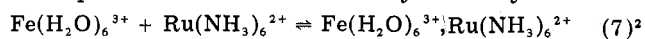
treated semiclassically by Marcus<sup>6</sup> and Hush<sup>5</sup> in terms of reorganizations in the inner and outer coordination spheres. The magnitude of the frequency factor for electron transfer,  $\nu_{et}$ , depends on the resonance or delocalization energy whether it is treated as a resonance, surface-crossing, or electron-tunneling phenomenon.<sup>4</sup> More recently, quantum mechanical treatments have been given which include the role of nuclear tunneling between vibrational levels of the reactants and products through the activation barrier.<sup>7</sup>

Application of the Franck-Condon principle to electron transfer means that the vertical process 1  $\rightarrow$  5 in Figure 1A cannot occur thermally. Electron hopping between surfaces is far too rapid to be driven thermally since thermal activation occurs by transitions to higher vibrational levels and solvent modes which are slow on the electronic time scale. The vertical process can be driven by light, and the optical transition has been observed in mixed-valence ions<sup>5b,8a</sup> like the Ru(II)-Ru(III) ion in eq 6 (pyz is pyrazine).<sup>3</sup> The



optical transition, which has been termed intervalence transfer (IT) by Hush,<sup>5b</sup> leaves Ru(II) and Ru(III) in sites having the equilibrium coordination spheres of the opposite oxidation state (Figure 1A) until vibrational relaxation can occur.

In Figure 1B is shown a reaction coordinate diagram for electron transfer within an ion pair for a reaction like eq 8 which is favored thermodynamically. For such



(4) N. Sutin in "Inorganic Biochemistry", Vol. 2, G. L. Eichborn, Ed., Elsevier, New York, N.Y., 1973, p 611.

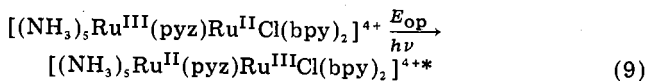
(5) (a) N. S. Hush, *Trans. Faraday Soc.*, **57**, 557 (1961); (b) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967); *Electrochim. Acta*, **13**, 1005 (1968); *Chem. Phys.*, **10**, 361 (1975).

(6) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); **43**, 679 (1965); R. A. Marcus and N. Sutin, *Inorg. Chem.*, **14**, 213 (1975), and references therein.

(7) N. R. Kestner, J. Logan, and J. Jortner, *J. Phys. Chem.*, **78**, 2148 (1974); W. Schmickler, *Ber. Bunsenges. Phys. Chem.*, **77**, 991 (1973); S. G. Christov, *ibid.*, **79**, 357 (1975); P. P. Schmidt, *J. Chem. Phys.*, **56**, 2775 (1972); V. G. Levich, *Adv. Electrochem. Eng.*, **4**, 249 (1966); R. R. Dogonadze in "Reactions of Molecules at Electrodes", N. S. Hush, Ed., Oxford University Press, London, 1971.

(8) (a) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10**, 247 (1967); (b) B. Mayoh and P. Day, *Inorg. Chem.*, **13**, 2273 (1974); *J. Am. Chem. Soc.*, **94**, 2885 (1972).

cases the extent of reorganization of the coordination spheres is less than for self-exchange because the energy balance condition at 2' and 3' is met in part by the energetically favorable nature of the electron-transfer process. The vertical process 4'  $\rightarrow$  5', which leads to the reversal of eq 8, has been observed optically in unsymmetrical mixed-valence ions (eq 9). In the



complex in eq 9, the differences in inner coordination sphere ligands lead to an oxidation-state asymmetry. Light-driven electron transfer (eq 9) occurs against a chemical potential to give a transient, high energy oxidation state isomer of the system.<sup>9,10</sup>

IT transitions are of inherent interest because of what they are: long-range, directed electron-transfer processes between separated redox sites. As discussed below they can also provide an experimental basis for relating optical and thermal electron transfer and for understanding the properties of mixed-valence complexes.

### Electron Transfer in Mixed-Valence Complexes

According to Marcus<sup>6</sup> and Hush<sup>5</sup> the activation barrier to electron transfer for a reaction like 8 is given by eq 10 where  $\Delta G^\circ_{R'}$  is the free-energy change within

$$\Delta G^* = (\lambda/4)(1 + \Delta G^\circ_{R'}/\lambda)^2 \quad (10a)$$

$$\Delta G^* = \lambda/4 \quad (10b)$$

the ion pair upon electron transfer, and  $\lambda$  is the reorganizational parameter.<sup>11</sup> For a self-exchange reaction or for a symmetrical mixed-valence ion, the free energy change is zero (Figure 1A), giving eq 10b.

$\lambda$  includes contributions from inner ( $\lambda_i$ ) and outer ( $\lambda_o$ ) sphere reorganization (eq 11).<sup>4-7</sup> Expressions have been

$$\lambda = \lambda_i + \lambda_o \quad (11)$$

given for  $\lambda_i$  in terms of the bond distance changes and force constants needed to take the redox sites to the inner-sphere configurations at the top of the reaction barrier for self-exchange.<sup>5,6</sup> Using a dielectric continuum model for the solvent,  $\lambda_o$  is given by eq 12 where

$$\lambda_o = e^2 \left( \frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{d} \right) \left( \frac{1}{n^2} - \frac{1}{D_s} \right) \quad (12)$$

$e$  is the unit electron charge,  $n^2$  and  $D_s$  are the optical and static dielectric constants of the medium,  $r_1$  and  $r_2$  are the molecular radii at the redox sites, and  $d$  is the internuclear separation between redox sites. For a reaction like 8 there are two reaction partners,  $Fe(H_2O)_6^{3+}$  and  $Ru(NH_3)_6^{2+}$ , and their contributions to  $\lambda$  are taken to be half the  $\lambda$  values for the  $Fe(H_2O)_6^{3+/2+}$

(9) G. M. Brown, R. W. Callahan, and T. J. Meyer, *J. Am. Chem. Soc.*, **96**, 7829 (1974); G. M. Brown, R. W. Callahan, and T. J. Meyer, *Inorg. Chem.*, **14**, 1443 (1975).

