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Charge-Transfer Perturbations of the Electronic Contributions to Bimolecular Reactions. Nonadiabatic Effects Observed in Energy-Transfer and Electron-Transfer Reactions[1]

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Abstract: The rates of intermolecular *energy* transfer between (^{2}E)Cr(polypyridyl)$_3^{3+}$ and Co(III) complexes and the rates of intermolecular electron transfer between Co(polypyridyl)$_3^{3+}$ and Co(sep)$^{2+}$ have been found to be sensitive to weak charge-transfer perturbations for certain combinations of reactants. The variations in (^{2}E)Cr(III)/Co(III) quenching rates appear to be largely dictated by the electronic terms in a collisional mechanism. The intermolecular d-orbital donor–acceptor overlap decreases exponentially with donor–acceptor separation. Thus, the rates for Co(NH$_3$)$_6^{3+}$ and Co(NH$_3$)$_5$F^{2+} with the large Cr^{III}–polypyridyl donors are about 0.1% of the expected limits imposed by diffusion and spin statistics. However, for a given donor, the quenching rates for Co(NH$_3$)$_5$X^{2+} and related complexes increase in the order X = F < Cl < Br < NCS < N$_3$. The effect of ligands in enhancing quenching can be described in terms of a weak charge-transfer perturbation between the (^{2}E)Cr(PP)$_3^{3+}$ donor and an oxidizable ligand (X) of the acceptor. This perturbation may be discussed either in terms of a superexchange contribution to the electron-exchange integral or in terms of an increase in the effective mean orbital radius along the donor–acceptor axis. The latter approach leads to a simple correlation of variations in rate with the reciprocal of the energies of the charge-transfer perturbation. These observations have led to a search for related effects in those simple electron-transfer reactions which are suspected of being relatively nonadiabatic, i.e., reactions in which the electronic matrix element may make a contribution to the rate. The electron-transfer systems chosen for this study have used weak ion-pair charge-transfer interactions to perturb [Co(PP)$_3^{3+}$,X$^-$]–M^{II} electron-transfer rates. For M^{II} = Co(sep)$^{2+}$, but not for Ru(NH$_3$)$_6^{2+}$, the electron-transfer rates are susceptible to such perturbations for X$^-$ = I$^-$, NO$_2^-$, and ascorbate. The effect of these electron-transfer rates varies inversely with the energetics of the [Co(PP)$_3^{3+}$,X$^-$] → [Co(PP)$_3^{2+}$,·X] charge-transfer interaction. These effects, and comparisons with the component self-exchange reactions, show that the Co(PP)$_3^{3+}$/Co(sep)$^{2+}$ reaction is relatively nonadiabatic in the absence of any charge-transfer perturbations; but the reaction becomes more adiabatic as the magnitude of the energy gap to the perturbing charge transfer state decreases. In the absence of CT perturbations, the Co(phen)$_3^{3+}$/Co(sep)$^{2+}$ reaction would occur with about 0.4% of the rate based only on Franck–Condon contributions (i.e., for the adiabatic limit). Much smaller effects of the counterions (X$^-$) are found for Co(PP)$_3^{3+}$–Ru(NH$_3$)$_6^{2+}$ and Co(NH$_3$)$_6^{3+}$–Co(sep)$^{2+}$ reactions, in accord with the expectations that ruthenium reactions may be relatively adiabatic and that the [Co(NH$_3$)$_6^{3+}$,X$^-$] → *[Co(NH$_3$)$_6^{2+}$,·X] energy gap should be relatively large.

Among the more fundamental problems limiting quantitative understanding of electron-transfer processes is ambiguity about the manner in which the transfer probability varies with donor–acceptor separation. A persistent concern with this issue has originated from studies of electron transport between widely separated prosthetic groups in biological systems.[2] "Electron tunneling" has been implicated in solvated-electron,[3a] radical ion,[3b] and excited-state[3c,4] reactions in rigid media. There have also been a few recent studies of electronic relaxation in molecular systems synthesized so as to maintain donor–acceptor separations with known covalent linkages.[5-9] Inferences from these studies have not been entirely consistent. Some of the apparent inconsistencies may reflect the complicated nature of the systems studied and the elaborate interpretations of results which are usually required. On the other hand, some inconsistencies may reflect differences in factors other than the separation distance which contribute to donor–acceptor interactions in the varied systems investigated. If some factors other than distance contribute to donor–acceptor coupling, then inferences about complex systems must take account of these additional interactions. Information from relatively simple systems would be very useful in evaluating various possible contributions to donor–acceptor interactions. We have investigated some simple bimolecular reactions in which it is possible to systematically vary some of the factors which may contribute to donor–acceptor coupling.

The rate variations of simple bimolecular reactions can usually be factored into the separate contributions of nuclear rearrangements and of purely electronic properties of the donor and acceptor orbital systems.[10-16] The large rate variations in transition-metal electron-transfer reactions are usually a consequence of corresponding variations in nuclear distances which accompany net transfer of charge.[10-16] For example, Franck–condon factors

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have been found to dominate the reactivity of $(^1A)Co(III)/(^4T)Co(II)$ couples[9-11] in keeping with the large change in bond length which accompanies electron transfer. This is so despite the accompanying changes of spin multiplicity which one might expect to maximize the contributions of purely electronic factors. Even with such dominant Franck–Condon factors, it appears that purely electronic terms can contribute to the observed rate constants[2-8,13b,14-20] in many electron-transfer reactions of transition-metal complexes. Unequivocal assignment of the reported discrepancies between calculated (based on Franck–Condon contributions only) and observed electron-transfer rates to variations in donor–acceptor electronic interactions is generally precluded by uncertainties in knowledge of bond lengths, vibrational frequencies, and free-energy changes. As a consequence, there is little *experimental* documentation of the details of purely electronic interactions in electron-transfer reactions of transition-metal complexes. Theoretical estimates of these quantities (e.g., ref 13b, 19c, and 20b) seem to involve many assumptions and can be in error by a few orders of magnitude. Thus, it is still not firmly established how changes in electronic properties such as spin multiplicity, donor–acceptor overlap, or orbital symmetry affect the observed rates of bimolecular electron-transfer reactions.

We have been investigating energy-transfer reactions of electronically excited transition-metal complexes in order to gain some insight into the factors contributing to the electronic matrix elements of bimolecular reactions. While many details differ (such as the nature of the operator coupling reactant and product surfaces, specific wave functions, etc.) in bimolecular *electron-* and *energy*-transfer reactions, formalisms describing the rates of the collisionally activated reactions are qualitatively similar;[13,15a,20-22] both reaction classes may be described as nonradiative electronic transitions within the collision complex. For example, the transition probabilities (or rate constants) for both processes may be derived from the Fermi Golden rule,[11-13,15,21,22]

$$P_{ab} = (2\pi/\hbar)(H_{ab})^2\rho$$

(H_{ab} is the vibronic matrix element; ρ is the density of product states). For electron transfer this is commonly expressed, assuming separability of nuclear and electronic motion in the vibronic matrix element, H_{ab}, as

$$k_e = K_o\nu_e \exp[-\Delta G_e^*(\mathrm{FC})/RT]$$

(K_o is an outer-sphere association constant for the reactants; ν_e is a frequency term which can reflect the electronic matrix element for weak reactant–product coupling; $\Delta G_e^*(\mathrm{FC})$ is the Franck–Condon term expressed as an activation free energy). It is customary to treat the changes in solvent and coordination sphere nuclear coordinates as separate contributions to the Franck–Condon term.

In contrast, it has been traditional to express the Franck–Condon contribution in energy-transfer reactions in terms of a spectral overlap integral,[21]

$$k_q = K_o\nu_q \int \epsilon_D \epsilon_A \, d\omega$$

(where ϵ_D and ϵ_A are normalized probabilities for donor emission and acceptor absorption at frequency ω, respectively; the other variables are defined as above). In both classes of reactions the electronic term, ν_i^{el} (i = e for electron transfer; i = q for energy transfer; in the weak coupling limit), is of the form[2-5,11,13,15,21,22]

$$\nu_i^{el} = a_i(H_i^\circ)^2 \exp[-2\alpha_i r_{DA}] \qquad (1)$$

where the a_i are constants of proportionality; the H_i° are sums of interaction terms giving rise to reactant/product coupling; the α_i^{-1} are mean orbital radii of the donor and the acceptor; r_{DA} is the donor–acceptor separation; i = e or q. The exponential factor can be interpreted as donor–acceptor overlap approximated in the assymptotic solution of the wave equation and valid for $r_{DA} \gg \alpha_i^{-1}$. Empirical equations very similar to eq 1 have been used to represent the electronic matrix element in those gas-phase atom–molecule reactions which produce ion pairs.[16]

Even for simple coordination complexes, eq 1 predicts "nonadiabatic" electron-transfer rates for plausible values of α_i^{-1}; e.g., for the $Co(NH_3)_6^{3+,2+}$ couple values of $\alpha_e^{-1} \sim 180$ pm and $r_{DA} = 650$ pm (van der Waals contact) would result in a value of k_e which is ~0.1% of the value based only on Franck–Condon contributions. Therefore, a search for such electronic effects in simple reactions seems in order.

Our investigations of bimolecular energy-transfer reactions have been motivated by the expectation that Franck–Condon factors should make relatively small contributions for some of these reactions, and that the reaction rates should reflect more directly the variations in electronic terms than has been found to be the case for electron-transfer reactions. The Laporte forbidden electronic transitions involving d orbitals of transition-metal complexes are promoted by multipole interactions,[23] and work in several laboratories[20,24-26] has demonstrated that intermolecular energy-transfer reactions of these systems very often proceed by means of a collisional mechanism. These *energy*-transfer reactions tend to have smaller intrinsic Franck–Condon barriers than do the *electron*-transfer reactions of the same complexes (because no charge is transferred, bond length changes are smaller, etc.). As a consequence, even a moderately favorable donor–acceptor energy gap can result in reactions which are insensitive to Franck–Codon factors. This has been nicely illustrated in Wilkinson and co-workers' studies of Cr(III) quenching of organic triplets,[24] wherein sufficiently large donor–acceptor energy differences (i.e., $E[^3D] - E[(^2E)Cr(III)]$) resulted in $\Delta G_q^*(\mathrm{FC}) \rightarrow 0$ and limiting values of k_q which varied with the steric bulk of the acceptor.

