a triplet of triplets spectrum but the ring flip modulates these couplings and an alternating line-width effect occurs (Figure 6i). The positions of the outermost lines and, largely, the central one are unaffected while the more intense lines to low field interchange, as do their high-field counterparts, and exhibit line broadening. The individual lines can be observed at low temperatures (Figure 6ii). Exchange also interchanges the two inner lines of the outer triplets, which are on opposite sides of the center. Figure 6i exhibits the CIDEP characteristic of a radical from a symmetric radical pair, formed from a triplet precursor, with pure ST_0 RPM polarization. The low-field lines are in emission and the high-field ones in absorption, and this latter exchange connects lines of opposite phase. At exchange rates too slow to cause line broadening, population is transported between the two environments and a line is observed in each position whose intensity is the average of the original ones. For radicals with symmetric ST_0 polarization this average is zero.

As the temperature is lowered ST_{-1} polarization, asymmetric in its hyperfine dependence, is added to the ST_0 effects and the low-field signals become more intense than those at high field. Now exchange produces a nonzero emissive average and the innermost members of the outer triplets in the spectrum both appear in emission. A novel CIDEP pattern is observed with a single emissive line among the absorptive high-field ones (Figure 6ii). The entire exchange behavior from very slow exchange affecting line intensities, to line broadening, and eventual line sharpening is predicted by a simple two-site exchange model.[25]

Concluding Remarks

Flash photolysis ESR provides positive identification of transient free radicals shortly after their formation. CIDEP in turn provides a direct link between the photophysics of the system and its photochemistry. The multiplicity of the precursor involved in forming a precise radical is obtained.

RPM polarization arises in both ESR and NMR (CIDNP) in spin-correlated pairs. These are essential reaction intermediates between the excited state of the molecule produced in the flash and the subsequent free radicals. The spin evolution that occurs within them controls the amount of geminate product formed and the future course of the reaction. These intermediates have not long been recognized but they can now be studied directly in new experiments.[26,27] Thus microwave transitions can be induced in the radical pair held within a magnetic field to affect the S–T mixing within it and, consequently, the product or escaping radical yield. This is the radical yield detected magnetic resonance (RYDMR) technique. Similar experiments can be performed by measuring the yield as a static magnetic field only is applied, since S–T_0 mixing occurs via the different magnetic fields at the electrons of the two radicals in the pair. This is why high magnetic fields affect radical reactions.

Previous accounts of CIDEP have been concerned with basic polarization effects and their interpretation. Here we have discussed some of the further information available from the study of the time dependence and line shapes of polarized signals. It has been shown that spin-polarized radicals provide the opportunity for a wide range of exchange studies, opening up new possibilities in the slow-exchange, and very-slow-exchange, situations. The analysis of the spectra, and their time dependence, is more involved than with conventional ones but is well understood. CIDEP is a common phenomenon and it yields complex information in a direct manner. The experiment is not difficult to perform and has a remarkably wide range of applications. It should be one of the major weapons in the armory of the photochemist and, at a fundamental level, it provides a continuous challenge to the physical chemist and theoretician.

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Modifications of Transition-Metal Reaction Patterns through the Manipulation of Superexchange Couplings

JOHN F. ENDICOTT

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Our training as chemists conditions us to think in terms of orbitals and even to construct mechanistic arguments based on the presumed properties of orbitals. In keeping with this bias it would be natural to expect

John F. Endicott is a Professor of Chemistry at Wayne State University. An Oregonian by birth, he received much of his early education there, culminating in a B.A. from Reed College. His Ph.D. in physical chemistry is from The Johns Hopkins University and he learned inorganic chemistry during a postdoctoral period with Henry Taube at Stanford University. He spent a few years on the faculty at Boston University before moving to Detroit in 1969. His research interests have always involved the fundamental problems of chemical reactivity.

that electronic selection rules and symmetry requirements be clearly manifested in the observed variations of single-electron-transfer rates. Certainly there have been a variety of attempts to attribute specific electron-transfer rate patterns to variations in electronic factors.[1-6] However, the work required to move nuclei

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from their reactant to their product configurations (often characterized by a nuclear reorganizational parameter, λ) has been found to contribute so much to the activation barrier for electron-transfer reactions that little room has been left for unequivocal demonstrations of the effects of purely electronic factors.[6-11] Nevertheless, several developments during the past decade have brought the issues related to these electronic contributions into relatively sharp focus: (1) Miller's systematic study of solvated electron reactions in rigid glass matrices;[12] (2) the evolution of protein systems[13-15] and/or synthetic donor–acceptor systems with peptide[16] or rigid organic[17] spacers in which large donor–acceptor distances can be defined with some certainty; (3) the systematic study of classes of bimolecular reactions in which purely electronic factors, such as the energy gap to certain low-lying excited states, can promote what are otherwise electronically forbidden electron-transfer processes.[19,20]

Such electronic factors can play a role only when the donor and acceptor are very weakly coupled. While the effects of weak electronic couplings are often small relative to the effects of nuclear reorganizational barriers, variations in electronic factors can alter observed rates by several orders of magnitude. More importantly, studies of these effects can lead to insights into the properties of donor and acceptor wave functions in the critical region far from the nuclei of origin. Among the systems in which these issues are crucial to the understanding of electron-transfer reaction patterns are several biological electron-transfer systems in which donor and acceptor prosthetic groups are separated by several tens of angstroms. Notable among these are bacteriochlorophylls in which the donor–acceptor separation has been established by X-ray crystallography.[21] There has been speculation that neighboring groups in these systems can alter the donor and/or acceptor wave functions in such a way that the electronic coupling is appreciably enhanced.[22]