(10) T. J. Meyer, *Adv. Chem. Ser.*, No. 150, Chapter 7 (1976); G. M. Brown, R. W. Callahan, E. C. Johnson, T. J. Meyer, and T. R. Weaver, *Am. Chem. Soc. Symp. Ser.*, No. 5, 66 (1975).

(11) For outer-sphere reactions like reactions 1-3 and 7-8,  $k$  is given by  $k = \nu_{et} Q \exp(-\Delta G^*/RT)$ , where  $Q$  is the ion-pairing constant.<sup>3-5a</sup> The expression given by Marcus,  $k = pZ \exp(-U(d)/RT) \exp(-\Delta G^*/RT)$ , is slightly different in that  $U(d)$  is the work required to bring the reactants together from an infinite separation,  $Z$  is the collision frequency between two neutral molecules in solution ( $\sim 10^{11} M^{-1} s^{-1}$ ), and  $p$  is the probability of adiabatic surface crossing over the reaction barrier.

Table I  
 $\lambda_i$  and  $\lambda_o$  (in Acetonitrile) for Intramolecular Electron Transfer in Mixed-Valence Ions

Ion	$E_{op}, 10^3 \text{ cm}^{-3}$ ( $\lambda_{max}, \text{nm}$ )	$\lambda_i,$ kcal/mol	$\lambda_o,$ kcal/mol	Ref
$[(\text{NH}_3)_5\text{Ru}^{\text{III}}(4,4'\text{-bpy})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{5+}$	8.9 (1130)	10.0	15.4	13
$[(\text{bpy})_2\text{ClRu}^{\text{III}}(\text{pyz})\text{Ru}^{\text{II}}\text{Cl}(\text{bpy})_2]^{3+}$	7.7 (1300)	16.1	6.0	3a
$[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{pyz})\text{Ru}^{\text{II}}\text{Cl}(\text{bpy})_2]^{4+}$	10.4 (960)	12.9	10.0	14

and  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  self-exchange reactions,  $\lambda_{11}$  and  $\lambda_{22}$  in eq 13.<sup>6</sup>

$$\lambda = \frac{\lambda_{11} + \lambda_{22}}{2} \quad (13)$$

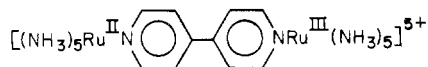
The treatments given by Marcus and Hush have been tested using outer-sphere electron-transfer rate data.<sup>4</sup> The difficulty with this approach is that self-exchange rate constants are hard to measure, and comparisons using rate constants usually fail to give direct insight into the underlying theory because of possible cancellation of effects. Direct insight can be gained using mixed-valence ions.

Hush has shown that for symmetrical mixed-valence ions the energies of the optical ( $E_{op}$ , Figure 1A, eq 6) and thermal ( $E_a$ , Figure 1A, eq 4) electron-transfer processes are related by eq 14 which follows from eq

$$E_{op} = 4E_a = 4E_{inner} + 4E_{outer} = \lambda = \lambda_i + \lambda_o = \lambda_i + e^2 \left( \frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{d} \right) \left( \frac{1}{n^2} - \frac{1}{D_s} \right) \quad (14)$$

10b, 11, and 12 if  $T\Delta S^* \sim 0$ . Mixed-valence ions offer several advantages in the study of electron-transfer processes: (a) the electron donor and acceptor sites are held in fixed chemical positions and complications arising from preequilibria like eq 1 and 7 do not appear; (b) from eq 14, estimates of the thermal activation barrier are easily available by spectroscopic measurements of IT band energies; (c) estimates for the extent of delocalization of the optical electron can also be obtained from IT bands.<sup>3a,5b,8</sup> Equation 14 applies only to ions like  $[(\text{bpy})_2\text{ClRu}^{\text{II}}(\text{pyz})\text{Ru}^{\text{III}}\text{Cl}(\text{bpy})_2]^{3+}$  where electron delocalization is small enough to leave the Ru(II) and Ru(III) sites relatively unperturbed.<sup>3,5b,8</sup>

From eq 14, in a series of solvents the IT band energy should vary linearly with  $((1/n^2) - (1/D_s))$  and the intercept of the plot should give  $\lambda_i$ .<sup>12</sup> The expected linear relationship was first observed by Tom, Creutz, and Taube<sup>13</sup> for the ion



and has since been found for  $[(\text{bpy})_2\text{ClRu}^{\text{II}}(\text{pyz})\text{Ru}^{\text{III}}\text{Cl}(\text{bpy})_2]^{3+}$  and for the unsymmetrical ion  $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{pyz})\text{Ru}^{\text{II}}\text{Cl}(\text{bpy})_2]^{4+}$ .<sup>14</sup> The importance of such experiments is that they allow numerical values to be obtained for the separate inner- and outer-sphere contributions to the activation barrier. Data for the three ions are given in Table I.

The data are consistent with several predictions. If eq 11 and 13 are correct,  $\lambda_i$  for the unsymmetrical ion

(12) The value at the intercept corresponds to the measurement of  $E_{op}$  in a solvent like  $\text{CCl}_4$  where there is no permanent dipole moment.

(13) G. M. Tom, C. Creutz, and H. Taube, *J. Am. Chem. Soc.*, **96**, 7827 (1974).

(14) R. W. Callahan, T. J. Meyer, M. J. Powers, and D. J. Salmon, *Inorg. Chem.*, **15**, 1457 (1976).

