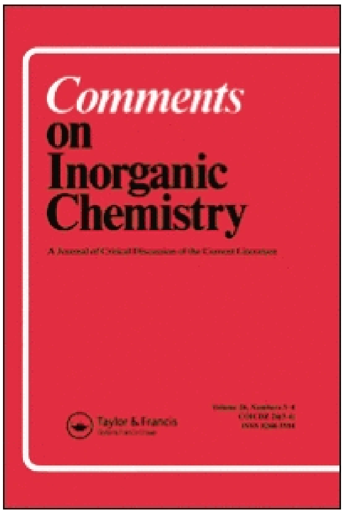

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Intramolecular Electron Transfer Reactions of Ion Pairs: Thermal, Optical, and Photochemical Pathways

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To cite this Article Haim, Albert(1985) 'Intramolecular Electron Transfer Reactions of Ion Pairs: Thermal, Optical, and Photochemical Pathways', Comments on Inorganic Chemistry, 4: 3, 113 — 149

To link to this Article: DOI: 10.1080/02603598508072256

URL: http://dx.doi.org/10.1080/02603598508072256

Intramolecular Electron Transfer Reactions of Ion Pairs: Thermal, Optical, and Photochemical Pathways

It has been recognized for several years that bimolecular electron transfer reactions[1] (as well as other reactions[2]) proceed via a sequence of elementary steps, namely, formation of the precursor complex, intramolecular electron transfer within the precursor complex, and dissociation of the successor complex. For outer-sphere reactions, the precursor and successor complexes are ion pairs or outer-sphere complexes. For inner-sphere reactions, the precursor and successor complexes are binuclear complexes in which a bridging ligand connects the two metal centers. Under conditions where the stability of the precursor complex is low (Q_{IP} or $Q_p << 1$) and the electron transfer step k_{et} is rate determining, experimental kinetic measurements yield second-order rate constants k_{exp} which are equal to the product of the equilibrium constant for the formation of the precursor complex and the rate constant for electron transfer, $k_{exp} = Q_{IP}k_{et}$ or Q_pk_{et}.[3] The overwhelming majority of electron transfer reactions of transition metal complexes—both outer-sphere and inner-sphere reactions—conform to the above trend, and under these circumstances kinetic measurements do not yield direct information about the act of electron transfer itself.

Since the values of k_{et} and its associated activation parameters are crucial to an understanding of the electron transfer process, a great deal of effort has been expended in developing approaches toward obtaining the elementary constants k_{et}. In the present Comment we

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Comments Inorg. Chem.
1985, Vol. 4, No. 3, pp. 113–149
0260-3594/85/0403-0113/$30.00/0

summarize the approaches that have been utilized and the salient mechanistic features that have been uncovered. Only outer-sphere reactions are treated since inner-sphere, intramolecular electron transfer reactions have been reviewed recently.[3,4] Both thermal and photochemical intramolecular electron transfer reactions are considered and the area of optical electron transfer in ion pairs is also reviewed. The trends are discussed on the basis of nuclear (Franck–Condon) and electronic (adiabatic and nonadiabatic electron transfer) factors. Some problems are pointed out and the need for additional work in certain areas is indicated.

SATURATION KINETICS IN THERMAL REACTIONS

The strategy[5] employed in obtaining values of k_{et} (however, see below) for outer-sphere reactions involves the use of transition metal complexes of high and opposite charge. Under these circumstances, substantial ion-pair formation between reactants is obtained at relatively low concentrations and kinetic studies provide values of both Q_{IP} and k_{et}. The first system where the approach was realized involved the reaction between $Co(NH_3)_5OH_2^{3+}$ and $Fe(CN)_6^{4-}$.[5] In view of the success of the approach, systematic studies were undertaken and studies of the $Fe(CN)_6^{4-}$ reduction of complexes of pentaamminecobalt(III) with pyridines or carboxylate anions[6–8] and of the reduction of $Co(NH_3)_5OS(CH_3)_2^{3+}$ by a variety of pyridine complexes of pentacyanoferrate(II)[9] were published. All of these reactions display saturation kinetics, e.g., the functional dependence of the pseudo-first-order rate constant k_{obs} with respect to the concentration $[E]$ of the excess reagent is given by Eq. (1).

$$k_{obs} = \frac{a[E]}{1 + b[E]} \qquad (1)$$

Such functional dependence clearly demonstrates substantial association between the reactants and the proposed mechanism,[5–9] as exemplified for the $Co(NH_3)_5py^{3+}$–$Fe(CN)_6^{4-}$ reaction (py = pyridine) is given by Eqs. (2) and (3).

$$Co(NH_3)_5py^{3+} + Fe(CN)_6^{4-} \xrightleftharpoons{Q_{IP}} Co(NH_3)_5py^{3+}|\,Fe(CN)_6^{4-} \qquad (2)$$

$$\mathrm{Co(NH_3)_5py^{3+} | Fe(CN)_6^{4-}} \xrightarrow{k_{\mathrm{et}}} \text{products } (\mathrm{Co^{II}, Fe^{III}}) \qquad (3)$$

According to this interpretation, $b = Q_{\mathrm{IP}}$ and $a/b = k_{\mathrm{et}}$. However, it must be noted that there is an ambiguity[10] in the mechanistic interpretation of Eq. (1). The functional dependence in Eq. (1) demonstrates that an ion pair is formed but provides no information as to whether the formation of the ion pair precedes the act of electron transfer or electron transfer proceeds via a direct bimolecular reaction between the free ions.[10] The complete mechanism is given as Scheme I. In this interpretation $b = Q_{\mathrm{IP}}$ and $a/b = k_{\mathrm{et}} + k_b/Q_{\mathrm{IP}}$.

Scheme I

$$\begin{tikzcd}
\mathrm{Co(NH_3)_5py^{3+} + Fe(CN)_6^{4-}} \arrow[rr, shift left, "Q_{\mathrm{IP}}"] \arrow[dr, "k_b"'] & & \mathrm{Co(NH_3)_5py^{3+} | Fe(CN)_6^{4-}} \arrow[ll, shift left] \arrow[dl, "k_{\mathrm{et}}"] \\
& \begin{array}{c}\text{products}\\ (\mathrm{Co^{II}, Fe^{III}})\end{array} &
\end{tikzcd}$$

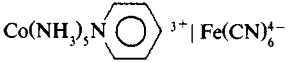
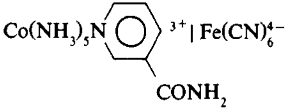
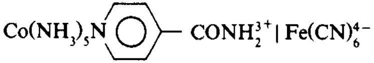
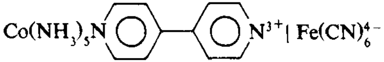
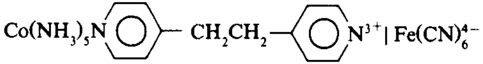
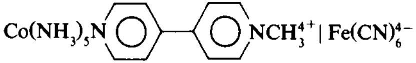
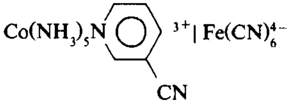
Unfortunately, the experimental information is insufficient to decide whether the k_{et} or the k_b pathway (or a combination of both) consummates the reaction. In the absence of evidence one way or another, we will assume that $k_b = 0$ and thus k_{et} is the effective pathway. This assumption is in keeping with accepted theoretical notions[11] regarding the mechanism of electron transfer. The reactants are *first* brought together and *then* suitable fluctuations in the inner- and outer-coordination shells take place in order to reach the intersection region where electron transfer is obtained under Franck–Condon restrictions.

THERMODYNAMIC AND STRUCTURAL CONSIDERATIONS ABOUT ION PAIRS

Values of Q_{IP} and of the associated thermodynamic parameters for a variety of amminecobalt(III)–cyanoferrate(II) ion pairs are listed in Table I. The values were obtained by kinetic methods.[5–9] Included in Table I are values of the equilibrium constants for ion-pair formation between $\mathrm{Ru(NH_3)_5py^{3+}}$ and $\mathrm{Fe(CN)_6^{4-}}$, $\mathrm{Ru(CN)_6^{4-}}$, or $\mathrm{Os(CN)_6^{4-}}$ obtained by static methods.[12] It will be seen that there is excellent agreement between the kinetic and the static measurements

TABLE I

Equilibrium constants (25°C) and enthalpy and entropy changes for ion-pair association between transition metal complexes (ionic strength 0.10 M)

Ion Pair	Q_{IP}, M^{-1}	ΔH, kcal/mole	ΔS, eu	Reference
$Co(NH_3)_5OH_2^{3+} \mid Fe(CN)_6^{4-}$	1.5×10^3			5
	2.4×10^3	~0	15	6
	2.5×10^3			7
	5.3×10^3			7
	2.3×10^3			7
	2.8×10^3			7
	3.2×10^3			7
	1.3×10^3			7

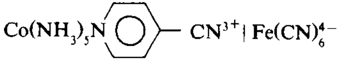
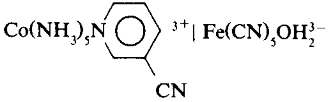
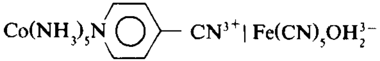
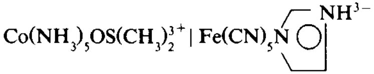
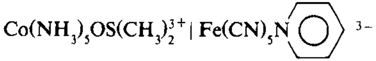
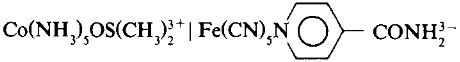
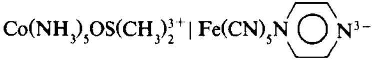
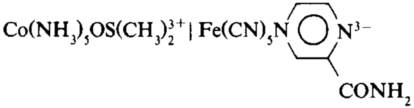
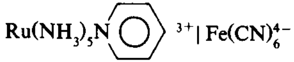
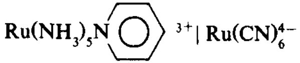
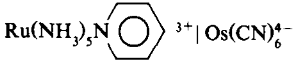
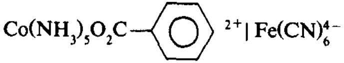
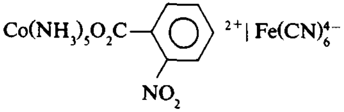
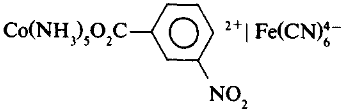
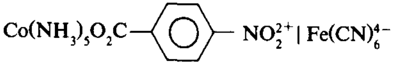
	2.5×10^3			7
	8.0×10^2			a
	6.0×10^2			a
$Co(NH_3)_5OS(CH_3)_2^{3+} \mid Fe(CN)_5NH_3^{3-}$	4.2×10^2	~0	12	9
	4.5×10^2	~0	12	9
	4.9×10^2	~0	12	9
	6.0×10^2	~0	12	9
	3.6×10^2	~0	12	9
	5.6×10^2	~0	13	9

TABLE I
(Continued)

	2.5×10^3			12
	2.7×10^3			12
	2.9×10^3			12
$Co(NH_3)_5O_2CCH_3^{2+} \| Fe(CN)_6^{4-}$	3.0×10^2	~0	11	8
	2.4×10^2	~0	11	8
	2.8×10^2	~0	11	8
	1.5×10^2	~0	10	8
	2.9×10^2	~0	11	8

(a) A. P. Szecsy and A. Haim, J. Am. Chem. Soc. **104**, 3063 (1982).