Kinetic Formalisms

It is convenient to discuss electron-transfer rates in terms of a semiclassical formalism, such as that developed by Newton, Sutin, and co-workers.[23,24] The electron-transfer rate constant can be written as

$$k_{ELT} = K_0 \kappa_{el} \kappa_{nu} \nu_{nu} \qquad (1)$$

where K_0 is an equilibrium constant for bringing the reactants to a critical distance of separation r, κ_{el} is the electronic transmission coefficient (or retardation factor), κ_{nu} is the nuclear transmission coefficient (or retardation factor), and ν_{nu} is the frequency of nuclear motions coupled to the electron-transfer process and where it is assumed that nuclear and electronic motions can be separated (Born–Oppenheimer approximation). In the semiclassical approach, the transmission coefficients can be written as

$$\kappa_{el} = 2P/(1 + P)$$

and

$$\kappa_{nu} = \Gamma \exp(-\Delta G^{\ddagger}_{cl}/RT)$$

where $P = 1 - \exp(-\nu_{el}/2\nu_{nu})$, ν_{el} is the frequency of electronic motion in the transition state, Γ is a nuclear tunneling correction factor, and the work associated with the nuclear reorganization required for the transition state is given by

$$\Delta G^{\ddagger}_{cl} = (\lambda/4)(1 + \Delta G^{\circ}/\lambda)^2 \qquad (2)$$

In eq 2, λ is the classical nuclear reorganizational parameter,[7,9] and ΔG° is the free energy change associated with the electron-transfer step. In this description, reactant and product potential energy (PE) surfaces are constructed and the PE of their crossing region determines κ_{nu}. The effects of purely electronic factors on electron-transfer reactivity patterns appear only through ν_{el}, where[24b]

$$\nu_{el} = H_{RP}^2 S \qquad (3)$$

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in which H_{RP} is the donor–acceptor interaction energy in the reactant-to-product surface crossing region and

$$S = \frac{4}{h\nu_{nu}}\left(\frac{2\pi^3}{2\lambda_0 RT + (\lambda_{in}h\nu_{in})\ \mathrm{csch}\ (h\nu_{in}/2kT)}\right)^{1/2}$$

with λ_0 the solvent contribution and λ_{in} the first coordination sphere contribution to λ, and ν_{in} the mean vibrational frequency of first coordination sphere vibrational modes associated with the nuclear reaction coordinate.

Overview of Studies of Electronic Factors in Electron-Transfer Reactions: The Distance Dependence

The formalisms described above illustrate the important feature that purely electronic factors can only be important when H_{RP} is very small; i.e., for $\nu_{el} < 2\nu_{nu}$. Several authors[5,6,8,23–25] have proposed that H_{RP} varies exponentially with the distance (r_{DA}) of separation of donor and acceptor:

$$H_{RP} \cong J_{RP}\ \exp(-\alpha r_{DA}) \tag{4}$$

An intuitively appealing rationalization of eq 4 can be based on Dexter's theory of exchange-induced energy transfer.[25] In this approach, J_{RP} is an exchange coupling constant, based on the value of H_{RP} evaluated at $r_{DA} = 0$, the exponential term is an approximate overlap integral, based on the asymptotic (or spherical wave) solutions of the wave equation for the donor and acceptor, and α is a radial parameter characteristic of the donor–acceptor system (for example α^{-1} would be the Bohr radius for donor and acceptor hydrogen atoms). Expressions of the same form as eq 4 can be obtained from electron tunneling models.[5] The exchange and tunneling formalisms are at least partly interconvertible.

One can define two limiting classes of reactions for which H_{RP} might be small enough to influence reaction patterns: (1) reactions for which $r_{DA} > \alpha^{-1}$ and (2) reactions for which the electron-transfer process is forbidden so that $J_{RP} \sim 0$.

There has been a great deal of recent interest in unimolecular electron-transfer systems in which the donor and acceptor are held at fixed distances of separation. Much of this research has involved modified protein and metalloenzyme substrates. The results of this work[13–15] have so far seemed a bit confusing, partly because it is difficult to unequivocally evaluate the nuclear factors (κ_{nu}) in such reactions and partly because the nature of the substrates makes the isolation and systematic variation of key parameters difficult.[26]

The most elegant studies to date of the variations in electron-transfer rates with changes in r_{DA} have involved the electron-transfer relaxation rates in homologous series of compounds in which the donor and acceptor are covalently linked by means of relatively rigid bridging groups of variable length and in which the electron donor is prepared by means of fast radical reactions using the pulse radiolysis technique.[12d,16c,18] Particularly simple results have been obtained for the series of $(NH_3)_5Os^{II}-L-Co^{III}(NH_3)_5$ complexes in which
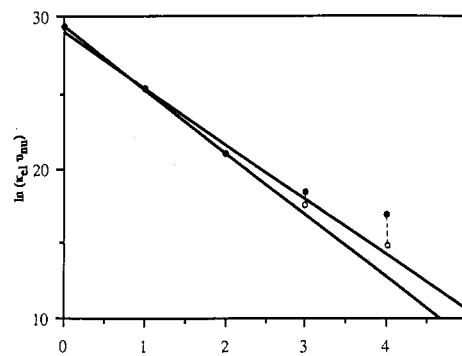
Figure 1. Plot of $[\ln k_{ELT} + \Delta H^*/RT]$ vs the number of L-proline units in the bridge of $(NH_3)_5Os^{II}-L-Co^{III}(NH_3)_5$. Closed circles are for mean electronic relaxation rate and the open circles are for the slow component of a biphasic decay. Data from ref 16c.