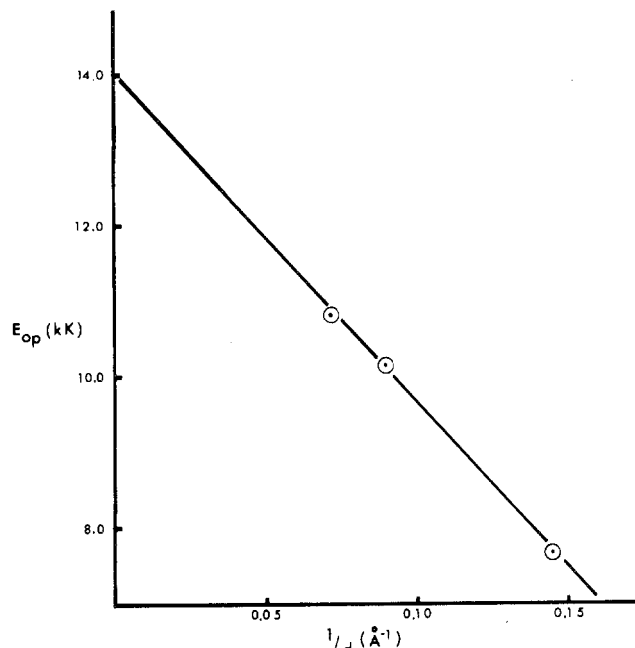


Figure 2. Plot of  $E_{op}$  ( $10^3 \text{ cm}^{-1}$ ) vs.  $1/d$  ( $\text{\AA}^{-1}$ ) in acetonitrile at  $22 \pm 2^\circ \text{C}$  (taken from ref 16).

should be equal to one-half the sum of the  $\lambda_i$  values for the two symmetrical ions. The calculated (13.0 kcal/mol) and experimental (12.9 kcal/mol) values are in good agreement. As predicted by eq 12,  $\lambda_o$  is lower when  $-\text{RuCl}(\text{bpy})_2$  is one of the redox sites because its molecular radius is larger than the radius for  $-\text{Ru}(\text{NH}_3)_5$  (5.8  $\text{\AA}$  average vs. 3.5  $\text{\AA}$ ).  $E_{inner}$  ( $=\lambda_i/4$ ) is small for the pentaammine dimer, which is expected since Ru-N bond distances are nearly the same in salts of  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$ .<sup>15</sup>

The role of the distance separating redox sites has been investigated by IT band measurements in the series of ions  $[(\text{bpy})_2\text{ClRu}(\text{L})\text{RuCl}(\text{bpy})_2]^{3+}$  (L = pyrazine, 4,4'-bipyridine, or *trans*-py-CH=CH-py) where  $d$  varies from 6.9 to 13.2  $\text{\AA}$ .<sup>16</sup> If delocalization is small, the two redox sites should act as uncoupled oscillators and  $\lambda_i$  should be independent of  $d$ . A dependence on  $d$  arises in  $\lambda_o$  (eq 12) and therefore in  $E_{op}$  (eq 15). The

$$E_{op} = \left[ \lambda_i + e^2 \left( \frac{1}{2r_1} + \frac{1}{2r_2} \right) \left( \frac{1}{n^2} - \frac{1}{D_s} \right) \right] - \frac{e^2}{d} \left( \frac{1}{n^2} - \frac{1}{D_s} \right) \quad (15)$$

dependence on  $d$  appears because in a dimer or ion pair, solvent molecules are shared between the redox sites and the extent of solvent reorganization for electron transfer is less than it would be for isolated redox sites.

For the three mixed-valence ions, the linear relationship between  $E_{op}$  and  $1/d$  predicted by eq 15 has been found (Figure 2),<sup>16</sup> the slope and intercept of the

(15) H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).

line in Figure 2 are in reasonable agreement with values calculated using eq 15, and it has been verified that  $\lambda_i$  is essentially independent of solvent. From the plot in Figure 2, it can be determined that  $E_a$  increases from 5.5 kcal/mol with pyrazine as the bridging ligand to 10.0 kcal/mol when there is an infinite separation between the redox sites.

The results described above are encouraging in that they make physical sense and suggest that IT band measurements can give detailed insight into the activation barrier for electron transfer. The ideal experiment will be to measure both IT band energies and the rate of intramolecular electron transfer directly for an ion like  $[(\text{bpy})_2\text{ClRu}^{\text{II}}(\text{pyz})\text{Ru}^{\text{III}}\text{Cl}(\text{bpy})_2]^{3+}$ . With the results of both experiments in hand, the reaction profile could be mapped completely, including both the frequency factor and the activation barrier (eq 5). The direct measurement will be difficult;  $k$  has been estimated to be  $\sim 10^{10} \text{ s}^{-1}$  for  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{3+}$  in acetonitrile at 25 °C.<sup>3</sup>

The IT data have been shown to be consistent with the rate of outer-sphere self-exchange between  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{py})\text{Cl}]^+$  and  $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{py})\text{Cl}]^{2+}$ .<sup>17</sup> The complexes have virtually the same properties as the Ru(II) and Ru(III) sites in  $[(\text{bpy})_2\text{ClRu}^{\text{II}}(\text{bpy})\text{Ru}^{\text{III}}\text{Cl}(\text{bpy})_2]^{3+}$ . In electron transfer in both the mixed-valence ion and within the ion-pair  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{py})\text{Cl}^+, \text{Ru}^{\text{III}}(\text{bpy})_2(\text{py})\text{Cl}^{2+}]^{3+}$ , the electron donor and acceptor sites are held in close proximity and the major difference between the two is in accounting for the preequilibrium in the outer-sphere reaction (compare reactions 1–3 with reaction 4).<sup>18</sup> Good agreement has been obtained between the experimental self-exchange rate constant and a predicted value estimated using the IT data in Figure 2 to obtain  $E_a$  at the appropriate  $d$ , the Fuoss equation to estimate the ion-pairing constant, and  $k = \nu_{\text{et}} Q \exp(-E_a/RT)$ ,<sup>3a,4,16</sup> which takes into account the ion-pairing step.<sup>11</sup> In the future, such comparisons promise to give considerable insight into the details of outer-sphere electron-transfer processes.<sup>16</sup>