(compare the Q_{IP} values 2.4 × 10^3 M^{-1} and 2.5 × 10^3 M^{-1} for the ion pairs $Co(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$ and $Ru(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$, respectively, at 0.10 M ionic strength).

Values of Q_{IP} for $3+|4-$ ion pairs fall in the range (1.3–5.3) × 10^3 M^{-1}, whereas for $3+|3-$ ion pairs the observed range is (3.6–8.0) × 10^2 M^{-1} and for $2+|4-$ ion pairs the range is (1.5–3.0) × 10^2 M^{-1}. The stabilities of the ion pairs increase with an increase in the charge product of the constituent ions, as expected for an association driven by electrostatic interactions. Estimates of Q_{IP} can be obtained by utilization of the Fuoss–Eigen formulation, Eqs. (4)–(6).[6]

$$Q_{IP} = \frac{4\Pi N d^3}{3000} \exp(-U(d)/RT) \qquad (4)$$

$$U(d) = \frac{z_+ z_- e^2}{D_s d(1 + \kappa d)} \qquad (5)$$

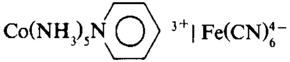
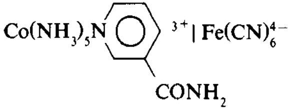
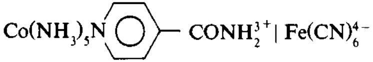
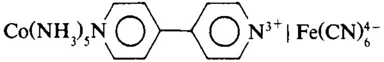
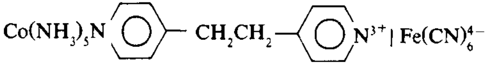
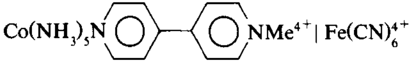
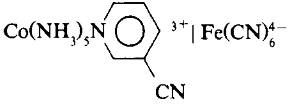
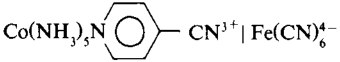
$$\kappa = (8\Pi N e^2 \mu / 1000 D_s RT)^{1/2} \qquad (6)$$

Definitions: N, Avogadro's number; d, distance of closest approach; R, gas constant; T, absolute temperature; z_+ and z_-, charges of cation and anion, respectively; e, electronic charge; D_s, static dielectric constant of solvent; μ, ionic strength. Introducing the numerical values of the constants for water at 25 °C, Eq. (4) becomes Eq. (7). This equation is applicable to spherical ions.

$$Q_{IP} = 2.523 \times 10^{21}\, d^3 \exp(-7.131 \times 10^{-8}\, z_+ z_- / d(1 + 3.285 \times 10^7\, d\mu^{1/2})) \qquad (7)$$

For nonspherical ions, the appropriate value of d is obtained by adding the radii equivalent to the spheres of equal volume.[13] Values of the radii for the anionic and cationic complexes listed in Table II fall in the ranges (4.5–5.0) × 10^{-8} cm and (3.3–4.3) × 10^{-8} cm, respectively. Taking middle range values of 4.7 × 10^{-8} cm and 3.8 × 10^{-8} cm for anion and cation, respectively, we calculate values of Q_{IP} equal to 3.2 × 10^2 $M^{-1}(-4|+3)$, 85 M^{-1} $(-3|+3)$ and 55 $M^{-1}(-4|+2)$. It will be seen that the measured values are consistently

TABLE II
Rate constants (25°C) and enthalpy and entropies of activation for intramolecular electron transfer in ion pairs (ionic strength 0.10 M)

Ion Pair	k_{et}, s^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	Reference
	1.5×10^{-2}			6
	5.0×10^{-2}			7
	3.6×10^{-2}			7
	2.4×10^{-2}			7
	1.0×10^{-2}			7
	4.7×10^{-2}			7
	3.5×10^{-1}			7
	1.5×10^{-1}			7

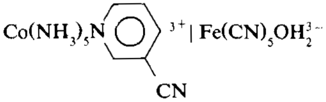
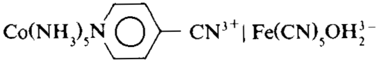
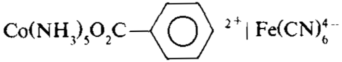
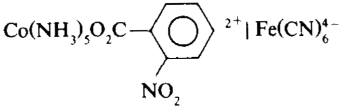
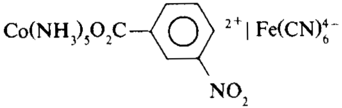
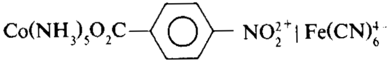
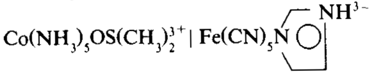
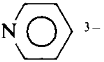
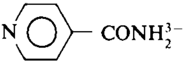
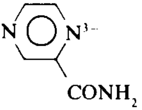
	7.1×10^{-1}			a
	4.6×10^{-1}			a
$Co(NH_3)_5O_2CCH_3^{3+} \mid Fe(CN)_6^{4-}$	3.7×10^{-4}			8
	6.2×10^{-4}			8
	2.8×10^{-3}			8
	9.1×10^{-4}			8
	7.6×10^{-4}			8
$Co(NH_3)_5OS(CH_3)_2^{3+} \mid Fe(CN)_5NH_3^{3-}$	1.3	22.6	17	9
	2.6	22.1	17	9

TABLE II
(Continued)

$Co(NH_3)_5OS(CH_3)_2^{3+}$ | $Fe(CN)_5N$ 	1.5×10^{-1}	24.0	18	9
$Co(NH_3)_5OS(CH_3)_2^{3+}$ | $Fe(CN)_5N$ 	5.0×10^{-2}	24.5	17	9
$Co(NH_3)_5OS(CH_3)_2^{3+}$ | $Fe(CN)_5N$ 	8.9×10^{-3}	26.0	18	9
$Co(NH_3)_5OS(CH_3)_2^{3+}$ | $Fe(CH)_5N$ 	4.7×10^{-3}	26.2	18	9

(a) A. P. Szecsy and A. Haim, J. Am. Chem. Soc. **104**, 3063 (1982).

higher (by factors of 4 to 10) than the values calculated from Eq. (7). It has been suggested[6,9,14] that the increased stability of the ion pairs compared with that expected on the basis of the simple electrostatic model may be associated with specific hydrogen-bonding interactions within the ion pairs. In fact, there is strong evidence for the existence of hydrogen bonds between ammonia nitrogen and cyanide nitrogen in salts of cationic ammine complexes and anionic cyanide complexes.[15] Therefore, the H-bonding hypothesis for the ion pairs in solution appears to be quite reasonable.

From Table I it will be seen that ion-pair formation is an entropy driven process, with the enthalpy term being near zero. The increase in entropy upon ion-pair association is expected on the basis of the decrease in solvation attending charge neutralization. The entropy change, calculated by differentiating the free energy with respect to temperature,[13] is given for the Fuoss–Eigen formulation by Eqs. (8) and (9).

$$\Delta S^0_{\mathrm{IP}} = R \ln\left(\frac{4\Pi N d^3}{3000}\right) - \frac{\partial U(d)}{\partial T} \tag{8}$$

$$\frac{\partial U(d)}{\partial T} = \frac{U(d)}{2T(1+\kappa d)}\left(\frac{2\,\partial \ln D_s}{\partial \ln T} + \kappa d \frac{\partial \ln D_s}{\partial \ln T} + \kappa d\right) \tag{9}$$

For water at 25 °C $\delta \ln D_s / \delta \ln T = -1.368$ and Eq. (8) becomes Eq. (10). Values

$$\Delta S^0_{\mathrm{IP}} = 1.99 \ln 2.523 \times 10^{21}\, d^3$$

$$+ \frac{7.095 \times 10^{-8} z_+ z_-}{d(1 + 3.285 \times 10^7\, d\mu^{1/2})^2}(-2.736 - 7.779 \times 10^7\, d\mu^{1/2}) \tag{10}$$

of ΔS^0_{IP} for $-4|+3, -3|+3$, and $-4|+2$ ion pairs calculated from Eq. (10) are 14.5, 11.1 and 10.0 eu, respectively. The calculated values are in excellent agreement with the observed values (15, 12 and 11 eu for $-4|+3, -3|+3$, and $-4|+2$ ion pairs, respectively).

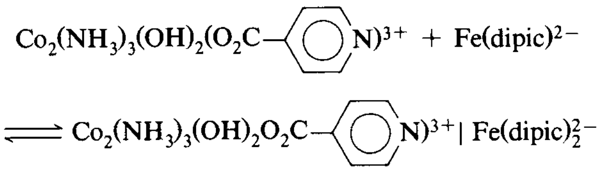
The thermodynamic parameters for ion-pair formation estimated by utilization of the Fuoss–Eigen formulation (Eqs. (7) and (10)) can be combined with thermodynamic measurements for the free ions in order to obtain the thermodynamic changes associated with the intramolecular electron transfer within the ion pairs. The calculation is carried out by means of the thermodynamic cycle presented in Scheme II (X = $G, S,$ or H).[12,16] ΔG_1^{IP} (from the measured value of $Q_{\mathrm{IP}} = 2.5 \times 10^3\ \mathrm{M}^{-1}$) and ΔG_2^{IP} (estimated from Eq. (7) with d = 8.9×10^{-8} cm and with an empirical[12] correction) are -4.60 and -2.54.

Scheme II

$$\begin{tikzcd}
\mathrm{Ru(NH_3)_5py^{3+}} + \mathrm{Fe(CN)_6^{4-}} \arrow[r, "\Delta X^0_{12}"] \arrow[d, "\Delta X_1^{\mathrm{IP}}"] & \mathrm{Ru(NH_3)_5py^{2+}} + \mathrm{Fe(CN)_6^{3-}} \arrow[d, "\Delta X_2^{\mathrm{IP}}"] \\
\mathrm{Ru(NH_3)_5py^{3+}} | \mathrm{Fe(CN)_6^{4-}} \arrow[r, "\Delta X^0_{\mathrm{et}}"] & \mathrm{Ru(NH_3)_5py^{2+}} | \mathrm{Fe(CN)_6^{3-}}
\end{tikzcd}$$

kcal/mole, respectively. ΔG^0_{12} (from E^0 values) is 2.88 kcal/mole. Therefore ΔG^0_{et} = 4.94 kcal/mole. It will be seen that the stability difference between the ion pairs (ΔG^0_{et} = 4.94 kcal/mole, $Q_{\mathrm{et}} = 2.33 \times 10^{-4}$) is larger than that between the free ions (ΔG^0_{12} = 2.88 kcal/mole, $Q_{12} = 7.72 \times 10^{-3}$). To be sure, this is a consequence of the higher stability of the $-4|+3$ ion pair as compared to the $-3|+2$ ion pair. Values of ΔS_1^{IP} and ΔS_2^{IP} (estimated from Eq. (10) with $d = 8.9 \times 10^{-8}$ cm) are 13.9 and 7.5 eu. ΔS^0_{12} (calculated from the reaction entropies[17] for the $\mathrm{Ru(NH_3)_5py^{3+/2+}}$ and $\mathrm{Fe(CN)_6^{3-/4-}}$ couples, 17 and 23 eu, respectively) is 40 eu.[18] Therefore, ΔS^0_{et} = 34 eu. It will be seen that the entropy change associated with the intramolecular electron transfer within the ion pair is a substantially positive quantity. This result is readily accommodated on the basis of the important charge redistribution ($-4|+3$ to $-3|+2$) attending the internal electron transfer and the concomitant desolvation. It is noteworthy that the entropy change associated with charge redistribution within the ion pair is substantially larger than that for charge neutralization in the formation of the ion pairs from the free ions and is almost equal to the entropy change for electron transfer between the free ions. Finally, from the ΔG and ΔS values, we calculate $\Delta H_1^{\mathrm{IP}} = -0.46$ kcal/mole, $\Delta H_2^{\mathrm{IP}} = -0.30$ kcal/mole, ΔH^0_{12} = 14.9 kcal/mole, and ΔH^0_{et} = 15.1 kcal/mole. As noted earlier, ion-pair formation is essentially a thermoneutral process whereas the electron transfer process, whether between the free ions or within the ion pair, is a substantially endothermic process. The endothermicity is, to be sure, related to the desolvation attending electron transfer from the -4 ion to the $+3$ ion.

