for hydrogen atom abstraction from some of the complexes suggest that they are chemically significant.

Acknowledgment. We thank the National Science Foundation (Grant CHE-83-08078 to N.J.C.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (S.R.C.), for financial support. We also thank Peter Haaland and Jeffrey C. Hayes for preliminary experiments.

Registry No. **1**, 39333-53-4; **2**, 102977-65-1; **3**, 82917-94-0; **4**, 57175-17-4; **5**, 102977-66-2; **6**, 86949-29-3; **7**, 102977-67-3; **8**, 89710-99-6; **9**, 102977-68-4; **10**, 102977-69-5; **11**, 102977-70-8; **12**, 102977-71-9; **13**, 71531-99-2; **14**, 102977-72-0; **15**, 11084-56-3; **16**, 11084-55-2; **17**, 11133-01-0; $[W(\eta\text{-}C_5H_5)_2(C_2H_4)(CH_2Ph)][Br]$, 102977-73-1.

Experimental Probes of the Electronic Matrix Element Contributions to Bimolecular Reactions. The Electronic Energy Transfer Reactions of (^{2}E)-Chromium(III)-Polypyridyl Complexes with Transition-Metal Acceptors[1]

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Received August 9, 1985

Abstract: The rates have been determined for quenching of (^{2}E)Cr(polypyridyl = PP)$_3^{3+}$ donors by a few dozen cobalt(III) complexes. The quenching rates for the cobalt(III) acceptors have been found to be as much as three orders of magnitude slower than the diffusion limit but independent of the donor–acceptor energy gap. This and other evidence indicates that the rates of these reactions are limited by electronic rather than by Franck–Condon factors. In accord with this interpretation the rates decrease with increasing donor and acceptor separation (r_{DA}). The distance dependence is compatible with expectation for energy transfer mediated by an exchange mechanism with k_q proportional to $\exp(-2\alpha r_{DA})$ and $\alpha = 5.5 \pm 0.5$ nm^{-1}. The rates also respond to charge-transfer perturbations, with the rates increasing as the energy of the perturbing charge-transfer excited (CT) states decreases. This effect can be interpreted either (a) in terms of the superexchange contribution to the donor–acceptor interaction energy or (b) as the result of polarizabion of the donor and acceptor wave functions by CT-induced dipole moments. Either interpretation results in an inverse dependence (of k_q or α, respectively) on the energy of the perturbing CT state. The correlations of experimental data suggest that low-energy CT states of the donor and acceptor tend to interfere.

The fundamental factors governing reactivity patterns of bimolecular energy transfer reactions in solution are in a general way common to many classes of important chemical and physical interactions. For example there have been several explicit comparisons of energy and electron transfer reaction dynamics[2-6] and the role of donor–acceptor exchange interactions is important in many aspects of spectroscopy.[7] Much of the recent interest in energy transfer reactions arises from the perception that many of these reactions are relatively sensitive to the purely electronic factors[2-6,8-11] which make significant contributions to chemical reactivity, but which are often obscured by much larger nuclear (or Franck–Condon) factors in other chemical reactions.[12-16]

The migration of electronic excitation energy between donor and acceptor centers is itself a fundamental concern in either understanding or in manipulating the behavior of reactive electronic excited states.[6,8-10,17-19] Those energy-transfer reactions in which the individual electronic transitions are dipole allowed have attracted the most attention and are well-understood theoretically.[8-10,17,20,21] In contrast, those reactions in which both of the individual electronic transitions are dipole forbidden have received less experimental or theoretical attention. However, the

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perceived relationships between electron- and energy-transfer processes have stimulated several recent studies of the dipole forbidden, intermolecular energy transfer between the metal centered, d-orbital excited states of transition-metal complexes.

Comparisons between the rates of bimolecular energy transfer and electron transfer (or other simple chemical) reactions can be conveniently formulated in terms of the Fermi–Golden rule, assuming that electronic and nuclear motions can be treated separately (Born–Oppenheimer approximation)

$$k = g_s K_0 (2\pi / hL)\langle V\rangle^2 N\rho \qquad (1)$$

where g_s is a statistical weight based on the changes in spin multiplicities; K_0 is an outer-sphere association constant; L has dimensions of energy and is a function of reorganizational energies or relaxation times;[12,14] $\langle V\rangle$ is the matrix element describing the electronic coupling of reactant and product potential energy surfaces; N is a Franck–Condon factor describing the dependence of the reaction rate on nuclear parameters (changes of bond length and angle, ΔQ; vibrational frequencies, ω, of the normal vibrational modes involved in these nuclear displacements; the energy difference, ΔE; between the thermally equilibrated reactants and products); and ρ is a density of states parameter. Since energy transfer processes involve at least two electrons, while electron transfer generally involves a single electron, one expects a detailed difference in the formulation of $\langle V\rangle$ for the two processes but very similar forms for N. This overall qualitative similarity in the logical structure of the dynamic behavior of certain classes of energy-transfer and electron-transfer systems has proved to be instructive and stimulating.[2-5] However, there are several different mechanisms possible for donor–acceptor coupling in energy-transfer processes,[8-17,20,21] and these are not all neatly mapped onto electron-transfer or other chemical processes.

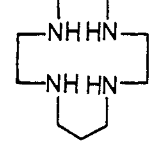
Systematic discussions of chemical processes usually use eq 1 to describe the "unimolecular" decay of a reactant pair within a collision complex. By analogy with the nonradiative relaxation of molecular excited states,[22] the discussion of energy-transfer reactions is facilitated by reference to the different limiting forms expected of N when the individual electronic transitions involve either a very large or a very small change in nuclear coordinates.[23] However, the theoretical formalisms appropriate to relaxation of electronic excited states are not trivially mapped onto bimolecular processes, if only because coupling strengths and energy gaps are typically much smaller in the bimolecular reactions. To emphasize that caution is necessary, we have used four limiting categories to classify energy transfer reactions: (a) Category 1 reactions are those which approximate the unimolecular "strong-coupling" limit[22] and can be described semiclassically in terms of the crossing of greatly displaced reactant and product potential energy curves. (b) In category 2 the reactant and product potential energy surfaces do not formally intersect (donor and acceptor states have molecular geometries very similar to those of the respective ground states) and semiclassical descriptions of the relaxation process are in terms of nuclear and electronic tunneling parameters. (c and d) Intermediate categories 3 and 4 are approached from 1 and 2, respectively. These categories are formally distinguished by relationships between the parameters characterizing the potential energy surfaces (ΔE the energy difference between the zeroth vibrational states of the donor and acceptor electronic excited states; λ the nuclear reorganizational energy difference between the reactants with their equilibrium coordinates and the products with these same nuclear coordinates; and ω_{ave} the mean frequency of the vibrational modes associated with the reactant–product nuclear displacement):[23] (a) for category 1, $|\Delta E| < \lambda$ and $\lambda \gg \hbar\omega_{ave}$; (b) for category 2, $|\Delta E| > \lambda$ and $\lambda \sim \omega_{ave}$; (c) for category 3, $|\Delta E| > \lambda$ and $\lambda \sim \hbar\omega_{ave}$; and (d) for category 4, $|\Delta E| \leq \lambda$ and $\lambda \sim \hbar\omega_{ave}$. The very small gaps characteristic of the category 4 limit make their theoretical discussion difficult,[8-10] and we have elsewhere[24] discussed the interpretation of energy-transfer rates which approach this behavior. Only those energy-transfer reactions which approximate category 1 or category 3 behavior can be used in relatively simple, direct analogies to ordinary electron-transfer processes.

Transition-metal donor excited states must have lifetimes of more than a few hundred ns to be useful in the study of bimolecular reactions in fluid solution, and the most common such species are the polypyridyl (PP) complexes of ruthenium(II) or of chromium(III). Energy-transfer reactions in which the excited states of Ru^{II}–polypyridyl complexes are quenched by Cr^{III}–amine complexes[2b,2c,25] are characterized by very small values of λ and appear to fall in or near to category 2.[23,24] Such systems cannot be readily compared to simple electron-transfer systems. In contrast, the excited states of Co^{III} are appreciably distorted[26] and should result in values of $\lambda > \hbar\omega_{ave}$ for the $(^2E)Cr(PP)_3{}^{3+}$–Co^{III} energy-transfer reactions. As a result these energy-transfer reactions should have many features in common with simple electron-transfer processes. In this report we examine several aspects of the $(^2E)Cr(PP)_3{}^{3+}$–Co^{III} systems with a special view of determining the properties of the electronic matrix element, $\langle V\rangle$, in such reactions.