One feature of interest in mixed-valence ruthenium chemistry is that routes to mixed-valence polymers such as  $[(\text{bpy})_2\text{ClRu}(\text{pyz})[\text{Ru}(\text{bpy})_2(\text{pyz})]_2\text{RuCl}(\text{bpy})_2]^{9+/8+/7+}$ <sup>10</sup> and  $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{Ru}(\text{bpy})_2(\text{pyz})\text{Ru}(\text{NH}_3)_5]^{8+/7+}$ <sup>19a</sup> are known and IT bands have been observed in such ions.<sup>10,19</sup> Using the insight gained from the dimeric mixed-valence ions and the synthetic chemistry of the polymers, it may be possible in the future to design and interpret experiments where long-range electron transfer occurs through metal polymer chains.

The good agreement between experiment and theory for the dimeric mixed-valence ions need not extend to related systems. Apparent breakdowns may appear where specific solvent effects occur such as H bonding

to aquo and cyano ions, where physical changes in the bridging ligand may be important,<sup>20</sup> or most importantly, where delocalization is extensive.

In the mixed-valence ions  $[(\text{bpy})_2\text{ClRu}^{\text{II}}(\text{L})\text{Ru}^{\text{III}}\text{Cl}(\text{bpy})_2]^{3+}$  discussed above there is good experimental evidence for discrete Ru(II) and Ru(III) sites. The barrier to intramolecular electron transfer (eq 4, Figure 1A) arises because changes in oxidation state cause differences in inner and outer coordination spheres. Orbital overlap between Ru(II) and Ru(III) leads to delocalization and partial charge transfer in the ground state because of mixing of the properties of the different sites in the combined wave functions.

If delocalization is slight, IT bands appear having properties consistent with the treatment given by Hush,<sup>5b</sup> and the Hush theory relates optical and thermal electron transfer. With increased delocalization, the coordination spheres at the Ru(II) and Ru(III) sites are distorted from the equilibrium positions for isolated Ru(II) and Ru(III) ions and the distortions make the sites more nearly alike. The distortions, which are energetically unfavorable, are driven by the increased resonance energy as delocalization increases.

The effects of increased delocalization are shown in Figure 3B. As the sites become more nearly alike, the displacement between the (2,3) and (3,2) curves is decreased and the splitting between the upper and lower surfaces is increased. The two changes, one in vibrational energy content and the other in electronic, tend to cancel each other out and the energy of the IT band may be relatively unchanged. However, in the Hush treatment for the optical transition, the metal sites should be treated as fractional valences with only partial electron transfer in  $\lambda_{\text{op}}$ , and appropriate intermediate bond distances and force constants should be used in  $\lambda_i$ . Also, any relation between  $E_{\text{op}}$  and  $E_a$  must take into account explicitly the resonance energy leading to the splitting between the surfaces in Figure 3B.<sup>5b,8b</sup> A further complication is that the probability of nuclear tunneling transitions through the barrier will increase as delocalization makes the barrier "thinner" (Figure 1B) and there may be no simple relationship between  $E_{\text{op}}$  and the thermally activated process.

With strong overlap, delocalization can become complete, giving equivalent redox sites on the vibrational time scale (Figure 3C). A thermal barrier no longer exists, and the question of intramolecular electron transfer becomes one of electronic motion in a molecular orbital delocalized over both sites just as in a delocalized  $\pi$  orbital in benzene. Low energy absorption bands can appear,<sup>21</sup> but they are molecular transitions between delocalized levels (Figure 3C) and involve no directional charge-transfer character unless the molecule is unsymmetrical.

Taube's group has prepared a series of pentaammine mixed-valence ions,  $[(\text{NH}_3)_5\text{Ru}(\text{L})\text{Ru}(\text{NH}_3)_5]^{5+}$  (L = NCCN,<sup>21a</sup> NCC(R)CN<sup>-</sup>,<sup>21b</sup> pyrazine<sup>22</sup>), in which delocalization appears to be complete and the metal sites appear to be equivalent. The difference in properties between the bpy and pentaammine dimers is striking,

(20) H. Fischer, G. M. Tom, and H. Taube, *J. Am. Chem. Soc.*, **98**, 5512 (1976).

(21) (a) G. M. Tom and H. Taube, *J. Am. Chem. Soc.*, **97**, 5310 (1975); (b) H. Krentzien and H. Taube, *ibid.*, **98**, 6379 (1976).

(22) (a) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **91**, 3988 (1969); **95**, 1086 (1973); (b) J. K. Beattie, N. S. Hush, and P. R. Taylor, *Inorg. Chem.*, **15**, 992 (1976).

(16) R. W. Callahan, T. J. Meyer, M. J. Powers, and D. J. Salmon, *J. Am. Chem. Soc.*, **98**, 6731 (1976).

(17) By measuring the rate of the net reaction,  $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^+ + [\text{Ru}(\text{phen})_2(\text{py})\text{Cl}]^{2+} \rightarrow [\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^{2+} + [\text{Ru}(\text{phen})_2(\text{py})\text{Cl}]^+$ , for which  $K = 1.0$ .<sup>3a</sup>

(18) If the outer-sphere reaction rate is near the diffusion-controlled limit, corrections for diffusional effects must be made (R. M. Noyes, *Prog. React. Kinet.*, **1**, 129 (1961)) and the situation is more complicated.