Although the trends in the thermodynamic changes associated with ion-pair formation noted above appear to be general,[19] exceptions have been reported.[20] Thus, the enthalpy and entropy changes for ion-pair formation in Eq. (11) (dipic = dipicolinate) are -9 kcal/mole and -22 eu, respectively. The negative entropy change was taken[20] to indicate a highly ordered situation, and an ion-pair structure involving stacked aromatic rings was invoked.



(11)

The postulate of a stacked structure for the ion pair in Eq. (11) bears on the general question regarding the approach of two ions, one of which is spherical (or almost so) and the other asymmetric. In this case, a variety of relative orientations between the ions leads to various structures. There is no direct evidence regarding the structures of the ion pairs listed in Table I, but any indirect evidence bearing on this issue suggests that the most stable structure involves closest approach between the cyanide groups of the anion and the ammonia groups of the cation, as expected on the basis of electrostatic and hydrogen-bonding considerations. Perhaps the most direct evidence, although negative, pertains to the spectra of the $Fe(CN)_6^{4-}$–$Co(NH_3)_5L^{n+}$ (L = a pyridine) ion pairs. The spectra were obtained by mixing rapidly and at low temperatures the cobalt(III) complex with an excess of $Fe(CN)_6^{4-}$.[7] The ion pairs $Co(NH_3)py^{3+}|Fe(CN)_6^{4-}$ and $Co(NH_3)_5(N\text{-}Mebpy)^{4+}|Fe(CN)_6^{4-}$ (N-Mebpy is N-methyl-4,4′-bipyridinium) exhibit maxima at 445 nm (molar absorbance 160 M^{-1} cm^{-1}) and 470 nm (molar absorbance 240 M^{-1} cm^{-1}).[7] It was argued that had the $Fe(CN)_6^{4-}$ approached $Co(NH_3)_5(N\text{-}Mebpy)^{4+}$ on the side of the heterocyclic ligand, the expected maximum absorption would have been near 530 nm, the known[21-23] maximum for the charge transfer complex of $Fe(CN)_6^{4-}$ with N,N-dimethyl-4,4′-bipyridinium ion. In view of the difference between observed and expected maxima and the similarity of the spectra for the ion pairs of the pyridine and the N-methyl-4,4′-bipyridinium cobalt(III) complexes with $Fe(CN)_6^{4-}$, it was suggested[7] that the orientation of the ion pairs involves closest approach on the side of the ammonia ligands and the color of the ion pairs was assigned to a metal (Fe) to metal (Co) charge transfer band.[7] Some support for this assignment comes from a comparison of the measured rate constant ratio for electron transfer within the ion pairs $Co(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$ and $Co(NH_3)_5(N\text{-}Mebpy)^{4+}|Fe(CN)_6^{4-}$ with the value calculated from the optical transitions. The pertinent relationships between thermal electron transfer and optical electron transfer[24–26] are given by Eqs. (12) and (13)

$$k_{et} = \kappa \nu_n \exp(-\Delta G^*/RT) \tag{12}$$

$$\Delta G^* = E_{op}^2/4(E_{op} - E_0) \tag{13}$$

where ΔG^* is the reorganization free energy for thermal electron transfer, E_{op} is the energy of the optical transition, E_0 is the free energy[27] difference between the two oxidation state isomers of the ion pair, ν_n is a nuclear vibration frequency[11] taken to be $\sim 6 \times 10^{12}$ s^{-1},[25] and κ is the electronic factor which is equal to 1.0 for adiabatic reactions. The observed ratio of k_{et} for $Co(NH_3)_5(N\text{-}Mepby)^{4+}|Fe(CN)_6^{4-}$ to k_{et} for $Co(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$ is 3.1 and the calculated ratio from Eqs. (12) and (13)[27] (assuming that the electronic factor is equal to 1.0) is 4.2. The reasonable agreement between measured and calculated ratio provides support for the assignment of the electronic transitions for the ion pairs to a metal to metal charge transfer process and, thus, for an ion-pair structure whereby $Fe(CN)_6^{4-}$ approaches the ammonia side of the cobalt complex.

Evidence for approach between $Fe(CN)_6^{4-}$ and the ammine side of $Ru(NH_3)_5L^{3+}$ (L is a pyridine derivative) has also been advanced.[12] The energies of the intervalence transfer bands in the ion pairs $Ru(NH_3)_5L^{3+}|Fe(CN)_6^{4-}$ are not affected by the presence of bulky substituents on L.[12] Since intervalence bands are known[28] to vary appreciably with the distance between the centers of charge transfer, it was inferred[12] that the optical interaction in the ion pairs $Ru(NH_3)_5L^{3+}|Fe(CN)_6^{4-}$ took place over the same distance and thus that the ammonia ligands, rather than the pyridine ligand, provided the path for approach to $Fe(CN)_6^{4-}$.

FREE ENERGY RELATIONSHIPS

Most tests of Marcus' relationship for a series of related cross-reactions involve comparisons of second-order rate constants.[29] The reduction of $Co(NH_3)_5OS(CH_3)_2^{3+}$ by a series of $Fe(CN)_5L^{3-}$ complexes was shown to involve ion-pair formation between the reactants (see Table I) and values of k_{et} for reaction (14) were extracted from the kinetic data.[9]

$$Co(NH_3)_5OS(CH_3)_2^{3+} \mid Fe(CN)_5L^{3-} \xrightarrow{k_{et}} Co(NH_3)_5OS(CH_3)_2^{2+} \mid Fe(CN)_5L^{2-} \qquad (14)$$

The data, listed in Table II, provide an opportunity to test the relationship between k_{et} and the standard free energy change for a series of reactions that proceed in the intramolecular regime. The pertinent relationships are given in Eqs. (15) and (16).[11,13,26,30]

$$k_{et} = \kappa\nu_n e^{-\Delta G_{12}^*/RT} \qquad (15)$$

$$\Delta G_{12}^* = \frac{\Delta G_{11}^* + \Delta G_{22}^* + \Delta G_{et}^0}{2} + \frac{(\Delta G_{et}^0)^2}{8(\Delta G_{11}^* + \Delta G_{22}^*)} \qquad (16)$$

The ΔG_{ij}^* terms are the reorganization free energies for intramolecular electron transfer in the ion pairs for the cross-reactions (ΔG_{12}^*) and for the exchange reactions (ΔG_{11}^* and ΔG_{22}^*). ΔG_{et}^0 is the standard free energy change for reaction (14). Provided that the second term on the right-hand side of Eq. (16) is small and that the reorganization free energies for the $Fe(CN)_5L^{3-}$–$Fe(CN)_5L^{2-}$ exchanges are insensitive to the identity of L, a plot of $\ln k_{et}$ vs ΔE_{et}^0 for reaction (14) is predicted to be linear. Since $\Delta E_{et}^0 = E_1^0 - E_2^0 - 0.059$ (E_1^0 and E_2^0 are the reduction potentials of the Co(III)–Co(II) and Fe(III)–Fe(II) couples and -0.059 is the difference in the ΔE^0 values for the free ions and for the ion pairs; note that the $+3|-3$ ion pair—the reactant—is more stable than the $+2|-2$ product ion pair), it follows that $\ln k_{et}$ should be a linear function of E_2^0 with slope $-0.5/RT$ or -19.4. The experimental results,[9] displayed in Fig. 1, show that a linear relationship is obeyed with slope -21.6, in excellent agreement with the theoretical value of -19.4. Evidently, rate constants for intramolecular electron transfer in a series of related cross-reactions, just as second-order rate constants, vary with the square root of the corresponding equilibrium constants.

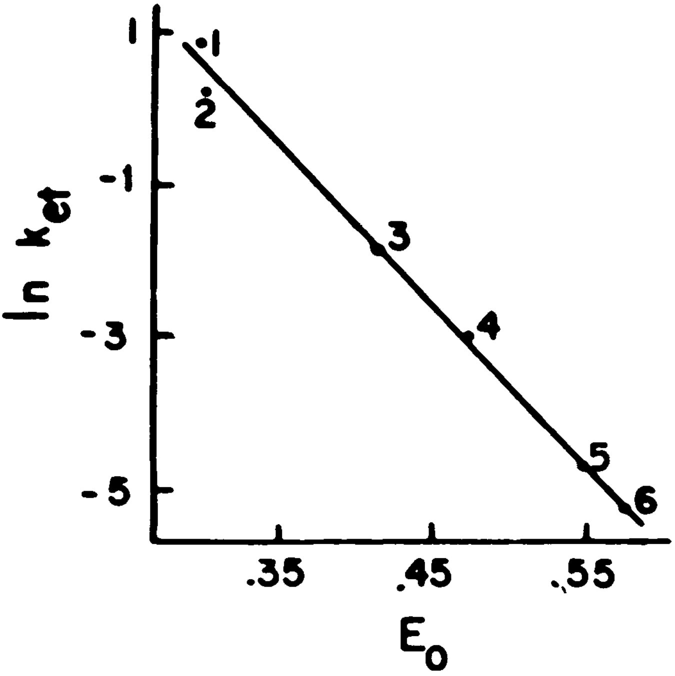


FIGURE 1 Plot of $\ln k_{et}$ vs E^0 for intramolecular electron transfer in $Co(NH_3)_5OS(CH_3)_2^{3+}$ $Fe(CN)_5L^{3-}$. k_{et} in s^{-1}, E^0 in volts vs NHE, 25 °C, ionic strength 0.10 M. 1, imidazole; 2, ammonia; 3, pyridine; 4, pyridine-4-carboxamide; 5, pyrazine; 6, pyrazine-2-carboxamide. Adapted from Ref. 9.

