# Experimental Probes of the Electronic Matrix Element Contributions to Bimolecular Reactions. Retardation Factors Associated with the Mismatching of Electronic Excited States in Outer-Sphere Redox Couples[1]

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**Abstract:** Simple outer-sphere electron-transfer reactions of cobalt(III)–cobalt(II) couples appear to become increasingly nonadiabatic as the electronic structures of the reactant and the product species become more different. A series of $Co^{III}$–$Co(sep)^{2+}$ reactions has been used to probe the effect. A retardation factor (or apparent transmission coefficient), $\beta_{ab}$, has been evaluated for each reaction with respect to the corresponding, relatively adiabatic $Co^{III}$–$Ru(NH_3)_6^{2+}$ and/or $Co^{III}$–$Cr(bpy)_3^{2+}$ reference reaction systems. The Marcus square-root relation has been used to evaluate Franck–Condon factors for the adiabatic surface crossings. Values of $\beta_{ab} \to 1$ as $\Delta E(T;0)$ (the vertical energy difference between the lowest energy triplet excited states of Co(III) and $Co(sep)^{3+}$) and $\Delta E(D;0)$ (the vertical energy difference between the lowest energy doublet excited and the quartet ground states of Co(II) and $Co(sep)^{2+}$) both approach zero. Thus self-exchange electron-transfer reactions in these systems tend to be relatively adiabatic. Values of $\ln \beta_{ab}$ decrease systematically as ($|\Delta E(T;0)| + |\Delta E(D;0)|$) increases, with $\beta_{ab} \simeq 0.002$ for the *cis*-$Co(en)_2(cyclohexylamine)Cl^{2+}$–$Co(sep)^{2+}$ reaction being the smallest value observed. This behavior of the retardation factor can be attributed to variations in the vibronic coupling between reactant and product potential energy surfaces.

There has been a continuing interest in the influence of donor–acceptor electronic interactions on the rates of electron-transfer reactions.[2-5] Some of the issues involved are frequently encountered in discussions of the distance dependence of electron-transfer reactions,[2-12] a concern which becomes very important in understanding biological electron-transport systems with widely separated prosthetic groups.

We have been attempting to develop some systematic approaches for investigating the effects of donor–acceptor electronic interactions on simple bimolecular reactions.[2,13] In the course of our studies we have inferred that the contributions of electronic factors to the ratios of degenerate (or self-exchange) electron-transfer reactions seem small compared to those of some related cross reactions involving different redox couples.[3,13b,14] A similar inference, based on different lines of evidence, has been made by Sutin and co-workers.[15] These observations are of fundamental importance insofar as they reflect on the criteria by which elec-

tronic factors are evaluated and to the extent that this behavior itself may originate from some sort of variations in the donor–acceptor electronic interactions. We report here our studies of the effect on electron-transfer rates of systematic variations in the electronic structures of donor and acceptor redox couples.

Franck–Condon models, most frequently the classical Marcus model,[16] have been very successful in correlating and rationalizing the larger features of electron-transfer rates.[4,12-20] Most such models are based on the Born–Oppenheimer approximation[21]

$$\psi_{BO}(r_e,q_n) \simeq \psi_e(r_e,q_n)\phi(q_n)$$

where $r_e$ and $q_n$ are electronic and nuclear coordinates, respectively, and $\psi_e$ and $\phi_n$ are the corresponding electronic and nuclear wave functions. The transition-state energy is evaluated in terms of the intersection of the potential energy surfaces based on the nuclear coordinates. In semiclassical approaches, the contributions of electronic factors are conveniently formulated in terms of a classical transmission coefficient,[4,17,20,22] using the Landau–Zener model for surface crossing; i.e.

$$k = K_0 \kappa \nu_{nu} \exp(-\Delta G^{\ddagger}/RT)$$

$$\kappa \sim 1 - P \qquad (1)$$

and

$$\ln P \simeq -2\pi H_{RP}^2/h\ \nu_{nu}|S_R - S_P| \qquad (2)$$

where $K_0$ is an outer-sphere association constant, $\Delta G^{\ddagger}$ is the activation free energy based on a Franck–Condon model, $H_{RP}$ is

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**Table I.** Visible Absorption Spectra of Some Co(III) Complexes

| complex | $^1A_1 \rightarrow \ ^1T_1$ $\lambda_{max}$,[a] nm | $^1A_1 \rightarrow \ ^1T_2$ $\lambda_{max}$,[a] nm | $E(^3T_1) - E(^1A_1),$ $10^3 \ cm^{-1}$ (estd)[b] | $E(^2E) - E(^4T_2),$ $10^3 \ cm^{-1}$ (estd for Co(II))[b] |
|---|---|---|---|---|
| $Co(NH_3)_6^{3+}$ | 475 | 339 | 13.4[c] | 7.4 |
| $Co(en)_3^{3+}$ | 466 | 339 | 13.8 | 7.2 |
| $Co(sep)^{3+}$ | 465 | 339 | 13.9 | 7.2 |
| $Co(NH_3)_5(cha)^{3+}$ | 478 (62) | 340 (55) | 12.9 | 7.7 |
| $Co(en)_2(NH_3)(cha)^{3+}$ | 460 (76) | 352 (70) | 13.5 | 7.4 |
| $Co([14]aneN_4)(NH_3)_2^{3+}$ | 465 (65) | 340 (78) | 14.3 | $\sim -5^d$ |
| $Co(NH_3)_5CN^{2+}$ | 440 (56) | 326 (52) | 16.1 | 6.7 |
| $Co(NH_3)_5Cl^{2+}$ | 525 | | 12.8 | |
| $cis$-$Co(en)_2(cha)Cl^{2+}$ | 525 (83) | 368 (93) | 12.1 | 8.0 |
| $Co(en)_2(CN)Cl^+$ | 458 (82) | 340 (sh) | 14.6 | |

[a] Entries for the first three compounds are literature values. Molar absorptivities ($cm^{-1} \ M^{-1}$) are in parentheses. The center of gravity of absorption in complexes of lower than $O_h$ symmetry is approximately assigned as $^1A_1 \rightarrow \ ^1T_1$ or $^1T_2$. [b] See text for details of estimates. [c] Reference 42. [d] Doublet ground state.

the electronic matrix element, $\nu_{nu}$ is the effective frequency of nuclear motion, and $S_R$ and $S_P$ are the slopes of the reactant and product potential energy surfaces in the neighborhood of the crossing point.

In most instances the contributions of electronic factors have been evaluated indirectly, with respect to some Franck–Condon model for the activation energy and a zero-order assumption that $\psi_e(r_e, q_n) = \psi_e^°(r_e, q_n^°)$, where $q_n^°$ corresponds to the nuclear coordinates of the potential energy minimum. In such an approach, rates which are found to be significantly smaller than those based on only the Franck–Condon term are classified as "nonadiabatic". It is becoming increasingly common to attribute any large discrepancies between observed and Franck–Condon-calculated rates to poor donor–acceptor overlap. More specifically, these assumptions underlie any identification of nonadiabatic reactions based on the Marcus square-root relation,[4] and the Marcus relation specifically predicts adiabatic cross-reaction behavior based only on the properties of the self-exchange reactions. Thus, the references cited above[3,13b,14,15] have evaluted the relative adiabaticities of cross-reactions based on deviations from behavior predicted by the square-root relation. The inference, in these previous studies, that self-exchange reactions tend to be more adiabatic than cross-reactions might in principle result from the contributions of any of several factors: (a) a large difference in the shapes of reactant and product potential energy surfaces for the cross-reactions but not for the self-exchange reactions;[23] (b) a large magnitude of electronic coupling (analogous to magnetic exchange interactions) for electronically degenerate compared to nondegenerate systems; (c) a failure of the implicit assumption that $\psi_e(r_e, q_n) = \psi_e^°(r_e, q_n^°)$. We have extended our experimental studies to include the systematic investigation of apparently nonadiabatic behavior in a number of near-degenerate electron-transfer systems. We find that the degree of apparent nonadiabaticity is systematic in certain electronic properties of the reactants and products. Our experimental observations and their implications are reported in this paper.