In some related work, we have found that quenching of excited-state $(^2E)Cr^{III}$–polypyridyl species by $(^1A_1)Co(III)$ complexes,

$$(^4A_2)Cr(PP)_3^{3+} + h\nu \rightarrow [(^4T)Cr(PP)_3^{3+}] \rightarrow (^2E)Cr(PP)_3^{3+}$$

$$(^2E)Cr(PP)_3^{3+} \rightarrow (^4A_1)Cr(PP)_3^{3+} + h\nu, \text{ or heat}$$

$$(^2E)Cr(PP)_3^{3+} + (^1A_1)Co(III) \xrightarrow{k_q} (^4A_2)Cr(PP)_3^{3+} + (^3T)Co(III) \ [\text{or } (^5T)Co(III)]$$

is relatively insensitive to Franck–Condon factors; i.e., estimated values of $\Delta G_q^*(\mathrm{FC})$ are relatively small and k_q appears to be independent of the donor–acceptor energy gap.[26] However, the cobalt complexes are usually very poor quenchers. These are therefore likely to be a set of reactions in which values of k_q are more responsive to variations in electronic than Franck–Condon factors. In the present report we describe studies which indicate

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that environmental charge-transfer perturbations can alter the electronic matrix elements in at least some bimolecular *energy*-transfer and *electron*-transfer reactions.

Experimental Section

Syntheses. Acidopentaammine–cobalt(III) complexes,[27] 1,4,8,11-tetraazacyclotetradecane ([14]aneN_4 or cyclam),[28] *trans*-Co^{III}([14]aneN_4)XY,[28,29] polypyridylchromium(III)[30] and -cobalt(III),[31] and (*S*)-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6.]eicosanecobalt(III) (Co(sep)$^{3+}$),[32,33] were prepared as described in the literature. Perchlorate or trifluoromethylsulfonate salts of the complexes (*trans*-1,2-diaminocyclohexane)bis(phenanthroline)cobalt(III) and tris(3,4,7,8-tetramethylphenanthroline)cobalt(III) were prepared by a variation of the literature method for polypyridylcobalt(III) complexes.[31] Proton NMR spectra and chemical analyses were used to characterize these complexes. The purity of previously reported complexes was established by comparison of spectra with literature reports and by differential pulse polarography. Commerical $Ru(NH_3)_6Cl_3$ was purified by recrystallization. Trifluoromethanesulfonic acid was purified by vacuum double distillation of the technical material. Sodium and lithium salts were prepared by neutralization of the respective carbonates with the acid. Ascorbic acid was purified by means of recrystallization after decolorization with activated charcoal, all in strictly deaerated and light-shielded environments. The recrystallization procedure was repeated at least twice. The solid samples thus obtained were used within 2 days. Stock solutions were used within 4–5 h. Reproducible results were not obtained unless these precautions were taken. All other reagents were of reagent grade or better.

Techniques. 1. Luminescence Quenching Studies. The techniques employed have evolved over a period of several years. Quenching rates were determined by using a combination of luminescence quenching (Stern–Volmer) and transient lifetime techniques.

Emission intensities were determined, using a Molectron UV1000 pumped Molectron DL-14 tuneable dye laser as the excitation source, at a wavelength selected to minimize filter effects and to optimize absorption by the Cr(III) substrate. For most studies we have used a coumarin-2 dye and peaked the excitation wavelength to maximize intensity at the detector.

Samples were deaerated by using a Cr(II) scrubbed nitrogen or argon stream for about 30 min prior to photochemical, stopped flow, or electrochemical studies. Samples for luminescence lifetime studies were contained in a standard 1-cm fluorescence cuvette fitted with a serum cap within a thermostated (±0.2 °C) PRA cell housing equipped with an Omega thermistor temperature sensor. Emitted light was collected perpendicular to the excitation beam with use of a 10 cm quartz collimating lens focussed to maximize intensity in a PAR Model 1250 optical multichannel analyzer (OMA) with a silicon intensified detector. The emission intensity of $(^2E)Cr(PP)_3^{3+}$ was measured at the emission maximum and was averaged over 10–30 measurements for each determination. A standard linear least-squares program was used to obtain Stern–Volmer constants, K_{sv}, from the concentration dependence of the reciprocal intensity. Absorption corrections[34,35] were made, as necessary, on the basis of the measured donor and acceptor absorbances at the excitation and emission wavelengths. Second-order quenching rate constants were obtained from the values of K_{sv} as $k_q = K_{sv}\tau_D^{-1}$, where the donor lifetimes (τ_D) were determined under the conditions of medium, temperature, deaeration, etc., used in the quenching experiments. Quenching rate constants obtained by using this approach were in satisfactory agreement with those obtained in early stages of this work with use of an Aminco-Bowman spectrometer to determine emission intensities.

2. Transient Lifetime Studies. The decay of the $(^2E)Cr(PP)_3^{3+}$ excited-state absorbance[36,37] was monitored with use of a standard Xenon Corp flash photolysis system. Ultraviolet excitation wavelengths were removed by surrounding the sample with a saturated solution of naphthalene in ethanol. Transient decay rates were monitored with a Nicolet Explorer III digital oscilloscope. Quenching rate constants were obtained from the dependence of the first-order decay rates on the concentration of quencher with use of standard least-squares analysis. We have also determined emission decay lifetimes at 25 °C and 15 °C with use of laser excitation, as described above, but with the scattered radiation focussed on a Jobin-Yvon H-100 spectrometer and the decay of the emission maximum detected with an RCA 7102 photomultiplier interfaced to either the Nicolet Explorer III or a Tektronix 7904 oscilloscope, by means of a Products for Research Inc., housing.

3. Electron-Transfer Studies. Kinetic studies were made on an Aminco stopped flow instrument thermostated at 25 °C. In order to avoid complications in the kinetic analysis arising from dissociation of $Co(PP)_3^{2+}$ ($\tau \sim 5$ s), we selected a monitoring wavelength in the 315–360-nm region for which the absorbance changes accompanying the aquation of the Co(II) product were minimized, and we adjusted the concentrations of the excess reagent, Co(sep)$^{2+}$ or $Ru(NH_3)_6^{2+}$, so that the electron-transfer reactions had less than one tenth the lifetime required for the $Co(PP)_3^{2+}$ dissociation. Precautions were taken to avoid complications due to the $Co(PP)_3^{3+}$–ascorbate reactions (which are reported to be relatively slow;[38] in our systems these reactions occurred on the same time scale, or more slowly, as the $Co(PP)_3^{2+}$ substitution reactions). In order to minimize such extraneous reactions it was necessary to keep ascorbate with the reducing agents and NO_2^- with $Co(PP)_3^{3+}$ until the electron-transfer process was initiated by the mixing of reagents. Reactant solutions of similar ionic strengths were mixed in the flow apparatus.

4. Electrochemical Studies. Electrochemical studies were performed with a PAR Model 174A polarographic analyzer. Either a PAR Model 303 static mercury drop electrode or a carbon paste electrode was used as the working electrode. A PAR or Orion Ag|AgCl reference electrode was used with an appropriate salt bridge. With the PAR Model 174 used in a cyclic differential pulsed mode, good quality waves for both cathodic and anodic scans were obtained for Co– and Cr–polypyridyls even at concentrations as low as 10^{-5} M.

Results

Quenching rate constants are summarized in Table I. In addition to the data in the table, we have determined Stern–Volmer quenching constants for $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5NCS^{2+}$ quenching of $(^2E)Cr(phen)_3^{3+}$ in 1 M HCl over the temperature range 0–30 °C. In each case we find similar apparent negative activation energies for K_{sv}, $E_a \simeq -42 \pm 8$ kJ mol^{-1}, presumably due to variations in donor lifetime.

Rate constants observed for the electron-transfer reactions of $Co(PP)_3^{3+}$ with excess [Co(sep)$^{2+}$] or [$Ru(NH_3)_6^{2+}$] under pseudo-first-order conditions exhibited excellent first-order dependence on [reductant]. Bimolecular rate constants for these reactions were obtained from k_{obsd}/[reductant] for various [X^-]. The bimolecular rate constants thus obtained for anion-promoted electron-transfer reactions are summarized in Table II. Our measurements of half-wave potentials are summarized in Table III. We found some medium dependence of $E_{1/2}$, especially for the Co(sep)$^{3+,2+}$ couple, as noted in Table III. The variations in $E_{1/2}$ with medium are generally quite small for the $Ru(NH_3)_6^{3+,2+}$ couple and we presume that the observed variations arise from variation in junction potentials. Where the variations in $E_{1/2}$ are larger for Co(sep)$^{3+,2+}$, they are likely to involve a specific interaction of the anion from the medium with the cobalt substrate as discussed below.

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$$(I_o/I)_{corr} = (I_o/I)_{obsd}\frac{1 - 10^{-(A_D+A_Q)l}}{1 - 10^{-A_Dl}}\,\frac{A_D}{A_D + A_Q}10^{-A_Q'l'}$$

where $(I_o/I)_{corr}$ is the corrected ratio, $(I_o/I)_{obsd}$ is the intensity ratio observed, A_D is the absorbance of the donor at the excitation wavelength, A_Q and A_Q' are the absorbances of the quencher at the excitation and emission wavelengths, respectively, and l and l' are the optical paths for absorption and emission, respectively.