NUCLEAR AND ELECTRONIC FACTORS

According to current concepts in electron transfer theory,[11] the rate of electron transfer is governed by two terms: a nuclear and an electronic factor. The precursor and successor complexes have different sizes and charge distributions. Consequently, their most stable configurations will occur in different regions of nuclear configuration space. The intramolecular electron transfer process that transforms the precursor complex into its electronic isomer, the successor complex, corresponds to the crossing of the system, as depicted in Fig. 2, from one surface to the other. The nuclear factor (Franck–Condon condition) corresponds to the changes in the positions of the nuclei—

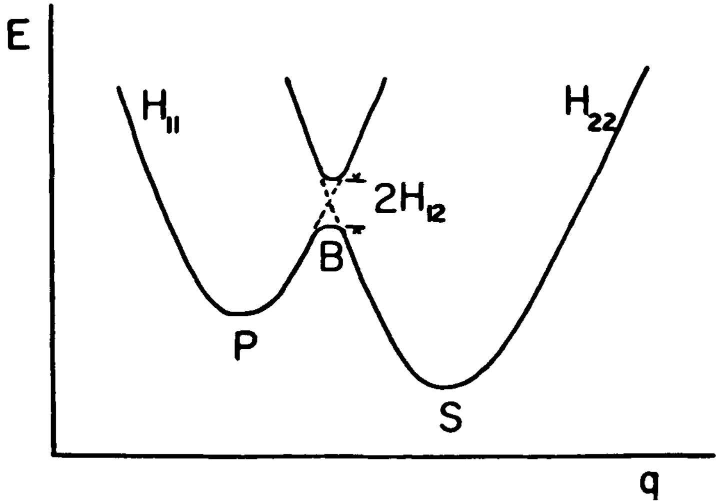


FIGURE 2 Schematic representation of zero-order and first-order surfaces for electron transfer. E = energy; q = nuclear coordinate; P = precursor ion pair; B = transition state for electron transfer within ion pair; S = successor ion pair; H_{11} = precursor ion pair surface; H_{22} successor complex surface; H_{12} = splitting at intersection region. Adapted from Ref. 4.

both inner-sphere (metal to ligand bond distances) and outer-sphere (orientation of solvent dipoles)—necessary to bring the precursor complex from its equilibrium configuration to that appropriate to the intersection region. In the latter configuration, the energies of the system before and after electron transfer are equal. The electronic factor corresponds to the probability of electron transfer once the intersection region has been reached and depends on the magnitude of H_{12}, the electronic coupling between metal centers.[31] If H_{12} is not too small (>0.5 kcal), every time that the required nuclear configuration is reached the electron is transferred, e.g., the system follows the path given by the lower surface and the process is referred to as adiabatic electron transfer. Alternatively, if H_{12} is too small, the system reaches the intersection region with enough momentum to jump to the upper surface and only occasionally is electron transfer consummated. This is referred to as nonadiabatic electron transfer.

One of the goals of measuring electron transfer reactions in the intramolecular mode is to assess the adiabaticity of the reactions. Unlike bimolecular electron transfer rate constants, rate constants for intramolecular electron transfer and their corresponding enthalpies and entropies of activation do not include the kinetic and thermodynamic parameters for assembling the reactants. Therefore, such rate constants are a measure of the intrinsic act of electron transfer and provide evidence about both nuclear and electronic factors. For a series of related reactions where the nuclear factors are expected to remain constant, the variations in reactivity, if any, can be utilized to assess adiabaticity. The observed trends for the reactions listed in Table II indicate that these reactions are proceeding at or near the adiabatic limit. Consider first the $Co(NH_3)_5OS(CH_3)_2^{3+}|Fe(CN)_5L^{3-}$ system. The excellent agreement between the dependence of the rate upon the driving force and the predictions based on Eqs. (15) and (16) show that κ is constant for all L. However, it cannot be ascertained whether κ is constant at 1 (adiabatic reaction) or at a value smaller than 1 (nonadiabatic electron transfer). Some information bearing on this issue comes from a consideration of the entropies of activation. The rate constant for intramolecular electron transfer is given by Eqs. (17) and (18) in the semiclassical[1,11] and transition state formalisms, respectively.[31]

$$k_{et} = \kappa \nu_n \exp(\Delta S^*/R) \exp(\Delta H^*/RT) \qquad (17)$$

$$k_{et} = (kT/h) \exp(\Delta S^\ddagger/R) \exp(\Delta H^\ddagger/RT) \qquad (18)$$

Since $kT/h \sim \nu_n$ and $\Delta H^* = \Delta H^\ddagger$, it follows that $\kappa \exp(\Delta S^*/R) = \exp(\Delta S^\ddagger/R)$. For nonadiabatic reactions $\kappa < 1$ and, if $\Delta S^* = 0$, $\Delta S^\ddagger$, the measured entropy of activation on the basis of Eq. (18), is negative. It is generally assumed that ΔS^* is near zero and therefore negative values of $\Delta S^\ddagger$ are taken as diagnostics of nonadiabaticity. However, before $\Delta S^\ddagger$ can be utilized to assess adiabaticity, a correction for the entropic driving force must be made.[17] The pertinent relation is given by

$$\Delta S^* = \Delta S^*_{int} + 0.5\Delta S^0 \qquad (19)$$

Eq. (19), where ΔS^*_{int} is the intrinsic reorganization entropy and ΔS^0 is the standard entropy change for the intramolecular electron transfer reaction. Because of the substantial desolvation attending electron transfer from anion to cation in an ion pair of the type $Co(NH_3)_5OS(CH_3)_2^{3+}|Fe(CN)_5L^{3-}$ (see above), ΔS^0 is a highly positive quantity estimated[17] at ~40 eu. On the basis of the dielectric continuum model[17] it is predicted that $\Delta S^*_{\text{int}} \sim 0$ and therefore, $\Delta S^* \sim 20$ eu. The measured[9] values of ΔS^* for the intramolecular electron transfer reactions of the $Co(NH_3)_5OS(CH_3)_2^{3+} \mid Fe(CN)_5L^{3+}$ ion pairs fall in the 17–18 eu range, in remarkable agreement with the 20 eu value estimated for ΔS^*. Therefore, we infer that $\kappa \sim 1$ and electron transfer takes place in the adiabatic regime.

Since the coupling between metal centers (H_{12} in Fig. 2) is a sensitive function of distance and orbital symmetry, the insensitivity[32] of k_{et} to the identity of L in the intramolecular electron transfer reactions of the $Co(NH_3)_5L^{n+} \mid Fe(CN)_6^{4-}$ ion pairs ($n = 2$, L is a carboxylate ligand; $n = 3$, L is a pyridine ligand) has been rationalized[8] on the basis of ion-pair contacts involving the ammonia sides of the cobalt(III) complexes rather than the sides with the unique ligand L. Again, the relative constancy of k_{et} implies a fairly constant κ, but it cannot be ascertained whether $\kappa \sim 1$ or $\kappa < 1$. Additional information on this question comes from a consideration of the rate comparisons presented in Table III.[8] The first-order rate constants for reductions by $Ru(NH_3)_6^{2+}$ were calculated as $k_{\text{et}} = k_{\text{obs}}/Q_{\text{IP}}$ from the measured (k_{obs}) second-order rate constants[6,33] and the ion-pair formation constants calculated by utilization of Eqs. (4)–(6). It will be seen (column 4 of Table III) that the ratios of the rate constants for internal electron transfer in $Ru(NH_3)_6^{2+}$ and $Fe(CN)_6^{4-}$ reactions are independent of the nature of the oxidant, as anticipated for cross-reactions that obey Marcus' relationship. The ratios can be calculated from the known reduction potentials and self-exchange rate constants for the $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+/2+}$ couples.[6,34,35] It is noteworthy that calculated (column 5) and observed (column 4) ratios are in

TABLE III
Comparison of rate constants (25°C) for reduction of Co(III) and Ru(III) complexes by $(Fe(CN)_6^{4-}$ and $Ru(NH_3)_6^{2+}$

Oxidant	k_{Fe}, s^{-1}	k_{Ru}, s^{-1}	$k_{\text{Ru}}/k_{\text{Fe}}$ Observed	$k_{\text{Ru}}/k_{\text{Fe}}$ Calculated
$Co(NH_3)_5O_2CCH_3^{2+}$	3.7×10^{-4} [a]	0.10[b]	2.8×10^2	2.2×10^2
$Co(NH_3)_5py^{3+}$	1.5×10^{-2} [c]	6.56[b]	4.4×10^2	1.7×10^2
$Ru(NH_3)_5py^{3+}$	9.7×10^3 [c]	4.5×10^6 [c]	4.6×10^2	1.7×10^2

(a) Reference 8.
(b) F.-R. Fan and E. S. Gould, J. Am Chem. Soc. **13**, 2647 (1974).
(c) Reference 7.

excellent agreement for oxidants that are σ electron acceptors (Co(III) complexes) as well as for $Ru(NH_3)_5py^{3+}$, a Π electron acceptor. The agreement for such a variety of systems indicates that the values of κ are the same for all these systems and, barring some fortuitous coincidence, that $\kappa = 1$ for all the systems, e.g., the electron transfer is adiabatic.

OPTICAL ELECTRON TRANSFER IN ION PAIRS

Metal to metal charge transfer bands have been observed in the following ion pairs: $Ru(NH_3)_6^{3+} \mid Fe(CN)_5L^{3-}$ (L is a substituted pyridine),[36] $Ru(NH_3)_5L^{3+} \mid M(CN)_6^{4-}$ (L is a substituted pyridine, M is Fe, Ru, Os),[12] $Co(NH_3)_6^{3+} \mid Ru(CN)_6^{4-}$ (in dimethylsulfoxide),[37] $CoA^{3+} \mid Fe(CN)_6^{4-}$ (A is ethylenediamine or sepulchrate),[38] and $[Eu\subset 2.2.1]^{3+} \mid M(CN)_6^{4-}$ (M is Fe, Ru, Os; $\subset$2.2.1. is 4,7,13,16,21-pentaoxo-1,10-diazabicyclo[8.8.5.]tricosane).[39] The wavelengths for the absorption maxima (molar absorbance) of selected ion pairs are listed in Table IV. It will be seen that for a given $M^{III}(NH_3)_5L^{3+}$ complex, the wavelength decreases with decreasing reducing power of the $M^{II}(CN)_5L^{n-}$ complex, and that, for a given $M^{II}(CN)_5L^{n-}$ complex, the wavelength increases with increasing oxidizing power of the $M^{III}(NH_3)_5L^{3+}$ complex. This is the expected trend for a metal to metal charge transfer band associated with an electron donor acceptor interaction, e.g., $E_{op} = I - A + C$, where E_{op} is the energy of the optical charge transfer transition, I is the ionization potential of the donor, A is the electron affinity of the acceptor, and C is a coulombic term.[36] An alternate treatment of the optical transitions is based on Eq. (13).[24] If E^0 is small compared to E_{op}, Eq. (20) is obeyed.[24]

$$E_{op} = 4\Delta G^* + E_0 \tag{20}$$

Although E_0 is really a free energy,[27] values of E_0 were taken[12] to be equal to ΔH^0_{et}, the enthalpy change associated with internal electron transfer in the ion pair (see Scheme II). Values of ΔH^0_{et} were estimated for a series of $Ru(NH_3)_5L^{3+} \mid M(CN)_6^{4-}$ ion pairs (L is a nitrogen heterocycle; M is Fe, Ru, or Os) under the assumption that ΔS^0_{et} is constant along the series, and plots of E_{op} vs ΔH^0_{et} were found