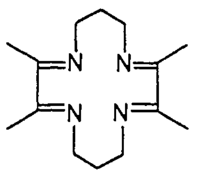
Experimental Section

Materials. Acidopentamminecobalt(III),[27] *trans*-(1,4,8,11-tetraazacyclotetradecane = [14]aneN$_4$)cobalt(III)XY,[28-31] *trans*-(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradecane-1,3,8,10-tetraene = Me$_4$-[14]tetraeneN$_4$)cobalt(III),[29,32-34] *cis*- and *trans*-$Co^{III}(en)_2XY$,[35-39] and (*S*,1,3,6,10,13,16,19-octaazabicyclo(6.6.6)eicosane = sep)cobalt(III)[40,41]

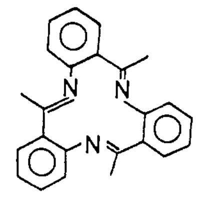
Sep



[14]aneN$_4$



Me$_4$[14]tetraeneN$_4$



Bzo$_3$[12]hexaeneN$_3$

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were prepared as described in the literature cited. Dr. T. Ramasami generously supplied the sample of [*trans*-Co([14]aneN$_4$)(NH$_3$)$_2$]Cl$_2$.

The synthesis of Fe(Me$_4$[14]tetraeneN$_4$)Br$_3$ has been reported.[42] The Fe(Me$_4$[14]tetraeneN$_4$)X$_2^+$ complexes are relatively labile and the bromo complex was dissolved in solutions of 1 M in Br$^-$ or Cl$^-$ to generate the respective trans dihalo complexes. The Fe(Me$_4$[14]tetraeneN$_4$(OH$_2$)$_2$)$^{3+}$ complex was prepared as PF$_6$ salt from the dibromo complex by the addition of HPF$_6$.

WARNING. We have found the [Fe(N$_4$)X$_2$]ClO$_4$ complexes to be extremely hazarous and strongly recommend against isolation of the perchlorate salts.

Commerical [Ru(NH$_3$)$_6$]Cl$_3$ and [Rh(NH$_3$)$_5$Cl]Cl$_2$ (Matthey–Bishop) were purified by recrystallization.

Trifluoromethanesulfonic acid was purified by vacuum double distillation of the technical grade material. The sodium and lithium salts were prepared by neutralization of the respective carbonates.

All other materials were commercial, reagent or better grade.

The Co(NH$_3$)$_6^{3+}$ and Co(en)$_3^{3+}$ complexes were N-deuterated by repeated (5–6) recrystallizations from D$_2$O. Shifts in the N–H stretching frequency were used to monitor the progress and extent of deuteration. On the basis of relative intensities of ν(N–H) and ν(N–D) we estimate that the complexes were more than 96% deuterated.

Techniques. The quenching rates reported in this study have been determined by observations of the quencher concentration dependencies of excited state lifetimes. Most of the studies have monitored the excited state luminescence decay by using a N$_2$-laser pumped, dye laser excitation source, a Jobin-Yvon H-100 spectrometer, a RCA 7102 photomultiplier, and a Nicolet Explorer III for detection.[4b] Samples were kept in a thermostated housing (±1 °C) for the luminescence measurements. All samples were deaerated by using a Cr^{2+}-scrubbed stream of N$_2$.

Charge-Transfer Energies. Values of E_{CT} are for the vertical transitions: (a) observed in (X$^-$)Co^{III}L$_5$ $\rightarrow$ *[•X)Co^{II}L$_5$] absorptions, E_{CT}(Co) or (b) estimated for the intermolecular {(^{2}E)Cr^{III}(PP)$_3$, (X$^-$)Co^{III}L$_5$} $\rightarrow$ {Cr^{II}(PP)$_3$, (•X)Co^{III}L$_5$} transitions, E_{CT}(Cr).[4b] Values of E_{CT}(Cr) were obtained from $\Delta E^f + 4D_q(X) + \Delta E_\lambda$ (where ΔE^f is the difference in formal potentials for the (^{2}E)Cr^{III}(PP)$_3$/Cr^{II}(PP)$_3$ and the •X/X$^-$ couples in aqueous solutions;[43,44] $4D_q(X)$ is the amount of ligand field stabilization energy contributed to Co(III) by the ligand X$^-$; ΔE_λ is the value of λ for the charge-transfer transition). The values of E^f used were 1.42,[22] 2.6,[44] 2.0,[44] 1.62,[45] 1.4,[46] and 1.0[47] V for the (^{2}E)Cr(phen)$_3^{3+}$/Cr(phen)$_3^{2+}$, •Cl/Cl$^-$, •Br/Br$^-$, •NCS/NCS$^-$, •N$_3$/N$_3^-$, and •NO$_2$/NO$_2^-$ couples, respectively. Tabulated values of $D_q(X)$[48] have been used. Values of $E_\lambda \simeq 40$ kJ mol^{-1}, estimated for solvent reorganizational contributions,[49] have been used for reactions of all but the nitro complexes; a value of $E_\lambda \simeq 130$ kJ mol^{-1} has been used for the latter to take into account internal reorganization[47] as well as solvent reorganizational contributions. For the *trans*-Co(N$_4$)X$_2$ quenchers we have used $k_q/2$ in the correlations, assuming that there is a statistical factor of about 2 favoring the CT-enhancement of rates of these complexes over the corresponding Co(NH$_3$)$_5$X complexes.

To evaluate k_{en} for each reaction, we considered the quantities k_q/K_0. Owing to uncertainties in the absolute values of K_0 and compensating for factors other than size and LMCT-perturbations which may also contribute to k_{en}, all the correlations are based on rate ratios: $(k_q'/k_q)_{corr} = (k_q/k_q^{ref})\cdot(K_0^{ref}/K_0)$. For Figure 1 we used Co(NH$_3$)$_6^{3+}$ as the reference system. For the correlations with E_{CT}, the reference systems were the following: (a) Co(NH$_3$)$_6^{3+}$ for Co^{III}(NH$_3$)$_5$X; (b) *trans*-Co([14]aneN$_4$)(NH$_3$)$_2^{3+}$ for *trans*-Co([14]aneN$_4$)XY$^+$ and for *trans*-Co(Me$_4$[14]tetraeneN$_4$)XY$^+$; the average values of k_q for *trans*-Co(N$_4$)(NH$_3$)$_2^{3+}$ and *trans*-Co(N$_4$)(OH$_2$)$_2^{3+}$ for the *trans*-Co(N$_4$)(OH$_2$)X^{2+} complexes (N$_4$ = [14]aneN$_4$, Me$_4$[14]tetraeneN$_4$).

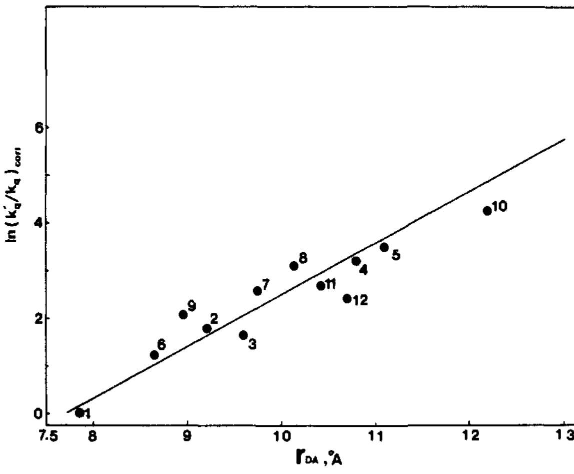

Figure 1. Distance dependence of the electronic matrix element for (^{2}E)Cr(PP)$_3^{3+}$–Co^{III} reactions. Data from Table II.

The Association Constant K_0. We have used the standard procedures, as for example described by Brown and Sutin,[50] in estimating K_0. This estimate employs a mean value of r_{DA} based on the geometric mean of the van der Waals radii along three Cartesian axes.[50]

For ions with nonspherical charge distributions (e.g., Co^{III}(NH$_3$)$_5$X^{2+} or *cis*-Co(en)$_2$X$_2^+$) estimates of K_0 should in principle take account of higher order electrostatic interactions than the ion–ion Coulombic interactions which are the basis of the standard treatment. We have ignored such higher order corrections.

In the solutions of high ionic strengths which we have employed, the bimolecular reactions are expected to have diffusion limited rates of (1–6) × 10^9 M^{-1} s^{-1} ($g_s \simeq 1$) depending on charge types (i.e., from [+3, +3] to [+3, +1], respectively). Few of our reactions have approached this limit, but for those few we have employed the simple stationary state expression

$$k_q(\text{obsd}) = k_d k_{en}/(k_{-d} + k_{en})$$

to estimate k_{en} when k_q(obsd) is greater than 10% of k_d.

Results

The bimolecular quenching data obtained in this study (at 15 °C) are summarized in Table I.

We have made systematic studies of the temperature dependence of k_q for the Co(phen)$_3^{3+}$, Co(NH$_3$)$_5$F^{2+}, and Co(NH$_3$)$_5$NCS^{2+} quenching of (^{2}E)Cr(phen)$_3^{3+}$ (in 1 M NaCF$_3$SO$_3$ over the temperature range −6 to 35 °C). the observed rates increased very slightly with temperature, consistent with a first order preexponential temperature dependence of the rate constant (see Figure S-1)[51] or possibly with a small temperature coefficient for K_0. From Figure S-1 we infer that $\Delta H^\ddagger = 0 \pm 2$ kJ mol^{-1} for each of these reactions.