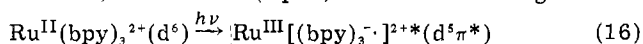
(19) (a) R. W. Callahan, T. J. Meyer, M. J. Powers, and D. J. Salmon, *Inorg. Chem.*, **15**, 894 (1976); (b) G. M. Brown, T. J. Meyer, D. O. Cowan, F. Kaufman, C. LeVanda, M. D. Rausch, and P. V. Røling, *ibid.*, **14**, 506 (1975).

but can be explained. For spin-paired  $d^5$ - $d^6$  Ru(II)-Ru(II) systems, IT<sup>3,13</sup> and self-exchange rate data<sup>2,3a</sup> show that the reorganizational energies needed to make the Ru(II) and Ru(III) sites equivalent ( $E_a$  in Figure 1A) are low:  $\sim 5.5$  kcal/mol in acetonitrile for [(bpy)<sub>2</sub>ClRu(pyzo)RuCl(bpy)<sub>2</sub>]<sup>3+</sup> from IT measurements.<sup>3a</sup> Because of the low distortion energies, the transition region from slight to complete delocalization is small energetically. What may appear to be subtle changes in molecular structure can be sufficient to give complete delocalization if overlap is sufficiently enhanced.

The difference between the pentaammine and bpy complexes is probably that the  $-\text{Ru}^{\text{II}}(\text{NH}_3)_5$  site is more strongly reducing and  $d\pi$  electron density more readily available for delocalization.<sup>23</sup> Mixing of  $d\pi(\text{Ru}(\text{II}))$  with  $\pi^*(\text{pyz})$  "carries" the Ru(II) wave functions across the bridging ligand for overlap with the electron-deficient Ru(III) site. In the bpy complex, competitive back-bonding to bpy decreases  $d\pi$ - $\pi^*(\text{pyz})$  mixing both by stabilizing  $d\pi$  orbitals and by decreasing their radial extensions. Backbonding to bpy ties up the available  $d\pi$  electron density and the extent of delocalization is too small to overcome the reorganizational barrier.

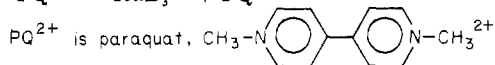
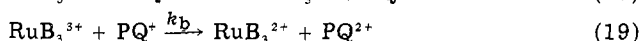
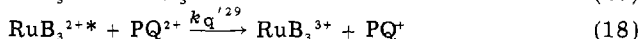
### Electron Transfer Reactions of Excited States

All molecular excited states are potential redox reagents since the absorption of light leads to excitation of an electron to a higher level where it is more weakly bound, and at the same time to an electron hole in a lower level. Ru(bpy)<sub>3</sub><sup>2+</sup> and related polypyridine complexes of Ru(II) absorb light strongly in the visible because of low-lying metal to ligand CT (charge transfer) transitions (eq 16).<sup>24a</sup> The resulting excited



states can be relatively long-lived in solution ( $\sim 600$  ns for Ru(bpy)<sub>3</sub><sup>2+\*</sup>)<sup>24b</sup> and are known to have considerable Ru(III)-bpy<sup>-</sup> character.<sup>25</sup> Ru(bpy)<sub>3</sub><sup>2+\*</sup> has been used as a sensitizer in energy-transfer processes,<sup>26</sup> but of more interest here is its reactivity as an electron-transfer reagent.

Electron-transfer quenching of Ru(bpy)<sub>3</sub><sup>2+\*</sup>, which was first proposed by Gafney and Adamson,<sup>27</sup> can readily be shown by microsecond flash photolysis (reactions 17-19). At relatively high quencher con-



centrations and low concentrations of Ru(bpy)<sub>3</sub><sup>2+</sup>, excitation and quenching occur during the flash, the redox products are formed in small but spectrally detectable amounts, and back electron transfer between

(23) H. Taube, *Surv. Prog. Chem.*, **6**, 1 (1973).

(24) (a) G. M. Bryant, T. E. Ferguson, and H. K. J. Powell, *Aust. J. Chem.*, **24**, 257 (1971); (b) F. E. Lytle and D. M. Hercules, *J. Am. Chem. Soc.*, **91**, 253 (1969).

(25) (a) K. W. Hipps and G. A. Crosby, *J. Am. Chem. Soc.*, **97**, 7042 (1975), and references therein; (b) J. Van Houten and R. J. Watts, *ibid.*, **98**, 4853 (1976); (c) R. Benasson, C. Salet, and V. Balzani, *ibid.*, **98**, 3722 (1976).

(26) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coord. Chem. Rev.*, **15**, 321 (1975), and references therein.

(27) H. D. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, **94**, 8238 (1972).

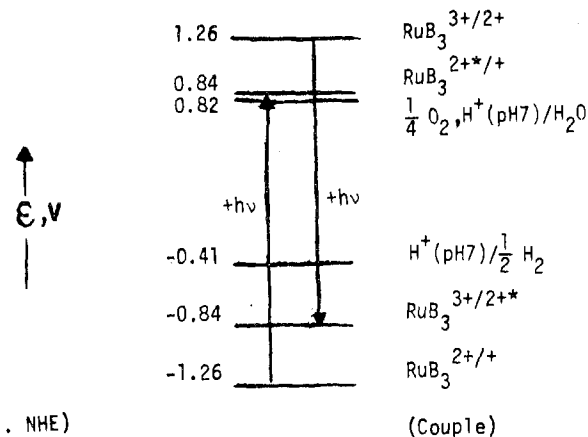
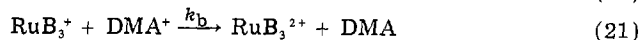
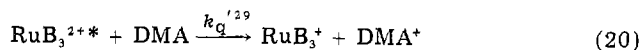


Figure 3. Redox potential diagram.