TABLE IV

Absorption maxima for metal to metal charge transfer bands (molar absorbances) of ion pairs, reduction potentials of acceptor and donor ions, and rate constants for intramolecular electron transfer

Ion Pair	λ_{max}, nm(A, M^{-1} cm^{-1})	$E^0_{acceptor}$	E^0_{donor}	k_{et}, s^{-1}	Reference
$Ru(NH_3)_6^{3+}$|$Fe(CN)_6^{4-}$	714[a]	0.05	0.43		b
$Ru(NH_3)_6^{3+}$|$Ru(CN)_6^{4-}$	549[a]	0.05	0.94		36
$Ru(NH_3)_6^{3+}$|$Fe(CN)_5py^{3-}$	725[a]	0.05	0.48		36
$Ru(NH_3)_5py^{3+}$|$Fe(CN)_6^{4-}$	910 (33)	0.31	0.43	1×10^6	12
$Ru(NH_3)_5py^{3+}$|$Ru(CN)_6^{4-}$	643 (38)	0.31	0.94	7×10^{-1}	12
$Co(NH_3)_6^{3+}$|$Fe(CN)_6^{4-}$	440 (300)	$\sim$0	0.43	2×10^{-2}	38
$Co(NH_3)_6^{3+}$|$Ru(CN)_6^{4-}$	360 (580)[c]	$\sim$0	0.94	1×10^{-8}	37
$Co(en)_3^{3+}$|$Fe(CN)_6^{4-}$	430 (105)	−0.16	0.43	1×10^{-4}	38
$Cosep^{3+}$|$Fe(CN)_6^{4-}$	430 (106)	−0.30	0.43	7×10^{-5}	38
$Eu{\subset}2.2.1^{3+}$|$Fe(CN)_6^{4-}$	530 (110)	−0.18	0.43	6×10^{-2}	39
$Eu{\subset}2.2.1^{3+}$|$Ru(CN)_6^{4-}$	434 (120)	−0.18	0.94	9×10^{-9}	39

(a) From solids.

(b) J. C. Curtis and T. J. Meyer, J. Am. Chem. Soc. **100**, 6284 (1978).

(c) In dimethysulfoxide.

to be linear (see Fig. 3) with slopes 1.08 ± 0.17, 1.23 ± 0.33, and 0.94 ± 0.26 for Fe, Ru, and Os, respectively,[12] in excellent agreement with the predictions of Eq. (20). A similar trend holds for the salts $[Ru(NH_3)_6]$ $[Fe(CN)_5L]$ (L is CO, $(CH_3)_2SO$, or a nitrogen heterocycle).[36] Since values of ΔH^0_{et} or ΔG^0_{et} are not available for the internal electron transfer in the solid state, E_{op} was plotted vs ΔG^0_{12}, the free energy change associated with the electron transfer reaction of the free ions in solution.[36] A linear relation of slope 1.39 ± 0.09 was obtained (see Fig. 4), in fair agreement with the prediction based on Eq. (20). Although the slopes of the lines in Fig. 3 are in reasonably good agreement with Eq. (20), it was thought[12] that there were some problems with the intercepts which have the values 13.5 ± 2, 18.4 ± 4, and 18.6 ± 5 kcal/mole for Fe, Ru, and Os, respectively. Consider the $Ru(NH_3)_5L^{3+}$ | $Fe(CN)_6^{4-}$ ion pairs. The calculated value of the intercept is $(\lambda_{11} + \lambda_{22})/2$, where λ_{11} and λ_{22} are the reorganization terms for the ruthenium and iron couples, respectively. Each of the terms is made up of an inner- and an outer-shell contribution. The inner-shell contributions for ruthenium[13] and iron[12] are 4.0 and 1.4 kcal/mole, respectively. The outer-shell contributions, calculated from Eq. (21), are 21 and 20 kcal/mole, respectively.

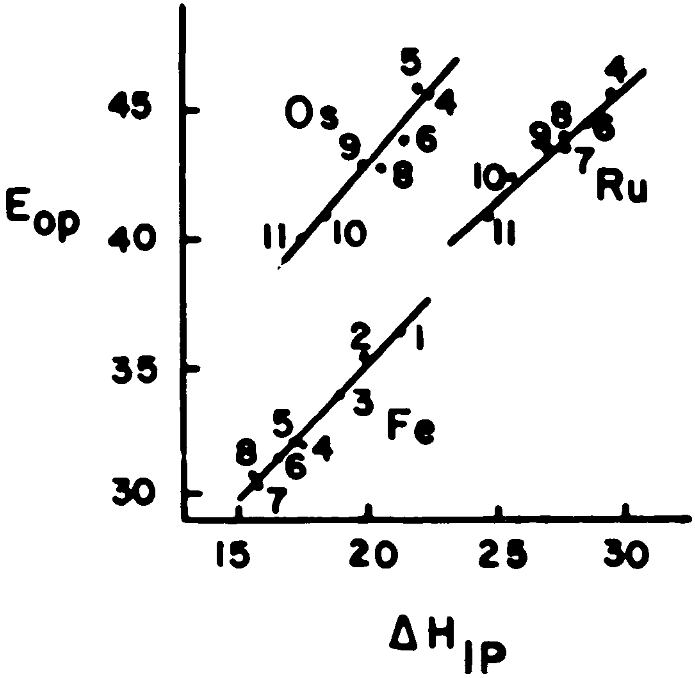


FIGURE 3 E_{op} vs ΔH^0_{IP} for ion pairs $Ru(NH_3)_5L^{3+}|M(CN)_6^{4-}$ (M = Fe, Ru, Os). E_{op}, energy of intervalence transfer band, kcal/mole; ΔH^0_{IP}, enthalpy change for internal electron transfer in the ion pair, kcal/mole. 1, imidazole; 2, 2, 5-dimethylpyrazole; 3; pyrazole; 4, 4-methylpyridine; 5, 4-tert-butylpyridine; 6, pyridine; 7, 4-chloropyridine; 8, 4-bromopyridine; 9, 3-chloropyridine; 10, 3, 5-dichloropyridine; 11, 3, 5-dimethylpyrazine. Adapted from Ref. 12.

$$\lambda_0 = e_0^2 \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{d}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \tag{21}$$

Therefore, $(\lambda_{11} + \lambda_{22})/2 = 23$ kcal/mole, in rather poor agreement with the observed intercept of 13.5 kcal/mole if E_0 in Eq. (20) is taken to be ΔH^0_{IP}. Correction of the optical transitions for the effect of spin-orbit coupling[12] yields an intercept of 12.6 kcal/mole, still in poor agreement with the theoretical value 23 kcal/mole. The disagreement between experimental and calculated intercept was ascribed[12] to a breakdown of the solvent polarization model caused by specific solvent effects. However, since E_0 in Eq. (20) is a free energy,[27] the intercept in the plot of E_{op} vs ΔH^0_{IP} is $4\Delta G^* - T\Delta S^0_{IP}$. From $4\Delta G^* = 23$ kcal/mole and $\Delta S^0_{IP} = 39$ eu,[12] we calculate

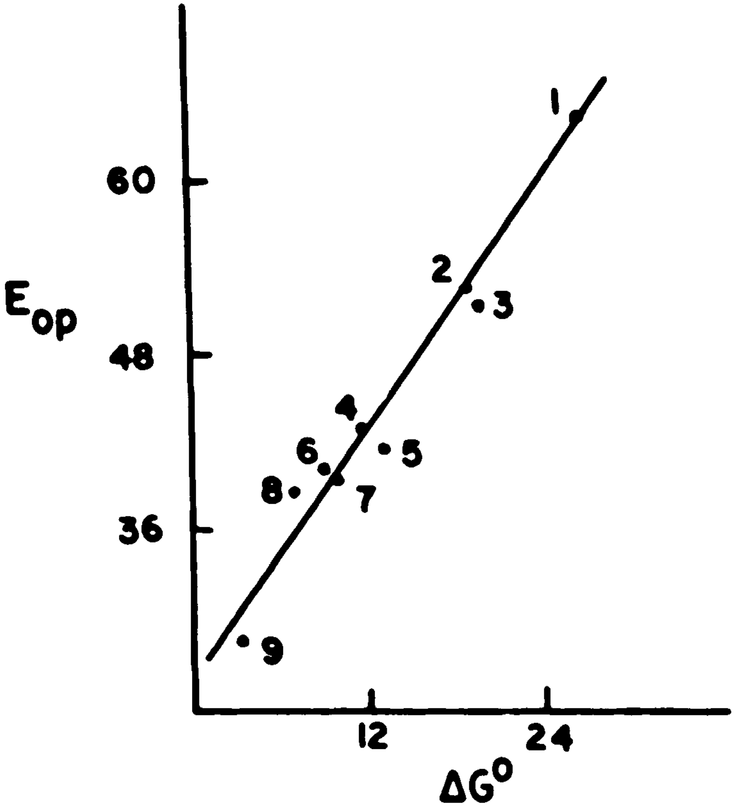


FIGURE 4 E_{op} vs ΔG^0 for ion pairs $Ru(NH_3)_6^{3+}|Fe(CN)_5L^{3-}$, $Ru(NH_3)_6^{3+}|M(CN)_6^{4-}$ (M = Fe, Ru), and $Ru(NH_3)_5py^{3+}|M(CN)_6^{4-}$ (M = Fe, Ru). E_{op}, energy of intervalence transfer band, kcal/mole; ΔG^0, standard free energy change from difference in reduction potentials for the two couples, kcal/mole. 1, L = CO; 2, $Ru(NH_3)_6^{3+}|Ru(CN)_6^{4-}$; 3, L = dimethylsulfoxide; 4, L = pyrazine; 5, $Ru(NH_3)_5py^{3+}|Ru(CN)_6^{4-}$; 6, $Ru(NH_3)_6^{3+}|Fe(CN)_6^{4-}$; 7, L = pyridine; 8, L = imidazole; 9, $Ru(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$. Adapted from Ref. 36.

an intercept of 11.3 kcal/mole, in acceptable agreement with the spin-orbit coupling corrected experimental values of 12.6 ± 2, 15.5 ± 4, and 10.1 ± 5 kcal/mole for the Fe, Ru, and Os systems, respectively. The agreement indicates that Eq. (20) provides a useful relationship between the energy of the optical electron transfer and the thermodynamics of the corresponding thermal process. Moreover, the agreement suggests that the reorganization parameters for the self-exchange reactions of the $Fe(CN)_6^{4-/3-}$, $Ru(CN)_6^{4-/3-}$ and $Os(CN)_6^{4-/3-}$ complexes are equal to each other.