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Table I. Kinetic Parameters for Co(III) Quenching of $(^2E)Cr(PP)_3^{3+}$

	intensity quenching $10^{-6}k_q$, M^{-1} s^{-1}		lifetime quenching[b] $10^{-6}k_q$, M^{-1} s^{-1}			
quencher	$Cr(phen)_3^{3+}$	$Cr(bpy)_3^{3+}$	$Cr(phen)_3^{3+}$	$Cr(bpy)_3^{3+}$	no. in Figure 1	medium
A. Flash Photolysis						
$Co(NH_3)_6^{3+}$			3.5 ± 0.8	4.3 ± 0.5		1 M HCl (25 °C)
$Co(NH_3)_5OH_2^{3+}$			4.3 ± 0.5	4.0 ± 0.5		1 M HCl (25 °C)
$Co(NH_3)_5CN^{2+}$				5.0 ± 0.5		1 M HCl (25 °C)
$Co(NH_3)_5Cl^{2+}$			41 ± 5			1 M $NaHSO_4$ (25 °C)
$Co(NH_3)_5Br^{2+}$			106 ± 10			1 M $NaHSO_4$ (25 °C)
$Co(NH_3)_5NCS^{2+}$				186 ± 10		1 M $NaHSO_4$ (25 °C)
$Co(NH_3)_5N_3^{2+}$				160 ± 10		1 M $NaHSO_4$ (25 °C)
$Co(N_4)(OH_2)_2^{3+}$ [c]				1.8 ± 0.1		1 M $NaClO_4$, pH 2 (25 °C)
$Co(N_4)Cl_2^+$ [b]				25 ± 5		1 M $NaClO_4$, pH 2 (25 °C)
$Co(N_4)(OH_2)N_3^{2+}$ [c]				163 ± 20		1 M $NaClO_4$, pH 1 (25 °C)
Hg^{2+}(aq)			<0,1			1 M $NaClO_4$, pH 1 (25 °C)
B. Luminescence Quenching						
$Co(NH_3)_5OH_2^{3+}$	3.5 ± 0.2 (130)					1 M HCl (15 °C)
			3.5 ± 0.2			1 M $NaHSO_4$ (15 °C)
$Co(NH_3)_5F^{2+}$	1.6 ± 0.5 (88)	2.0 ± 0.3 (70)				1.5 M $NaHSO_4$ (25 °C)
$Co(NH_3)_5Cl^{2+}$	53 ± 8 (130)				1	1 M HCl (15 °C)
$Co(NH_3)_5Br^{2+}$			152 ± 12		2	1 M $NaHSO_4$ (15 °C)
$Co(NH_3)_5NO_2^{2+}$			71 ± 8		3	1 M $NaHSO_4$ (15 °C)
$Co(NH_3)_5NCS^{2+}$	257 ± 30 (110)					1 M HCl (25 °C)
	393 ± 40 (130)					1 M HCl (15 °C)
			252 ± 30		4	1 M $NaHSO_4$ (15 °C)
$Co(NH_3)_5N_3^{2+}$	321 ± 30 (130)					1 M HCl (15 °C)
			237 ± 20		5	1 M $NaHSO_4$ (15 °C)
$Co(N_4)(OH_2)_2^{3+}$ [c]	1.02 ± 0.12 (400)		1.06 ± 0.08			1 M $NaHSO_4$ (15 °C)
$Co(N_4)(OH_2)Cl^{2+}$ [c]	1.02 ± (400)		21 ± 2			1 M $NaHSO_4$ (15 °C)
$Co(N_4)Cl_2^+$ [c]	51 ± 5 (400)		54 ± 2		6	1 M $NaHSO_4$ (15 °C)
$Co(N_4)(OH_2)Br^{2+}$ [c]	24 ± 5 (400)					1 M $NaHSO_4$ (15 °C)
$Co(N_4)(NO_2)_2^+$ [c]	41 ± 5 (400)		54 ± 3		7	1 M $NaHSO_4$ (15 °C)
$Co(N_4)(OH_2)N_3^{2+}$	147 ± 10 (400)		122 ± 10		8	1 M $NaHSO_4$ (15 °C)
$Co(N_4)(NCS)Cl^+$ [c]	40 ± 4 (400)		62 ± 15		9	1 M $NaHSO_4$ (15 °C)
$Co(N_4)(NCS)_2^+$ [c]	180 ± 20 (400)		163 ± 15		10	1 M $NaHSO_4$ (15 °C)
$Co(N_4)(NCS)N_3^+$ [c]	311 ± 25 (400)		301 ± 20		11	1 M $NaHSO_4$ (15 °C)
$Co(N_4)N_3Cl^+$ [c]	242 ± 21 (400)				12	1 M $NaHSO_4$ (15 °C)
$Co(N_4)(N_3)^{2+}$	421 ± 40 (400)		434 ± 40		13	1 M $NaHSO_4$ (15 °C)
$Co(CN)_6^{3-}$	⩽0.2 ± (90)	⩽1 (70)				1.5 M $NaHSO_4$ (25 °C)
$Ru(NH_3)_6^{3+}$	⩽0.2 (90)	⩽1 (70)				1.5 M $NaHSO_4$ (25 °C)
$Rh(NH_3)_5Cl^{2+}$	⩽0.2 (90)					1.5 M $NaHSO_4$ (25 °C)

[a] k_q based on: $K_{SV} = k_q\tau_D$ where τ_D is the independently determined excited-state lifetime under the same conditions of medium, temperature, etc. (lifetimes in µs in parentheses). [b] k_q based on the [Co(III)] dependence of the first-order decay of $(^2E)Cr(PP)_3^{3+}$, monitored by absorbance in flash photolysis or emission in luminescence quenching. [c] N_4 = [14]aneN_4(cyclam).

Discussion

A. Energy Transfer. Our earlier work has shown that $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, and related complexes are relatively poor quenchers of $(^2E)Cr(PP)_3^{3+}$.[26] We have now shown that certain coordinated ligands can be effective in increasing the quenching efficiency of these Co(III) acceptors. Our observations on these systems to date include the following:

1. Complexes such as $Ru(NH_3)_6^{3+}$, $Rh(NH_3)_5Cl^{2+}$, and $Co(CN)_6^{3-}$, for which $E(^*Q) > E(^2E)$, are ineffective as quenchers of (^2E)Cr(III), while complexes such as $Co(NH_3)_6^{3+}$ and $Co(OH_2)_6^{3+}$ which have very low energy acceptor states do act as quenchers, but with k_q insensitive to donor–acceptor energy gap or other components of Franck–Condon factors.[26,39]
2. Amines, ammonia, water, polypyridyl, F^-, CN^-, and tetraamine macrocycle ligands bound to Co(III) have no special effect beyond the size effect noted earlier;[24,26] deviations from the size effect are less than a factor of 2 in k_q.
3. Coordination of larger halides (X = Cl, Br) or pseudo-halides (X = NCS, N_3) in $Co^{III}(NH_3)_5X$ complexes generates more efficient quenchers: e.g., $10^{-7}k_q \simeq$ 0.2, 4, 15, 24, 25 for X = F, Cl, Br, NCS, N_3, respectively (for the $Cr(phen)_3^{3+}$ donor in 1 M $NaHSO_4$).
4. Similar enhancements of the quenching rates occur in *trans*-ethylenediamine and [macrocycle(N_4)]cobalt(III) complexes and can be approximately factored into the individual contributions of X^-.[40]

It is especially interesting that the effectiveness of ligands X^- in promoting quenching, in the energy gap independent region for $Co^{III}(NH_3)_5X$ complexes, increases as the standard potential of the $\cdot X/X^-$ couple in water *decreases*. Since the rates of these reactions do not seem to be sensitive to the usual Franck–Condon parameters,[26,29] the observed variations may be taken as measures of the different contributions of the electronic matrix element. That is, since $k_q = K_0\nu_q \exp[-\Delta G_q^*(FC)/RT]$, it appears that $\Delta G_q^*(FC) \sim 0$ for these reactions.[24,26] Therefore, the variations in values of k_q (where k_q is 1 to 4 orders of magnitude smaller than the diffusion limit), can be taken as kinetic manifestations

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(39) Energy transfer is usually formulated in terms of very weak donor–acceptor coupling and an interaction Hamiltonian which is an expression of instantaneous charge fluctuation at each center. Multipole expansion of these dispersion forces leads to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, or $H_{DA} = H_{DD} + H_{DQ} + H_{QQ}$.[21] The first two terms are relatively long range and depend on spectral overlap parameters; these interactions do not appear to be the dominant factors in the *Cr(III)/Co(III) energy-transfer reactions. At short range, electron-exchange interactions (H_{EX}) are believed to be much more important than quadrupole–quadrupole interactions.[21] In this limit also, the Franck–Condon component of the quenching rate is usually expressed as a donor–acceptor spectral overlap integral.[21,22] For a small intrinsic Franck–Condon barrier and for a large energy gap the Franck–Condon factor should approach unity and the quenching rates should become independent of spectral overlap, energy gap, etc. This is in accord with observations on these[26] and related systems.[24]

(40) There is an additional enhancement in k_q in reactions with cis acceptors. In our factoring of effects for trans complexes, we have assumed the interaction to be with one ligand at a time so that the effects of two ligands can be linearly averaged. "Cis effects" will be discussed elsewhere.