## Experimental Section

**A. Materials.** We have synthesized a number of coordination complexes for this study. The complexes used were characterized by their visible–ultraviolet and infrared spectra and by means of elemental analysis. The spectroscopic data are summarized in Tables I and II, and elemental analyses are presented with the synthetic procedures below.

**[Co(NH₃)₅CN]Cl₂ and [Co(NH₃)₅NH₂C₆H₁₁]Cl₃.** These pentammine complexes were prepared by the reaction of NaCN or cyclohexylamine with $[Co(NH_3)_5O_3SCF_3](CF_3SO_3)_2$[24] in predried acetone. Generally, a 5- to 10-fold excess of the ligand, dissolved or dispersed in 25–50 mL of dry acetone, was added to 1 g of the trifluoromethylsulfonate (tfms) salt and the mixture was refrigerated overnight. The products, recovered by rotary evaporation of acetone, were recrystallized from aqueous NaCl at pH 4.0. In addition to spectroscopic data in Tables I and II, the $^1H$ NMR spectrum of $Co(NH_3)_5NH_2C_6H_{11}^{3+}$ was also consistent with literature reports on analogous compounds.[24]   Anal. Calcd for [Co-

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**Table II.** Characteristic Infrared Spectral Functions and Assignments for Some Co(III) Complexes

| complex | bands obsd, cm⁻¹ | assignment |
|---|---|---|
| $Co(NH_3)_5CN^{2+}$ | 2180 | $\nu(C\equiv N)$ |
| $Co(NH_3)_5(cha)^{3+}$[a] | 1440, 1380, 1360, 840 | $\delta(CH_2)$ and $\rho_r$ (CH₂) deformation modes |
| $Co([14]aneN_4)(NH_3)_2^{3+}$ | 1610, 1320, 865,[a] 820 | $\delta(NH_2)$, $\delta(CH_2)$, $\rho_r(NH_2)$, $\rho_r(CH_2)$ |
| $Co(en)_2(CN)Cl^+$ | 2185, 1595, 1150, 1050, 750 | $\nu(C\equiv N)$, $\delta(NH_2)$, $\nu(C-N)$, $\nu(C-C)$, $\rho_r(NH_2)$ |

$(NH_3)_5CN]Cl_2$: C, 4.98; H, 6.27; N, 29.0. Found: C, 4.76; H, 5.92; N, 29.8. Calcd for $[Co(NH_3)_5NH_2C_6H_{11}]Cl_3 \cdot HCl \cdot H_2O$: C, 17.3; H, 6.98; N, 20.8. Found: C, 17.6; H, 6.66; N, 20.9.

**[Co(en)₂(NH₃)NH₂C₆H₁₁]Cl₃.** This complex was prepared by the reaction of 1.3:1:1 molar ratios of freshly prepared NaNH₂, [*cis*-Co-(en)₂Cl₂]Cl, and NH₂C₆H₁₁, dispersed in either tetrahydrofuran or dioxane. The reaction proceeded slowly at room temperature. After about 24 h, the solvent was evaporated and the crude material was recrystallized as the chloride salt from aqueous HCl. The product obtained was yellowish orange and exhibited broad $^1H$ NMR multiplets at 1.4 ppm for $NH_2C_6H_{11}$ and complex multiplets centered at 2.7 ppm for the methylene groups of ethylenediamine (in D₂O). The ratio found for ethylenediamine:cyclohexylamine (C–H) protons was 1.2:1.0 (expected 1.38:1.0). This material was further purified on a Dowex 50W-X2 (200–400 mesh) 15 × 0.8 cm column employing a 0.5 M $HCF_3SO_3$–$NaCF_3SO_3$ mixture as eluant with $[H^+] = 0.02$ M. Two yellow-orange bands were separated. The minor band, <5% of the total [Co(III)], moved faster and was not further characterized. The predominant species (>90%) eluted as a distinct band and exhibited the characteristic $^1H$ NMR spectrum.

**[Co(en)₂(CN)Cl]Cl.** To prepare this complex, we dispersed 3 g of [*cis*-Co(en)₂Cl₂]ClO₄ in methanol and added 0.3 g of NaCN. The mixture was stirred at room temperature for 6–8 h. The methanol was removed by rotary evaporation, and the remaining solid was dissolved in a minimum amount of water and then *carefully* acidified in a well-ventilated hood. The solution remaining after removal of HCN was concentrated by rotary evaporation. For purification, a Sephadex LH-20 resin was preswollen with a 80:20 methanol:water mixture. The concentrate was added to the Sephadex column, and the products were eluted with aqueous methanol. Two major bands were observed: a fast-moving orange band and a slower yellow band. The orange product was separated, and the resulting spectroscopic data are in Tables I and II. For the large-scale preparations needed for our kinetic studies, the reaction products were separated on a Dowex 50W-X2 column (15 × 0.8 cm) with a 0.5 M $NaCF_3SO_3$ eluant. The orange band moved fastest on this column also.

**[Co(phen)₂(CN)₂]ClO₄.** This complex was prepared by the addition of ~2 g of $[Co(phen)_3](ClO_4)_3$ dissolved in 20 mL of methanol. The reaction mixture was stirred for 8 h and then the solvent was removed at reduced pressure. The resulting solid was rinsed with ice cold water, and the crude product was mixed with water and stirred for 15 min. The mixture was filtered, and the remaining solid was recrystallized from acidic (HClO₄) methanol. In addition to the spectroscopic characterization (Tables I and II), we have used the quasireversible electrochemistry to characterize this complex. The differential pulse voltammogram indicated only one electroactive species in dimethylformamide (DMF), with $E_{1/2} = -0.36$ V vs. SCE ($E_{pa} - E_{pc} \simeq 60$ mV); this compares to a literature report of –0.39 V vs. SCE in a different medium[26] and to +0.14 V vs. SCE for $Co(phen)_3^{3+}$.

WARNING: The perchlorate salts used in this study are explosive and potentially hazardous.

[Co([14]aneN$_4$)(NH$_3$)$_2$]Cl$_3$.[27] We used a procedure similar to that reported for [Co(Me$_4$[14]tetraeneN$_4$)]Cl$_3$.[28] Three grams of [*trans*-Co([14]aneN$_4$)Cl$_2$]Cl were added to about 50 mL of liquid ammonia condensed in a conical flask. The mixture was kept at ca. −70 °C in a dry ice–acetone bath for 3 h, and then the ammonia was allowed to evaporate slowly. This procedure was repeated twice. Following the final, complete evaporation of NH$_3$, the crude product was recrystallized from water. The purified product was characterized by means of the spectra summarized in Tables I and II and elemental analysis. Anal. Calcd for [Co([14]aneN$_4$)(NH$_3$)$_2$]Cl$_3$·HCl·H$_2$O: C, 26.4; H, 7.32; N, 18.50. Found: C, 26.47; H, 7.61; N, 18.2.