We have found that N–H deuteration has no significant effect on the quenching rate. In 1 M HCl at 15 °C we found $k_q = (6.7 \pm 0.3) \times 10^6$ and $(6.4 \pm 0.3) \times 10^6$ M^{-1} s^{-1}, respectively, for Co(NH$_3$)$_6^{3+}$ and Co(ND$_3$)$_6^{3+}$ and $k_q = (3.7 \pm 0.2) \times 10^6$ and $(3.9 \pm 0.2) \times 10^6$ M^{-1} s^{-1}, respectively, for Co(en)$_3^{3+}$ and Co(d-en)$_3^{3+}$ (figures S-2 and S-3).[51]

In the present study we have extended the earlier investigation[4a,13a] of the dependence of k_q on the separation distance of the (^{2}E)Cr(polypyridyl)$_3^{3+}$ donor and the Co^{III} quencher in the collision complex by using donors with bulky substituents. The van der Waals separation distance has been based on the approach of Brown and Sutin.[50] Our observations are summarized in Table II and in Figure 1.

There is a general tendency for k_{en}/k_{en}^{ref} to increase as E_{CT}(Cr) decreases (Table I). This becomes a relatively good correlation when E_{CT}(Co) is taken into account. Thus, a plot of $(k_{en}/k_{en}^{ref})^{1/2}$ vs. $\Sigma(1/E_{CT}) = [1/E_{CT}(\text{Cr}) - 1/E_{CT}(\text{Co})]$ has less scatter than

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(51) Supplementary material. See paragraph at end of paper.

Table I. Parameters for the Bimolecular Quenching of $(^2E)Cr(phen)_3^{3+}$

no. in figure 2	quencher	ε (727 nm) M^{-1} cm^{-1}	medium, 1 M (pH)	$10^{-6}k_q$[a] M^{-1} s^{-1}	~K_0[b] M^{-1}	~$E(^*X^0)$[c] kJ mol^{-1}	~E_{CT}- (Cr)[d] kJ mol^{-1}	~E_{CT}- (Co)[e] kJ mol^{-1}
	$Co(NH_3)_6^{3+}$	0.25	$NaCF_3SO_3$ (2)	1.4 ± 0.1	0.13	127		
			HCl	7.5 ± 1	0.13			
			HBr	14 ± 2	0.13			
	$Co(NH_3)_5OH_2^{3+}$	1.62	$NaCF_3SO_3$ (2)	0.95 ± 0.05	0.13	90		
	$Co(NH_3)_5F^{2+}$	0.27	$NaCF_3SO_3$ (2)	4.2 ± 0.2	0.28	126		
1	$Co(NH_3)_5Cl^{2+}$	0.33	$NaCF_3SO_3$ (2)	35 ± 2	0.28	125	210	438
			HCl	76 ± 2				
			HBr	93 ± 5				
2	$Co(NH_3)_5Br^{2+}$	1.90	$NaCF_3SO_3$ (2)	123 ± 10	0.28	123	163	383
3	$Co(NH_3)_5NO_2^{2+}$	2.3	$NaCF_3SO_3$ (2)	97 ± 8	0.28	132	237	498
4	$Co(NH_3)_5NCS^{2+}$	1.0	$NaCF_3SO_3$ (2)	154 ± 10	0.28	115	159	393
			HCl	112 ± 4				
5	$Co(NH_3)_5N_3^{2+}$	6.1	$NaCF_3SO_3$ (2)	223 ± 5	0.28	112	115	400
	cis-$Co(en)_2Cl_2^+$		HCl	116 ± 5	1.12			
6	*trans*-$Co(en)_2Cl_2^+$		HCl	88 ± 3	1.12	94	215	392
	cis-$Co(en)_2(NCS)_2^+$		HCl	730 ± 40 (831)	1.12			
7	*trans*-$Co(en)_2(NCS)_2^+$		HCl	115 ± 10	1.12	117	154	360
	cis-$Co(en)_2(NO_2)_2^+$		HCl	273 ± 15	1.12			
	trans-$Co(en)_2(NO_2)_2^+$		HCl	157 ± 15	1.12	165	230	431
	cis-$Co(en)_2(aniline)Cl^{2+}$		HCl	285 ± 15[f]	0.45	117		
	cis-$Co(en)_2(NH_2CH_2C_6H_5)Cl^{2+}$		HCl	443 ± 20[f]	0.45	117		
	cis-$Co(en)_2(py)Cl^{2+}$		HCl	300 ± 15[f]	0.45	117		
	cis-$Co(en)_2(cha)Cl^{2+}$		HCl	99 ± 15[f]	0.45	117		
	$Co([14]aneN_4)(NH_3)_2^{3+}$	18	$NaCF_3SO_3$ (2)	1.07 ± 0.08	0.89	143		
	$Co([14]aneN_4)(OH_2)_2^{3+}$	16	$NaCF_3SO_3$ (2)	0.66 ± 0.05	0.89	104		
8	$Co([14]aneN_4)Cl_2^+$	15	$NaCF_3SO_3$ (2)	45 ± 3	2.08	90	210	386
9	$Co([14]aneN_4)(OH_2)Cl^{2+}$	18	$NaCF_3SO_3$ (2)	22 ± 1	1.36	95	210	(406)
10	$Co([14]aneN_4)(NO_2)_2^+$	12	$NaCF_3SO_3$ (2)	57 ± 4	2.08	128	227	468
11	$Co([14]aneN_4)(NCS)Cl^+$	14	$NaCF_3SO_3$ (2)	86 ± 3	2.08	103	180	374
12	$Co([14]aneN_4)(OH_2)N_3^{2+}$	11	$NaCF_3SO_3$ (2)	132 ± 10	1.36	103	105	368
13	$Co([14]aneN_4)(NCS)_2^+$	14	$NaCF_3SO_3$ (2)	154 u 10	2.08	117	149	367
14	$Co([14]aneN_4)(N_3)_2^+$	49	$NaCF_3SO_3$ (2)	557 ± 30	2.08	102	105	347
15	$Co([14]aneN_4)(NCS)N_3^+$	31	$NaCF_3SO_3$ (2)	381 ± 30	2.08	109	127	362
	$Co([14]tetraeneN_4)(OH_2)_2^{3+}$	9	$NaCF_3SO_3$ (2)	1.3 ± 0.1	0.89	136		
16	$Co(Me_4[14]tetraeneN_4)(NO_2)_2^+$	15	$NaCF_3SO_3$ (2)	150 ± 10	2.08	165	227	468
17	$Co(Me_4[14]tetraeneN_4)(OH_2)N_3^{2+}$	27	$NaCF_3SO_3$ (2)	216 ± 20	1.36	134	105	357
18	$Co(Me_4[14]tetraeneN_4)(NCS)_2^+$	13	$NaCF_3SO_3$ (2)	364 ± 25	2.08	138	149	347
19	$Co(Me_4[14]tetraeneN_4)(NCS)N_3^+$	30	$NaCF_3SO_3$ (2)	412 ± 35	2.08	133	127	349
20	$Co(Me_4[14]tetraeneN_4)(N_3)_2^+$	39	$NaCF_3SO_3$ (2)	464 ± 40	2.08	131	105	344
	$Co(Me_4[14]tetraeneN_4)Cl_2^+$		HCl	14 ± 1	2.06		210	372
	$Co(Me_4[14]tetraeneN_4)Br_2^+$		HBr	168 ± 15	2.08		153	345
	$Fe(Me_4[14]tetraeneN_4)(OH_2)_2^{3+}$		$NaCF_3SO_3$ (2)	1.2 ± 1	0.89			
	$Fe(Me_4[14]tetraeneN_4)Cl_2^+$		HCl	8 ± 1	2.08			
	$Fe(Me_4[14]tetraeneN_4)Br_2^+$		HBr	53 ± 4	2.08			
	$Ru(NH_3)_6^{3+}$		HCl	≤0.01				
	$Rh(NH_3)_5Cl^{2+}$		HCl	≤0.01				

[a] Quenching rates from luminescence lifetime quenching except as indicated; 15 ± 1°. [b] Calculated ion pair association constant; based on procedures described in ref 50. [c] Estimated energy for the lowest energy, vibrationally equilibrated triplet excited states for Co(III) complexes. Lowest excited state for other complexes as noted. The $(^3T^\circ)Co(III)$ estimates are referenced to the value reported (ref 26) for $Co(NH_3)_6^{3+}$; the difference in triplet energies are based on values of ligand field stabilization and splitting parameters reported in the literature (ref 69–71). In this treatment we have held the Racah parameter constant for axial substitution within a family of complexes or averaged Racah parameters for O_h complexes where they are reported. [d] Estimated energy for the vertical, intermolecular charge-transfer transition: $\{(^2E)Cr(phen)_3^{3+}, X^-{-}Co^{III} \rightarrow {}^*\{Cr(phen)_3^{2+}, {}^\bullet X{-}Co^{III}\}$. $E_{CT}(Cr) = \Delta E^f + 4Dq(X) + E_\lambda$; ΔE^f = difference in formal potentials for $(^2E)Cr(phen)_3^{3+}/Cr(phen)_3^{2+}$ and $^\bullet X/X^-$; $Dq(X)$ the contribution of X^- to the LFSE of Co(III); E_λ, the estimated reorganizational energy for the vertical transition E_λ = 40 kJ mol^{-1} except for NO_2^-; E_λ = 130 kJ mol^{-1} for NO_2^-).[44,45] [e] Experimental energies for the absorption maxima for the lowest energy $[Co^{III} - X^-] \rightarrow {}^*[Co^{II}{-}X^\bullet]$ charge-transfer transitions. [f] Quenching rates from luminescence intensity quenching.