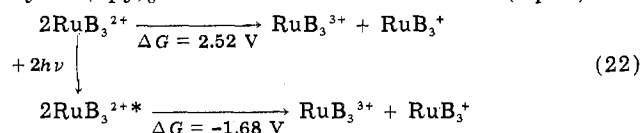
them (reaction 19) can be followed directly.<sup>28</sup> Consistent with the presence of both oxidizing (Ru<sup>II</sup>) and reducing (bpy<sup>-</sup>) sites, flash photolysis has also been used<sup>30,31</sup> to show that reductive quenching (e.g., reactions 20, 21)<sup>31</sup> can also occur to give the strongly re-



DMA is *N,N*-dimethylaniline

duced complex Ru(bpy)<sub>3</sub><sup>+</sup>, in which an electron has been added to a  $\pi^*(\text{bpy})$  level.<sup>30,31</sup>

The thermodynamic properties of Ru(bpy)<sub>3</sub><sup>2+\*</sup> as a redox reagent have been estimated experimentally by measuring its rate of quenching by a series of nitroaromatic compounds having slightly varying oxidizing strengths.<sup>32</sup> From the data, the formal potential for the Ru(bpy)<sub>3</sub><sup>3+/2+\*</sup> couple was estimated; this allows the effect of optical excitation on the redox properties of Ru(bpy)<sub>3</sub><sup>2+</sup> to be summarized as in the redox potential diagram in Figure 3.<sup>33</sup> The values cited are reduction potentials in water vs. NHE.<sup>34</sup> In the excited state, both the oxidizing (RuB<sub>3</sub><sup>2+\*</sup> + e<sup>-</sup> → RuB<sub>3</sub><sup>3+</sup>) and the reducing (RuB<sub>3</sub><sup>2+\*</sup> - e<sup>-</sup> → RuB<sub>3</sub><sup>3+</sup>) properties of the system are enhanced by 2.10 V, the excited-state energy. The effect is shown graphically in Figure 3 as a light-driven crossing of the energies for Ru(II) acting as oxidant and reductant. The crossing means that the high stability with respect to disproportionation enjoyed by Ru(bpy)<sub>3</sub><sup>2+</sup> is lost in the excited state (eq 22).



(28) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974).

(29) In the emission quenching experiment, the total rate of quenching, both energy and electron transfer, is measured. For the  $k_q'$  values in eq 18 and 20,  $k_q' \leq k_q$  even if quenching is solely by electron transfer.  $k_q'$  refers to the production of free, observable redox products. Following electron-transfer quenching within the reactant ion pair, e.g., RuB<sub>3</sub><sup>2+\*</sup>, PQ<sup>2+</sup> → RuB<sub>3</sub><sup>3+</sup>, PQ<sup>+</sup>, back electron transfer to give RuB<sub>3</sub><sup>2+</sup>, PQ<sup>2+</sup> can occur competitively and decrease the amount of redox product formation observed.

(30) C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **98**, 6384 (1976).

(31) C. P. Anderson, T. J. Meyer, D. J. Salmon, and R. C. Young, *J. Am. Chem. Soc.*, **99**, 1980 (1977).

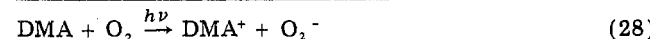
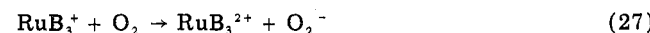
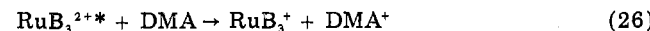
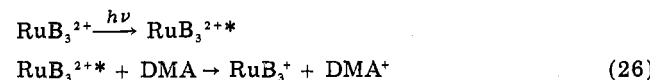
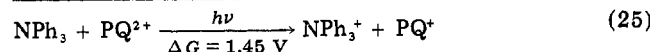
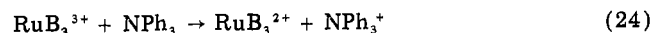
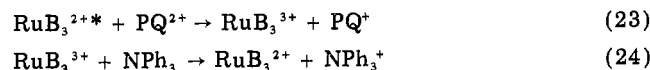
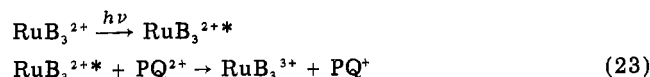
(32) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **97**, 2909 (1975).

(33) T. J. Meyer, "Photoredox Catalysis", presented to International Workshop on Fundamental Research in Homogeneous Catalysis, Dec 13-16, 1976, Palermo City, Italy.

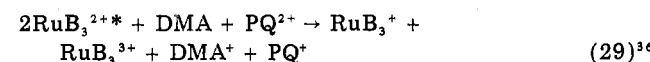
(34) C. Creutz and N. Sutin, *Inorg. Chem.*, **15**, 496 (1976).

The data in the diagram show something far more striking. Standard potentials for the oxidation and reduction of water are also given, and from the data it is apparent that  $Ru(bpy)_3^{2+}$  is thermodynamically capable of both oxidizing and reducing water at pH 7.<sup>33</sup> The reduction potential data only outline thermodynamic possibilities. The redox chemistry of water is complicated because transformations between stable forms ( $2H_2O \rightarrow O_2$ ;  $H_2O \rightarrow H_2$ ) involve multielectron steps and are often slow. The excited state has not been observed to liberate either  $H_2$  or  $O_2$  from water, but even if it is incapable of reacting with water at a significant rate, chemically modified forms may be, or it may be possible to use the excited state to drive coupled redox systems which can.