Literature procedures were used to prepare [Co(NH$_3$)$_6$](ClO$_4$)$_3$,[29] [Co(en)$_3$](ClO$_4$)$_3$,[30] [Co(phen)$_3$](ClO$_4$)$_3$,[31] [Co(NH$_3$)$_5$Cl](ClO$_4$)$_2$,[32] [*cis*-Co(en)$_2$Cl(NH$_2$C$_6$H$_{11}$)](ClO$_4$)$_2$,[25] Co(sep)Cl$_3$,[14,33,34] [Co(bpy)$_3$](ClO$_4$)$_3$,[35] [Co(chda)$_3$]Cl$_3$ (where chda = 1,2-cyclohexanediamine),[36] [Co(bzo[12]hexaeneN$_3$)$_2$](NO$_3$)$_3$,[37,38] and [Co(Me$_4$[14]tetraeneN$_4$)-(NH$_3$)$_2$](ClO$_4$)$_3$.[28] Intermediate materials were prepared as in the literature cited, and all other materials were reagent grade.

**B. Physical Characterizations.** Electronic absorption spectra were determined on a Cary 14 spectrophotometer. Infrared spectra were determined of samples in KBr pellets with a Perkin-Elmer 283 spectrometer. Proton NMR spectra were determined with either a Varian T-60 or a Nicolet NT-300 instrument with D$_2$O or CH$_3$OD solvents and Me$_4$Si or TSP(aq) as the internal references. Electrochemical determinations employed a Princeton Applied Research Model 174A polarographic analyzer used in the differential pulsed mode with platinum, calomel, and hanging mercury drops (or carbon paste) as the counter, reference, and working electrodes, respectively. The differential pulse voltammograms were usually recorded in 0.1 M NaCF$_3$SO$_3$ at a scan rate of 10 or 20 mV s$^{-1}$.

**C. Kinetic Studies.** The reductions of a series of Co(III) complexes were monitored at 25 °C in 0.20 M NaCF$_3$SO$_3$. Reactions were run under pseudo-first-order conditions, with the choice of excess reagent dictated by considerations of solubility and of the relative instability of reagents such as Cr(bpy)$_3$$^{2+}$ [39,40] and Co(sep)$^{2+}$.[14] Then, for reactions of Cr(bpy)$_3$$^{2+}$, we used [Co(III)] ≫ [Cr(bpy)$_3$$^{2+}$]. The Cr(bpy)$_3$$^{2+}$ reductant was generated in the reactant solutions in order to minimize complications due to formation of aquo–chromium(II) species. This was achieved by mixing, in the stopped-flow system, a solution containing Cr(bpy)$_3$$^{3+}$ and the Co(III) oxidant, with a solution containing Co(sep)$^{2+}$. Concentrations were adjusted so that the Co(sep)$^{2+}$ reductions of the various Co(III) oxidants were very slow (<0.1 s), while the Cr-(bpy)$_3$$^{3+}$–Co(sep)$^{2+}$ reaction was 90% complete in <5 ms. The [Co(III)] was adjusted so that the half-life of the Co(III)–Cr(bpy)$_3$$^{2+}$ reactions was less than 20% of the half-life for aquation of Cr(bpy)$_3$$^{2+}$.[40] These reactions were monitored at 560 nm, where the molar absorptivity of Cr-(bpy)$_3$$^{2+}$ is estimated to be 4500 M$^{-1}$ cm$^{-1}$,[34,40] and the resulting pseudo-first-order plots were linear for 2.5–4 half-lives. Typical reactant

concentration ranges were as follows: [Cr(bpy)$_3$$^{3+}$] = (4–10) × 10$^{-3}$ M; [Co(sep)$^{2+}$] = (0.2–1.0) × 10$^{-4}$ M; [Co(III)] = (2–200) × 10$^{-4}$ M; [H$^+$] = (0.1–1.0) × 10$^{-4}$ M; [NaCF$_3$SO$_3$] = 0.2 M. The dependence of $k_{obsd}$ on [Cr(bpy)$_3$$^{3+}$], [Co(sep)$^{2+}$], and added excess bpy was examined for the Co(NH$_3$)$_6$$^{3+}$–Cr(bpy)$_3$$^{2+}$ reaction, but only the excess [Co(NH$_3$)$_6$$^{3+}$] had any measurable effect for our reaction conditions.

Many of the Co$^{III}$–Co(sep)$^{2+}$ reactions reported here are relatively slow, so precautions had to be taken to avoid complications resulting from the acid decomposition of Co(sep)$^{2+}$, on the one hand,[33a] and the excessive increase in pH due to released ammonia or amine, on the other. The specific conditions employed for each cross-reaction were evolved after some preliminary studies in each case but were generally such that (1) that the smallest acid concentration possible be employed which would be sufficient to maintain pH <7 over the course of the reaction (viz. initial pH ∼4.5) and (2) that the concentrations of Co(III) counter reagents (or [Co(sep)$^{2+}$], if in excess) be so chosen that the time constants of the Co$^{III}$–Co(sep)$^{2+}$ reactions were at least an order of magnitude smaller than those expected for the acid decomposition of Co(sep)$^{2+}$.[33a] In practice these conditions required that 10[Co(sep)$^{2+}$] < [H$^+$], [Co(III)] as large as possible, and blank determinations to monitor the acid decomposition of Co(sep)$^{2+}$ under the chosen reaction conditions. The progress of these reactions was generally observed in the 260–340 nm region, depending on the UV–vis spectra of the Co(III) oxidants. Pseudo-first-order plots of the absorbance changes were linear to 3–5 half-lives. For many of the reactions with $t_{1/2}$ < 6 × 10$^2$ s, we used [Co(sep)$^{2+}$] > [Co(III)]. Reagent concentrations were typically adjusted within the following ranges: [Co(sep)$^{2+}$] = (0.6–15) × 10$^{-4}$ M; [Co(III)] = (0.6–200) × 10$^{-4}$ M; [H$^+$] = (0.4–1.0) × 10$^{-3}$ M; [NaCF$_3$SO$_3$] = 0.20 M. Reactions of Ru(NH$_3$)$_6$$^{2+}$ were run by using the usual precautions of deaeration, exclusion of light, and pH 4–6.

The very limited solubility of Co(bzo$_3$[12]hexaeneN$_3$)$_2$$^{2+}$ in water forced us to use an 80:20 water:methanol medium for the studies of Co(bzo$_3$[12]hexaeneN$_3$)$_2$$^{3+}$.

A Guilford Model 250 spectrophotometer equipped with a thermostated cell holder was used for the slower kinetic runs. The faster reactions were studied with use of an Aminco stopped-flow system. Syringe techniques were used to transfer deaerated solutions. Solutions of Ru-(NH$_3$)$_6$$^{2+}$ and Co(sep)$^{2+}$ were obtained by the zinc dust reductions of solutions of the respectively trivalent complexes in an Ar or N$_2$ atmosphere. Generally a variation of 4–25 times was employed for the concentration of the reagent in excess (the excess in concentration always exceeded 10-fold), and 4–16 determinations of pseudo-first-order rates were made to establish the bimolecular rate law and to derive second-order rate constants.

**Evaluation of the Apparent Adiabatic Rate Ratios ($R_{ad}$).** The fundamental issue of concern is whether or not the transmission coefficient, $\kappa$, is significantly different from unity at the saddle point of the multidimensional electron-transfer reaction surface. This is especially a concern in view of the considerable success of adiabatic Franck–Condon models, especially the Marcus and Hush models, in accounting for the rates of electron-transfer reactions. More particularly, careful analysis has shown that adiabatic, Franck–Condon models account for most of the activation barrier even for reactions involving Co(III)–Co(II) couples.[13b-f,14,17,19] However, there are systematic deviations, spanning a few orders of magnitude,[13b-f,15] and semiclassical[17,20] and quantum mechanical[3,8,11,12,20,22] models do predict nonadiabatic behavior even for simple electron-transfer reactions.