Table II. Distance Dependence for the Quenching of $(^2E)Cr(PP)_3^{3+}$ by Co(III) Complexes[a]

donor	quencher	K_0, M^{-1}[b]	^{r}DA, nm[c]	$\ln k_q/M^{-1}$ s^{-1}	no. in Figure 1
$Cr(phen)_3^{3+}$	$Co(NH_3)_6^{3+}$	0.13	0.78	15.83	1
$Cr(4,7\text{-}Me_2phen)_3^{3+}$	$Co(NH_3)_6^{3+}$	0.20	0.84	14.99	6
$Cr(4,7\text{-}Ph_2phen)_3^{3+}$	$Co(NH_3)_6^{3+}$	0.30	0.89	14.57	9
$Cr(phen)_3^{3+}$	$Co(en)_3^{3+}$	0.36	0.92	15.02	2
$Cr(4,7\text{-}Me_2phen)_3^{3+}$	$Co(en)_3^{3+}$	0.51	0.98	14.59	7
$Cr(4,7\text{-}Ph_2phen)_3^{3+}$	$Co(en)_3^{3+}$	0.74	1.04	14.90	11
$Cr(phen)_3^{3+}$	$Co(sep)^{3+}$	0.46	0.96	15.42	3
$Cr(4,7\text{-}Me_2phen)_3^{3+}$	$Co(sep)^{3+}$	0.63	1.01	14.31	8
$Cr(4,7\text{-}Ph_2phen)_3^{3+}$	$Co(sep)^{3+}$	0.94	1.07	15.36	12
$Cr(phen)_3^{3+}$	$Co([14]aneN_4)(NH_3)_2^{3+}$	0.89	1.08	14.55	4
$Cr(phen)_3^{3+}$	$Co(phen)_3^{3+}$	1.04	1.12	14.40	5
$Cr(4,7\text{-}Ph_2phen)_3^{3+}$	$Co(phen)_3^{3+}$	1.65	1.22	14.12	10

[a] 15 ± 1°; 1 M HCl; emission lifetime quenching. [b] Association constants estimated as in Table I. [c] Estimated van der Waals contact distance (see ref 50).

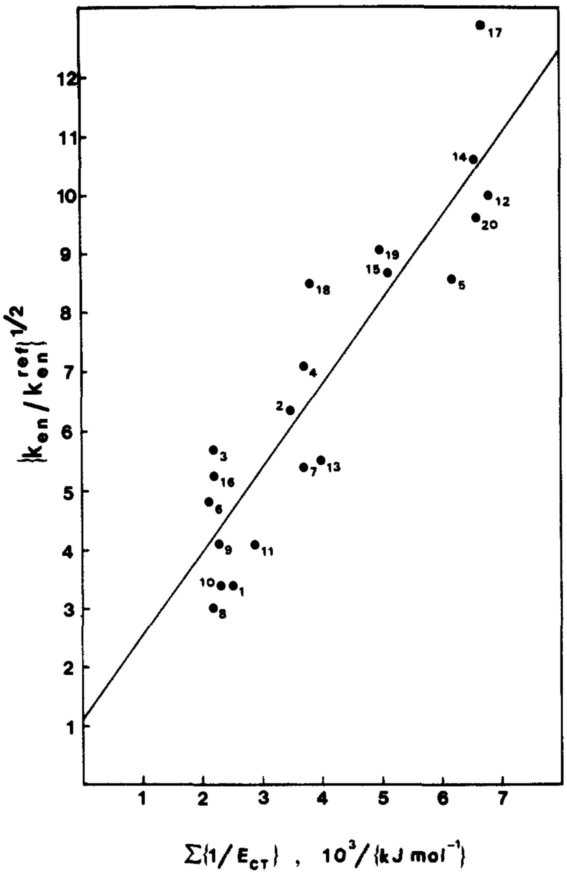

Figure 2. Variations in relative quenching rates with ligand-to-metal charge-transfer interactions. Correlation is based on eq 1, 4, and 9 with $\Sigma(1/E_{CT}) = 1/E_{CT}(Cr) - 1/E_{CT}(Co)$ and data from Table I. Points numbered as indicated in Table I (1 M $NaCF_3SO_3$). For least-squares correlation: slope = 1.43×10^3 kJ mol^{-1}; intercept = 1.08; r = 0.91.

the others that we have attempted, although a plot of ln(k_{en}/k_{en}^{ref}) vs. $\Sigma(1/E_{CT})$ is only slightly worse (Figure S-2). In our preliminary studies[4,52] of these reactions, we used a correlation with $[1/E_{CT}(Cr) + 1/E_{CT}(Co)]$, but with the current data, which are more consistent in medium and represent a wider range of quenchers, we find that this does not generate nearly as good a correlation as the one shown in Figure 2.

We have now examined the (^{2}E)Cr(PP)$_3^{3+}$–Co^{III} energy-transfer reaction patterns in a variety of ionic media: $NaHSO_4$, HCl, NaCl, HBr, $HClO_4$, $NaClO_4$, and $NaCF_3SO_3$. The observed values of k_{en} vary appreciably from medium to medium (see Table I). Most of the studies reported in this paper have employed 1 M $NaCF_3SO_3$ as the medium in which CT and ionic association effects are minimized while solubilities are acceptable. While quenching rates are comparable in bisulfate, trifluoromethanesulfonate, and perchlorate media, k_q tends to be much larger in chloride and bromide media. The larger values of k_q found in halide media may indicate the importance of a (halide)-to-(^{2}E)Cr(PP)$_3^{3+}$ CT perturbation, similar to those found in some electron-transfer systems.[4b,53] However, we have not made a thorough study of these effects, and we cannot at present distinguish between CT perturbations and the effects of specific ionic association in such systems.

Fortunately, many of the effects of these smaller variations appear to be relatively unimportant in the k_{en}/k_{en}^{ref} ratios. There does seem to be a tendency toward larger quenching constants when the "innocent" ligands are unsaturated. This effect is manifested in the larger rates observed for Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)$_2^{3+}$ than for Co([14]aneN$_4$)(OH$_2$)$_2^{3+}$ and in the relatively large value of k_q observed when Am = py, aniline, or benzylamine in the Co(en)$_2$AmCl^{2+} quenchers.

Several of these effects of medium or "innocent" ligands appear to make their largest percentage contributions to k_{en} when $\Sigma(\Delta E_{CT})^{-1}$ is relatively small.

Discussion

The principle aim of this study has been to investigate the contributions of the electronic matrix element to a simple class of bimolecular reactions. In order to accomplish this, it is first necessary to evaluate the contributions of Franck–Condon factors to the observed patterns of reactivity. As this work has evolved, it has become apparent that many transition-metal energy-transfer reactions are accompanied by very small displacements of the nuclear coordinates and that this situation is best approximated as occurring between nearly nested, nonintersecting reactant and product potential energy surfaces (e.g., category 2 behavior).[23,24] In this limit, the energy-transfer process is governed by the probability of electronic and nuclear tunneling between the potential energy surfaces, and the energy-transfer rates are very sensitive to the number of vibrational states which are available to accept large fractions of the excess excitation energy.[8-10,23,24] The contributions of $\langle V \rangle$, N, and ρ are difficult to separate in this limit, and, consequently, reactions which fall into, or near, category 2 are not readily used as experimental probes of the electronic matrix element.

The systems which would be most useful for the purposes of the present study are those for which the energy-transfer process results in a relatively large nuclear displacement, but the donor–acceptor energy gap is large enough that $N \sim 1$. The ligand-field excited states of cobalt(III) complexes are greatly distorted,[26] with Stokes-shifts predicted to be of the order of 5×10^3 cm^{-1}. For example, for the (^{2}E $\rightarrow$ ^{4}A$_2$)Cr(phen)$_3^{3+}$ donor–(^{3}T$_{1g}$ $\leftarrow$ ^{1}A$_{1g}$)Co(NH$_3$)$_6^{3+}$ acceptor, energy-transfer system, $\Delta E \sim 5 \times 10^3$ cm^{-1}, $\lambda \sim 2.5 \times 10^3$ cm^{-1}, and $\hbar\omega_{ave}$ (Co-ligand) $\sim$400 cm^{-1}. Thus the (^{2}E)Cr(PP)$_3^{3+}$–Co^{III} energy-transfer systems are likely to exhibit the desired patterns of behavior.