Values of the rate constants for internal electron transfer in ion pairs calculated by utilization of Eqs. (12) and (13) are presented in Table IV. At first glance, the equations appear to give reasonable results for relative rate constants. Thus, the ratio of the rate constants for internal electron transfer in the ion pairs $ML_6^{3+} \mid Fe(CN)_6^{4-}$ and $ML_6^{3+} \mid Ru(CN)_6^{4-}$ are 1.4×10^6, 2×10^6 and 6.7×10^6 for $Ru(NH_3)_5py^{3+}$, $Co(NH_3)_6^{3+}$ and $[Eu\subset 2.2.1]^{3+}$, respectively. According to the Marcus relationship for cross-reactions, ratios of rate constants for two reductants reacting with a common oxidant are predicted to be independent of the identity of the oxidant. The relative constancy of k_{et} ratios for $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ ion pairs conforms to this prediction. However, other considerations render the calculations somewhat suspect. Based on the difference in the reduction potentials of the $Fe(CN)_6^{3-/4-}$ and $Ru(CN)_6^{3-/4-}$ couples, the reactivity ratio is calculated to be $\sim 2 \times 10^4$ $(\log(k_{et}^{Fe}/k_{et}^{Ru})\ \alpha\ 8.45\Delta E^0)$. If the discrepancy between the latter value and the $\sim 2 \times 10^6$ value estimated from the optical spectra is ascribed to a difference in the rate constants for self-exchange in the $Fe(CN)_6^{3-/4-}$ and $Ru(CN)_6^{3-/4-}$ couples, we estimate a rate constant for iron about 10^4 higher than for ruthenium. Although there is very little information about the redox reactivity of the $Ru(CN)_6^{3-/4-}$ couple, the 10^4 ratio for Fe to Ru exchange rates is rather unlikely. The rate constant for self-exchange between $Ru(CN)_6^{3-}$ and $Ru(CN)_6^{4-}$ can be estimated from the measured[40] rate constant for the reductive quenching of $^*Ru(bpy)_3^{2+}$ by $Ru(CN)_6^{4-}$. The measured value, $1 \times 10^7\ M^{-1}\ s^{-1}$, when combined with the known E^0 values for $^*Ru(bpy)_3^{2+}/Ru(bpy)_3^{+}$ (0.84 v)[41] and $Ru(CN)_6^{3-/4-}$ (0.94)[12] and the rate constant for self-exchange between $^*Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{+}$ $(1 \times 10^8\ M^{-1}\ s^{-1})$[41] gives a rate constant for self-exchange in $Ru(CN)_6^{3-/4-}$ (by utilizing the electrostatically corrected Marcus relationship[6]) of $1.2 \times 10^4\ M^{-1}\ s^{-1}$. This value is very similar to the $1.9 \times 10^4\ M^{-1}\ s^{-1}$ for self-exchange in $Fe(CN)_6^{3-/4-}$. Additional support for the similarity of rate constants for self-exchange in the $Fe(CN)_6^{3-/4-}$ and $Ru(CN)_6^{3-/4-}$ couples comes from a consideration of the relative rates of $^*Ru(bpy)_3^{2+}$ quenching by $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$.[40,41] The measured rate constants are 7.2×10^9 and $1 \times 10^7\ M^{-1}\ s^{-1}$, respectively. However, before these rate constants can be utilized to determine the relative rate constants for exchange in the Ru and Fe systems, it must be ascertained whether diffusion- or activation-controlled reactions are obtained. Undoubtedly, the $Ru(CN)_6^{4-}$ quenching of $^*Ru(bpy)_3^{2+}$ is activation controlled. However, it is very likely that the corresponding $Fe(CN)_6^{4-}$ is diffusion controlled.[41,42] The diffusion-controlled rate constant for the $^*Ru(bpy)_3^{2+}$–$Fe(CN)_6^{4-}$ reaction calculated[41] from Eqs. (22) and (23)[43]

$$k_d^0 = [4\pi N(D_A + D_B)d/1000]\,((w_0/RT)/[\exp(w_0/RT) - 1]) \quad (22)$$

$$\log k_d = \log k_d^0 + 2Z_AZ_B\alpha\mu^{1/2}/(1 + \beta d\mu^{1/2}) \quad (23)$$

is 3.1×10^9 M^{-1} s^{-1} at $\mu = 0.10$ M[41] and 7.3×10^{10} M^{-1} s^{-1} at $\mu = 0$, compared with the observed[40] values of 7.2×10^9 M^{-1} s^{-1} at $\mu = 0.10$ M and 7.2×10^{10} M^{-1} s^{-1} at $\mu = 0$. From the good agreement between observed calculated values, it was inferred[41,42] that the $^*Ru(bpy)_3^{2+}$–$Fe(CN)_6^{4-}$ is diffusion controlled. Under these conditions the ratio of the measured rate constants for quenching of $^*Ru(bpy)_6^{2+}$ by $Fe(CN)_6^{4-}$ and $Ru(CN)_{16}^{4-}$ cannot be utilized to estimate the rate constant for the self-exchange of the $Ru(CN)_6^{3-/4-}$ couple. However, a value of 1.5×10^{11} M^{-1} s^{-1} for the hypothetical activation-controlled $^*Ru(bpy)_3^{2+}$–$Fe(CN)_6^{4-}$ reaction can be estimated[41] from the rate constants for self-exchange in the $^*Ru(bpy)_3^{2+}$–$Ru(bpy)_3^{+}$ (1×10^8 M^{-1} s^{-1})[44] and $Fe(CN)_6^{3-/4-}$ (1.9×10^4 M^{-1} s^{-1})[34] couples and their E^0 values (0.84 and 0.42 v, respectively)[45,12] by utilization of the Marcus relationship corrected for electrostatics.[6,34] If the 1.5×10^{11} M^{-1} s^{-1} value is accepted, then the ratio of the rate constants for the activation-controlled reactions of $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ with $^*Ru(bpy)_3^{2+}$ is 1.5×10^4. The excellent agreement between the latter value and the value 2×10^4 estimated from the difference in reduction potentials between the $Fe(CN)_6^{3-/4-}$ and $Ru(CN)_6^{3-/4-}$ couples implies equal (or nearly so) rate constants for self-exchange. If the latter conclusion is accepted—and the estimates made above appear to be quite reliable—it is evident that the rate constants calculated from the optical transitions are in error since they require a 10^4 difference in rate constants for self-exchange between $Fe(CN)_6^{3-/4-}$ and $Ru(CN)_6^{3-/4-}$.

In addition to the difficulties with the relative rate constants calculated from the optical transitions, there are problems with the absolute values of the rate constants. In the single case where a measured value is available, the comparison between calculated (1×10^6 s^{-1}) and measured (1.7×10^3 s^{-1}) rate constants for internal electron transfer in the ion pair $Ru(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$ is not encouraging. Possible reasons for the failure of Eqs. (12) and (13) to provide acceptable estimates of k_{et} may be advanced by considering various possible relative orientations of cation and anion in the ion pairs. For instance, the ion pairs for optical and for thermal electron transfer may have different (isomeric) structures.[10] Under these circumstances, Eqs. (12) and (13) would provide a value of k_{et} for a hypothetical thermal reaction of the ion pair involved in the optical electron transfer. It is also conceivable that the dominant and the reactive ion pairs in the thermal reaction have different structures.[10] Under these circumstances, the experimental value of k_{et} obtained under the assumption that the dominant and the reactive ion pair are the same would not be the correct rate constant for intramolecular electron transfer in the reactive ion pair, and comparison with the value of k_{et} calculated from Eqs. (12) and (13) would not be appropriate.[46]

Unfortunately, with the exception of the $Ru(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$ ion pair, there are no outer-sphere systems where both optical and thermal electron transfer have been observed, and therefore tests for the validity of Eqs. (12) and (13) for systems which are clearly not in the inverted region cannot be made. Additional work in this area is indicated. We have made a beginning[38] by measuring the charge transfer spectra and formation constants for the ion pairs $CoL^{3+}|Fe(CN)_6^{4-}$ (L is 3 en or sepulchrate); but the thermal electron transfer rates have not been measured yet. Estimates of k_{et} for these ion pairs can be made from the known rate constants for self-exchange of the couples and their reduction potentials. The results, 8×10^{-8} s^{-1} and 1×10^{-5} s^{-1} for the ethylenediamine and sepulchrate systems, respectively, are in poor agreement with the values estimated from the optical transitions (4×10^{-4} and 7×10^{-5} s^{-1}, respectively). The comparisons are not encouraging so far, but clearly the thermal rates must be measured in these systems.

INTRAMOLECULAR ELECTRON TRANSFER IN ION PAIRS FORMED BY EXCITED STATES

The photochemical equivalent of saturation kinetics in thermal reactions is represented by the phenomenon of static quenching. It is manifested experimentally by upward curvature in Stern–Volmer plots (plots of I_0/I vs quencher concentration, I_0 and I being the emission intensity in the absence and presence of quencher, respectively) and by differences in emission and lifetime quenching measurements. There are only three papers[41,42,47] which address the question of static quenching via outer-sphere ion association between transition metal complexes.

In the first paper,[47] luminescence and lifetime studies of the excited state[48] *Ru(bpy)$_3^{2+}$ were carried out in the presence of anionic complexes such as Mo(CN)$_8^{4-}$, IrCl$_6^{3-}$ and PtCl$_4^{2-}$. For most of the pairs studied, intensity and lifetime Stern–Volmer plots were linear and had the same slope, an indication of only dynamic quenching. However, for Ru(bpy)$_3^{2+}$–Mo(CN)$_8^{4-}$ in water and *Ru(bpy)$_3^{2+}$–PtCl$_4^{2-}$ in dimethylformamide, it was found[47] that addition of the quencher decreased the intensity faster than the lifetime, and therefore it was inferred that static quenching was obtained. The mechanistic interpretation of the results is shown in Scheme III for Mo(CN)$_8^{4-}$. (The PtCl$_4^{2-}$ system is not considered here because it apparently involves energy transfer.[49])

Scheme III

$$\begin{tikzcd}
\mathrm{Ru(bpy)}_3^{2+} + \mathrm{Mo(CN)}_8^{4-} \arrow[r, shift left, "Q_{\mathrm{IP}}"] \arrow[r, leftarrow, shift right] \arrow[d, "h\nu"] & \mathrm{Ru(bpy)}_3^{2+} | \mathrm{Mo(CN)}_8^{4-} \arrow[d, "h\nu"] \\
{}^{*}\mathrm{Ru(bpy)}_3^{2+} + \mathrm{Mo(CN)}_8^{4-} \arrow[r, "k_q"] \arrow[d, "1/\tau_0"] & {}^{*}\mathrm{Ru(bpy)}_3^{2+} | \mathrm{Mo(CN)}_8^{4-} \arrow[d, "k_{\mathrm{et}}"] \\
\mathrm{Ru(bpy)}_3^{2+} & \mathrm{Ru(bpy)}_3^{+} | \mathrm{Mo(CN)}_8^{3-}
\end{tikzcd}$$

On the basis of Scheme III, where it is assumed that the excited state ion pair produces no detectable luminescence nor does it dissociate to yield *Ru(bpy)$_3^{2+}$ and Mo(CN)$_8^{4-}$, lifetime and intensity quenching measurements are governed by Eqs. (24) and (25), respectively.

$$\tau_0/\tau = 1 + k_q\tau_0\,[\mathrm{Mo(CN)}_8^{4-}] \tag{24}$$

$$I_0/I = (1 + k_q\tau_0\,[\mathrm{Mo(CN)}_8^{4-}])\,(1 + Q_{\mathrm{IP}}[\mathrm{Mo(CN)}_8^{4-}]) \tag{25}$$

Values of k_q and Q_{IP} derived from the measurements are 9×10^9 M^{-1} s^{-1} and 3×10^2 M^{-1}, respectively, at ionic strength 0.0104 M. The experimental value of Q_{IP} is in good agreement with the value 1.4×10^2 M^{-1} calculated from Eqs. (4)–(6). This is in contrast with the amminecobalt(III)–cyanoferrate(II) ion pairs where experimental and calculated values differ by several-fold, presumably because of the extra stabilization due to hydrogen bonding. To be sure, hydrogen-bonding interactions are not obtained in the $Ru(bpy)_3^{2+}$–$Mo(CN)_8^{4-}$ system, and the electrostatic interaction is apparently sufficient to account for the ion association. When the measured value of k_q (9×10^9 M^{-1} s^{-1}) is compared with the value 1.1×10^{10} M^{-1} s^{-1} at ionic strength 0.0104 calculated from Eqs. (22) and (23), it becomes evident that the $Mo(CN)_6^{4-}$–$*Ru(bpy)_3^{2+}$ reaction is controlled by diffusion. Under these circumstances, the rate constant for intramolecular electron transfer within the excited state ion pair (k_{et} in Scheme III) cannot be obtained.