Table II. Summary of Kinetic Parameters for Electron-Transfer Reactions:[a]

$$\mathrm{M^{II}} + \mathrm{Co(PP)_3}^{3+} \xrightarrow{\mathrm{X}^-} \mathrm{M^{III}} + \mathrm{Co(PP)_3}^{2+}$$

oxidant	X^-	$[X^-]$, M	$10^{-4}k_e(\mathrm{Co(sep)}^{2+})$, $M^{-1}\,s^{-1}$	$10^{-4}k'_e(\mathrm{Ru(NH_3)_6}^{2+})$, $M^{-1}\,s^{-1}$
$\mathrm{Co(phen)_3}^{3+}$	CF_3SO_3	0.10	0.48 ± 0.04	0.93 ± 0.08
	I	0.01	0.92 ± 0.08	1.05 ± 0.09
		0.05	1.25 ± 0.08	1.20 ± 0.08
		0.09	1.42 ± 0.10	1.2 ± 0.1
	NO_2	0.01	1.1 ± 0.1	1.12 ± 0.08
		0.05	2.2 ± 0.2	1.20 ± 0.09
		0.09	3,4 ± 0.3	1.2 ± 0.1
	ascorbate	0.005	4.0 ± 0.3	0.99 ± 0.09
		0.01	7.8 ± 0.8	1.18 ± 0.08
		0.025	18 ± 2	1.4 ± 0.1
		0.05		1.6 ± 0.2
	NCS	0.02	1.25 ± 0.15	1.08 ± 0.08
		0.05	1.51 ± 0.13	1.4 ± 0.1
		0.09	1.78 ± 0.2	1.7 ± 0.1
	HCO_2	0.05	2.25 ± 0.05	
		0.09	4.2 ± 0.1	
	CH_3CO_2	0.01	1.05 ± 0.05	
		0.05	1.75 ± 0.07	1.02 ± 0.05
		0.10	2.2 ± 0.1	1.02 ± 0.05
	Cl	0.10	0.48 ± 0.05	0.95 ± 0.05
$\mathrm{Co(5\text{-}nitro(phen))_3}^{3+}$	CF_3SO_3	0.10	1.1 ± 0.1	1.65 ± 0.12
	NO_2	0.01	2.0 ± 0.1	
		0.02	3.0 ± 0.2	
		0.05	4.7 ± 0.3	
		0.10		
	ascorbate	0.01	6.8 ± 0.8	1.8 ± 0.1
		0.02	10.6 ± 0.8	1.9 ± 0.2
		0.05	17.9 ± 0.9	2.1 ± 0.2
$\mathrm{Co(3,4,7,8\text{-}Me_4phen)_3}^{3+}$	$CF_3SO_3^-$	0.10	0.24 ± 0.01	0.44 ± 0.03
	NO_2^-	0.02	0.45 ± 0.03	
		0.05	0.95 ± 0.03	
		0.10	1.6 ± 0.08	
	ascorbate	0.01	1.1 ± 0.1	0.50 ± 0.03
		0,025	1.9 ± 0.1	0.56 ± 0.03
		0.05	3.0 ± 0.2	0.61 ± 0.03
		0.08		
$\mathrm{Co(phen)_2(chn)}^{3+}$	$CF_3SO_3^-$	0.10	0.036 ± 0.003	0.091 ± 0.005
	ascorbate	0.012	0.2 ± 0.1	0.096 ± 0.004
		0.025	0.3 ± 0.1	0.10 ± 0.002
		0.05	0.5 ± 0.2	0.10 ± 0.02
$\mathrm{Co(NH_3)_6}^{3+}$	$CF_3SO_3^-$	0.20	$(14 \pm 1) \times 10^{-6}$ [b,c]	
	I^-	0.10[d]	$(13 \pm 1.5) \times 10^{-6}$ [e]	
	NO_2^-	0.05[d]	$(20 \pm 1) \times 10^{-6}$ [e]	
		0.20[d]	$(20 \pm 2) \times 10^{-6}$ [e]	
	ascorbate	0.10[d,f]	$(21 \pm 2) \times 10^{-6}$ [e]	
	acetate[g]	0.025[d]	$(22 \pm 1) \times 10^{-6}$ [e]	
		0.05[d]	$(29 \pm 2) \times 10^{-6}$ [e]	
		0.075[d]	$(34 \pm 2) \times 10^{-6}$ [e]	
		0.10[d]	$(38 \pm 2) \times 10^{-6}$ [e]	

[a] 25 °C; ionic strength = 0.1 M ($[\mathrm{NaCF_3SO_3}] + [\mathrm{NaX}]$). [b] Pseudo-first-order rate constants were obtained by using a large excess (≥20-fold) of $[\mathrm{Co(NH_3)_6}^{3+}]$ over $[\mathrm{Co(sep)}^{2+}]$ with $[\mathrm{Co(sep)}^{2+}]$ typically at 1×10^{-4} M and $[\mathrm{H}^+]$ being maintained at 10^{-3} M with use of $\mathrm{NaCF_3SO_3}$ or at about 10^{-4} M with use of 10^{-3} M $\mathrm{NaCH_3CO_2}$ buffer. When precautions were taken to exclude O_2 and to avoid excessive increases in pH due to released NH_3, pseudo-first-order plots were linear for 3 to 5 half-lives and only a single stage was observed (260–270 nm). Conditions were adjusted so that the lifetime reported[32c] for the acid-induced, $\mathrm{Co(sep)}^{2+}$ decomposition would be more than 12 times longer than the lifetime for reaction with $\mathrm{Co(NH_3)_6}^{3+}$. [c] Average of nine determinations. [d] 0.2 M ionic strength. [e] Average of four determinations. [f] Ascorbate used as buffer; $[\mathrm{H}^+] \sim 6 \times 10^{-5}$ M. [g] The variations of bimolecular rates with $[\mathrm{CH_3CO_2}^-]$ were analyzed according to eq 4 to obtain a value of 0.71 $M^{-1}\,s^{-1}$ for the acetate ion pair.

of variations in the electronic transmission coefficient. For very small values of the electronic transmission coefficient, ν_q^{el} may be considered to be a function of donor–acceptor overlap (at a separation r_{DA}) and of the various contributions (ν_q°) to the electronic matrix element at $r_{DA} = 0$[2,3-5,7,13-15,19b,c,21,22,41]

$$\nu_q^{el} \simeq \nu_q^{\circ} \exp[-2\alpha_q r_{DA}] \qquad (2)$$

The effect of ligands X in enhancing the quenching rates for a given donor–acceptor separation (r_{DA}) might in principle be discussed in terms of either (a) "superexchange" contributions to the mixing Hamiltonian (and hence to ν_q°), or (b) variations

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(41) Brocklehurst, B. *J. Phys. Chem.* **1979**, *83*, 536.

Table III, Electrochemical Parameters[a]

couple	medium	$E_{1/2}$, V vs. SCE	$E_{pa} - E_{pc}$, mV	full width at half height E_{pc}, mV
$Co(phen)_3^{3+,2+}$	0.1 M $NaCF_3SO_3$	0.14 ± 0.01[b]	68 ± 2	140
$Co(Me_4phen)_3^{3+,2+}$	0.1 M $NaCF_3SO_3$	0.08 ± 0.01[b]	62 ± 4	148
$Co(NO_2phen)_3^{3+,2+}$	0.1 M $NaCF_3SO_3$	0,20 ± 0.01[b]	68 ± 2	145
$Co(phen)_2(chn)^{3+,2+}$	0,1 M $NaCF_3SO_3$	0.07 ± 0.01[b]	70 ± 2	145
$Co(sep)^{3+,2+}$	0.1 M $NaCF_3SO_3$	−0.54 ± 0.01[c]	61 ± 2	110
	0.1 M NaI	−0.535 ± 0.005[c]	60 ± 2	110
	0.1 M $NaNO_2$	−0.572 ± 0.005[c]	59 ± 2	109
	0.1 M NaAscorbate	−0,568 ± 0.005[c]	59 ± 2	116
	0.1 M $NaCH_3CO_2$	−0.585 ± 0.005	61 ± 2	110
$Ru(NH_3)_6^{3+,2+}$	0.1 M $NaCF_3SO_3$	−0.186 ± 0.005[c]	58 ± 2	108
	0.1 M NaI	−0.182 ± 0.005[c]	58 ± 2	108
	0.1 M $NaNO_2$	−0,195 ± 0.005[c]	58 ± 2	111
	0.1 M NaAscorbate	−0.188 ± 0.005[c]	58 ± 2	108
	0.1 M $NaCH_3CO_2$	−0.190 ± 0.005[c]	59 ± 2	109

[a] 25 °C; 10 mV s^{-1} scan rate; 25 mV (p-p) modulation amplitude; $[H^+] = 1 \times 10^{-5}$ M. [b] Carbon paste electrode. [c] Hanging mercury drop electrode.

in the *effective* donor–acceptor *orbital radius* (hence as variations in α_q). The latter is more convenient for a phenomenological comparison and may in these systems be rationalized in terms of the contributions of the charge-transfer-induced dipole moment to the distribution of electron density along the donor–acceptor axis. Thus, for α_q^{-1} the mean orbital radius along the donor–acceptor axis, a first-order perturbation arising from the charge-transfer-induced dipole moment, will increase the effective radius by an amount δr_{CT}, as in

$$\alpha_q^{-1} = (\alpha_q^\circ)^{-1} + \delta r_{CT} \simeq (\alpha_q^\circ)^{-1} + \frac{1}{e}\left(\frac{\partial \mu_{CT}}{\partial F}\right)F(\alpha_q^\circ) + ...$$

where μ_{CT} is the induced dipole moment, F is the polarizing field intensity (or potential gradient), and $(\alpha_q^\circ)^{-1}$ is the mean orbital radius in the absence of an external perturbation. For a charge-transfer perturbation, the polarizability can be represented[42] as,

$$\partial \mu_{CT}/\partial F \simeq eC/E_{CT}$$

where E_{CT} is the energy gap to the high-energy, perturbing charge-transfer state and C is a proportionality constant. For small δr_{CT} and resulting from several charge-transfer interactions,

$$\alpha_q \sim \alpha_q^\circ - (\alpha_q^\circ)^2 \sum_i \frac{C_iF_i(\alpha_q^\circ)}{E_{CT}(i)} \qquad (3)$$

where the first-order contributions of i CT perturbations are considered. For a closely related series of reactants (i.e., for similar values of ν_q°, α_q°, r_{DA}, and F), substitution of eq 3 in eq 2 implies approximately linearly increasing values of ln k_q with increasing $\sum_i 1/E_{CT(i)}$ (provided electronic coupling remains weak). This is in reasonable accord with the observation for $Co(NH_3)_5X^{2+}$ and *trans*-Co([14]aneN$_4$)XY$^{(3-n)+}$ (n = 0, 1, 2) quenchers of $(^2E)Cr(PP)_3^{3+}$ as indicated in Figure 1. In this figure, we have (a) referenced the quenching rates of the pentaammine and [14]aneN$_4$ complexes to the quenching rates (i.e., k_q°) found for the respective $Co(NH_3)_5OH_2^{3+}$ and *trans*-Co([14]aneN$_4$)(OH$_2$)$_2^{3+}$ complexes, in order to take account of any variations in "cis effects", (b) made allowance for the effect of variations in charge type on K_0, (c) taken account of a statistical factor of two in comparing rates of quenching by Co(N$_5$)X^{2+} and *trans*-Co(N$_4$)X$_2^+$ complexes (i.e., and X$^-$-perturbed encounter is approximately twice as probable in the latter than in the former class of compounds), and (d) allowed for variations in the van der Waals contact distances (r_{DA}) with use of parameters discussed elsewhere.[26a,43] In our estimates of E_{CT} we have considered "ligand-to-metal" charge-transfer contributions in the encounter complexes of the types,