the bridging ligand L is a synthetic polypeptide constructed from isonicotinic acid (imine function bonded to Os) and poly(L-proline) (carboxylate function bonded to Co). In these molecules the lifetime for electronic relaxation is shorter than the mean conformational lifetime, so the rates are relatively uncomplicated by conformational rearrangements, and the donor and acceptor centers are the same through the series of molecules. Thus, nuclear reorganizational energies vary little (as reflected in $\Delta H^* = 42.7$–53.1 kJ mol^{-1}) while the electron relaxation rates, $(NH_3)_5Os^{II}-L-Co^{III}(NH_3)_5 \xrightarrow{k_{ENT}} (NH_3)_5Os^{III}-L-Co^{II}(NH_3)_5$, vary by a factor of 10^6 (the $Co^{II}(NH_3)_5$ product exchanges ligands with the solvent very rapidly and is not detected). The small variations observed in ΔH^* can be readily attributed to variations in the solvent contribution to the nuclear reorganizational energy λ_0. Thus, for $\lambda = \lambda_0 + \lambda_{in}$, the contributions from the first coordination spheres (λ_{in}) should be nearly constant, independent of the number of proline groups in the bridge. However, λ_0 does vary with r_{DA}.[7,10,23,24] It is necessary to correct k_{ELT} for this contribution in order to assess the distance dependence of κ_{el}. To accomplish this it is necessary to evaluate ΔG^*. For reactions in water at 25 °C, $4T\Delta S^*_0/\lambda \cong -0.015$[10] for the solvent contributions and ΔS^*_{in} is negligible.[27–29] Consequently, $\Delta G^* \cong \Delta H^*$. Since $K_0 = 1$ for unimolecular processes, $k_{ELT}\ \exp(\Delta H^*/RT) \cong \kappa_{el}\nu_{nu}$. Figure 1 shows that $|\ln k_{ELT} + \Delta H^*/RT|$ varies in proportion to the number of proline groups in the bridge, and since each proline contributes about 3.1 Å to r_{DA},[16] $\alpha^{-1} \cong 1.4 \pm 0.2$ Å. Further, for $n = 0$, $\kappa_{el}\nu_{nu} \cong 5.7 \times 10^{12}$ s$^{-1} \cong kT/h$, strongly suggesting that electron transfer in this complex is electronically allowed (a more accurate[24] estimate would be $\nu_{nu} \cong 1.3 \times 10^{13}$ s^{-1} and $\kappa_{el} \cong 0.5$).

While the above analysis may have to be modified as more systems are examined (e.g., see ref 12d), the work of Isied et al. has been an important conceptual advance. This is largely because the skillful use of simple molecular systems has allowed these workers to isolate the distance dependence from other factors affecting electron-transfer rates.

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(27) If the Os(III)–Os(II) and Ru(III)–Ru(II) couples behave similarly, $\Delta S^*_{Os-Co} \cong 0$ for the Os(II)–Co(III) couples in question since $\Delta S^*_{exch} \sim -20$ eu for the various self-exchange electron-transfer reactions while $\Delta S^°_{Os-Co} \cong 24$ eu and $\Delta S^*_{Os-Co} = \Delta S^*_{exch}(1 - 4\alpha^2) + \Delta S^°_{Os-Co}(1 + 2\alpha)/2,$[31] where $\alpha = \Delta G_{Os-Co}/\lambda \cong 0.21$. See also: Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.
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## More General Features of Donor–Acceptor Electronic Couplings

The distance dependence of κ_{el} is only one aspect of the general problems relating to the influence of electronic factors on electron-transfer rates. Several other issues can be formulated with reference to eq 4: (1) How much does α vary with changes of donor and/or acceptor orbitals? (2) To what extent is H_{RP} sensitive to the medium containing the donor and acceptor? (3) The exchange interpretation offered above suggests that there will be an angular component to eq 4 as r_{DA} becomes small and the donor and acceptor are fixed in their relative orientations (i.e., when asymptotic solutions of the wave equation are not valid). (4) Electronic and nuclear motions may be coupled near the transition state so the factorization in eq 1 is probably not rigorously correct. (5) The coupling between the electronic relaxation time and solvent relaxation times may also complicate the evaluation of κ_{el}.[23b,30,31]

The general issues raised above are not unique to electron-transfer reactions.[32] The general formalisms describe the nonradiative relaxation of an excited electronic configuration (e.g., $(NH_3)_5Os^{II}-L-Co^{III}(NH_3)_5$) to form products of a different electronic configuration (e.g., $(NH_3)_5Os^{III}-L-Co^{II}(NH_3)_5$). The most important constraint on the systems useful for study of the influence of electronic factors is that H_{RP} should be small. A practical constraint is that the nuclear reorganizational contributions be readily evaluated with eq 1 and semiclassical formalisms. Thus some reaction classes are likely to be much more useful than are others in systematic investigations of κ_{el}. For example, the classical, halide-bridged, inner-sphere electron-transfer reactions[33] and any reactions for which $\Delta G° > \lambda$ (i.e., reactions in the "inverted region") are not likely to be useful for this purpose since donor–acceptor coupling (H_{RP}) is usually large in the former[34] while κ_{nu} is difficult to evaluate for the latter. Among the useful reactions will be those for which electronic relaxation is quantum mechanically forbidden. We have found certain d-orbital-to-d-orbital energy-transfer reactions (Cr^{III} donors, Co^{III} acceptors)[19] and orbitally forbidden electron-transfer cross reactions (Co^{III} acceptors, high-spin Co^{II} donors)[20] to be useful probes of contributions to κ_{el}. In fact, the reaction patterns found in the energy-transfer reactions have been useful in designing electron-transfer systems in which κ_{el} can be systematically investigated.