The major experimental problem can be regarded as one of determining the configuration coordinates of the saddle point. For example, the Marcus–Hush formalisms imply that the saddle point can be, at least approximately, constructed as the intersection of zero-order parabolic potential energy surfaces (i.e., with $\psi_e(r_e,q_n) = \psi^0(r_e,q_n^0)$). With this view in mind, we have used the square-root relation[16]

$$k_{ab}(\text{calcd}) = (k_{aa}k_{bb}K_{ab}f_{ab})^{1/2} \qquad (3)$$

(where the $k_{ii}$ are the self-exchange rate constants of the component redox couples (denoted as "a" and "b"), $K_{ab}$ is the equilibrium constant for the cross-reaction, log $f_{ab}$ = (log $K_{ab}$)$^2$/4 log ($k_{aa}k_{bb}/A_{aa}A_{bb}$), and the $A_{ii}$ are the pre-exponential coefficients of the respective self-exchange rate constants[16]) to evaluate the behavior based on the zero-order potential energy surfaces. The effects of a perturbation which is electronic in orgin can then be considered (e.g., see ref 13c). The perturbation can be handled in several ways, and a detailed discussion is presented below. However, this approach enables us to use the simple Marcus–Hush treatment, and parabolic potential energy surfaces in the initial evaluations.

Several interrelated considerations and experimental difficulties in determining accurate values of $k_{aa}$, $K_{ab}$, etc., have led us to use rate ratios, rather than individual rate constants, in our search for the kinetic manifestations of electronic factors. In principle, one should evaluate the

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(27) Abbreviations: sep = (*S*)-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]-eicosane; bzo$_3$[12]hexaeneN$_3$ = 3,4:7,8:11,12-tribenzo-1,3,9-triazoduodeca-1,3,5,7,9,11-hexaene; [14]aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane; Me$_4$-[14]tetraeneN$_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; cha = cyclohexylamine; chda = *trans*-1,2-diaminocyclohexane.
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limiting adiabatic rate constant, $k_{ab}$(adiabatic), determined only by the configuration coordinates of the actual saddle point on the reaction surface. Then $\kappa = k_{ab}$(obsd)$/k_{ab}$(adiabatic). In practice the actual saddle point is not known, and the uncertainties in the ground-state structural parameters lead to uncertainties, often of the order of $\kappa$ or larger, in values of $k_{ab}$(adiabatic) based on $k_{ab}$(calcd). Furthermore, in developing a series of studies involving systematic variations in some perturbations or other, one must nearly always use some reagents for which key parameters (e.g., $k_{aa}$, $K_{ab}$, bond lengths, force constants, etc.) are unknown. If the more poorly characterized reagents are a series of oxidants (viz. Co(III) complexes), then the *first order* contributions of the oxidants nearly cancel in a rate ratio (e.g., as based on eq 3; see below), but the second-order contributions of driving force, through $f_{ab}$ in eq 3, do not. Finally, a simple experimental probe is in most ways less equivocal than an elaborate calculation based on any theoretical model.

Ideally, the reference reactions selected should be adiabatic so that $k_{ab}$(obsd)$/k_{ac}$(obsd) $= \alpha_{cb}\kappa_{ab}$ (for $\alpha_{cb}$ a constant depending only on reagents "b" and "c"). The semiclassical formalism (e.g., eq 1 and 2 and ref 17 and 20) suggest that $\kappa$ depends exponentially on the ratio of the electronic matrix element to the effective nuclear frequency. Thus, as the effective nuclear frequency associated with the reaction coordinate becomes smaller, one expects $\kappa$ to approach unity rapidly, even for similar values of $H_{RP}$. In practical terms, the most useful reference reactions are expected to be those which minimize first coordination sphere reorganization (i.e., those components corresponding to the relatively high frequency vibrations).

For two reductants ("b" and "c") and a common oxidant ("a"), eq 3 implies

$$k_{ab}(obsd)/k_{ac}(obsd) = \alpha_{cb}'(f_{ab}/f_{ac})^{1/2} = \alpha_{cb}$$

where $\alpha_{cb}' = (k_{bb}K_{cb}/k_{cc})^{1/2}$; these relations, of course, assume that both reactions are adiabatic and that parabolic surfaces are appropriate for the zero-order wave functions (harmonic approximations). If the reactions of "a" with both "b" and "c" were nonadiabatic (but the self-exchange reactions were adiabatic)[41]

$$k_{ab}(obsd)/k_{ac}(obsd) = \alpha_{cb}\kappa_{ab}/\kappa_{ac}$$

where $\kappa_{ab}$ and $\kappa_{ac}$ are the electronic transmission coefficients of the reactions indicated. For the ideal reference reaction, as discussed above, $\kappa_{ac} \simeq 1$. Even for this ideal situation, one must evaluate $\alpha_{cb}$ in order to obtain $\kappa_{ab}$. The contribution of first-order terms, $\alpha_{cb}$, will be known for the probe and reference couples ("b" and "c", respectively). However, evaluation of the second-order component, $(f_{ab}/f_{ac})^{1/2}$, requires at least one additional reference reaction, unless $f_{ab} \simeq f_{ac}$.

We use these concepts, based on eq 3, to develop criteria for the deviations of a set of probe reactions from the behavior expected in the adiabatic limit. If we assume that the various reference reactions are well behaved (i.e., that $k_{ac}$(obsd) $= k_{ac}$(calcd) $= k_{ac}$(adiabatic), etc.), then we can set $k_{ab}$(obsd) $\simeq \beta_{ab}k_{ab}$(adiabatic), where $\beta_{ab}$ is a retardation factor which reflects any contributions to the rate which are not contained in the simple Franck–Condon models. If the only source of discrepancy in fitting data to eq 3 were in the deviations from limiting adiabatic behavior, then $\beta_{ab} \rightarrow \kappa_{ab}$ under the conditions discussed above. The Co-(sep)$^{2+}$ reductions of various Co(III) complexes were used for probe reactions; the Ru(NH$_3$)$_6$$^{2+}$ and Cr(bpy)$_3$$^{2+}$ reductions of these complexes have served as our reference reactions. The ratio of rate constants, $R$(Co:Ru) $= k$(obsd:Co$^{III}$ + Co(sep)$^{2+}$)$/k$(obsd:Co(III) + Ru(NH$_3$)$_6$$^{2+}$), was used as our principle index of reaction patterns. We have used three approaches for estimating the contributions of second-order terms (i.e., $f_{ab}/f_{ac}$)$^{1/2}$) to this ratio: (1) calculations based on eq 3; (2) an extrapolation of $f_{ab}/f_{ac} \rightarrow 1$ based on the ratios $R$(Co:Ru) and $R$(Co:Cr) $= k$(obsd:Co$^{III}$ + Co(sep)$^{2+}$)$/k$(obsd:Co$^{III}$ + Cr(bpy)$_3$$^{2+}$); (3) determination of $f_{ab}/f_{ac}$ based on values of $R$(Cr:Ru) $= k$(obsd:Co$^{III}$ + Cr(bpy)$_3$$^{2+}$)$/k$(obsd:Co$^{III}$ + Ru(NH$_3$)$_6$$^{2+}$). The first of these approaches is straightforward, but it requires precise knowledge of several parameters. The second and third require further comment.