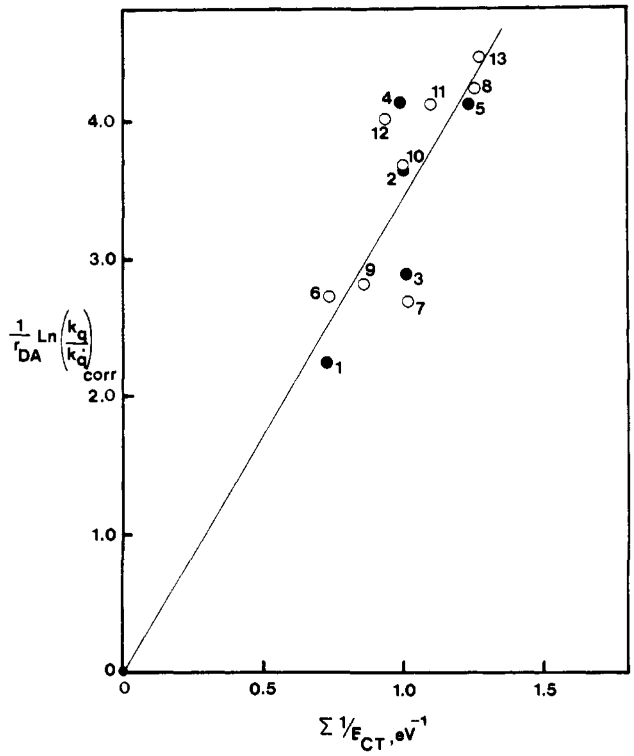

Figure 1. Variations in quenching efficiency with charge-transfer properties of ligands coordinated to Co(III) in $(^2E)Cr(phen)_3^{3+}$ + Co(III) reactions. For numbering of entries refer to Table I; k_q° is the quenching rate constant of $Co(NH_3)_5OH_2^{3+}$ for pentaammine quenchers and the quenching rate constant of Co([14]aneN$_4$)(OH$_2$)$_2^{3+}$ for the Co([14]aneN$_4$)XY quenchers. The abscissa takes into account both $[(^2E)Cr^{III}, {}^-X\text{–}Co^{III}] \rightarrow [{}^*Cr^{II}, \cdot X\text{–}Co^{III}]$ and $({}^-X\text{–}Co^{III}) \rightarrow {}^*(\cdot X\text{–}Co^{II})$ charge-transfer energies, and is interpreted as the difference in CT perturbations of the halo (or pseudo-halo) complexes and the aquo complexes used as reference systems. This referencing amounts to an approximate correction for "cis effects" and solvent CT contributions. These terms could amount to ~3–4 eV for aquo and amine complexes. When X ≠ Y, average values have been estimated as the inverses of the individual components of E_{CT}. The estimates of van der Waals contact distances are r_{DA} (nonhalo ligands) = 0.95 nm (NH$_3$, H$_2$O); 1.2 nm ([14]aneN$_4$).

$$[(^2E)Cr(PP)_3^{3+}, X^-\text{–}Co^{III}] \xrightarrow{E_{CT}(Cr)} {}^*[Cr(PP)_3^{2+}, \cdot X\text{–}Co^{III}]$$

and

$$[(^2E)Cr(PP)_3^{3+}, X^-\text{–}Co^{III}] \xrightarrow{E_{CT}(Co)} {}^*[(^2E)Cr(PP)_3^{3+}, \cdot X\text{–}Co^{II}]$$

Values of E_{CT}(Co) have been obtained from the optical spectra

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[42] Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley-Interscience: New York, 1969.

[43] Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

($E_{\max}$ of the π component of $X^- \rightarrow Co^{III}$). Values of E_{CT}(Cr) have been estimated on the basis of the (^{2}E)Cr(PP)$_3^{3+}$ potentials[36,44] and the estimated $\cdot$X–Co^{III}/X$^-$–Co^{III} potentials (based on $E^f \sim E^f(\cdot X/X^-) + 4D_q[X]$).[45–49] We have neglected the complementary ionization processes (i.e., Cr(III) and Co(III) charge-transfer-to-solvent perturbations) since they are of relatively high energy and expected to be more or less constant through the series of compounds. The figure considers a single donor, (^{2}E)Cr(phen)$_3^{3+}$, so the relatively low energy $^2E \rightarrow$ phen CT contribution would make a constant contribution, probably shifting the absolute value of the origin of the abcissa by less than 0.5 eV^{-1}.

The scatter of data in Figure 1 corresponds (within one standard deviation in ln $k_q/k_q°$) to about 25% deviation of $(k_q/k_q°)_{\mathrm{corr}}$ from the values predicted by the correlation line. This is about as good as one can expect in view of the cumulative errors in the ratio $k_q/k_q°$ and the uncertainties in r_{DA} and E_{CT}.

Finally, it is important to note that one implication of Figure 1 is that CT perturbations may contribute in some small way to the quenching rates of aquo and amine complexes. Such contributions could amount to ~0.3 eV^{-1} in $1/E_{CT}$. On the basis of Figure 1 and the various additional contributions to $\sum 1/E_{CT}$, we estimate that in the absence of CT perturbations the rate of (^{2}E)Cr(phen)$_3^{3+}$ quenching by Co(III) complexes would be $\sim 10^5$ M^{-1} s^{-1} ($r_{DA} \sim 1$ nm). This is a factor of about 10^4 smaller than the diffusional limit.

B. Electron Transfer. The inferences from *energy-transfer* studies, outlined above, suggest that variations of the bimolecular rate constants with weak charge-transfer perturbations can be used to probe contributions of the electronic matrix element. But, while it is experimentally feasible to study *energy-transfer* reactions for which $\Delta G^*(FC) \sim 0$, this is not a very practical approach to the study of contributions of the electronic matrix elements to *electron-transfer* reactions. Of necessity, a search for such contributions must involve reactions with conveniently measurable rates, and therefore reactions with significant Franck–Condon contributions. Any CT perturbations introduced must be sufficiently subtle that Franck–Condon factors are not much changed. The perturbations we have selected to probe *electron-transfer* reactions arise from the weak outer-sphere association of cationic complexes with anionic species from the medium. The optical absorptions resulting from such ion-pair associations are well known[50] and their energetics are well understood.[48,49] The systems selected for study involved the Co(PP)$_3^{3+,2+}$, Co(sep)$^{3+,2+}$, and Ru(NH$_3$)$_6^{3+,2+}$ couples, all complexes in which first coordination sphere substitution is very slow. Our studies have involved the outer-sphere Co(sep)$^{2+}$ or Ru(NH$_3$)$_6^{2+}$ reductions of Co(PP)$_3^{3+}$ complexes.

Association between Co(PP)$_3^{3+}$ and anionic species in solution give rise to weak charge-transfer absorption in the high-energy visible-to-ultraviolet spectral regions. These transitions can be attributed to the process:

$$[\mathrm{Co(PP)_3^{3+}, X^-}] + h\nu \xrightarrow{*E_{CT}(X)} *[\mathrm{Co(PP)_3^{2+}}, \cdot \mathrm{X}]$$

These interactions are weak and do not significantly alter the ground-state structural properties of the Co(PP)$_3^{3+}$ complexes. Our strategy has, therefore, been to investigate the effect of variations with $*E_{CT}(X)$ of the Co(PP)$_3^{3+}$–Co(sep)$^{2+}$ electron-transfer rate (k_e^{Co}). The cobalt reactants were chosen for investigation because electronic terms have often been postulated to contribute to electron-transfer reactions involving Co(III)–Co(II) couples.[13b,14,17,19,51] Since reactions involving Ru(III)–Ru(II) couples generally seem more "adiabatic,"[19,43,52,53] we have used the Co(PP)$_3^{3+}$–Ru(NH$_3$)$_6^{2+}$ reactions run in identical media (k_e^{Ru}) as reference reactions. A relatively adiabatic set of reference reactions is essential since any variations in Franck–Condon factors would have similar kinetic effects on both the reference and the test sets of reactions.

On the basis of the well known Marcus square-root relation,[10]

$$k_{e,ab} = (k_{e,aa}k_{e,bb}K_{ab}f_{ab})^{1/2}$$

and literature parameters[19,32,43,54] one would predict, if all the reactions were "purely adiabatic", $k_e^{Co}/k_e^{Ru} \simeq 12$. In 0.1 M NaCF$_3SO_3$ at 25 °C we find $k_e^{Co}/k_e^{Ru} = 0.5$ for the Co(phen)$_3^{3+}$/Co(sep)$^{2+}$. That the Co(phen)$_3^{3+}$/Co(sep)$^{2+}$ reaction (in NaCF$_3$SO$_3$) is about 1% of the predicted rate is suggestive of contributions of electronic factors. With anions X$^-$, which are relatively easy to oxidize (thus exhibiting relatively low-energy charge-transfer spectra of the [Co(PP)$_3^{3+}$, X$^-$] ion pairs), k_e^{Co} increases

$$k_e^{Co} = \frac{k_e^{Co}(S) + K_x k_e^{Co}(X)[X]}{1 + K_x[X^-]} \tag{4}$$

where k_e^{Co}(S) is the value of k_e^{Co} in the 0.10 M NaCF$_3$SO$_3$ medium, K_x is the ion-pair formation constant, and k_e^{Co}(X) is the electron-transfer rate to the ion pair. The parameters obtained by fitting the kinetic data in Table II to eq 4 are presented in Table IV. Differences in the numerical values of K_x listed for Co(sep)$^{2+}$ and Ru(NH$_3$)$_6^{2+}$ require some comment. Equation 4 indicates that rate data are useful in obtaining values of K_x only when $k_e^{M(II)}(X) > k_e^{M(II)}(X)$. For the Ru(NH$_3$)$_6^{2+}$ reactions this condition is not fulfilled and there is great uncertainty in the resulting values of K_x. In addition, the K_x values are undoubtedly composite quantities reflecting properties of all three partners in the reaction, so different measurements may result in slightly different numerical values. Finally, an increase in electronic coupling (or transmission coefficient) could result in an increase in the distribution of distances (r_{DA}) over which electron transfer occurs; for anion-promoted coupling, larger values of r_{DA} would correspond to larger values of K_x.[55] The negligible variations in

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(44) Brunschwig, B. S.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 7568.