A. A Semiclassical Formalism for Category 1 Systems. Energy-transfer rates in, or near, the category 1 regime are most conveniently treated as classical surface crossing processes, so that the rate constants can be described by using a modified classical formalism, as has been done in simple electron-transfer systems[2,6,12,14,54]

$$k_q = g_s K_0 \kappa_{el} \nu_{nu} \Gamma \exp(-\Delta G^*(FC)/RT) \qquad (2)$$

where κ_{el} is the electronic transmission coefficient; ν_{nu} is the effective nuclear frequency appropriate to the reaction coordinate; Γ is the nuclear tunneling coefficient; and ΔG^*(FC) is the classical Franck–Condon activation free energy. In principle, the activation free energy is a function of the nuclear displacements (ΔX_i), related vibrational frequencies (ω_i), and the energy difference between minima of the donor and acceptor potential energy surfaces (ΔE or, allowing for small entropy contributions, $\Delta G°$). A useful representation of κ_{el} is based[12,14,54] on the Landau-Zener model for surface coupling

$$\kappa_{el} = 2[1 - \exp(-\nu_{el}/2\nu_{nu})]/[2 - \exp(-\nu_{el}/2\nu_{nu})] \qquad (3)$$

in which ν_{el} is the effective electronic frequency. On the basis of such an approach, electronic factors can only contribute to the observed reactivity patterns if $\nu_{el} < 2\ \nu_{nu}$. Obviously, eq 2 is equivalent to eq 1, where $N = \Gamma \exp[-\Delta G^*(FC)/RT]$ and $\nu_{el} = (2\pi/L)\langle V \rangle^2$. Contributions of the major factors in eq 2, to the observed quenching rates, are discussed in turn.

1. The Statistical Factors (g_s and K_0). For the (^{2}E)Cr(PP)$_3^{3+}$–Co^{III} reactions g_s = 1. Absolute values of K_0 are somewhat uncertain, but the relative values used in our correlations are expected to be reliable estimates of the variations expected

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(54) This formulation is based on arguments of Dexter[21] and the related approach to electron transfer reactions, ref 12 and 14 and: (a) Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798. (b) Newton, M. D. *Int. J. Quantum Chem. Symp.* **1980**, *14*, 363. (c) Newton, M. D. *ACS* Symp. Ser. **1982**, 255. (d) Tembe, B.; Friedman, H. L.; Newton, M. D. *J. Chem. Phys.* **1982**, *76*, 1490.

with changes in molecular size or charge type.

2. The Electronic Factor. The magnitude of the electronic frequency, ν_{el}, is determined by the effectiveness of donor–acceptor coupling, δ_{Da}, when the reactants in a collision complex have nuclear coordinates appropriate to the intersection region of the reactant and product potential energy surfaces. The magnitude of the electronic matrix element, $\langle V \rangle$, depends on the operators coupling the reactant and product potential energy surfaces and on the overlap of the donor and the acceptor orbitals.[5-17,21] In discussion of the various experimental contributions to $\langle V \rangle$, it is useful to consider separately the coupling constants (described by the appropriate Hamiltonian operators) and the donor–acceptor overlap integral[5,21,54]

$$\langle V \rangle \sim J_{DA}{}^0 \exp(-\alpha r_{DA}) \qquad (4)$$

where r_{DA} is the distance of separation of donor and acceptor orbital centers, α^{-1} can be approximately intepreted as a mean donor–acceptor orbital radius,[7,21] and $J^0{}_{DA}$ is proportional to the sum of Hamiltonian interaction terms evaluated at $r_{DA} = 0$. While eq 4 provides a useful basis for discussion of the purely electronic contributions to reactivity patterns, $\langle V \rangle$ actually must involve sums over many configurations, and the separation of component contributions (i.e., $J^0{}_{DA}$ and α) in eq 4 is likely to be somewhat artificial. In practice, the contributions to $\langle V \rangle$ are best evaluated experimentally. However, one must first evaluate the Franck–Condon contributions to k_q.

3. The Franck–Condon Factor. A semiclassical expression of the form $\Gamma \exp((-\Delta G^*(FC)/RT)$ should adequately describe the Franck–Condon contributions to k_q in the surface crossing limit (category 1), where $\Delta G^*(FC) \simeq E_a = (\lambda/4)\,(1 + \Delta E^\circ{}_{DA}/\lambda)^2$, and λ is a function of the changes in bond lengths (ΔX_D and ΔX_A, respectively), the vibrational frequencies coupled to these bond length changes ($\omega_{i,D}$, $\omega_{i,A}$, $\omega_{f,D}$, and $\omega_{f,A}$ for the initial (i) and final (f) state frequencies, respectively), the difference in energies (ΔE) of the minima of the reactant and product potential energy surfaces, a solvation component ($\Delta G_s{}^*$) accompanying any change of size of the donor or/and acceptor, and a nuclear tunneling factor (Γ) if the vibrational quanta are large compared to $2kT$). In the limit that the reactant and product surfaces are nested (category 2), one expects a very weak dependence on ΔE and/or decreases in k_q with increasing $|\Delta E|$.[8-10,15,16] Both the temperature coefficient, E_a, and the reorganizational parameter, λ, need to be evaluated in order to ascertain whether the $(^2E)Cr(PP)^{3+}$–Co^{III} systems are better described by category 1 or by category 2 Franck–Condon terms.

a. Temperature Dependence. The classical free energy of activation can be described by

$$\Delta E^*(FC) = (\lambda/4)\,(1 + \Delta E/\lambda)^2 \qquad (5)$$

provided the reactant and product surfaces are similar in shape. There may be a very weak tendency of k_q to increase with T for the $(^2E)Cr(PP)_3{}^{3+}$–Co^{III} reactions, but plots of $\ln(k_q/T)$ vs. $1/T$ (Figure S-1) are independent of temperature and $\Delta H^* \simeq 0 \pm 2$ kJ mol^{-1}. Thus, either (a) $\Delta E \sim \lambda$ and these energy-transfer reactions are in an intermediate reaction regime (category 3) only slightly removed from the category 1 limit or (b) λ is very small and these reactions are best treated in the category 2 limit.

b. The Reorganizational Components. In principle, λ could be estimated in the surface crossing limit with reference to the degenerate energy transfer reactions

$$(^*X^0)ML_6 + M'L_6 \overset{k_R}{\rightleftharpoons} ML_6 + (^*X^0)M'L_6$$

(where $^*X^0$ indicates the lowest energy, vibrationally equilibrated electronic excited state, the prime is an arbitrary label, and R = D or A). For such a reaction, eq 2 becomes

$$k_r = g_s K_0 \kappa_{el} \nu_{nu} \Gamma \exp(-\lambda_R/4RT) \qquad (6)$$

in which λ_R is the intrinsic free energy barrier to the migration of electronic excitation energy, since $\Delta E = 0$. Unfortunately, there are three problems with such an approach: (i) the experimental values of k_r for the reactions of interest are almost never available; (ii) the calculation of k_r from molecular parameters is only feasible for reactions with an appreciable displacement of nuclear coordinates (category 1); (iii) when the nuclear displacement is very small there is no easily identified reorganizational parameter which can be transferred from the degenerate to the cross energy transfer reactions. The $(^2E)Cr^{III}$–$(^4A_2)Cr^{III}$ energy-transfer reactions, involving nested potential energy surfaces and $\Delta E \simeq 0$, correspond to a limiting situation which is very difficult to treat theoretically;[9] however, since this is a weakly coupled (category 2) situation in which eq 6 is not applicable, the experimental rates of the degenerate energy-transfer reactons are not helpful in understanding the cross-reaction reactivity patterns. Estimates of the Franck–Condon factor, N_R, can be made when structural information is available for both the ground state and the excited state by using approaches common in the study of electron-transfer reactions,[12-14,54] or from Stokes-shifts. For reactions near the category 2 limit, the appropriate parameters are $N_R \simeq 1$ and $\lambda_R \simeq 0$. However, it is to be emphasized that these hypothetical values have meaning only in the treatment of cross-energy transfer reactions of the category 1 type and that they are not appropriate estimates of the tunneling parameters for degenerate, category 2 type reactions.[55]

For degenerate, energy-transfer reactions of the category 1 (or category 3 type), assuming classical behavior and harmonic vibrations

$$\lambda_R{}^{in}/4 = \frac{n}{2}\,\frac{f_D f_A}{f_D + f_A}(\Delta X)^2 \qquad (7)$$

(for n equivalent changes ΔX in bond length; and f_D and f_A the effective force constants, for the donor and acceptor, respectively, appropriate to these changes in bond length). For a "cross reaction" (i.e., for donor and acceptor chemically distinct), $\lambda \simeq (1/2)(\lambda_D + \lambda_A)$. In the $(^2E)Cr^{III}$–Co^{III} energy-transfer systems, $\lambda_D \simeq 0$, $\lambda_A > 0$ so $\lambda \simeq \lambda_A/2$.