The $Mo(CN)_8^{4-}$–$Ru(bpy)_3^{2+}$ system illustrates another feature of studies with ions of high and opposite charge. In order to obtain substantial ion-pair association, high reactants concentrations are necessary and this implies the use of high ionic strengths. However, ion-pair formation constants decrease with increasing ionic strength, and unless the highest concentrations compatible with the prevalent ionic strength are utilized, less association is obtained. Thus, as indicated above, at 1.04×10^{-2} M ionic strength and with $[Mo(CN)^{4-}]_8 = (1.0\text{–}10) \times 10^{-4}$ M, curvature was observed in the intensity Stern–Volmer plots, and good evidence for static quenching was presented.[47] However, at ionic strength 0.50 M and with $[Mo(CN)_8^{4-}] = (5.0\text{–}80) \times 10^{-4}$ M, intensity and lifetime Stern–Volmer plots are linear and have the same slope,[50] and there is no evidence, at the concentrations used, for ion-pair association. To be sure, higher concentrations could have been used at the 0.50 M ionic strength, but this would imply changing the cation concentration by a considerable amount. However, redox potentials[51,52] and rate constants[53] for ions such as $Mo(CN)_8^{4-}$ and $Fe(CN)_6^{4-}$ are very sensitive to the *concentration and identity of the cation*, and the use of constant ionic strength may represent an unsatisfactory approach for such ions.[54]

Electron transfer quenching of $*Ru(bpy)_3^{2+}$ and $*Ru(phen)_3^{2+}$ by $Co(C_2O_4)_3^{3-}$, $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ has also been interpreted[42] on the basis of ion-pair formation between the quencher and *Ru(bpy)$_3^{2+}$. Unfortunately, the measurements were not carried out at constant ionic strength and the calculation of k_q and Q_{IP} from the data involved an assumed dependence of k_q and Q_{IP} upon ionic strength.[55] An iterative procedure which combined intensity and lifetime measurements yielded values of k_q and Q_{IP} at infinite dilution. The values of k_q and Q_{IP} obtained were 7.3×10^{10} M^{-1} s^{-1} and 3.6×10^3 M^{-1} for Ru(bpy)$_3^{2+}$–Fe(CN)$_6^{4-}$, 5.1×10^{10} M^{-1} s^{-1} and 2.0×10^3 for Ru(bpy)$_3^{2+}$–Fe(CN)$_6^{3-}$, and 3.8×10^{10} M^{-1} s^{-1} and 1.9×10^3 M^{-1} for Ru(bpy)$_3^{2+}$–Co(C$_2$O$_4$)$_3^{3-}$. It will be seen that the resulting values of k_q are very similar to those calculated from Eqs. (22) and (23) for diffusion-controlled reactions (4.3×10^{10} M^{-1} s^{-1} for a +2, −4 reaction and 3.3×10^{10} M^{-1} s^{-1} for a +2, −3 reaction). The quenching mechanism for Fe(CN)$_6^{4-}$ is similar to that for Mo(CN)$_8^{4-}$, namely, reductive quenching. For Fe(CN)$_6^{3-}$ or Co(C$_2$O$_4$)$_3^{3-}$ the mechanism is oxidative quenching as shown in Scheme IV.

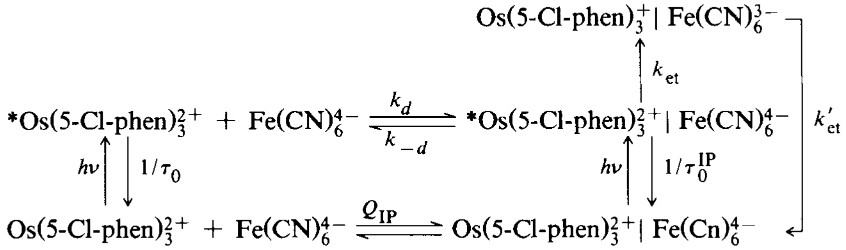
Scheme IV

$$\begin{tikzcd}
\mathrm{Ru(bpy)_3^{2+}} + \mathrm{Fe(CN)_6^{3-}} \arrow[r, shift left] \arrow[d, "h\nu"] & \mathrm{Ru(bpy)_3^{2+} | Fe(CN)_6^{3-}} \arrow[l, shift left] \arrow[d, "h\nu"] \\
{}^*\mathrm{Ru(bpy)_3^{2+}} + \mathrm{Fe(CN)_6^{3-}} \arrow[r, "k_q"] \arrow[d, "1/\tau_0"] & {}^*\mathrm{Ru(bpy)_3^{2+} | Fe(CN)_6^{3-}} \arrow[d, "k_{et}"] \\
\mathrm{Ru(bpy)_3^{2+}} & \mathrm{Ru(bpy)_3^{3+} | Fe(CN)_6^{4-}}
\end{tikzcd}$$

Since the reactions of *Ru(bpy)$_3^{2+}$ with the quenchers are diffusion controlled, values of k_{et} cannot be obtained from the studies. Additional studies of the quenching of *Ru(bpy)$_3^{2+}$ by Fe(CN)$_6^{4-}$ or Fe(CN)$_6^{3-}$ have been carried out at constant ionic strength, with no evidence for static quenching at 0.10 M or 0.50 M. Values of k_q at 0.50 M are 3.5×10^9 and 6.5×10^9 M^{-1} s^{-1} for Fe(CN)$_6^{4-}$ and Fe(CN)$_6^{3-}$, respectively.[56] It is not surprising that evidence for static quenching was not obtained in these studies. Values of Q_{IP} calculated from Eqs. (4)–(6) are 14 and 10 M^{-1} for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{-3}$, respectively. In order for bimolecular quenching to be diffusion controlled, it is necessary that $k_{et} >> k_{-d}$, where k_{-d} is the rate constant for the dissociation of the excited state ion pair into $*Ru(bpy)_3^{2+}$ + quencher. Values of k_{et} calculated from the Marcus relationship corrected for electrostatics (rate constant and E^0 values for the $Fe(CN)_6^{3-/4-}$ couple at 0.50 M ionic strength are 9.6×10^3 M^{-1} s^{-1} and 0.45 v, respectively; corresponding values for $*Ru(bpy)_3^{2+}$–$Ru(bpy)_3^{+}$ and for $Ru(bpy)_3^{3+}$–$*Ru(bpy)_3^{2+}$ are 1×10^8 M^{-1} s^{-1}, 0.82 v, and 1×10^8 M^{-1} s^{-1}, -0.84 v, respectively) are 6.6×10^9 and 4.5×10^{12} s^{-1} for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$, respectively. Comparison of these values with the values of k_{-d} calculated from Eqs. (22) and (23)–7.1×10^7 and 2.0×10^8 s^{-1} for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$, respectively—confirm that the reactions are indeed diffusion controlled. These calculations bring out another feature of interest for the excited state ion pair. If the lifetime of the excited state $*Ru(bpy)^{2+}$ ($\tau_0 = 6.0 \times 10^{-7}$ s, $k = 1.7 \times 10^6$ s^{-1}) is assumed to be unaffected by ion pairing, clearly there will be no detectable luminescence coming from the excited state ion pair since the competing internal electron transfer is so much faster than luminescence emission.

Finally, we consider the $*Os(5\text{-}Cl\text{-}phen)^{2+}$–$Fe(CN)_6^{4-}$ system[41] which appears to be the only system with detectable ion pairs for which the quenching of the excited state is not controlled by diffusion but rather by electron transfer. Both emission and lifetime studies suggest the presence of ion pairs in this system. The emission studies display the upward curvature characteristic of static quenching. The lifetime studies show that the rate of disappearance of $*Os(5\text{-}Cl\text{-}phen)^{2+}$ first increases with increasing concentration of $Fe(CN)_6^{4-}$, but that at high concentrations (>0.10 M) a finite limiting rate is reached. This observation indicates that the *ion pair fluoresces.* Moreover, since the limiting lifetime and the quantum yield for emission of the excited state ion pair were found to be considerably smaller than the corresponding values for the excited free ion, internal electron transfer in the excited ion pair is implicated. All the observations could be fitted quantitatively by the mechanism depicted in Scheme V with the following values of the constants at 0.10 M ionic strength: $k_{et} = 1.6 \times 10^8$ s^{-1}, $k_{-d} = 1.0 \times 10^8$ s^{-1}, $k_d = 8.2 \times 10^9$ M^{-1} s^{-1}, $Q_{IP} = 36$ M^{-1}, and $\tau_0 = \tau_0^{IP} = 6.6 \times 10^{-8}$ s.[41]

Scheme V



$$\begin{tikzcd}
 & \mathrm{Os(5\text{-}Cl\text{-}phen)_3^{+} \mid Fe(CN)_6^{3-}} \arrow[dd, bend left=60, "k'_{et}"] \\
{*}\mathrm{Os(5\text{-}Cl\text{-}phen)_3^{2+} + Fe(CN)_6^{4-}} \arrow[r, shift left, "k_d"] \arrow[d, shift left, "1/\tau_0"] & {*}\mathrm{Os(5\text{-}Cl\text{-}phen)_3^{2+} \mid Fe(CN)_6^{4-}} \arrow[l, shift left, "k_{-d}"] \arrow[u, "k_{et}"'] \arrow[d, shift left, "1/\tau_0^{IP}"] \\
\mathrm{Os(5\text{-}Cl\text{-}phen)_3^{2+} + Fe(CN)_6^{4-}} \arrow[u, shift left, "h\nu"] \arrow[r, shift left, "Q_{IP}"] & \mathrm{Os(5\text{-}Cl\text{-}phen)_3^{2+} \mid Fe(Cn)_6^{4-}} \arrow[l, shift left] \arrow[u, shift left, "h\nu"]
\end{tikzcd}$$

Since some of the parameters utilized to fit the lifetime data were approximated as the corresponding values for Ru(bpy)$_3^{2+}$, it is important to confirm the validity of the values of k_{et} derived from the lifetime studies. Calculations of k_{et} from the cross-relation corrected for electrostatics[6,34] were carried out[41] utilizing the following auxiliary information (first and second numbers at ionic strength 1.0×10^{-3} and 0.10 M, respectively): E^0 for Fe(CN)$_6^{3-/4-}$, 0.38, 0.42 v; E^0 for Os(5-Cl-phen)$_3^{+}$/*Os(5-Cl-phen)$_3^{2+}$ 0.72, 0.72 v; rate constants for self-exchange, 27, 1.9×10^4 M^{-1} s^{-1} for Fe and 4.5×10^7, 1.0×10^8 M^{-1} s^{-1} for Os. The calculated values of k_{et}, 1.3×10^8 and 5.3×10^8 s^{-1} at ionic strength 1.0×10^{-3} and 0.10 M, respectively, are in reasonable agreement with the values of 8.7×10^7 and 1.6×10^8 s^{-1} derived from the lifetime measurements, and provide additional support for the validity of the latter values.