(45) A similar approximation has been employed in the discussion of photohomolysis threshold energies.[46] A somewhat better estimate would be based on the enthalpy cycle,

$$\begin{tikzcd}
X^- \text{-} Co^{III} + H_2O \arrow[r, shift left, "\Delta H_1^\circ"] \arrow[d, shift right, "\Delta H_3^\circ"'] & H_2O\text{-}Co^{III} + X^- \arrow[l, shift left] \arrow[d, shift left, "\Delta H_4^\circ"] \\
(e^-) + \cdot X\text{-}Co^{III} + H_2O \arrow[u, shift right] \arrow[r, shift left, "\Delta H_2^\circ"] & H_2O\text{-}Co^{III} + \cdot X + (e^-) \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

where $\Delta H_3° \simeq -E^f$. Enthalpy parameters are not available and our approximation sets $\Delta H_4° \simeq -E^f(\cdot X/X^-)$ and $(\Delta H_1° - \Delta H_2°) \sim D_q[X]$. Values of D_q[X] were taken from Wentworth and Piper.[47] We have neglected the solvent reorganizational contributions to E_{CT}(Cr) since they seem to be relatively small in ion-pair C–T transitions.[37,38]

(46) Endicott, J. F. *Inorg. Chem.* **1977**, *16*, 494.

(47) Wentworth, R. A. D.; Piper, T. S. *Inorg. Chem.* **1965**, *4*, 709.

(48) Endicott, J. F.; Ferraudi, G. J.; Barber, J. R. *J. Phys. Chem.* **1975**, *79*, 630.

(49) Cannon, R. D. *Adv. Inorg. Chem. Radiochem.* **1979**, *21*, 179.

(50) (a) Waysbort, D.; Evenor, M.; Navon, G. *Inorg. Chem.* **1975**, *14*, 514, (b) Elsbernd, H.; Beattie, J. K. *Ibid.* **1968**, *7*, 2468, (c) Yokoyama, H.; Yamatera, H. *Bull. Chem. Soc. Jpn*, **1971**, *44*, 1725, (d) Yoneda, H. *Ibid.* **1955**, *28*, 125.

(51) (a) Rillema, D. P., Endicott, J. F. *Inorg. Chem.* **1972**, *11*, 2361, (b) *Ibid.* **1976**, *15*, 1459.

(52) That Ru(III)–Ru(II) couples should appear relatively more adiabatic than Co(III)–Co(II) couples is plausible on the basis of either the somewhat larger 4d than 3d orbital radii or the smaller nuclear frequency, ν_e^{nu}, expected for Ru. In regard to the latter, and using the Landau–Zener framework to describe the probability of surface crossling,[14,15,19b,c]

$$\kappa_e = \frac{2(1 - \exp[-\nu_e^{el}/2\nu_e^{nu}])}{(2 - \exp[-\nu_e^{el}/2\nu_e^{nu}])}$$

and when $\nu_e^{el} > \nu_e^{nu}$, the transmission coefficient (κ_e) approaches 1. The limiting condition $\nu_e \rightarrow \nu_e^{el}$ is more accessible when vibrational quanta are large than when they are small; the effective nuclear frequencies are typically about 10 times larger for Co(III)–Co(II) than for Ru(III)–Ru(II) since in the former ν_e^{nu} is dominated by metal–ligand frequencies and in the latter by solvent frequencies.

(53) Thorson, W. R.; Delos, J. B.; Boorstein, S. A. *Phys. Rev. A* **1971**, *4*, 1052.

(54) Meyer, T. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 2369.

(55) In principle each possible (donor, acceptor, anion) aggregate, i should be associated with an electron-transfer probability, $\sigma_i(D,A,X; r,\theta)$. The CT perturbations should be introduced into $\sigma_i(D,A,X; r,\theta)$, and the net rate computed on the basis of the distribution of aggregates and the sum over r and θ. For purposes of our phenomenological comparisons we have made the very simple assumption that this complex sum can be approximated by $K_x k_e^{Co}$(X) and that it is sufficient to consider perturbations in k_e^{Co}(X).

Table IV, Parameters for Assessment of Anionic Perturbations of Electron-Transfer Reactions[a]

		for Co(sep)$^{2+}$		for Ru(NH$_3$)$_6$$^{2+}$			
oxidant	X	K_X, M^{-1}	$10^{-4}k_e^{Co}(X)$, M^{-1} s^{-1}	K_X,[b] M^{-1}	$10^{-4}k_e^{Ru}(X)$, M^{-1} s^{-1}	$E_{CT}^{\ddagger}$,[c] eV	$-\ln(k_e^{Co}(X)/k_{calcd}^{Co})$[d]
Co(phen)$_3$$^{3+}$	CF$_3$SO$_3$		0.48 ± 0.04		0.93 ± 0.08		
	I	30 ± 3	1.8 ± 0.2		1.1 ± 0.1	1.56	3.3
	NO$_2$	8 ± 2	7,5 ± 0.8		1.1 ± 0.1	1.19	2.7
	ascorbate	35 ± 5	22,3 ± 1.8	~11	2.5 ± 0,2	0.89	1.7
	NCS	45 ± 5	2.0 ± 0.2	~20	2.0 ± 0.1	1.75	3.2
	Cl		(0.48)[e]		(0.95 ± 0.05)[e]	2.70	4.6
	HCO$_2$		(4.2)				
	CH$_3$CO$_2$	29 ± 3	2.6 ± 0.2		(1.02 ± 0.05)[e]		
Co(NO$_2$phen)$_3$$^{3+}$	CF$_3$SO$_3$		1.1 ± 0.1		1.65 ± 0.12		
	NO$_2$	7 ± 2	12 ± 1			1.22	2.72
	ascorbate	22 ± 4	34	~10	3.0 ± 0.3	0.93	1.82
Co(Me$_4$phen)$_3$$^{3+}$	CF$_3$SO$_3$		0.24 ± 0.01		0.44 ± 0.03		
	NO$_2$	10 ± 2	1.35 ± 0,10			1.22	3.45
	ascorbate	17 ± 3	6.4 ± 0.5	~11	1.0 ± 0.1	0.93	2.2
Co(phen)$_2$(chn)$^{3+}$	CF$_3$SO$_3$		0.036 ± 0.003		0.09 ± 0.01		
	ascorbate	20 ± 4	0.85 ± 0.05	~12	0.14 ± 0.04	0.95	2.46

[a] Data from Table II fitted to eq 3. [b] Values of K_X in Ru(NH$_3$)$_6$$^{2+}$ reactions are subject to considerable uncertainty since $k_e^{Ru}(X) < 3 k_e^{Ru}(S)$. [c] Transition-state CT perturbation estimated according to eq 5. [d] Values of k_{calcd}^{Co} were obtained by using the Marcus square-root relation. [e] Value in 0.1 M NaX.

the rates of the Ru(NH$_3$)$_6$$^{2+}$ reaction for CF$_3$SO$_3$$^-$, I$^-$, or NO$_2$$^-$ media demonstrate that these variations in the ionic medium do not greatly alter the intrinsic reorganizational energies or reaction free energies of the electron-transfer reactions. That there are small rate variations in ascorbate and NCS$^-$ media suggests that either (1) the Franck–Condon factors are not rigorously constant, (2) thermodynamic factors vary, or/and (3) even reactions of Ru(NH$_3$)$_6$$^{2+}$ are not wholly adiabatic and their rates are, therefore, susceptible to variations in electronic factors. Since $E_{1/2}$ for the Ru(NH$_3$)$_6$$^{3+,2+}$ couple is insensitive to the medium, significant variations in the driving force seem unlikely.

The Co(sep)$^{2+}$ reactions are appreciably more medium sensitive. These variations in rate with changes in the ionic medium can be placed in two categories: (1) those which appear to be a characteristic property of the sepulchrate complex; and (2) those which require an appropriate combination of oxidant and reductant.

We have taken the medium dependence of the Co(sep)$^{3+,2+}$ potential to be an indication of specific interactions between the Co(sep) couple and anionic species. In this assessment we note that potentials for the Ru(NH$_3$)$_6$$^{3+,2+}$ couple are only very weakly medium dependent under our conditions (0.1 M ionic strength; 25 °C); this couple is, therefore, useful as an external reference. The differences in $E_{1/2}$ of the Co(sep)$^{3+,2+}$ and Ru(NH$_3$)$_6$$^{3+,2+}$ couples in various media are $\delta\Delta E° = 0$, 22, 26, and 41 mV, respectively, for X$^-$ = I$^-$, NO$_2$$^-$, ascorbate, and acetate. These variations in potential alone, with no differences in reorganizational energies, would lead to some variations in electron-transfer rate constants.

The absorption maxima of ion-pair charge-transfer bands are about 1.6 V greater for Co(NH$_3$)$_6$$^{3+}$, X$^-$[49] than estimated for Co(PP)$_3$$^{3+}$, X$^-$.[56] Thus any medium dependence of the Co(NH$_3$)$_6$$^{3+}$/Co(sep)$^{2+}$ reactions is not likely to have its origin in CT perturbations, and we have chosen the Co(NH$_3$)$_6$$^{3+}$–Co(sep)$^{2+}$ reaction as a reference with respect to which the intrinsic kinetic effects of medium variations may be evaluated, relatively free of CT perturbations. If there were no alterations of reorganizational barriers, the observed values of $\delta\Delta E°$ would lead to $k_e^{Co} = 0.14$, 0.21, 0.24, and 0.31 M^{-1} s^{-1}, respectively (I$^-$, NO$_2$$^-$, ascorbate, and acetate) for this reaction; we find $k_e^{Co} = 0.13$, 0.20, 0.21, and 0.71 M^{-1} s^{-1} (0.2 M ionic strength; 25°), respectively. It is clear that the intrinsic kinetic effects of the variations in X$^-$ are small and largely a consequence of the observed variations in the potential of the Co(sep)$^{3+,2+}$ couple.