Laporte-Forbidden Energy-Transfer Reactions at or near the Classical Surface Crossing Limit

The principal advantage of using energy-transfer systems in studies of κ_{el} is that κ_{nu} tends to make a relatively small contribution, since no net charge is transferred and λ_0 and λ_{in} tend to be smaller than in comparable electron-transfer reactions. To be useful in the present context, the energy-transfer process must

be dipole forbidden, and thus short range and collisionally activated.[25] Energy-transfer reactions involving the d-orbital excited states of transition-metal complexes can meet these conditions. For example, the quenching of the lowest energy ^2E excited state of Cr-(III) complexes by Co(III) complexes

$$(^2E)Cr(III) + (^1A_1)Co(III) \xrightarrow{k_q}$$
$$(^4A_2)Cr(III) + (^3X)Co(III)$$
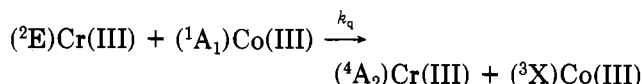
involves Laporte (d-orbital-to-d-orbital) and spin-forbidden transitions at each metal center, and the overall process is Laporte forbidden, but spin allowed. Under such circumstances, donor–acceptor coupling is mediated by a purely quantum mechanical interaction which results from the indistinguishability of electrons (the "exchange" interaction).[25] Since the lowest energy triplet excited states of Co(III) complexes have appreciably longer metal–ligand bonds than do the corresponding ground states,[35] eq 1–4 are expected to be applicable. That the coupling is weak is indicated by the relative inefficiency of these processes; thus k_q is about 0.1% of the diffusion limited rate for[19]

$$(^2E)Cr(phen)_3^{3+} + (^1A_{1g})Co(NH_3)_6^{3+} \rightarrow$$
$$(^4A_2)Cr(phen)_3^{3+} + (^3T_{1g})Co(NH_3)_6^{3+}$$
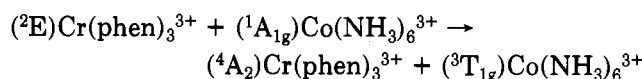
For this reaction, $\lambda \cong 37$ kJ mol^{-1}, $\Delta G \cong -36$ kJ mol^{-1}, and $\Delta G^*_{cl} = 0$ kJ mol^{-1}. This places the energy-transfer process in the surface-crossing regime with $\kappa_{nu} \cong 1$. Very similar conditions obtain for a series of Co(III)–hexaamine quenchers with $(^2E)Cr(phen)_3^{3+}$, $(^2E)Cr-(4,7-Me_2phen)_3^{3+}$, and $(^2E)Cr(1,7-Ph_2phen)_3^{3+}$ donors. If one assumes energy transfer occurs only at the van der Waals contact distance, this series can be employed to estimate[19c] $\alpha^{-1} = 1.82 \pm 0.17$ Å, based on eq 1 and 4. Thus the value of α^{-1}, characteristic of these (^2E)-Cr(III)–$(^1A_1)$Co(III) energy-transfer reactions, appears to be about 25% larger than the value of α^{-1} obtained for the $(NH_3)_5Os^{II}-L-Co^{III}(NH_3)_5$ electron-transfer reactions. At this stage it is not clear whether this difference is significant, but it is qualitatively consistent with the expectation that excited-state orbitals should be a little more diffuse than ground-state orbitals. The similarity of the results from such different studies is very encouraging.

When a coordinated amine (or ammine) of the Co(III) quencher is replaced by a relatively easily ionized ligand (Cl$^-$, Br$^-$, NCS$^-$, etc.), the complex becomes a much more efficient quencher. For many of these quenchers, the energy of the lowest energy triplet state is lower than that of $Co(NH_3)_6^{3+}$, a situation which could result in $-\Delta G° > \lambda$ and some important contributions from κ_{nu}. However, the reaction order does not parallel variations in $\Delta G°$; furthermore, $\Delta H^* \sim 0$ and identical reactivities are found for perprotio and perdeuterio complexes.[19c] Consequently, variations in quenching efficiency must be attributed to variations in κ_{el}. The enhancement of quenching rates, relative to those of related hexaamine complexes, tends to parallel the ease of oxidizing the non-amine ligands; i.e., the smaller the formal potential for the couple X + e$^-$ = X$^-$, the better the $Co(Am)_5X^{2+}$ complex quenches $(^2E)Cr(phen)_3^{3+}$. This suggests[19] that enhanced donor–acceptor electronic coupling in these systems is mediated by *intermolecu-*

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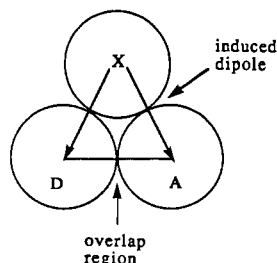
Figure 2. Schematic illustration of CT-induced dipoles in $(^2E)Cr(III)-(^1A_1)Co(III)$ systems. In principle, the interactions should be summed over $0° \leq \beta \leq 180°$ (β is the ADX angle) and a range of r_{DA} values. The optimum combinations of β and r_{DA} undoubtedly vary from system to system. The shaded area represents the region of maximum overlap.

lar, $X^- \rightarrow Cr(III)$, charge-transfer (CT) excited states.

The possibility of CT perturbations influencing H_{RP} is important because it demonstrates a simple mechanism by means of which "innocent" species in the environment of the donor and acceptor can alter the probability of energy transfer or electron transfer. Perhaps more importantly, these observations suggest that certain simple electronic properties of the reacting systems can be systematically altered in probing κ_{el}.

Energy Transfer: Theoretical Models for the CT Perturbations

The effects of CT perturbations on electron- and energy-transfer rates can be visualized in terms of the polarization of the electron density in the overlap region, between the donor and acceptor, through the interactions with the CT-induced dipole moments, μ_i (see Figure 2). These CT perturbations of κ_{el} can be described, with reference to eq 4, by an effect on the numerical value of either $\alpha^{19b,20a}$ or J_{RP}.[19c,20d,e] The former approach is intuitively useful and provides a qualitative guide for experimental studies, while CT perturbations on J_{RP} have the advantage of logical rigor. For weak perturbations, the two approaches are interconvertible through a first-order Taylor series expansion of the exponential. Only the second argument is outlined here.