The lowest energy excited state of $Co(NH_3)_6{}^{3+}$ is the $^5T_{2g}$, but the $^1A_{1g} \rightarrow {}^5T_{2g}$ transition is a strongly forbidden two-electron process. Thus, the lowest energy acceptor excited state is $(^3T_{1g})Co(NH_3)_6{}^{3+}$. In order to estimate λ_A for the $(^3T_{1g})Co(NH_3)_6{}^{3+}$–$(^1A_{1g})Co(NH_3)_6{}^{3+}$ energy-transfer system, we assume that $\lambda_A = \lambda_A{}^{in} + \lambda_A{}^{out}$ (for the inner- and outer-sphere contributions, respectively) and use the ground state structural parameters with the excited state distortions inferred by Wilson and Solomon.[26] For the e_g distortion coordinate in the $(^3T_{1g})Co(NH_3)_6{}^{3+}$–$(^1A_{1g})Co(NH_3)_6{}^{3+}$ system, $f_D = 191$ N m^{-1},[27] $f_A = 228$ N m^{-1},[56] $n = 4$, and $\Delta X = 11$ pm; for the a_{1g} coordinate, the respective parameters are 237 and ~230 N m^{-1}, and 2 pm. Thus, $\lambda_A{}^{in}$ (classical) $\simeq$ 68 kJ mol^{-1}. The vibrational quanta and the nuclear displacements are not very large, and $\lambda_A{}^{in}$ (quantum) $\simeq$ 64 kJ mol^{-1}. The Stokes-shift for the $^3T_{1g} \rightarrow {}^1A_{1g}$ transition would be $\sim 5 \times 10^3$ cm^{-1},[27] and since this is approximately equal to λ_A for the degenerate energy-transfer reaction, this consideration also indicates that $\lambda_A \sim 60$ kJ mol^{-1}. Due to the change in size of the solvating cavity, there should be a small contribution from $\lambda_A{}^{out}$. On the basis of the coordination sphere expansion there would be some difference in ground state and excited state solvation energies: a simple Born charging model and correlations of hydration energy with ionic size[57] suggest a difference of ~10 kJ mol^{-1}. This leads to $\lambda_A \simeq 74$ kJ mol^{-1}. Therefore, $\lambda \simeq 37$ kJ mol^{-1} for the $(^2E)Cr(PP)_3{}^{3+}$–$(^1A_{1g})Co(NH_3)_6{}^{3+}$ energy-transfer reactions.

c. The Energy Gap Dependence of k_q. Since the estimated value of $\lambda \sim 3 \times 10^3$ cm^{-1} (37 kJ mol^{-1}) for the $(^2E)Cr(PP)_3{}^{3+}$–$(^1A_{1g})Co(NH_3)_6{}^{3+}$ energy transfer is much larger than the mean energy of the vibrational modes associated with the nuclear reorganization (~400 cm^{-1}), and since $\Delta E \sim -\lambda$, these

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[55] The rate of energy migration between $Cr(NH_3)_6{}^{3+}$ centers in the solid state appears to be very inefficient: Flint, C. D.; Greenough, P.; Matthews, A. P. *J. Chem. Soc., Dalton Trans.* **1972**, 368.

[56] Schmidt, K. H.; Muller, A. *Inorg. Chem.* **1975**, *14*, 2183.

[57] Phillips, C. S. G.; Williams, R. J. P. *Inorg. Chemistry*; Oxford University Press: New York, 1965; pp 161–163.

reactions fall into the category 3 regime. Thus, eq 5 with a typical energy gap of $\Delta E \simeq -45$ kJ mol^{-1} leads to $\Delta G^{*} \simeq 0.4$ kJ mol^{-1}. For $\Delta E \sim -\lambda$, $N \sim 1$, and rate retardations (or rate variations) depend largely on $\langle V \rangle$.

Figure 3 indicates that, for Co^{III} acceptors with ligands which are relatively difficult to ionize ($E[X^- \rightarrow \bullet X + e^-] > 3$V) and for complexes which are comparable in size, the quenching efficiencies (k_q) are insensitive to the donor–acceptor energy gap. This is as one would expect for systems with $\Delta E \sim -\lambda$.

d. Other Probes of Franck–Condon Contributions. In principle the Franck–Condon factor can be sensitive to isotopic substitution of the atoms involved in the critical nuclear motions across the reaction coordinate.[46] Our failure to observe a difference in quenching rates for $Co(NH_3)_6^{3+}$ and $Co(ND_3)_6^{3+}$ is most likely a consequence of the very small nuclear tunneling contribution expected in λ when $N \sim 1$.

e. Summary of Probes of Franck–Condon Contributions to k_q. The energy gap independence of k_q in $(^2E)Cr(PP)_3^{3+}$–Co^{III} energy-transfer reactions, when the Co(III) quenchers are similar in size and do not have low energy ligand-to-metal charge-transfer bands, argues strongly that Franck–Condon factors are of minor significance in determining the inefficiency of energy trasnfer (2–3 orders of magnitude smaller than k_d) in the $(^2E)Cr(PP)_3^{3+}$–Co^{III} systems. This can be attributed to relatively small values of λ in the moderately exoergic reactions. One does expect some variations in λ through the series of acceptors used, but these variations should not have large effects on k_q when $\lambda \sim -\Delta E$. The temperature independence of k_q and the insensitivity of k_q to isotopic substitution are consistent with $N \sim 1$. Since $k_q \ll k_d$, we conclude that $\kappa_{el} \ll 1$ for these systems.

B. The Donor–Acceptor Coupling Mechanism. Vibronic coupling of the donor and acceptor may be achieved by means of a Coulombic (dipole–dipole, dipole–quadrupole, etc.) or an exchange mechanism.[6,8-10,17,20,21] Since the individual electronic transitions are both Laporte and spin forbidden, the Coulombic coupling mechanisms lead to very small probabilities for energy transfer. Thus, for a typical $(^2E)Cr(PP)_3^{3+}$–Co^{III} system, the critical Förster quenching radius[17,20] is $R_0 \simeq 6$ Å, and the rate constant for energy transfer is less than ca. 2×10^3 s^{-1} for any of the Coulombic coupling mechanisms.[10,17b] Consistent with this analysis, we find that there is no correlation of the spectral overlap integral (approximated as the absorptivity of Co^{III} at 727 nm,[58] see Table I) and the quenching rates.

We infer that the electron-exchange mechanism is the dominant means of donor–acceptor coupling in $(^2E)Cr(PP)_3^{3+}$–Co^{III} energy-transfer systems 1; (for a similar inference regarding energy migration in Cr^{III} solids see ref 9). Following Dexter, the Franck–Condon contribution to the energy-transfer rate in exchange-coupled systems is often formulated in terms of a spectral overlap integral normalized for acceptor absorptivity.[59] Owing to the great difference in line shapes for the donor emission and acceptor absorbance,[58] this spectral overlap integral is effectively a constant in the $(^2E)Cr(PP)_3^{3+}$–Co^{III} systems.

C. Probes of the Electronic Matrix Element $\langle V \rangle$ (or κ_{el}). Variations in k_q are possible for the $(^2E)Cr(PP)_3^{3+}$–Co^{III} reactions even within the range of ΔE_{DA} represented in Figure 3. Such variations are observed for variations in quencher size or for quenchers with relatively low-energy charge-transfer excited states. These are the kinds of physical parameters which should affect the electronic matrix element, and, in the semiclassical formalism represented by eq 2, which should alter the contributions of κ_{el}. These issues are developed further below.

Most discussions of the electronic contributions to bimolecular reactions have focussed on the overlap or distance dependence of $\langle V \rangle$,[2-5,52,60-64] often treating α in eq 4 as an invariant. Our studies have probed the distance dependence systematically by varying the mean van der Waals sizes of donor and acceptor (using acceptors with no low-energy charge-transfer bands). We have also expanded on the observation[4b] that k_{en} for $(^2E)Cr(PP)_3^{3+}$–Co^{III} systems increases for quenchers with low-energy CT bands (mean sizes held approximately constant), and we have developed a more rigorous critique of this phenomenon.