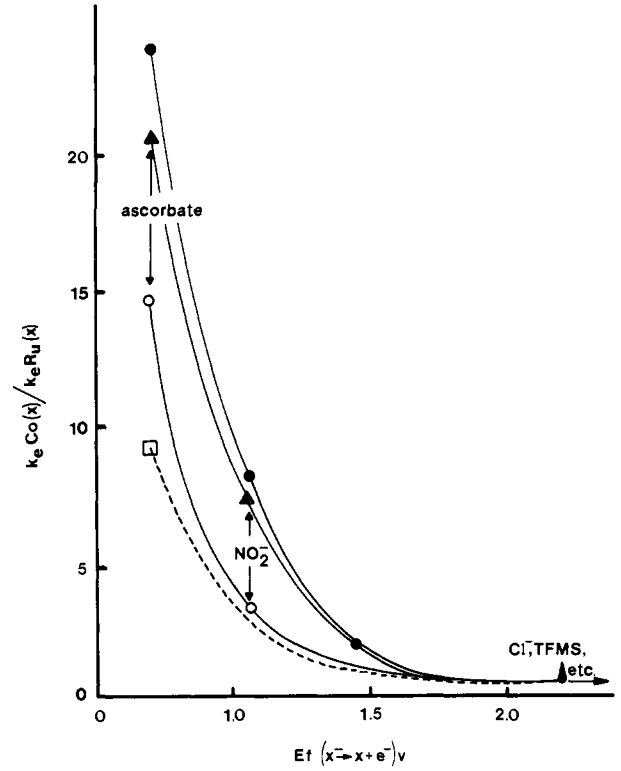

Figure 2. Variation of electron-transfer rates with the formal potential for oxidation of anionic components of the medium. (See Table IV.)

The considerations in the preceding paragraphs demonstrate that the larger variations in rates of the Co(PP)$_3$$^{3+}$–Co(sep)$^{2+}$ reaction with changes in counterion (X$^-$) cannot be a property of either the Co(PP)$_3$$^{3+,2+}$ or the Co(sep)$^{3+,2+}$ couple. Rather, these effects of anionic species on the Co(PP)$_3$$^{3+}$–Co(sep)$^{2+}$ electron-transfer rate are a characteristic feature of this combination of reagents. The magnitude of these effects increases with the ease of oxidizing X$^-$ (Figure 2), i.e., with rates increasing inversely with the X$^-$ → Co^{III}(PP)$_3$ charge-transfer energy gap qualitatively analogous to our observations on energy-transfer reactions in the preceding section.

Direct application of eq 1–3 to electron-transfer reactions is complicated by the considerable Franck–Condon barrier to electron transfer. We have proposed that CT perturbations are effective in increasing the coupling, δ, between reactant and product potential energy surfaces. Thus, we must consider the

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[56] These assumptions in estimation of ion-pair CT transitions have been verified by examination of ion-pair CT spectra of the Co(PP)$_3$$^{3+}$, X$^-$ systems (Ramasami, T.; Endicott, J. F., work in progress).

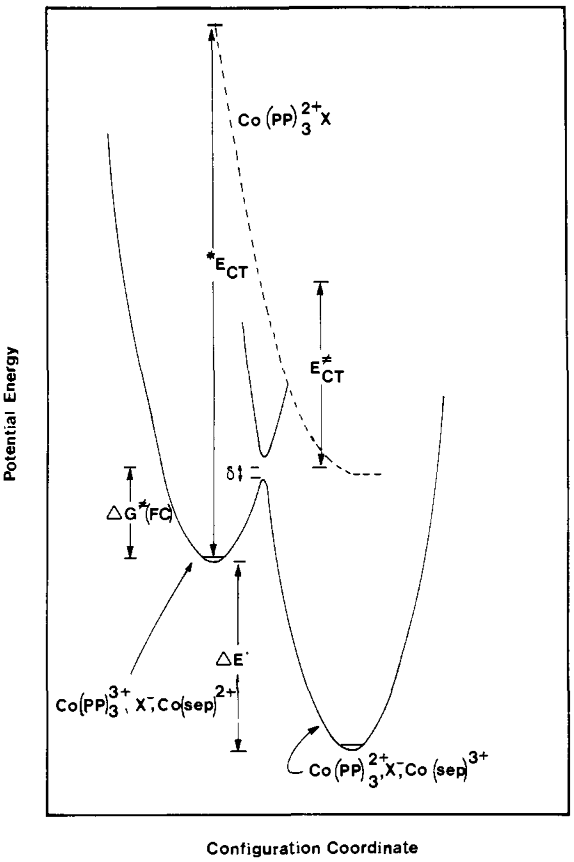

Figure 3. Qualitative representation of energy terms considered in analysis of charge-transfer perturbation of electron-transfer rates. Relative energies based on parameters for the [Co(phen)$_3^{3+}$, ascorbate, Co(sep)$^{2+}$] system. Harmonic vibrational contributions are assumed. Solid lines indicate the two-dimensional representation of the potential energy surface for the Co(phen)$_3^{3+}$ + Co(sep)$^{2+}$ reaction. The crossling point, $\Delta G^{\ddagger}$(FC), is based on values of the self-exchange parameters. Splitting of the surfaces at the crossling point is ~2δ. The (Co(PP)$_3^{2+}$, ·X) surface, dashed line, is based on the estimated (Co(PP)$_3^{3+}$, X$^-$) → *(Co(PP)$_3^{2+}$, ·X) charge-transfer absorption maximum (*E_{CT}) and the equilibrium constant for the corresponding thermal reaction; these points are connected with a harmonic surface.

magnitude of the perturbation at the point where the surfaces cross (see Figure 3). The energy of the system at the surface crossing point, $\Delta G^{\ddagger}$(FC), can be evaluated from the usual Franck–Condon models of the electron-transfer reaction coordinate.[11-15]

The perturbing, ion-pair charge-transfer state, *[X$^-$ → Co^{III}(PP)$_3$], is a vibronic state reached by a vertical electronic transition from the surface crossing region. The energy of this state can be estimated by assuming (a) a quadratic dependence of the CT energy on the nuclear coordinates, (b) that changing the neighboring anion does not significantly alter the Franck–Condon parameters for electron transfer, (c) that the configuration coordinates of the surface crossing region are not significantly changed by the CT perturbation, and (d) that the Franck–Condon-only activation energy is given by the usual Marcus [10] expression,

$$\Delta G^{\ddagger}(\mathrm{FC}) = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ}}{\lambda}\right)^2$$

where λ is Marcus' reorganizational parameter and ΔG° is the free energy change for the electron-transfer process. Then the CT perturbation at the surface crossing is given by,

$$E_{\mathrm{CT}}^{\ddagger} = E_{\mathrm{CT}}^{*} - \Delta G^{\ddagger}(\mathrm{FC}) + \left[\frac{\Delta G^{\ddagger}(\mathrm{FC})}{\lambda} - 2\left(\frac{\Delta G^{\ddagger}(\mathrm{FC})}{\lambda}\right)^{1/2}\right][E_{\mathrm{CT}}^{*} - \Delta G^{\circ}(\mathrm{Co,X})] \quad (5)$$

where ΔG°(Co,X) is the free energy change for the Co(PP)$_3^{3+}$ + X$^-$ → Co(PP)$_3^{2+}$ + °X reaction.

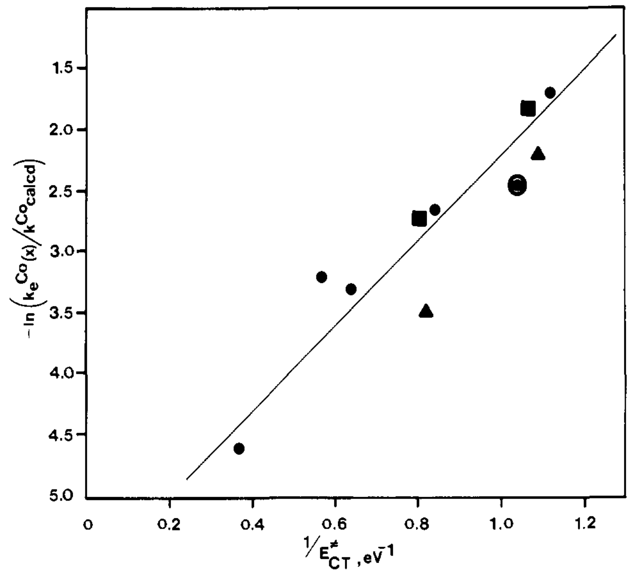

Figure 4. Variations in electron-transfer rates with charge-transfer properties of ion pairs in Co(PP)$_3^{3+}$ + Co(sep)$^{2+}$ reactions. Calculated rate constants are based on observed (or estimated) self-exchange rate constants. The value of $E_{CT}^{\ddagger}$ is based on the estimate of the energy of the vertical (Co(PP)$_3^{3+}$, X$^-$)‡ → (Co(PP)$_3^{2+}$, ·X)‡ transition for the system with nuclear coordinates appropriate to the transition state for electron transfer. See Table IV. Oxidants: Co(phen)$_3^{3+}$, ●; Co(NO$_2$phen)$_3^{3+}$, ■; Co(Me$_4$phen)$_3^{3+}$, ▲; Co(phen)$_2$(chn)$^{3+}$, ⊙.

For the correlation in Figure 4 we have based *E_{CT} on the observed CT maxima for [Co(en)$_3^{3+}$, X$^-$] ion pairs,[49] correcting for differences in Co(en)$_3^{3+,2+}$ and Co(PP)$_3^{3+,2+}$ reorganizational parameters and potentials. The Co(phen)$_3^{3+,2+}$ self-exchange rate constant has been taken as 20 M^{-1} s^{-1} and self-exchange parameters have been estimated for the other polypyridyl complexes on the basis of the ratios of their reduction rates with Ru(NH$_3$)$_6^{2+}$. Values of k_{calcd}^{Co} have been determined from the Marcus square-root relation[10] with use of reported or estimated self-exchange parameters and data from Table III.