For most of the reactions which we have examined, it has been necessary to base our estimates of $\beta_{ab}$ on the expected variations in $(f_{ab}/f_{ac})^{1/2}$ as the redox properties ($E_a$° and $k_{aa}$) of the oxidant are altered. Typical behavior for $R$(Cr:Ru), based on eq 3, is shown in Figure 1. This figure emphasizes that (a) even in a classical Franck–Condon model (for reductants M and M', and adiabatic reactions) $R$(M:M') varies in nearly a hyperbolic manner with $E_a$°, (b) $R$(M:M') is relatively insensitive to variations in $k_{aa}$, and (c) for truly adiabatic reactions the ratios $R$(M:M') may be used to obtain rough estimates ($E_a$$^f$) of $E_a$°. In the present context the inferred values of $E_a$$^f$ have been used parametrically in estimating
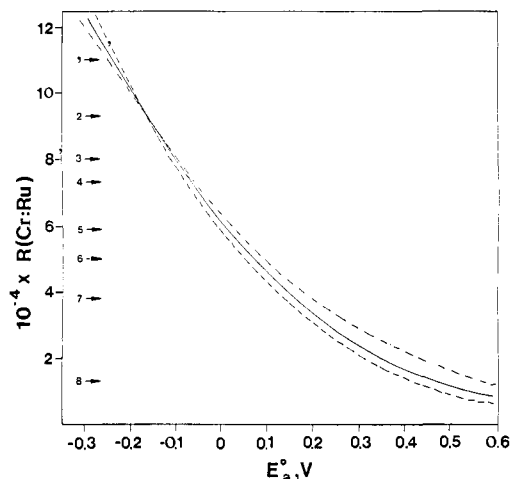


**Figure 1.** Calculated variations in the ratio, $R$(Cr:Ru), of rate constants for Cr(bpy)$_3$$^{2+}$ and Ru(NH$_3$)$_6$$^{2+}$ reductions of a series of oxidants, with standard potential and self-exchange parameters of the oxidant. Calculations are based on eq 3 as described in the text. The counter reagent self-exchange rate constant has been taken as $10^{-4}$ M$^{-1}$ s$^{-1}$ (solid line), $10^{-2}$ M$^{-1}$ s$^{-1}$ (dashed line), and $10^{-6}$ M$^{-1}$ s$^{-1}$ (dotted line). The observed ratios for several Co(III) oxidants are indicated on the left: Co(en)$_3$$^{3+}$ (1); Co(NH$_3$)$_5$CN$^{2+}$ (2); Co([14]aneN$_4$)(NH$_3$)$_2$$^{3+}$ (3); Co(NH$_3$)$_6$$^{3+}$ (4); Co(en)$_2$(CN)Cl$^+$ (5); Co(NH$_3$)$_5$(cha)$^{3+}$ (6); Co(en)$_2$(cha)NH$_3$$^{3+}$ (7); Co(en)$_2$(cha)Cl$^{2+}$ (8).

values of $(f_{ab}/f_{ac})^{1/2}$ in the second and third approaches mentioned above.

The necessary redox parameters ($K_b$° and $k_{bb}$) are well-known for the various reducing agents that we have employed, but they are not generally known for the Co(III) oxidants (the Co(en)$_3$$^{3+,2+}$ couple is an exception). Therefore, we have used methods 2 and 3 in our estimations of $\beta_{ab}$, as noted in Table III. The inferred values of $\beta_{ab}$ are included in Table III.

## Results and Discussion

We have attempted in this study to better define the allegedly greater adiabaticity of degenerate compared to nondegenerate electron-transfer systems. On systematic examination we find that such an effect does exist, as elaborated below.

While it is well established that nuclear reorganizational factors usually dominate electron-transfer rates,[4,11-20] the significance and the origin of electronic contributions to these rates remain matters of some concern. If some purely electronic factors were contributing to observed rates, then simple electronic perturbations may well give rise to systematic variations in the adiabaticity of the reactions. One would prefer to examine a single class of such electronic perturbations without varying any other significant parameter. This is almost never possible. As a consequence it is necessary to examine the effects of such electronic perturbations on the rates of apparently nonadiabatic probe reactions, with suitable referencing to more adiabatic systems where perturbations in electronic factors does not have any influence. These considerations have led us to the rather intricate rate-ratio comparison, described in detail above. The pertinent observed kinetic parameters are summarized in Table III. These experimental observations show a considerable variation in rate ratios, and these variations are well outide the range expected for the reductants used. It is shown below that these variations in the observed rate ratios are systematic in the electronic structures of reactants and products.

The molecular electronic properties most available for manipulation inevitably fall into one of two categories: (a) variations in the donor–acceptor overlap integral achieved by means of variations in the distance of closest approach ($r_{DA}$); or (b) variations in the mixing of donor and acceptor wave functions induced by the perturbing effects of low-energy electronic excited states. During the past few years we have been investigating the perturbational effects of low-energy charge-transfer excited states on electron-transfer reactions.[13]

The perturbing electronic excited states may be either intramolecular or intermolecular, and we have elsewhere discussed the

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(41) If the self-exchange reactions were not adiabatic a more complex ratio, $\alpha_{cb}k_{bb}\kappa_{ab}/k_{cc}\kappa_{ac}$, results since one does not expect cancellation of the electronic factors.

**Table III.** Kinetic Parameters for the Reactions of Co(sep)²⁺, Ru(NH₃)₆²⁺, and Cr(bpy)₃²⁺ with Co(III) Oxidants[a]

| oxidant | second-order rate constants, $k$(obsd), M⁻¹ s⁻¹, for | | | $E$, V (estd)[b] | observed rate ratios[c] | | calcd | |
|---|---|---|---|---|---|---|---|---|
| | Co(sep)²⁺ | Ru(NH₃)₆²⁺ | Cr(bpy)₃²⁺ | | R(Cr:Ru) × 10⁻⁴ | R(Co:Ru) | $R_{ad}$[d] | $\beta_{ab}$[e] |
| Co(NH₃)₆³⁺ | 0.15 ± 0.01 (9) | 0.006[f] | 440 (10) | -0.06 | 11 | 25 | 39 | 0.64,[g] 0.8[h] |
| Co(en)₃³⁺ | 0.05 ± 0.01 (7) | ~0.002 (4) | 215 (5) | -0.24[j] | 11 | 25 | 64 | 0.39,[i] 0.52[h] |
| Co(chda)₃³⁺ | 0.07 ± 0.01 (5) | 0.0025 (4) | | -0.26[j] | | 29 | 68 | 0.4[i] |
| Co(NH₃)₅(cha)³⁺ | 0.14 ± 0.01 (5) | 0.07 ± 0.01 (5) | | +0.085 | | 2 | 26 | 0.08,[g] 0.11[h] |
| cis-Co(en)₂(NH₃)(cha)³⁺ | 0.32 ± 0.01 (4) | 0.032 ± 0.006 (4) | (3.5 ± 0.1) × 10³ (3) | +0.18 | 5.0 | 10 | 21 | 0.48,[g] 0.63[h] |
| Co(phen)₃³⁺ | (4.8 ± 0.2) × 10³ (6) | (9.3 ± 0.3) × 10³ (6) | (1.2 ± 0.1) × 10³ (5) | +0.38[j] | 3.8 | 0.51 | 11 | 0.046[i] |
| meso-Co(bzo₃[12]hexaeneN₃)₂³⁺ | 100 ± 7 (5) | 55 ± 6 (4) | | +0.06[j] | | 1.8 | 26 | 0.069[i] |
| rac-Co(bzo₃[12]hexaeneN₃)₂³⁺ | 780 ± 60 (4) | (1.4 ± 0.1) × 10³ (4) | | +0.06[j] | | 0.56 | 26 | 0.021[i] |
| Co(Me₄[14]tetraeneN₄)(NH₃)₂³⁺ | 36 ± 4 (5) | 1.1 ± 0.1 (4) | | | | 27 | 28 | 0.98[i] |
| Co([14]aneN₄)(NH₃)₂³⁺ | 0.104 ± 0.008 (5) | (4.5 ± 0.2) × 10⁻² (4) | (3.6 ± 0.2) × 10³ (5) | -0.105 | 8.0 | 2.3 | 44 | 0.05,[g] 0.02–0.04[h] |
| Co(NH₃)₅CN²⁺ | 0.58 ± 0.03 (5) | 4.6 ± 0.2 (5) | (4.3 ± 0.2) × 10⁵ (4) | -0.168 | 9.3 | 0.12 | 52 | 0.0023,[g] 0.003[h] |
| Co(NH₃)₅Cl²⁺ | 58 ± 4 (6) | 260 ± 20 (5) | (8 ± 1) × 10⁵[k] | ~+0.5 | ~0.3 | 0.22 | ~0.8 | ~0.028,[g] 0.06[h] |
| cis-Co(en)₂(cha)Cl²⁺ | 0.82 ± 0.06 (6) | 45 ± 2 (5) | (5.7 ± 0.4) × 10⁵ (5) | +0.46 | 1.3 | 0.018 | 8 | 0.0023,[g] 0.002[h] |
| cis-Co(en)₂(CN)Cl⁺ | 1.20 ± 0.05 (5) | 0.10 ± 0.01 (4) | (5.9 ± 0.3) × 10³ (4) | +0.005 | 5.9 | 12 | 32 | 0.38,[g] 0.47[h] |