The general form of the perturbations of J_{RP} can be constructed from the exchange integrals

$$\int \Psi^R_{*Cr} \Psi^R_{Co} (H_{exch}) \Psi^P_{Cr} \Psi^P_{*Co} \, d\tau \quad (5)$$

in which the unperturbed wave functions, $^0\Psi^x_i$ (x = R or P for reactants or products; i = *Cr, Co, Cr, or *Co; the asterisk denotes an electronically excited species), are corrected to first order for mixing with the perturbing excited state, whose energy is E_{CT} greater than that of the state X

$$\Psi^x_j = {}^0\Psi^x_j + \left(\frac{\gamma_i}{E_{CT(j)}}\right) {}^0\Psi^x_{CT(j)}$$

(j = Cr or Co; γ_j = a coupling parameter). In the exchange formalism, the contributions of product as well as reactant species must be considered. In principle, one should also consider the donor and acceptor metal ionization processes ("charge transfer to solvent"). The ionization processes are neglected here since the energies involved are relatively large (and difficult to determine). The effect of the CT perturbations on J_{RP} can be concisely written

$$J_{RP} \cong H°_{RP} + \frac{H_{RCT(*Cr)}\gamma_{*Cr}}{E_{CT(*Cr)}} + \frac{H_{PCT(*Co)}\gamma_{*Co}}{E_{CT(*Co)}} +$$

$$\dots \cong H°_{RP} + \sum \frac{H_{XCT(i)}\gamma_i}{E_{CT(i)}}$$

where the sum extends over all CT interactions. The integrals $H_{XCT(i)}$ cannot be readily evaluated. Their values may be either positive or negative, and the heuristic argument represented in Figure 2 suggests opposite signs for the coefficients of the terms in $E_{CT(*Cr)}$ and $E_{CT(Co)}$. The $E_{CT(*Cr)}$ term tends to dominate the sum in $(^2E)Cr(PP)_3{}^{3+}-Co(III)$ systems,[19c] so a reasonable approximation is $I \cong [H_{XCT(i)}\gamma_i]_{av}$, and

$$J_{RP} \sim H°_{RP} + I\sum_i \frac{\pm 1}{E_{CT(i)}} \quad (6)$$

(where the positive sign has been suggested for the $X^- \rightarrow Cr^{III}$ CT states and the negative sign for the $X^- \rightarrow Co^{III}$ CT states[19c]). It is usually possible to find some quenchers of each type studied for which $X^- \rightarrow M^{III}$ CT perturbations are not important, e.g., as in hexaamine–cobalt(III) complexes. The quenching rates for such complexes can be used as the reference rates relative to which the effects of CT perturbations can be evaluated. For a well-chosen reference system, $H°_{RP} \cong H_{RP}(ref)$, and

$$\frac{J_{RP}}{J_{RP}(ref)} \cong 1 + \frac{I}{H_{RP}(ref)}\sum_i \frac{\pm 1}{E_{CT(i)}} \quad (7)$$

For a few series of $(^2E)Cr(III)/Co(III)$ energy-transfer reactions, eq 7 is the basis for a reasonable correlation.[19c] A closely related treatment uses an estimate of the classical surface crossing rate (k_{cl}; see Figure 3 and the discussion below) instead of a reference reaction rate.

CT Perturbations of Electron-Transfer Reactions

Several conditions must be met in order that the effects of CT perturbations can be systematically studied in electron-transfer systems: (1) the systems to be studied must have small values of κ_{el}; (2) reaction rates must be conveniently measurable; and (3) it must be possible to systematically vary the CT perturbations.

One would expect electron-transfer processes to be "electronically inhibited" if the electron-transfer process (1) is accompanied by large changes in spin multiplicity, (2) is formally a multielectron process, or (3) involves poor overlap of the electron-transfer donor and acceptor orbitals (as when r_{DA} is large or when the donor and acceptor orbitals are orthogonal in a sterically constrained transition state). There is evidence that the spin constraint is not very rigorous in these reactions. Thus the reaction

$$(NH_3)_5Os^{II}-L-Co^{III}(NH_3)_5 \rightarrow$$

$$(NH_3)_5Os^{III}-L-Co^{II}(NH_3)_5$$
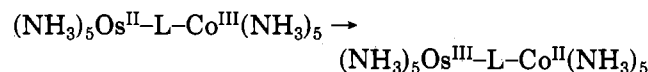
appears to be nearly adiabatic ($\kappa_{el} \sim 0.5$) when $r_{DA} \leq 8$ Å, even though the equilibrium cobalt(II) product has quartet spin multiplicity and the overall process is a singlet–triplet electronic transition. There is a possibility that such electron transfers are mediated by a low-spin Co(II) excited state.[36] In any event, spin relaxation processes are generally rapid enough[37-39] in