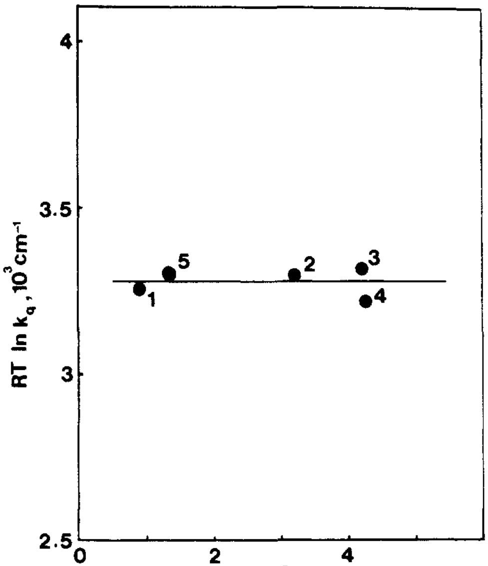

Figure 3. Dependence of k_q on the donor–acceptor energy gap for the $(^2E)Cr(phen)_3^{3+}$–Co^{III} electronic energy-transfer reactions. Data from Table I and ref 4. The $^3T_2$ state has been assumed to be the acceptor state in $Co(OH)_{26}^{3+}$, based on ref 55.

1. Distance Dependence of k_{en}. The data in Table II are in excellent accord with expectation based on eq 4 as shown in Figure 1. The linear correlation results in a value of $2\alpha = 10.9 \pm 1$ nm^{-1}, very much as we had inferred from some limited preliminary results.[4a] The simplest physical interpretation of this parameter is that the mean of the Cr-donor and Co-acceptor 3d-orbital radii is $\alpha^{-1} = 183 \pm 17$ pm. This is at least a plausible value for such a parameter.

Not all of our attempts to investigate the dependence on r_{DA} were as successful as implied by the data included in Figure 1. Two of the quenchers used, $Co(bzo_3[12]hexaeneN_3)_2^{3+}$ and $Co(chn)_3^{3+}$ (both provided by Dr. T. Ramasami), resulted in values of k_{en} (1.8 and 0.7×10^7 M^{-1} s^{-1}, respectively), which were about 10 times larger than we expected based on the estimated mean van der Waals radii of these species. Both of these compounds exhibit relatively intense near UV absorbancies, and there may be some contribution to k_{en} from relatively low-energy CT states as discussed in the next section. It may also be that these molecules deviate too much from the spherical shape for our simple analysis to be applicable.

2. Effects of Charge-Transfer Perturbations. Two approaches can be used to discuss the correlation of k_{en} with $\Sigma(E_{CT})^{-1}$: (a) conventional perturbation theory can be used to describe the effect of the charge-transfer excited states on $\langle V \rangle$[65,66] or (b) the CT perturbations can be visualized in terms of a perturbational increase in α^{-1} (eq 4) originating from the projection of the CT-

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[58] Since the $(^2E)Cr(PP)_3^{3+}$ emission is dominated by the electronic origin (O–O band), the emission band width is very narrow compared to the Co(III) absorption. As a consequence the spectral overlap integral is directly proportional to the acceptor absorptivitiy at 727 nm.

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induced dipole along the donor–acceptor axis.[4b] In either approach the effect of the perturbing excited state is treated as a superexchange contribution to the exchange integral.

a. The Perturbation Theory Approach. In the conventional perturbational approach we can write

$$J^0_{DA} \simeq \langle {}^2Cr,{}^1Co|H_{exch}|{}^4Cr,{}^3Co\rangle^0 + \langle {}^2Cr,{}^1Co|H_{exch}|CT\text{–}Cr\rangle^0\langle CT\text{–}Cr|H_{exch}|{}^4Cr,{}^3Co\rangle^0/E_{CT}(Cr) + \langle {}^2Cr,{}^1Co|H_{exch}|CT\text{–}Co\rangle^0\langle CT\text{–}Co|H_{exch}|{}^4Cr,{}^3Co\rangle^0/E_{CT}(Co) + \ldots \quad (8)$$

(where the quantities $({}^2Cr,{}^1Co)$, $({}^4Cr,{}^3Co)$, and (CT–M), are the reactant (R), product (P), and charge-transfer state wave functions ($S = {}^1/_2$), respectively, H_{exch} is the exchange operator, and the integrals are evaluated at $r_{DA} = 0$). For a rate ratio, $k_{en}/k_{en}{}^{ref}$, eq 8 takes the form

$$J^0_{DA}/J^0_{DRef} \simeq H^0_{RP}/H^0_{RP}(Ref) + H^0_{RCT}(Cr)H^0_{CTP}(Cr)/H^0_{RP}(Ref)E_{CT}(Cr) + H^0_{RCT}(Co)H^0_{CTP}(Co)/H^0_{RP}(Ref)E_{CT}(Co) + \ldots$$

or for $H^0_{RP} \simeq H^0_{RP}(Ref)$

$$k_{en}/k_{en}{}^{ref} \simeq J^0_{DA}/J^0_{DRef} \simeq 1 + [H^0_{RCT}(Cr)H^0_{CTP}(Cr)/H^0_{RP}(Ref)]/E_{CT}(Cr) + [H^0_{RCT}(Co)H^0_{CTP}(Co)/H^0_{RP}(Ref)]/E_{CT}(Co) + \ldots \quad (9)$$

The correlation in Figure 2 suggests that the numerators of the last two terms are approximately constants, nearly equal in magnitude but opposite in sign for the cobalt acceptors. The numerators of these terms are not likely to be identical with numerical magnitude, but their differences would be obscured by the fact that the $E_{CT}(Cr)$ term tends to dominate the correlations. Variations in the numerical magnitudes of the numerators might contribute to the scatter in Figure 2; but we have been unable to find any systematic deviations. A change of the acceptor metal, from low spin Co^{III} to low spin Fe^{III} in $M(Me_4[14]tetraeneN_4)X_2{}^+$ complexes, does appear to alter the dependence on $\Sigma(E_{CT})^{-1}$ (a factor of 2–3 smaller for the iron complexes; Table I) opposite to the direction expected for the changes in $E_{CT}(Cr)$ (expected to be slightly smaller for Fe than for Co). This suggests that the numerator of the $E_{CT}(Cr)$ term does vary some from quencher to quencher; unfortunately the correlated Fe^{III}–X^- charge-transfer state is a high energy state, and the pertinent spectroscopic information is not available which would enable us to properly use eq 9 in comparing the iron and cobalt quenchers.

The intercept of 1 ± 1 for the correlation in Figure 2 is in good agreement with eq 9. The correlation based on similar signs of the two charge-transfer perturbations has a large negative intercept. A negative intercept is not physically plausible (i.e., H^0_{RP} and H^0_{RP}(ref) should have the same sign), and this feature is strong experimental support for opposite signs of the last two terms in eq 9. The possible origin of this difference in sign for the effects of the $X^- \rightarrow Cr^{III}$ and $X^- \rightarrow Co^{III}$ charge-transfer perturbations is not readily apparent in this approach: evaluation of the H_{RCT} and H_{CTP} terms requires consideration of a large number of two-electron couplings whose magnitudes are very difficult to determine. Thus, the conventional perturbation treatment of superexchange interactions provides a systematic basis for representing the effects of low-energy charge-transfer excited states on the rates of energy-transfer reactions in the $({}^2E)Cr(PP)_3{}^{3+}$–Co^{III} systems, but it does not provide a convenient physical picture of at least one feature of the observations.

b. The Induced Dipole Model. The CT perturbations of energy rates are conveniently visualized in terms of changes in α^{-1} originating from projections of the CT induced dipoles along the donor–acceptor axis.[4b] A simple perturbation treatment[46] implies that α should be proportional to $\sum_i[E_{CT}(i)]^{-1}$ where the $E_{CT}(i)$ are the individual vertical energy gaps to the charge-transfer excited states. In such a treatment

$$\alpha \simeq \alpha^0 - (\alpha^0)^2\sum_i \frac{C_iF_i(\alpha^0)}{E_{CT(i)}} + \ldots \quad (10)$$

(where α^0 is the unperturbed inverse radial parameter, $F_i(\alpha^0)$ is the redox field strength for the unperturbed condition, and the C_i are polarizability constants with dimensions of area). On the basis of this approach, the difference in sign for the $E_{CT}(Cr)$ and $E_{CT}(Co)$ terms is a consequence of the opposing directions of the respective induced dipole components, projected along the Cr–Co axis, when X^- is anywhere between the metals. Qualitatively, this interpretation suggests that the donor and acceptor wave functions, in the overlap region between molecules, are polarized by low-energy CT excited states and that such polarizations can increase or decrease the electron density in the overlap region (depending on the sense of the CT-induced dipole moment). These effects can be approximated by a simple perturbation of the donor–acceptor overlap integral (where the unperturbed overlap integral is approximated by the overlap of spherical wave functions[21]). These very simple ideas are certainly more useful qualitative guides in designing and interpreting experiments than is the more conventional perturbation theory approach. However, energy transfer is inefficient in the systems considered ($k_{en}/k_{diff} \ll 1$) so that the approaches are approximately interconvertable; i.e., for the range of k_{en} values and with the uncertainties involved, it is not evident that one or the other approach provides a better description of the experimental data.