$Ru(bpy)_3^{2+}$  has been shown to be a potential photoredox catalyst. By using two one-electron transfer redox couples, the quenching and back electron transfer steps can be separated (reaction 23–25<sup>35</sup> and 26–28<sup>31</sup>)

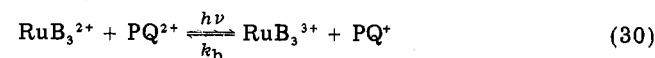


and visible light used to drive reactions transiently in the nonspontaneous direction as shown by flash photolysis. In a related experiment, flash photolysis of solutions containing both oxidant ( $PQ^{2+}$ ) and reductant (DMA) has been shown to lead to simultaneous oxidative and reductive quenching and therefore to the transient, chemically catalyzed disproportionation of  $Ru(bpy)_3^{2+}$  (eq 29).<sup>36</sup> Lin and Sutin have described



another interesting application where rate differences between the quenching of  $Ru(bpy)_3^{2+}$  by  $Fe(H_2O)_6^{3+}$  and the back reaction between  $Ru(bpy)_3^{3+}$  and  $Fe(H_2O)_6^{2+}$  have been exploited to achieve photogalvanic effects.<sup>37</sup>

In quenching schemes like reactions 17–19, rate data can be obtained for the quenching step by luminescence quenching measurements and for the back-reaction by flash photolysis. When used this way, flash photolysis becomes a relaxation technique in which a reaction at equilibrium is rapidly perturbed (eq 30) by the light



absorption, quenching sequence in reactions 17 and 18. Flash photolysis has proven to be an exceedingly valuable way of obtaining rate data which are usually inaccessible by other techniques.<sup>38</sup> Rate constants have

(35) T. J. Meyer, D. G. Whitten, and R. C. Young, *J. Am. Chem. Soc.*, **97**, 16 (1975).

(36) J. K. Nagle, R. C. Young, and T. J. Meyer, *Inorg. Chem.*, in press.

(37) C. T. Lin and N. Sutin, *J. Phys. Chem.*, **80**, 97 (1976); *J. Am. Chem. Soc.*, **97**, 3543 (1975).

(38) T. J. Meyer, *Israel J. Chemistry*, in press.

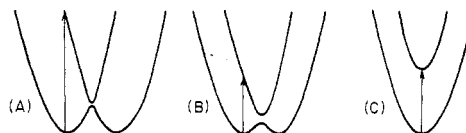


Figure 4. As in Figure 1 but showing the effects of delocalization: (A) slight delocalization; (B) intermediate delocalization; (C) complete delocalization.

been measured which are at or near the diffusion-controlled limit, e.g.,  $Ru(NH_3)_6^{2+} + RuB_3^{3+} \rightarrow Ru(NH_3)_6^{3+} + RuB_3^{2+}$ ,<sup>28</sup> and transient redox intermediates like  $O_2^-$  can be generated and their reactions observed.<sup>31</sup> The series of coupled reactions in 23–25 and in 26–28 show that there is an element of generality to the technique. The excited-state couples  $RuB_3^{3+/2+}$  and  $RuB_3^{2+}/+$  can be used catalytically to perturb redox equilibria, and rates can be measured for reactions like  $NPh_3^+ + PQ^+ \rightarrow NPh_3 + PQ^{2+}$ <sup>35</sup> and  $DMA^+ + O_2^- \rightarrow DMA + O_2$ ,<sup>31</sup> which do not involve Ru–bpy couples. The flash photolysis technique has also been used to estimate the  $RuB_3^{3+/2+}$  self-exchange rate.<sup>39</sup> Flash photolysis of solutions containing  $Ru(bpy)_3^{2+}$ ,  $Ru(phen)_3^{2+}$ , and  $Fe(H_2O)_6^{3+}$  results in excitation and quenching of both excited states to give  $Ru(bpy)_3^{3+}$  and  $Ru(phen)_3^{3+}$ , but  $Ru(phen)_3^{3+}$  is formed in slight excess. Following the flash, the equilibration reaction,  $Ru(phen)_3^{3+} + Ru(bpy)_3^{2+} \rightarrow Ru(phen)_3^{2+} + Ru(bpy)_3^{3+}$  ( $k(25^\circ C) = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in 1.0 M  $HClO_4$ ), for which  $K = 1.0$ , is observed directly.<sup>39</sup>

The flash photolysis and quenching experiments allow data to be obtained routinely<sup>40–42</sup> for reactions which occur in the “abnormal” or “inverted” free-energy region (Figure 1D).<sup>43</sup> Figure 1B–D shows the effect of an increasingly favorable free-energy change on the barrier to electron transfer. In Figure 1C the favorable nature of the electron transfer exactly cancels the reorganizational barrier. For such a case, an outer-sphere reaction would occur at the diffusion-controlled limit. According to eq 10a this will occur when  $-\Delta G^\circ_R' = \lambda$ . Reactions for which  $-\Delta G^\circ_R'/\lambda > 1$  are said to occur in the abnormal free-energy region (Figure 1D). From Figure 1D, reactions in this region have clear similarities with excited-state processes, and compared to other electron-transfer reactions, some peculiar properties. The reactant  $\rightarrow$  product surface crossings in Figures 1A and 1B are adiabatic processes; electron transfer by surface crossing in the abnormal region is nonadiabatic. Equation 10a predicts that for highly favored reactions ( $-\Delta G^\circ_R'/\lambda > 1$ ) there should be an inverse relationship between rate constant and driving force and reactions should become slower. This prediction has not been borne out by experiment,<sup>40</sup> and recent theoretical work has suggested that the usual reorganizational barrier to electron transfer can be circumvented by nuclear tunneling through the barrier or to high-energy vibronic levels within the product manifold.<sup>44</sup> In fact, there is both experimental evidence<sup>41,42</sup> and a theoretical

(39) F. R. Keene, R. C. Young, and T. J. Meyer, *J. Am. Chem. Soc.*, **99**, 2468 (1977).

(40) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969); *Israel J. Chem.*, **8**, 259 (1970).

(41) J. Nagle and T. J. Meyer, work in progress.

(42) C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **99**, 241 (1977).