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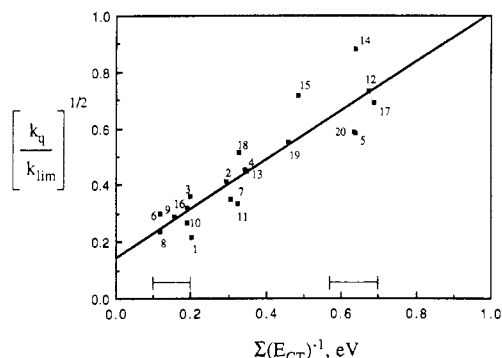
Figure 3. Correlation of relative rate constants for (^2E)Cr-$(phen)_3^{3+}$–$(^1A_1)$Co(III) energy-transfer excited states. The rate ratios were obtained from $k_q = sJ_{RP}^2 k_{lim}$ and $k_{lim} = f_L K_0 \nu_{nu}$ exp$(-2\alpha r_{DA})$. Parameters not defined in the text are as follows: s, a statistical factor equal to 1 for CoL_5X^{2+} complexes and 0.5 for $CoL_4X_2^+$ complexes; f_L, a factor referencing the rates of each family of quenchers to k_q for $Co(NH_3)_6^{3+}$ ($f_L = 1.0, 1.0, 1.1,$ and 0.8 for $Co(NH_3)_5X^{2+}$, $Co(en)_2X_2^{d+}$, $Co(L_1)X_2^+$, and $Co(L_2)X_2^+$ quenchers, respectively). Other numerical values used are $\alpha = 0.55$ Å^{-1} and $\nu_{nu} = 1.4 \times 10^{13}$ s^{-1} (based on ν_{Co-NH_3}). This treatment assumes that $J_{RP} \cong H^\circ_{RP} + H_{XCT}\sum(E_{CT})^{-1}$, where the sum extends over reactant and product species with the $X^- \to Cr^{III}$ contributions taken as positive and the $X^- \to Co^{III}$ contributions taken as negative. Estimated uncertainties in $\sum(E_{CT})^{-1}$ are indicated for limiting regions at the bottom of the figure. Quenching data are from ref 19c. All reactions at 25 °C in 1 M $NaCF_3SO_3$. Quenchers: 1, $Co(NH_3)_5Cl^{2+}$; 2, $Co(NH_3)_5Br^{2+}$; 3, $Co(NH_3)_5NO_2^{2+}$; 4, $Co(NH_3)_5NCS^{2+}$; 5, $Co(NH_3)_5N_3^{2+}$; 6, *trans*-$Co(en)_2Cl_2^+$; 7, *trans*-$Co(en)_2(NCS)_2^+$; 9, *trans*-$Co(L_1)(OH_2)Cl^{2+}$; 10, *trans*-$Co(L_1)$-$(NO_2)_2^+$; 11, *trans*-$Co(L_1)(NCS)Cl^+$; 12, *trans*-$Co(L_1)(OH_2)N_3^{2+}$; 13, *trans*-$Co(L_1)(NCS)_2^+$; 14, *trans*-Co-$(L_1)(NCS)N_3^+$; 16, *trans*-$Co(L_2)(NO_2)_2^+$; 17, *trans*-$Co(L_2)$-$(OH_2)N_3^{2+}$; 18, *trans*-$Co(L_2)(NCS)_2^+$; 19, *trans*-$Co(L_2)(NCS)N_3^+$; 20, *trans*-$Co(L_2)(N_3)_2^+$. $L_1 = 1,4,8,11$-tetraazacyclotetradecane; $L_2 = 2,3,9,10$-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene. Quenching rate constants for the more efficient reactions ($k_{obsd} > 10^8$ M^{-1} s^{-1}) have been corrected for diffusional effects using $k_{obsd}^{-1} = k_d^{-1} + k_q^{-1}$, where $k_d \cong 4 \times 10^9$ M^{-1} s^{-1} for $CoL_4X_2^+$ quenchers.

transition-metal complexes that serious rate retardations would not be expected.

Electron-exchange reactions between Co(III) and high-spin Co(II) complexes are spin allowed, but orbitally forbidden three-electron processes (i.e., three electrons must change orbitals). That such three-electron processes tend to be relatively forbidden is qualitatively indicated by the observation that the high-spin Co(sep)$^{2+}$ reductions of many Co(III) complexes are slower than the corresponding Ru(NH$_3$)$_6^{2+}$ reactions, whereas the simple classical arguments would predict the reverse order.[20]

Systematic variations of the CT perturbations of simple, "electronically forbidden" electron-transfer reactions have been accomplished by changing the anion in simple ion pairs.[20] For example, Co(phen)$_3^{3+}$ associates with anions X$^-$ to form ion pairs {Co(Phen)$_3^{3+}$,X$^-$}, many of which have resolvable CT absorptions in the visible to near-ultraviolet spectral regions. The energies of these CT transitions depend largely on the thermodynamics of the X/X$^-$ and Co(phen)$_3^{3+}$/Co(phen)$_3^{2+}$

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Table I
Estimated Superexchange Coupling Parameters for Several Systems Exhibiting CT Interactions

system	estimated $\bar{H}_{XCT}$,[a] eV M^{-1} s^{-1}	estimated $k_{cl}(K_0 \kappa_{nu} \nu_{nu})$[b]
$(^2E)Cr(PP)_3^{3+}$–$Co^{III}L_5X^c$	1.1	d
{Co(phen)$_3^{3+}$, X$^-$}–Co(sep)$^{2+\ e}$	0.72	3×10^5
{Co(phen)$_3^{3+}$, X$^-$}–Co([9]aneN$_3$)$_2^{2+\ f}$	0.72	8×10^6
{Co(OH$_2$)$_6^{3+}$, X$^-$}–Fe(bpy)$_3^{2+\ f}$	0.43	1×10^7
{Co((bzo)$_3$[12]hexaeneN$_3$)$_2^{3+}$, X$^-$}–Co(sep)$^{2+\ f}$	1.8	8×10^4
Co(NH$_3$)$_6$X^{2+}–Co(sep)$^{2+\ g}$	$\sim$2.5	(1 to 10^5)[h]

[a] The slopes obtained in plots of $(k_{obsd}/k_{cl})^{1/2}$ vs $\sum(E_{CT})^{-1}$. Based on data in the references cited. [b] Based on self-exchange parameters, equilibrium constant and Marcus square root relation, and/or the rates of relatively adiabatic reference reactions. $\bar{H}_{XCT}$ is an averaged coupling parameter for each series of reactions. [c] Reference 19b,c. [d] The "classical limit" for exchange-mediated energy-transfer reactions has been taken to be the nonradiative relaxation rate in a single molecule; i.e., we have used $k_{cl} \cong K_0 \nu_{nu}$ exp$(-2\alpha r_{DA})$ with $\alpha = 5.5$ nm^{-1}. [e] References 19b and 20a. [f] Reference 20b. [g] Reference 20e. [h] Range of values inferred from relatively adiabatic cross reactions used in ref 20e.