[a] 25 °C; 0.2 M NaCF₃SO₃; number of determinations in parentheses. [b] Estimates based on Figure 1 vs. NHE. [c] $R$(bc) = $k_{ab}$·$k_{ac}$ for the common oxidant "a". [d] Estimated value for the adiabatic ratio, $R$(CO:Ru)$_{ad}$. $^e\beta_{ab} = R$(Co:Ru)$_{obsd}$/$R$(Co:Ru)$_{ad}$. See text for details. [f] From ref 19; 0.1 M NaCF₃SO₃; 25 °C. $^g E^\circ$, parametric method 3. [h] From extrapolation of $(f_{ab}/f_{ac})^{1/2}$ → 1; method 2. [i] Calculated from eq 3; method 1. [j] Experimental value. [k] From: Candlin, J. P.; Halpern, J.; Trimm, D. L. *J. Am. Chem. Soc.* **1964**, *86*, 1019.
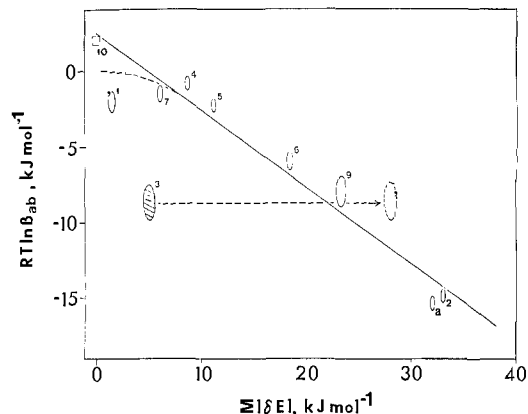


**Figure 2.** Variations in the discrepancy factors, $\beta_{ab}$, with the differences in excited-state energies for a Co(sep)²⁺ reduction of a series of Co(III) oxidants. Values of $\beta_{ab}$ are calculated as the ratio of the observed-to-expected ratios of rate constants for Co(sep)²⁺-to-Ru(NH₃)₆²⁺, $R$(Co:Ru), reductions of the indicated Co(III) complexes. Values of the expected rate ratios are based on eq 3 and known parameters or parameters interpolated with use of Figure 1. Only the lowest energy excited states are considered: i.e., $\sum|\delta E| = |E(^3T;Co^{III}) - E(^3T;Co(sep)^{3+})| + |E(^2E;Co^{II}) - E(^2E;Co(sep)^{2+})|$. Oxidants are numbered as in Figure 1 except for Co(NH₃)₅Cl²⁺ (9) and Co(sep)³⁺ (10). The left-hand-side entry for Co([14]aneN₄)(NH₃)₂³⁺ is based on triplet energies only; the right-hand-side entry for this oxidant includes the estimated sum of doublet- and quartet-state energy differences for Co(sep)²⁺ and Co([14]aneN₄)(NH₃)₂²⁺ where the ground-state spin multiplicities of these complexes are respectively quartet and doublet.

effects of metal-to-ligand and ligand-to-metal charge-transfer excited states on nonadiabatic, bimolecular reaction rates.[13] In the present study we have sought to determine whether the perturbations arising from the mixing of low-energy ligand-field excited states into the wave functions of reactant and product species had any influence on the relatively adiabatic features of Co(III)–Co(II) self-exchange reactions.[13c,13d,14] The experimental observations do indicate that in a series of closely related reactions, the rates of electron transfer do become more adiabatic as the reactants and products become more nearly electronically degenerate (Figure 2). The experimental observations are discussed in the following section, and models accommodating the observations are discussed in later sections.

**Correlation of the Retardation Factors ($\beta_{ab}$) with Electronic Properties of the Reactants.** We find that discrepancies from behavior based on eq 3 for simple Co(III) oxidants with Co(sep)²⁺ can be as much as a factor of $10^{-3}$. This is more or less consistent with the our previous observations[13] and is independent of the details of evaluation of $\beta_{ab}$.

The magnitudes of $\beta_{ab}$ factors seem to depend on a number of parameters. For example, the interactions of low-energy charge-transfer excited states can increase $\beta_{ab}$.[13] We have attempted to minimize the effects of charge-transfer interactions in the systems selected for this study. Our major interest in this work is the proposal that $\beta_{ab}$ decreases with increasing mismatch of the electronic structures of reactants and products. The possible contributions of other factors is discussed briefly below.

In evaluating the influence of metal-centered excited states, we have considered only the lowest energy, single electron excited states. For octahedral, Co(III) complexes the relevant state is the $^3T_{1g}$ state. Only for Co(NH₃)₆³⁺ do we have a reliable experimental determination of the vertical energy to this state.[42] We have used the hexammine complex as a reference and estimated $E(^3T_1)$ for the other complexes based on differences in the d–d spectra and a simple ligand-field model.[43,44] Thus, in the octahedral limit

(42) Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085.
(43) Wentworth, R. A. D.; Piper, T. S. *Inorg. Chem.* **1965**, *4*, 709.
(44) Jørgensen, C. K. "Absorption Spectra and Chemical Bonding in Complexes"; Pergamon Press: Oxford, 1962.

$$E(^1T_2) - E(^1T_1) = 16B$$

$$E(^3T_1) - E(^1A_1) = 10D_q - 3C$$

And $C \simeq 7.45B$ on the basis of the parameters listed by Wentworth and Piper[43] for $Co(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$. In complexes of lower symmetry, in which some or all the degeneracy of the T states is removed, we have assumed that all the triplet components (i.e., $^3E$, $^3A$, etc.) mix into the ground-state wave function and that it is sufficient to consider the mean triplet energy. The spectroscopic parameters employed are listed in Table I.

For high-spin cobalt(II) complexes we have used[44]

$$E(^2E) - E(^4T_2) = 20D_q{}' + 7B' + 4C'$$

where we have based $D_q{}'$ on the $D_q$ values of the corresponding Co(III) complexes with use of the emperical relation $D_q \simeq 2.44D_q{}'$ (based on published values for $Co(NH_3)_6{}^{3+,2+}$ and $Co(OH_2)_6{}^{3+,2+}$), $B' \simeq 835$ cm$^{-1}$, and $C' \simeq 4B'$. The resulting values of $E(^2E)$ are included in Table I.