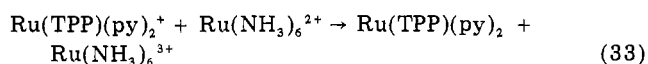
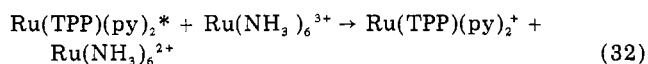
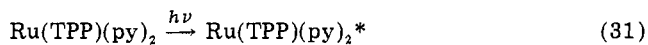
(43) R. A. Marcus, *J. Chem. Phys.*, **43**, 2654 (1965); **52**, 2803 (1970).

(44) (a) R. P. Van Duyne and S. F. Fischer, *Chem. Phys.*, **5**, 183 (1974);

(b) S. Efrima and M. Bixon, *Chem. Phys. Lett.*, **25**, 34 (1974); (c) W. Schmickler, *J. Chem. Soc., Faraday Trans.*, **72**, 307 (1976).

prediction<sup>44a</sup> that some falloff with rate should occur, but the effect is far less than predicted by eq 10a. That electron transfer in this region is not yet well understood is illustrated by recent flash photolysis studies which indicate that outer-sphere reactions like  $\text{RuB}_2(\text{CN})_2^+ + p\text{-CH}_3\text{-NC}_5\text{H}_4\text{OCH}_3 \rightarrow \text{RuB}_2(\text{CN})_2 + p\text{-CH}_3\text{-N}^+\text{C}_5\text{H}_4\text{OCH}_3$  may exceed the diffusion-controlled limit.<sup>41</sup> Using such systems it may be possible to obtain kinetic evidence for long-range electron transfer through intervening solvent molecules for reactions in the abnormal free-energy region.

Most of the applications discussed so far have used  $\text{Ru}(\text{bpy})_3^{2+}$  as the excited state. However, the participation of metal-complex excited states in electron-transfer reactions appears to be a general phenomenon with widespread opportunities for exploitation. Electron-transfer quenching has been shown to occur for a series of CT states ( $[\text{Ru}(\text{trpy})(\text{bpy})(\text{NH}_3)]^{2+}$ , etc.),<sup>45,46</sup> and for f-f ( $\text{Eu}(\text{phen})_3^{3+}$ )<sup>45</sup> and  $\pi\text{-}\pi^*$  ( $\text{Pd}(\text{OEP})$ ; OEP is octaethylporphyrin)<sup>45</sup> excited states. All of these examples have relied on the observation of luminescence as an indication for the existence of an excited state. The use of excited states as electron-transfer reagents may be far more widespread. Recent work has shown that even nonemitting excited states can be quenched at high quencher concentrations (e.g., reaction 31-33 in DMF; TPP is tetraphenylporphine),



and excited-state lifetimes can be estimated by observing product yields as a function of quencher concentration.<sup>47</sup> The full range and extent of excited state

(45) T. J. Meyer, D. G. Whitten, and R. C. Young, *J. Am. Chem. Soc.*, **98**, 286 (1976).

(46) C. T. Lin, W. Boettcher, M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **98**, 6536 (1976).

electron transfer reactivity is probably just beginning to appear.

### Concluding Remarks

Although often discussed separately and treated using different formalisms, charge transfer, thermal electron transfer, and intervalence transfer are obviously conceptually related processes and many of the ideas developed here should apply to all three. For example, in charge transfer in  $\text{Ru}(\text{bpy})_3^{2+}$ ,  $\text{Ru}^{\text{II}}\text{B}_3^{2+} + h\nu \rightarrow \text{Ru}^{\text{III}}(\text{B}_3^-)^{2+*}$ , and in intervalence transfer in an unsymmetrical mixed-valence ion,  $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{pyz})\text{Ru}^{\text{II}}\text{Cl}(\text{bpy})_2]^{4+} + h\nu \rightarrow [(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})\text{Ru}^{\text{III}}\text{Cl}(\text{bpy})_2]^{4+}$ , the electron-acceptor sites, ligand vs. metal, are different, but the processes are obviously similar. In the future it may be possible to explore the interrelationships between the three types of processes in detail to the mutual advantage of all three by using specially designed metal complexes and, where appropriate, new developments in short-time resolution spectroscopies. Hopefully, with continued experimental and theoretical advances, a unified treatment of electron transfer will evolve and perhaps the useful exploitation of metal complex excited states will become a reality.

*The work of my own described here is really that of my collaborators, and they are mentioned in the references cited. I would especially like to mention our collaboration with my colleague David Whitten and his group on much of the excited-state chemistry. This article was written in part while I was on sabbatical leave at The University of Sydney. I wish to acknowledge the hospitality of Professor Hans Freeman and his colleagues in the Department of Chemistry, exceedingly valuable conversations with Dr. Jim Beattie and Professor Noel Hush, and the W. R. Kenan Foundation, the A. P. Sloan Foundation, and the Department of Inorganic Chemistry at Sydney for sabbatical leave support. Financial support for my work on electron transfer has come from the Army Research Office, Durham, the National Science Foundation, and the Materials Research Center of The University of North Carolina.*

(47) R. C. Young, D. G. Whitten, and T. J. Meyer, submitted.

## The Aqueous Solution Chemistry of Methylmercury and Its Complexes

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The importance of methylmercury,  $\text{CH}_3\text{Hg}^{\text{II}}$ , in pollution of the environment by mercury became apparent in the 1960s following the surprising discovery that a large fraction of the mercury in fish was

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methylmercury, even though some of the fish were taken from lakes and rivers into which no methylmercury had been discharged. Subsequent studies of the biological cycle of mercury revealed chemical and microbiological pathways by which  $\text{CH}_3\text{Hg}^{\text{II}}$  can be formed from  $\text{Hg}^{\text{II}}$ .<sup>1-3</sup> The realization that methyl-

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