In the proposed mechanism depicted in Scheme V, the excited state ion pair undergoes three competing reactions, namely, electron transfer (1.6×10^8 s^{-1}), decay to the ground state (1.5×10^7 s^{-1}) and dissociation into the free ions (1.0×10^8 s^{-1}). It is instructive to note the interplay between the values of the rate constants that permits the observation of both internal electron transfer and fluorescence of the ion pair. For *Os(5-Cl-phen)$_3^{2+}$|Fe(CN)$_6^{4-}$, internal electron transfer is rather slow compared to diffusion and the radiative and nonradiative decay processes are rather fast. Under these circumstances, intramolecular electron transfer and fluorescence are detected. In contrast, for *Ru(bpy)$_3^{2+}$|Fe(CN)$_6^{4-}$, internal electron transfer is fast compared to diffusion and the radiative and nonradiative decay processes are rather slow. Under these circumstances, neither intramolecular electron transfer nor fluorescence of the excited state ion pair are detected, and the quenching of the excited state is diffusion controlled.

CHEMICAL CONSEQUENCES OF OUTER-SPHERE INTERVALENCE EXCITATION

This is quite an undeveloped subject. We are aware of only two systems where intervalence excitation leads to net, albeit with low quantum yields, transient or permanent changes. In the first,[45] it was found that excitation of the ion pair $Ru(NH_3)_5py^{+3}|Fe(CN)_6^{4-}$ produces the electronic isomeric ion pair $Ru(NH_3)_5py^{2+}|Fe(CN)_6^{3-}$ in 0.06 ± 0.03 yield. In the second,[57] excitation of the ion pair $Ru(NH_3)_5Cl^{2+}|Ru(CN)_6^{4-}$ produces $(NH_3)_5RuNCRu(CN)_5^-$ in 0.002 yield. Different reasons have been advanced to rationalize the low quantum yields in the two systems.[45,57] For $Ru(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$, it was noted[45] that cage separation of $Ru(NH_3)_5py^{2+}$ and $Fe(CN)_6^{3-}$ competes favorably with back electron transfer in $Ru(NH_3)_5py^{2+}|Fe(CN)_6^{3-}$ and the low quantum yield was ascribed[45] to a low efficiency for conversion of the Franck–Condon intervalence state $FC[Ru(NH_3)_5py^{2+}|Fe(CN)_6^{3-}]$ to the ground state $Ru(NH_3)_5py^{2+}|Fe(CN)_6^{3-}$. It was suggested[45] that the relaxation of the Franck–Condon intervalence state to the initial ground state $Ru(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$ may be faster than the process that establishes the solvent barrier to internal electron transfer in $Ru(NH_3)_5py^{2+}|Fe(CN)_6^{3-}$. The latter process is determined by the dielectric relaxation frequency of water ($10^{11}\ s^{-1}$) whereas the former involves the 10–100 times faster metal–ligand vibration frequencies. Support for this explanation comes from calculations of cage escape and internal electron transfer in $Ru(NH_3)_5py^{2+}|Fe(CN)_6^{3-}$. The implicitly proposed[45] sequence of events is given in Scheme VI.

Scheme VI

$$\begin{tikzcd}
Ru(NH_3)_5py^{3+}|\ Fe(CN)_6^{4-} \arrow[r, shift left, "h\nu"] & FC\ [Ru(NH_3)_5py^{2+}|\ Fe(CN)_6^{3-}] \arrow[l, shift left, "k_r"] \arrow[d, "k'_r"] \\
Ru(NH_3)_5py^{2+} + Fe(CN)_6^{3-} \arrow[r, shift left, "k_d"] & Ru(NH_3)_5py^{2+}|\ Fe(CN)_6^{3-} \arrow[l, shift left, "k_{-d}"] \arrow[ul, "k_{et}"]
\end{tikzcd}$$

Relaxation of the Franck–Condon excited state proceeds by two competing pathways: return to the ground state (k_r) or formation of the electronic isomer (k'_r). Since it was argued[45] that electron transfer is slow compared to cage separation ($k_{et} < k_{-d}$), the quantum yield of 0.06 is given by $k'_r/(k_r + k'_r)$. Confirmation of the inequality $k_{et} < k_{-d}$ comes from the following calculations. From the measured[6] value $4.3 \times 10^8\ M^{-1}\ s^{-1}$ for $k_f k_{et}/k_{-d}$ and the estimated[22] value 92 M^{-1} for k_f/k_{-d}, we calculate $k_{et} = 4.7 \times 10^6\ s^{-1}$. k_f is estimated as $3.0 \times 10^9\ M^{-1}\ s^{-1}$ by utilization of Eqs. (22) and (23), and therefore $k_{-d} = 3.3 \times 10^7\ s^{-1}$.

For the $Ru(NH_3)_5Cl^{2+}|Ru(CN)_6^{4-}$ system, the low quantum yield was ascribed[57] to fast back electron transfer compared to cage separation in the electronic isomer $Ru(NH_3)_5Cl^{+}|Ru(CN)_6^{3-}$ generated by intervalence excitation of the stable isomer. The proposed sequence of reactions is given by Eqs. (26)–30.[57]

$$Ru(NH_3)_5Cl^{2+}|\ Ru(CN)_6^{4-} \underset{k_{et}}{\overset{h\nu}{\rightleftharpoons}} Ru(NH_3)_5Cl^{+}|\ Ru(CN)_6^{3-} \tag{26}$$

$$Ru(NH_3)_5Cl^{+}|\ Ru(CN)_6^{3-} \underset{k_d}{\overset{k_{-d}}{\rightleftharpoons}} Ru(NH_3)_5Cl^{+} + Ru(CN)_6^{3-} \tag{27}$$

$$Ru(NH_3)_5Cl^{+} + H_2O \longrightarrow Ru(NH_3)_5OH_2^{2+} + Cl^{-} \tag{28}$$

$$Ru(NH_3)_5OH_2^{2+} + Ru(CN)_6^{4-} \longrightarrow (NH_3)_5RuNCRu(CN)_5^{2-} + H_2O \tag{29}$$

$$(NH_3)_5RuNCRu(CN)_5^{2-} + Ru(CN)_6^{3-} \longrightarrow (NH_3)_5RuNCRu(CN)_5^{-} + Ru(CN)_6^{4-} \tag{30}$$

According to the proposed interpretation, the observed quantum yield of 0.002 is a measure of competition between back electron transfer (k_{et}) and cage separation (k_{-d}) and therefore $k_{-d}/(k_{-d} + k_{et}) = 2 \times 10^{-3}$. k_d is estimated as $5.3 \times 10^9\ M^{-1}\ s^{-1}$ by utilization of Eqs. (22) and (23). k_d/k_{-d} is estimated as $5.7\ M^{-1}$ by utilization of Eqs. (4)–(6). Therefore, $k_{-d} = 9.3 \times 10^8\ s^{-1}$ and $k_{et} = 4.7 \times 10^{11}\ s^{-1}$. The latter value implies a rate constant for self-exchange in $Ru(NH_3)_5Cl^{2+/+}$ of $\sim 1 \times 10^5\ M^{-1}\ s^{-1}$, a reasonable[58] value. These considerations suggest high or even quantitative conversion of the Franck–Condon intervalence state $FC[Ru(NH_3)_5Cl^{+}|Ru(CN)_6^{3-}]$ to the unstable electronic isomer $Ru(NH_3)_5Cl^{+}|Ru(CN)_6^{3-}$. This inference is in sharp contrast with that reached for the very similar $Ru(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$ system, where, as indicated above, conversion of the Franck–Condon state to the unstable electronic isomer proceeds with a yield of only 6%. We have no explanation for the contrasting behavior of these two very similar systems, and can only suggest that additional work in these and related systems is clearly needed.

CONCLUSIONS

The present Comment demonstrates that a beginning has been made in the study of intramolecular electron transfer within ion pairs. The relationships between thermal, optical, excited state, and photochemical electron transfer have been emphasized, as has been the importance of comparing experimental measurements with those calculated from the Hush–Marcus theory. The subject of thermodynamics of ion-pair association is mature and useful equations are available for estimating, with a fair degree of confidence, free energy, entropy, and enthalpy changes for ion-pair formation. In contrast, the question of the structure of ion pairs in solution is wide open, and the ingenuity of workers in this field will be taxed before definitive structural information becomes available. Another topic, very powerful in principle but which has not been developed, deals with the relationship between optical and thermal electron transfer in ion pairs. So far, there is only one system where both thermal and optical electron transfer have been measured, and obviously many more comparisons are necessary. Additional work is also needed in excited state ion pair systems where both intramolecular electron transfer and fluorescence pathways can be detected and in photochemical systems where net chemical reactions (transient or permanent) follow optical excitation.

As an example of the type of systems where studies can yield much information, we cite the $\mathrm{Eu}{\subset}2.2.1^{3+}|\mathrm{M(CN)}_6^{4-}$ (M is Fe, Ru, Os; ⊂2.2.1. is 4,7,13,16,21-pentaoxo-1,10-diazabicyclo[8.8.5]tricosane) system for which a preliminary report was published recently.[39] The proposed scheme (Scheme VII) for the light-induced and thermal reactions in the system includes several of the issues raised in the present Comment, namely, ion-pair association between ground states of high and opposite charge (k'_d, k'_{-d}), outer-sphere intervalence transfer ($h\nu'$), intramolecular electron transfer of ground (k'_{et}) and excited (k_{et}) states. Static quenching and photochemistry following optical excitation are, in principle, implicit in the scheme, but have not yet been detected.

Scheme VII

$$\begin{tikzcd}
{}^*\text{EuC2.2.1}^{3+} + \text{M(CN)}_6^{4-} \arrow[r, shift left, "k_d"] & {}^*\text{EuC2.2.1}^{3+} | \text{M(CN)}_6^{4-} \arrow[l, shift left, "k_{-d}"] \arrow[d, "k_{et}"] \\
 & \text{EuC2.2.1}^{2+} | \text{M(CN)}_6^{3-} \arrow[d, shift left, "k'_{et}"] \\
\text{EuC2.2.1}^{3+} + \text{M(CN)}_6^{4-} \arrow[uu, "h\nu"] \arrow[r, shift left, "k'_d"] & \text{EuC2.2.1}^{3+} | \text{M(CN)}_6^{4-} \arrow[l, shift left, "k'_{-d}"] \arrow[u, shift left, "h\nu'"]
\end{tikzcd}$$

The synergism between theory and experiment that has characterized[59] the area of bimolecular, outer-sphere electron transfer reactions is also expected to be a key feature in the area of intramolecular, outer-sphere electron transfer.

Acknowledgments

Support of research on the topics featured in the present Comment by the National Science Foundation is gratefully acknowledged as are illuminating discussions with Dr. N. Sutin.

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