Qualitative comparison of the $\beta_{ab}$ parameters from Table III with the $E(^3T)$ and $E(^2E)$ parameters in Table I does indicate a correlation. We have tried several emperical correlations. The best by far is the simple correlation of ln $\beta_{ab}$ with

$$\sum |\delta E| = \{ |E(^3T;Co^{III}) - E(^3T;Co(sep)^{3+})| +$$
$$|E(^2E;Co^{II}) - E(^2E;Co(sep)^{2+})| \}$$

shown in Figure 2. It is important to observe that the difference in triplet-state energies tends to dominate $\sum |\delta E|$ and that $E(^3T;Co^{III}) > E(^3T;Co(sep)^{3+})$ for three of the oxidants while the reverse is true for most of the others (Table I). Since the rate constant for the $Ru(NH_3)_6{}^{3+}$–$Co(sep)^{2+}$ reaction was determined[14] under slightly different conditions from those employed in the present study, and since the $Co(en)_3{}^{3+}$–$Ru(NH_3)_6{}^{2+}$ reaction is so slow that the rate constant estimated provides only an upper limit, the experimental intercept in Figure 2 is necessarily uncertain. It is to be emphasized that the correlation in Figure 2 is empirical and that there is no basis for expecting a linear correlation over the full range of complexes.
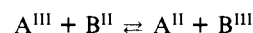
The large deviation from the correlation line in Figure 2 of the point for the $Co([14]aneN_4)(NH_3)_2{}^{3+}$–$Co(sep)^{2+}$ reaction is qualitatively consistent with the doublet ground state expected for $Co([14]aneN_4)(NH_3)_2{}^{2+}$[45] and the resulting mismatch with the electronic structure of high-spin $Co(sep)^{2+}$. The implication of Figure 2 is that the simple square-root relationship 3 fails to account for the reaction rates by an amount exponentially dependent on the absolute magnitude of the mismatch of the electronic energies of the reactants and products.

**Possible Models for the Dependence of Retardation Factors on Reactant and Product Electronic Structure.** Three possible origins of the effect illustrated in Figure 2 have been suggested in the introduction: (a) the shapes of the potential energy surfaces become more dissimilar as the electronic structures of reactants and products become more dissimilar; (b) enhanced coupling for electronically degenerate, compared to nondegenerate, reactants and products; and (c) $\psi_e(r_e,q_n) \neq \psi_e{}^o(r_e,q_n{}^o)$. The possibilities are discussed in turn below.

**Concerning the Possibility That Dissimilar Shapes of the Nuclear Potential Energy Surfaces Give Rise to the Small Values of $\beta_{ab}$.** Dissimilar slopes in the neighborhood of the saddle point imply very different effective force constants and/or nuclear displacements along the reactant and product reaction trajectories. This effect is likely to become important when the nuclear reorganizational barriers of the component couples are very different.[23] We find no evidence for such a contribution. On the contrary, the nuclear reorganizational energies of the $Co(en)_3{}^{3+,2+}$ and $Co(NH_3)_6{}^{3+,2+}$ couples are at least as badly mismatched to those of the $Co(sep)^{3+,2+}$ couple as are the reorganizational energies of $Co(phen)_3{}^{2+,2+}$, $Co(NH_3)_5Cl^{2+,+}$, $Co(NH_3)_5CN^{2+,+}$, etc. Yet

only the $Co(Am)_6{}^{3+}$–$Co(sep)^{2+}$ reactions, among those not complicated by charge-transfer perturbations, approach the limiting values of $\beta$ (or, by inference, $\kappa$) exhibited by the $Co(sep)^{3+,2+}$ couple. Further examples are provided by the $Co^{III}$–$Ru(NH_3)_6{}^{2+}$ and the $Co^{III}$–$Cr(bpy)_3{}^{2+}$ reactions which appear to conform relatively well to eq 3 even though there must be a considerable difference in the shapes of reactant and product potential surfaces for such couples. Thus, the degree of apparent nonadiabaticity (or $\beta$) does not correlate with the mismatch of nuclear reorganizational barriers, or by inference with purely vibrational factors.

**Concerning Possibly Enhanced Exchange Coupling in Electronically Degenerate Reactant–Product Systems.** Rather than seeking an explanation of the variations of $\beta$ with electronic structure in terms of a mismatch of purely vibrational factors, as discussed in the previous section, one could look for a purely electronic origin of the behavior observed. Exchange coupling of the reactant and product potential energy surfaces could, in principle, provide an appropriate model. The electron exchange interaction has been used to estimate the electronic matrix element in electron transfer[3,12,46] and in energy transfer,[47] as well as in discussions of molecular[48] and solid-state[3,12,46,49] magnetic interactions. While one must always be aware of the differences in Hamiltonian operators in these difference classes of phenomena, there are qualitative features of Dexter's treatment of dipole-forbidden energy-transfer processes which are helpful in discussions of electronic perturbations in electron-transfer processes.[13,50] The one-electron exchange integral, $\langle V \rangle$, for an electron-transfer reaction of the type

$$A^{III} + B^{II} \rightleftharpoons A^{II} + B^{III}$$

(the superscripts can be regarded as formal oxidation state designations) can be interpreted[46] as the interaction between composite orbital charge densities of the oxidized ($\rho^{III}$) and the reduced ($\rho^{II}$) species; i.e.

$$\langle V \rangle = \int \rho^{III} (e^2/r) \rho^{II} \, d\tau \qquad (4)$$

where

$$\rho^{III} = \phi(A^{III}) \phi(B^{III})$$

and $\rho^{II} = \phi(A^{II})\phi(B^{II})$, $\phi(X^{III})$ and $\phi(X^{II})$ are the respective redox orbital wave functions, and X = A or B. The charge densities ($\rho^i$) will be maximized in the spatial region between reactants, and the magnitudes of the $\rho^i$ in this region will be increased by any factor which mixes $\phi(A^i)$ with $\phi(B^i)$. For the ground states of cobalt(III) complexes, the lowest energy orbitals are filled, so there can be little mixing between $\phi(A^{III})$ and $\phi(B^{III})$, and $\rho^{III}$ would be expected to be very small. Such mixing as does occur can be described in terms of the contributions of the lowest energy triplet state to the ground state wave function through spin–orbit coupling: $\phi(X^{III}) = \phi^o(X^{III})[1 + \lambda_{SO}/E_T{}^X]$ (where $\phi^o(X)$ is the zero-order wave function, $\lambda_{SO}$ is a spin–orbit coupling parameter, and $E_T{}^X$ is the triplet-state energy of species X). For $\phi^o(A)\phi^o(B)$ $\sim 0$ and $E_T{}^B = E_T{}^A + \Delta E_T$, the dominant term in $\rho^{III}$ will be of the form $\gamma - \Delta E_T$ (where $\gamma$ is a constant) so that $\rho^{III}$ is expected to reach its maximum value when $\Delta E_T \rightarrow 0$. Although the zero-order terms should make a substantial contribution to $\rho^{II}$, it should be qualitatively similar in form to $\rho^{III}$; i.e., $\rho^{II}$ should maximize for equal doublet-state energies of the Co(II) species.

Thus the purely electronic, exchange-coupling model can provide a qualitative accounting for our observations. This approach has many attractive features, and a rigorous theoretical development

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(50) Note that electron transfer between low spin Co(III) and high spin Co(II) species is formally dipole forbidden.

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would be worthwhile. However, bond-length changes may play some role in the coupling, and a model combining vibrational and electronic coupling should also be considered.