redox couples.[10] These are weak ($K_x = 5$–50 M^{-1}), second coordination sphere complexes, so that variations of X$^-$ cannot greatly alter the nuclear reorganizational energies characteristic of the {Co(phen)$_3^{3+}$, X$^-$}/{Co(phen)$_3^{2+}$, X$^-$} couples, and κ_{nu} is expected to be approximately constant for such a series. That this is the case is demonstrated by the insensitivity of the electron-transfer rates to changes of X$^-$ for Ru(NH$_3$)$_6^{2+}$ reductions of {Co(phen)$_3^{3+}$, X$^-$} ion pairs (the only significant change from the rate observed for X$^-$ = CF$_3$S-O$_3^-$ was a 2-fold increase for the relatively reducing ascorbate ion, in contrast to a 60-fold range found in the Co(sep)$^{2+}$ reductions of {Co(phen)$_3^{3+}$, X$^-$}.[19b] These contrasting patterns of reactivity for Ru(NH$_3$)$_6^{2+}$ and high-spin Co(II) (Co(sep)$^{2+}$ or Co([9]aneN$_3$)$_2^{2+}$) toward the {Co(phen)$_3^{3+}$, X$^-$} ion pairs are qualitatively consistent with several points made above: (1) the Co(III)–Ru(II) reactions tend to be nearly adiabatic ($\kappa_{el} > 0.1$); (2) the Co(III)–high-spin Co(II) reactions tend to be electronically inhibited ($\kappa_{el} < 0.1$); (3) the inhibited electron-transfer rates can be promoted through contributions from relatively low-energy CT excited states.

More quantitative discussions of the effects of CT interactions can be formulated in terms of the perturbational variations as discussed above. It is useful to define $k_{cl} = K_0 \kappa_{nu} \nu_{nu}$ so that $\kappa_{el} = k(obsd)/k_{cl}$. Values of k_{cl} can be based on the {Co(phen)$_3^{3+}$, X$^-$}–Ru(NH$_3$)$_6^{2+}$ reactions, for which κ_{el} appears to be 0.5–1.[19b,20a-c] In applying eq 6 to such reactions, it is necessary to use $E_{CT(i)}$ values which are appropriate near the transition state,[19b,23b,40] i.e., as

$$E_{CT(i)} = E^*_{CT(i)} - E^\ddagger_{RP} + \delta_i$$

where $E^*_{CT(i)}$ is the activation energy obtained for the crossing point of the reactant and product nuclear PE surfaces and δ_i corrects for the energy differences ($\leq \sim$25%) of the CT excited states with ground-state and transition-state nuclear coordinates. Detailed expressions can be found elsewhere.[19b,20e,23b,40] These perturbations in $E_{CT(i)}$ have the effect of mixing nuclear and electronic terms.

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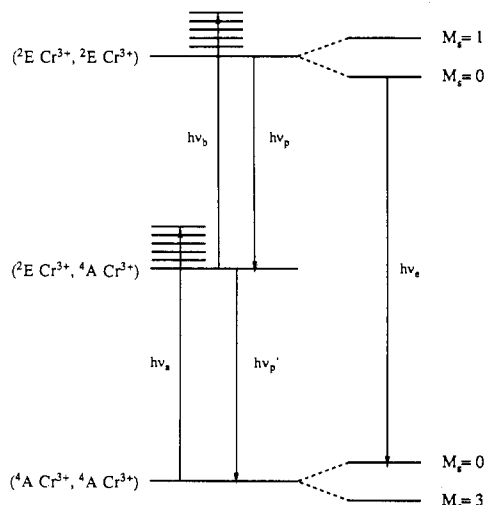
Figure 4. Qualitative energy level diagram illustrating upconversion in binuclear complexes. Coupling between excited states has been assumed to be stronger than coupling between ground states.

Table I summarizes the correlations which have been generated for the CT-enhanced relative electron-transfer rates $(k(\text{obsd})/k_{cl})$ in several electron-transfer and energy-transfer systems. It is remarkable that very similar electronic effects have been inferred for reactions as different as energy transfer and electron transfer.

A "Resonance" Effect in Electron-Transfer Reactions

The exchange interaction formalism suggests that the value of H_{RP} should increase as the reactants and products approach electronic degeneracy.[19a,20d,e] In experimental terms, this suggests that self-exchange electron-transfer reactions, which are necessarily electronically degenerate, should approach the $\kappa_{el} \simeq 1$ limit more closely than do cross reactions. A few different kinds of experimental studies have recently emerged in support of this hypothesis.[20d,e,41]

A Spectroscopic Analogue and the Possibility of "Photochemical Upconversion" in Simple Molecular Systems

The simultaneous electronic excitation of two weakly coupled metal centers by absorption of a single photon has been widely observed and discussed.[42-51] Some aspects of this work are as follows: (i) Simultaneous pair absorptions have been observed which are significantly more intense than the "parent", single-center

absorptions.[42,44,50] (ii) Dexter[51] used his theory of exchange-mediated energy transfer[25] as the basis of one of the first theoretical treatments of simultaneous pair absorptions. (iii) One of the most widely cited mechanisms for the intensity enhancement of simultaneous pair absorptions involves superexchange coupling to low-energy charge-transfer excited states.[43] Since identical selection rules apply to absorption and emission, there must exist multinuclear complexes for which the sequential absorption of two low-energy photons $h\nu_a$ and $h\nu_b$ is followed by relatively prompt radiative relaxation to the ground state with the emission of a higher energy photon $(h\nu_e)$ as illustrated in Figure 4. It seems likely that the appropriate systems will have weakly coupled ground states and reasonably long-lived, singly excited states. Binuclear Cr(III) complexes have many of the appropriate features, and simultaneous pair absorptions, mediated by bridging ligands, are well documented in Cr(III) dimers.[42] It seems likely that the right combination of weakly coupled complexes and CT perturbations will eventually be found which will promote efficient upconversion in Cr(III) complexes.