In assessing the significance of electronic terms in electron-transfer reactions one would prefer to compare the observed rate constants to the values these rate constants would have had if Franck–Condon terms alone contributed to the reactivity; i.e., one should consider the ratios k_{obsd}/k_{ad} where $k_{ad} = K_o\nu_e^{nu} \times \exp[-\Delta G^{\ddagger}(\mathrm{FC})RT]$. Unfortunately, current precision of structural parameters does not allow a sufficiently accurate calculation of k_{ad}. As a consequence we have based our evaluations (Figure 4) on a comparison to the self-exchange reactions of the reactant partners (in k_{calcd}^{Co} with use of the Marcus square-root relation). The ratio $k_{obsd}^{Co}/k_{calcd}^{Co}$ is always less than 1 for the Co(PP)$_3^{3+}$/Co(sep)$^{2+}$ reactions; e.g., $k_{obsd}^{Co}/k_{calcd}^{Co} \simeq 4 \times 10^{-3}$ for Co(phen)$_3^{3+}$/Co(sep)$^{2+}$ in the NaCF$_3$SO$_3$ medium. Since $k_{obsd}^{Co}/k_{calcd}^{Co} \geq k_{obsd}^{Co}/k_{ad}^{Co}$ (depending on how adiabatic the self-exchange processes are), ($k_{obsd}^{Co}/k_{ad}^{Co}$) $\ll 10^{-2}$ for the Co(PP)$_3^{3+}$/Co(sep)$^{2+}$ reactions in the limit of ($^1/E_{CT}^{\ddagger}$) → 0. For comparison, we note that for $\nu_e^{el} = \nu_e^{el,o}\exp[-2\alpha r_{DA}]$, with $\nu_e^{el,o} \sim 10^{15}$ s^{-1} and $\alpha = 5.5$ nm^{-1} as found in *energy*-transfer studies,[26] one finds $\nu_e^{el} \sim 10^{10}$ s^{-1} and $\nu_e^{el}/\nu_e^{nu} \sim 10^{-3}$ for the Co(III)–Co(II) reactions. The larger values of α commonly proposed[2-5,7,13,19b,c,22] would predict less adiabatic reactions.

However, it must be noted that the usual Franck–Condon analysis of Co(III)–Co(II) self-exchange reactions seems to indicate that they approach the adiabatic limit.[17,57] The tendency of self-exchange reactions to be more adiabatic than cross reactions of cobalt complexes suggests that one of the terms making a significant contribution to the electronic matrix element in elec-

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(57) Taube, H. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, Nevada, March 1982; American Chemical Society: Washington, DC, 1982; INOR 121.

tron-transfer reactions is the exchange integral for systems in which reactions and products are electronically degenerate. We have noted above that the observed CT perturbations of *electron-* or *energy*-transfer rates can be interpreted as a superexchange contribution, i.e., as a contribution somewhat similar in origin.

The standard deviation in Figure 4 is slightly larger than that in Figure 1. Some of the deviations from the correlation line in Figure 4 may be systematic, very likely a consequence of our assumption that self-exchange parameters (or even relative self-exchange parameters) for the $Co(PP)_3^{3+,2+}$ couples can be accurately extracted from the $Cr(PP)_3^{3+}/Ru(NH_3)_6^{2+}$ cross-reactions. At the level of these deviations, a factor less than 2 in $k_{obsd}^{Co}/k_{calcd}^{Co}$, we have no reason to expect that all of the $Co(PP)_3^{3+}/Ru(NH_3)_6^{2+}$ reactions are "uniformly nonadiabatic". At the present stage of these studies, such deviations are relatively small and do not affect the general features of our analysis,

C. Conclusions. In this study we have reported observatons on the kinetic behavior of some *energy*-transfer and *electron*-transfer reactions which indicate that the rates of reactions of each class can be perturbed by donor–acceptor charge-transfer interactions. The systematic nature of the variations in second-order rate constant with the magnitude of the perturbation can in each class of reactions be conveniently illustrated, with reference to eq 1 and 2, in a plot of ln k_i vs. $\sum_j 1/E_{CT(j)}$ (Figures 1 and 4).

The correlations in Figures 1 and 4 indicate qualitatively similar effects of charge-transfer perturbations on the rates of *energy*-transfer and *electron*-transfer reactions, Detailed differences in these correlations no doubt arise largely from differences in the coupling constants, C_i, which must reflect the differences (e.g., two and one electron, respectively) in the exchange integrals for the *energy-* and *electron*-transfer reactions. Quantitative comparison of the effects of CT perturbations on the rates of these two classes of reactions is also precluded by consideration of only $X^- \rightarrow M(III)$ ("LMCT") perturbations in the present study. Full development of a "superexchange" perturbation must also take account of the complementary metal ionization (or "MLCT" and "CT-to-solvent") contributions. Finally, the perturbations employed have been significantly different (first and second coordination sphere) in the two reaction classes.

Nevertheless, the present study does demonstrate that some classes of *energy-* and *electron*-transfer reactions are nonadiabatic ($\nu_i < k_BT/h$), and that nonadiabatic bimolecular reactions can become more adiabatic by introducing weak charge-transfer perturbations. These observations not only suggest that the response to CT perturbations might eventually become useful as a criterion for adiabaticity but they also suggest that long-range electron transfer between prosthetic groups in biological systems may be facilitated by the existence of redox polarizable functions in the protein or other medium separating electron-tansfer centers.

It is likely that donor–acceptor coupling can be enhanced by perturbations other than those of the various charge-transfer types. The value of $k_e^{Co}/k_e^{Ru} = 12$ calculated from self-exchange parameters is larger than any of the experimental ratios that we have found. Furthermore, in the reduction of $Co(phen)_3^{3+}$ ($CF_3SO_3^-$ media), $k_e^{Co}/k_e^{Ru} = 0.5$, with most of the effect arising from the $Co(phen)_3^{3+}/Co(sep)^{2+}$ reaction, for which k_e^{Co} is ~0.4% of the value on the basis of self-exchange reactions. In this system the $Ru(NH_3)_6^{2+}$ reactions appear to be relatively adiabatic; this suggests that k_e^{Co}/k_e^{Ru} might be a useful index of the adiabaticity of various cross-reactions. On this basis, the values of $k_e^{Co}/k_e^{Ru} \simeq 10$ found for the reactions with $Co(NH_3)_6^{3+}$ are suggestive of a relatively "adiabatic" reaction of $Co(sep)^{2+}$. These several observations suggest additional factors which might contribute to donor–acceptor coupling: (a) relatively large orbital radii (as with the 4d-Ru orbitals); (b) relatively small values of ν_e^{nu} (as when most of the Franck–Condon barrier arises from solvent) leading to $\nu_e^{el} > \nu_e^{nu}$ and $\kappa_e \sim 1$;[52] (c) a "resonance" effect resulting in an enhanced exchange interaction for electronically degenerate reactions (as in self-exchange reactions). We have noted elsewhere[26b] that there is no basis in principle for factoring these contributions to the electronic matrix element into separate contributions of the donor and acceptor. The experimental observations reported in this paper lend support to that view; we especially note that if future work supports the hypothesis that self-exchange reactions are in principle more adiabatic than cross reactions, then a simple factoring of the electronic matrix element would be very misleading.

The clarification of these issues and the discovery of additional molecular properties which perturb the donor–acceptor electronic matrix element seem likely as additional systematic studies of these phenomena evolve.

Registry No. $Cr(phen)_3^{3+}$, 15276-16-1; $Cr(bpy)_3^{3+}$, 15276-15-0; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(NH_3)_5OH_2^{3+}$, 14403-82-8; $Co(NH_3)_5CN^{2+}$, 19529-81-8; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5Br^{2+}$, 14970-15-1; $Co(NH_3)_5NCS^{2+}$, 14970-18-4; $Co(NH_3)_5N_3^{2+}$, 14403-83-9; $Co(N_4)(OH_2)_2^{3+}$, 46750-08-7; $Co(N_4)Cl_2^+$, 19973-61-6; $Co(N_4)(OH_2)N_3^{2+}$, 52658-59-0; $Co(NH_3)_5F^{2+}$, 15392-06-0; $Co(NH_3)_5NO_2^{2+}$, 14482-68-9; $Co(N_4)(OH_2)Cl^{2+}$, 18935-88-1; $Co(N_4)(OH_2)Br^{2+}$, 68108-79-2; $Co(N_4)(NO_2)_2^+$, 23507-13-3; $Co(N_4)(NCS)Cl^+$, 46931-41-3; $Co(N_4)(NCS)_2^+$, 47099-73-0; $Co(N_4)(NCS)N_3^+$, 86163-71-5; $Co(N_4)N_3Cl^+$, 46931-42-4; $Co(N_4)(N_3)^{2+}$, 86163-72-6; $Co(CN)_6^{3-}$, 14897-04-2; $Ru(NH_3)_6^{3+}$, 18943-33-4; $Rh(NH_3)_5Cl^{2+}$, 15379-09-6; $Co(phen)_3^{3+}$, 80711-15-5; $Co(sep)^{2+}$, 63218-22-4; $Ru(NH_3)_6^{2+}$, 19052-44-9; $Co(phen)_3^{3+}CF_3SO_3^-$, 86163-73-7; $Co(phen)_3^{3+}I^-$, 31415-56-2; $Co(phen)_3^{3+}NO_2^-$, 86176-93-4; $Co(phen)_3^{3+}$ascorbate, 86163-74-8; $Co(phen)_3^{3+}NCS^-$, 68369-95-9; $Co(phen)_3^{3+}HCO_2^-$, 86163-75-9; $Co(phen)_3^{3+}CH_3CO_2^-$, 86176-92-3; $Co(phen)_3^{3+}Cl^-$, 86163-76-0; $Co(3,4,7,8\text{-}Me_4phen)_3^{3+}$, 86176-94-5; $Co(phen)_2(chn)^{3+}$, 86163-77-1; Hg^{2+}, 7439-97-6.