3. Other Possible Contributions to the Electronic Matrix Element. The tendency for k_{en} to be relatively large when the quencher contains unsaturated ligands could originate from a CT perturbation. For example, such ligands seem to participate in metal-to-ligand CT perturbations of electron-transfer reations. However, the effect seems to be larger in electron-transfer systems,[67] possibly reflecting different sizes of ΔE_{CT}. Other explanations are possible (see below). Systems in which these effects as well as the isomer and anion effects make larger contributions need to be developed before definitive interpretations can be offered.

Banfield and Husain[68] raised the possibility that rate variations of spin-allowed energy-transfer reactions of transition-metal complexes may be correlated with Jørgensen's nephelauxetic parameter β,[69] and Balzani and co-workers[2] have made extensive use of this concept in their studies of transition-metal energy-transfer reactions. There may be some general similarities between the nephelauxetic concept and our concept of CT perturbations of the electron-exchange interaction, since both arguments can be viualized in terms of "expansion" of the acceptor (or donor) d-orbital system. However, the nephelauxetic interpretation is intramolecular while the CT interpretation necessarily combines intermolecular and intramolecular contributions, with the intermolecular terms dominating. We have examined the possibility of a correlation with parameters tabulated by Jørgensen but have found none, partly because the Racah parameter B_c ($\beta = B_c/B_i$; B_c for the complex, B_i for the free ion) varies so slowly in pentammine- and tetraammine-types of cobalt complexes that it is often treated as a constant.[48,69,70] We have also found that the effects of ligand substitution on the acceptor are much larger in magnitude for the $({}^2E)Cr(PP)_3{}^{3+}$–Co^{III} reactions discussed here than for the $({}^3CT)Ru^{II}$–Cr^{III} reactions on which Balzani et al. have based most of their inferences. Since the $({}^*CT)Ru^{II}$–Cr^{III} energy-transfer rates fall into the weak coupling regime (category 2), direct comparisons between these systems and the strongly coupled $({}^2E)Cr(PP)_3{}^{3+}$–Co^{III} systems are not very useful.[23,24]

The quenching patterns found for the low-spin iron(III)–$(Me_4[14]tetraeneN_4)$ complexes are qualitatively similar to those found for the cobalt(III) analogues, but the enhancement of k_q by the substitution of halide for aquo ligands are less dramatic for iron than for cobalt. These differences between the metals in their sensitivities of k_q to axial substituents are reversed in ordering from the expected variations of the nephelauxetic pa-

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rameter β for iron and cobalt,[69] and this effect appears to originate in differing sensitivities to CT perturbations.

Conclusions

The (^{2}E)Cr(PP)$_3^{3+}$–Co^{III} electronic energy-transfer reactions are characterized by large nuclear displacements with $\lambda > \hbar\omega_{ave}$, but with sufficiently large donor–acceptor energy gaps so that $\Delta E \sim \lambda$. In this regime, reaction rates are insensitive to the energy gap, and the Franck–Condon factors can be presumed to approximately equal unity. Nevertheless, the limiting rates of these reactions are 2–3 factors of ten smaller than expected for the diffusion limit. Variations in rate can be achieved in the (^{2}E)-Cr(PP)$_3^{3+}$–Co^{III} energy-transfer reactions by varying molecular parameters which should perturb the electronic matrix element. Thus, these reactions are useful as probes of the electronic matrix element contributions to bimolecular reactions. The contributions so far probed are the following:

1. The Distance Dependence of the Donor–Acceptor Coupling. This can be fitted to $\exp(-\alpha r_{DA})$ for the d-to-d energy-transfer reactions. Interpreted as a long range orbital overlap term, this yields 183 ± 17 pm for the mean orbital radial parameter (α^{-1}).

2. Perturbations from Low-Energy Charge-Transfer Excited States of the Donor–Acceptor Pair. Quenching rates of the (^{2}E)Cr(PP)$_3^{3+}$–Co^{III} reactions increase as the energy of low lying CT states decreases. These effects can be interpreted in terms of superexchange contributions to the two electron exchange integral coupling the reactant and product (Born–Oppenheimer) potential energy surfaces. In a very simple physical picture, the CT-induced dipole moment can be viewed as polarizing electron density along the donor–acceptor axis. These effects can be generalized to include a variety of environmetal perturbations on the quenching rates.

The properties inferred for the electronic matrix element in energy-transfer reactions have parallels for electron-transfer reactions. Indeed we have used information evolved during the project to design experimental probes of the electronic matrix element in electron-transfer reactions.[4b] One does find differences in the magnitudes of some of the effects; presumably these are related to the different properties of the one-electron (for electron-transfer) and the two-electron (for energy-transfer) exchange integrals. It should eventually be possible to evolve quantitative relationships between these two classes of reactions.

Acknowledgment. This study has profited from many critical discussions with Dr. T. Ramasami. We are also grateful to Dr. Ramasami for providing some of the compounds employed.

Registry No. Cr(phen)$_3^{3+}$, 15276-16-1; Cr(NH$_3$)$_6^{3+}$, 14695-95-5; Co(NH$_3$)$_5$OH$_2^{3+}$, 14403-82-8; Co(NH$_3$)$_5$F^{2+}, 15392-06-0; Co(NH$_3$)$_5$Cl^{2+}, 14970-14-0; Co(NH$_3$)$_5$Br^{2+}, 14970-15-1; Co(NH$_3$)$_5$NO$_2^{2+}$, 14482-68-9; Co(NH$_3$)$_5$NCS^{2+}, 14970-18-4; Co(NH$_3$)$_5$N$_3^{2+}$, 14403-83-9; *cis*-Co(en)$_2$Cl$_2^+$, 14875-15-1; *trans*-Co(en)$_2$Cl$_2^+$, 14403-91-9; *cis*-Co(en)$_2$(NCS)$_2^+$, 21169-85-7; *trans*-Co(en)$_2$(NCS)$_2^+$, 19314-33-1; *cis*-Co(en)$_2$(NO$_2$)$_2^+$, 20956-35-8; *trans*-Co(en)$_2$(NO$_2$)$_2^+$, 20084-72-4; *cis*-Co(en)$_2$(aniline)Cl^{2+}, 46753-03-1; *cis*-Co(en)$_2$(NH$_2$CH$_2$Ph)Cl^{2+}, 19306-83-3; *cis*-Co(en)$_2$(py)Cl^{2+}, 18430-51-8; *cis*-Co(en)$_2$(cha)Cl^{2+}, 28121-20-2; Co([14]aneN$_4$)(NH$_3$)$_2^{3+}$, 53176-75-3; Co([14]aneN$_4$)(OH$_2$)$_2^{3+}$, 46750-08-7; Co([14]aneN$_4$)Cl$_2^+$, 19973-61-6; Co([14]aneN$_4$)(OH$_2$)Cl^{2+}, 18935-88-1; Co([14]aneN$_4$)(NO$_2$)$_2^+$, 23507-13-3; Co([14]aneN$_4$)(NCS)Cl$^+$, 37739-58-5; Co([14]aneN$_4$)(OH$_2$)N$_3^{2+}$, 52658-59-0; Co([14]aneN$_4$)(NCS)$_2^+$, 47099-73-0; Co([14]aneN$_4$)(N$_3$)$_2^+$, 47099-77-4; Co([14]aneN$_4$)(NCS)N$_3^+$, 86163-71-5; Co([14]tetraeneN$_4$)(OH$_2$)$_2^{3+}$, 46750-08-7; Co([14]tetraeneN$_4$)(NO$_2$)$_2^+$, 47379-33-9; Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)N$_3^{2+}$, 59033-91-9; Co(Me$_4$[14]tetraeneN$_4$)(NCS)$_2^+$, 51240-28-9; Co(Me$_4$[14]tetraeneN$_4$)(NCS)N$_3^+$, 86163-71-5; Co(Me$_4$[14]tetraeneN$_4$)(N$_3$)$_2^+$, 60446-77-7; Co(Me$_4$[14]tetraeneN$_4$)Cl$_2^+$, 43225-24-7; Co(Me$_4$[14]tetraeneN$_4$)Br$_2^+$, 43225-25-8; Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)$_2^{3+}$, 76736-26-0; Fe(Me$_4$[14]tetraeneN$_4$)Cl$_2^+$, 101225-12-1; Fe(Me$_4$[14]tetraeneN$_4$)Br$_2^+$, 101225-14-3; Ru(NH$_3$)$_6^{3+}$, 18943-33-4; Rh(NH$_3$)$_5$Cl^{2+}, 15379-09-6; Cr(4,7-Me$_2$phen)$_3^{3+}$, 51194-72-0; Cr(4,7-Ph$_2$phen)$_3^{3+}$, 69178-81-0; Co(en)$_3^{3+}$, 14878-41-2; Co(sep)$^{3+}$, 72496-77-6; Co(phen)$_3^{3+}$, 18581-79-8.

Supplementary Material Available: Temperature dependencies, isotope effects, and alternative correlation of charge transfer perturbation of quenching rates (4 pages). Ordering information is given on any current masthead page.