Summary

It is difficult, but not impossible, to isolate the purely electronic contributions to electron-transfer reactions. Owing to the complexity of the problems, the most instructive studies to date have employed small molecules rather than proteins. Several important features have emerged from these studies.

The distance dependence inferred in some simple electron-transfer and energy-transfer reactions of transition-metal compounds is described by eq 4 with $\alpha^{-1} \simeq 1.4$–1.8 Å. This is within the range of values that have been inferred in more complex systems,[7d,12-18] but few of these studies have been able to adequately correct for κ_{nu} in the evaluation of κ_{el}. There is likely to be some dependence on the detailed properties of the donor and/or acceptor, as yet the information available does not permit evaluation of such factors.

It has also been possible to generate systematic electronic perturbations of reaction rates in certain small-molecule systems. The most readily investigated and perhaps the most common such perturbations increasing H_{RP} are introduced by low-energy charge-transfer excited states. These are most consistently described as perturbations on J_{RP} in eq 4, and a very simple treatment, eq 7, leads to similar magnitudes of the coupling coefficients, $H_{XCT} \sim 1$ eV (Table I), for the CT perturbations of *energy*-transfer and *electron*-transfer reaction rates. These effects are similar in magnitude to the analogous couplings found in charge-transfer complexes.[52]

This report has described the enhancement of donor–acceptor electronic coupling in reaction systems in terms of perturbational corrections to the donor and acceptor wave functions. The perturbations considered originate from the electronic interaction of the donor and acceptor with environmental species which are not necessarily linked to the donor and acceptor through covalent bonds. Much current discussion of donor–acceptor interactions in proteins has focused on "through-bond" interactions.[4,12,13,18] The formal treat-

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ments of these interactions often have much in common with the treatment of CT perturbations outlined above. While there may be some intuitive value in distinguishing "through-bond" and "through-space" interactions, it may be useful to replace them with the idea that induced dipole moments modify the "shape" of the electronic wave functions in spatial regions of maximum donor–acceptor orbital overlap. Induced dipole moments are directional, and this feature suggests the possibility of some tendency of the perturbations to favor charge or energy transfer along one spatial direction over any others. Although the basis of this inference is a simple heuristic model, the idea is interesting enough to warrant some experimental study. It could be important in understanding electron transport in complex systems.

Progress in the study of electronic effects in electron-transfer and energy-transfer reactions has been dramatic in the past decade, but many of the important fundamental issues are only beginning to be articulated and few implications of the patterns of behavior discussed above have been explored. This article has developed some of these issues. Further intensive studies are likely to lead to a detailed understanding of electron transport in biologically important protein systems. Other novel implications seem likely, such as the manipulation of the probability of photochemical upconversion (i.e., the annihilation of two excited states to produce a high-energy photon). The area of research should continue to provide challenges for significant experimental and theoretical study. Maybe we will even get the orbitals back into electron-transfer chemistry.

Intercalation and Binding of Carcinogenic Hydrocarbon Metabolites to Nucleic Acids

Ronald G. Harvey* and Nicholas E. Geacintov

Ben May Institute, The University of Chicago, Chicago, Illinois 60637, and Chemistry Department, New York University, New York, New York 10003

Two central dogmas underlie modern research in chemical carcinogenesis. The first is Miller's hypothesis[1] that the active forms of most carcinogens are electrophilic intermediates formed metabolically. The second is the assumption that the initiating step in the induction of tumors is the covalent binding of the active carcinogen species to a cellular macromolecule, generally presumed to be DNA. While there exists abundant evidence that formation of carcinogen–DNA adducts can result in mutations that lead ultimately to the induction of cancer, the details of the process at the molecular–genetic level remain obscure.

This Account reports recent advances in understanding the mechanism of interaction with nucleic acids of the active metabolites of one class of carcinogens, the polycyclic aromatic hydrocarbons (PAHs). That PAHs potentially play an important role in human cancer is suggested by their widespread environmental prevalence,[2,3] their relatively high tumorigenic potency, and their broad spectrum of activity in animal tissues.[4] Significant levels of benzo[a]pyrene and other carcinogenic PAHs are present in urban air, in auto exhaust, and in many common foods.[2,3] As a class, the PAHs rank second only to mycotoxin mold metabolites, e.g., aflatoxin, in relative carcinogenic potency. Moreover, PAHs are uniquely capable of selectively inducing diverse tumors in animal tissues, including mammary carcinoma, leukemia, sarcoma, etc., dependent upon the experimental conditions employed.[4] PAHs also offer significant advantages as model compounds for re-

Ronald G. Harvey was born in Ottawa, Canada. He received a B.S. in biology from UCLA in 1952. Following military service and two years as project leader at Sinclair Research Laboratories, Harvey, IL, he completed his academic studies at The University of Chicago, where he received a Ph. D. in chemistry in 1960. He subsequently joined the faculty of the Ben May Institute of The University of Chicago. Except for a year of postdoctoral study with D. H. R. Barton at Imperial College, University of London, his academic career has been entirely at The University of Chicago, where he is now Professor. His major research interests include the chemistry of polycyclic hydrocarbons, the mechanisms of chemical carcinogenesis, and novel synthetic methods.

Nicholas E. Geacintov was born in France and was educated at Syracuse University (New York State College of Forestry), where he received a Ph.D. in 1961 in polymer science. After postdoctoral work at the Polytechnic Institute of Brooklyn with Gerald Oster, he became interested in photochemistry. His primary interests at the present time involve applications of molecular spectroscopic techniques in various fields of biophysical chemistry, including the mechanisms of interactions of polycyclic aromatic mutagens and carcinogens with nucleic acids. He has been a member of the Chemistry Department at New York University since 1969.

*To whom correspondence should be addressed at The University of Chicago.

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