**A Possible Vibronic Model for the Retardation Factor.** One interpretation of the observations described in this paper is that eq 3 provides a reasonable description of the zero-order potential energy surfaces and the reactant-product surface crossing consistent with the Born-Oppenheimer approximation. However, when the electronic wave functions are strongly dependent on the nuclear coordinates, as when spin-orbit coupling mixes contributions from a distorted excited state into the ground-state wavefunction, then the nuclear coordinates required for resonance in the total wave function must be different from the coordinates appropriate to crossing of the zero-order potential energy surfaces. The condition for surface crossing may be taken as

$$E^R(r_e{}^\ddagger, q_n{}^\ddagger) = E^P(r_e{}^\ddagger, q_n{}^\ddagger)$$

where R and P designate the reactants and products, respectively, $r_e{}^\ddagger$ and $q_n{}^\ddagger$ are the respective electronic and nuclear coordinates at the surface crossing, and the energies are eigenvalues based on the Born-Oppenheimer wave functions. In the spirit of the Born-Oppenheimer approximation, this condition can be rewritten

$$E_e{}^R(r_e{}^\ddagger, q_n{}^\ddagger) = E_e{}^P(r_e{}^\ddagger, q_n{}^\ddagger) \tag{5}$$

and

$$E_n{}^R(q_n{}^\ddagger) = E_n{}^P(q_n{}^\ddagger) \tag{6}$$

(where the subscripts designate the electronic and nuclear contributions to the total energy; i.e., $E = E_e + E_n$). Minimization of $E_n(q_n{}^\ddagger)$ with respect to the nuclear coordinates leads to the zero-order function as as eq 3. However, the nuclear coordinates, $q_n{}^*$, of this energy minimum, $E^*$, do not necessarily satisfy the condition expressed in eq 5, and the minimization of energy with respect to both (5) and (6) will give a crossing point with energy $E^\ddagger$ such that $E^\ddagger \geq E^*$.[51]

The argument can be illustrated with respect to hexamine-type cobalt(III)-cobalt(II) couples. On the basis of ground-state crystal structures, the distortion coordinate when only the nuclear wave functions are considered is a "breathing" mode ($a_{1g}$ in $O_h$ symmetry).[13f,14,19] Spin-orbit coupling in a cobalt(III) species mixes some $^3T_{1g}$ character into the $^1A_{1g}$ ground state of these complexes, but the $^3T_{1g}$ states are distorted along both $a_{1g}$ and $e_g$ normal coordinates.[42] The amount of mixing will increase as $E(^3T_{1g}) - E(^1A_{1g}) = \Delta E(T)$ decreases. If the excited-state distortions are reasonably similar in the family of reactions investigated, then $E_e{}^R(r_e{}^*, q_n{}^*)$ will not be equal to $E_e{}^P(r_e{}^*, q_n{}^*)$ unless $\Delta E(T) = 0$. Since the excited-state distortions in these systems seem to involve a very large $e_g$ component,[42] one expects the actual reaction trajectory to be skewed from the $a_{1g}$-distortion pathway of the zero-order surfaces, formally by combining the zero-order $a_{1g}$ motion with a small amount of the $e_g$ motion. An analogous argument can be made regarding the effects of doublet excited-state mixing into the ground-state quartet-state wave functions of high-spin cobalt(II) species. Qualitatively, one expects that
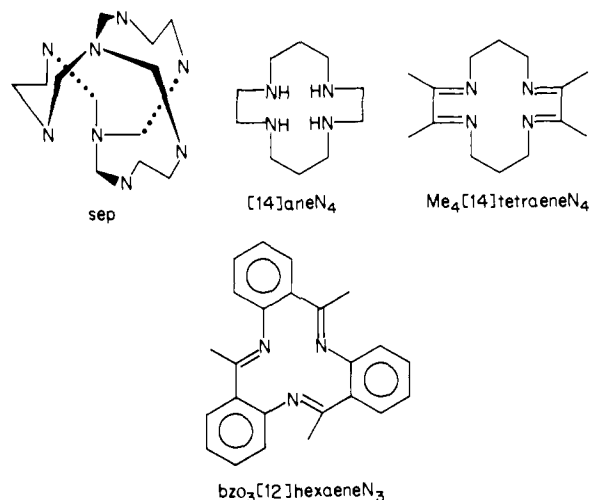
$$E^\ddagger = E^* + \sum_i (f_i/2)(\Delta X_i)^2$$

(where the $X_i$ are the nuclear displacements relating the actual configuration coordinates, $q_n{}^\ddagger$, of the surface crossing to the coordinates, $q_n{}^*$, based on the nuclear wave functions only;[51] the $f_i$ are the associated force constants).

While the vibronic coupling approach seems very plausible, it can be represented as a combination of nuclear and electronic models, since even here origin of the discrepancy is postulated to

Chart I



sep       [14]aneN₄       Me₄[14]tetraeneN₄

bzo₃[12]hexaeneN₃

arise from the contributions of the electronic wave function. Thus, to some reasonable degree of approximation, we can represent the electronic contribution to electron-transfer rates in the vibronic limit by

$$H_{RP} \sim \langle V \rangle \int \phi_n{}^R \phi_n{}^P \, dq$$

where $\langle V \rangle$ is an electron exchange integral, as discussed in the preceeding section, and $\int \phi_n{}^R \phi_n{}^P \, dq$ is a nuclear overlap integral.

**Observations on the Distance Dependence of Some Simple Electron-Transfer Rates.** One expects the electronic matrix element, $H_{RP}$ in eq 1, to decrease rapidly as the reactants are placed further apart.[2,3,6-10] We have made some very limited attempts to investigate such effects.

Beattie and co-workers[36] have previously noted that while $Co(en)_3{}^{3+}$ and $Co(chda)_3{}^{3+}$ differ considerably in size, they exhibit very similar reactivities. Our observations are somewhat similar (Table III), although uncertainties (arising from possible reductant decomposition) in the very slow $Ru(NH_3)_6{}^{2+}$ reactions do make it difficult to draw firm conclusions based on the rate ratios in Table III. However, we do wish to point out that the *ratios* of rate constants reported by Beattie and co-workers[36] *do show* the trend expected on the basis of our analysis. Thus for the $V^{2+}$ and $Cr(bpy)_3{}^{2+}$ reductions of $Co(en)_3{}^{3+}$ and $Co(chda)_3{}^{3+}$ the ratios are $1.3 \times 10^{-5}$ and $0.65 \times 10^{-5}$, respectively. Since the redox potentials for all the couples involved are very similar, one expects $f_{ab} \simeq f_{ac}$, and no second-order correction to the rate ratio is necessary. There will be a small ($\leq 20\%$) correction, increasing the ratio, owing to the effect of the different radii of the reducing agents on the reactant outer-sphere association constants. For[2-12] $H_{RP} \sim A \exp(-\alpha r_{DA})$, and using mean radii[52] of 4.4 and 5.5 Å for the oxidants (based on parameters cited by Beattie and co-workers), one finds $\alpha \sim 0.4$ Å$^{-1}$. Given the experimental uncertainties, this is not unreasonable (values of $\alpha$ between 0.5 and 1 Å$^{-1}$ have been estimated in the literature[2-6,8,9,12,13]). The electronic structures of these oxidants are similar, so retardations of rate such as those discussed above are not expected to be a complication in these comparisons.

In another attempt to investigate the same issue, we have made a comparison of the electron-transfer reactivities of a few complexes with aromatic ligands: $Co(phen)_3$, *meso*-$Co(bzo_3[12]$-hexaeneN₃)₃²⁺, and *rac*-$Co(bzo_3[12]hexaeneN_3)_2{}^{3+}$. The values of $\beta_{ab}$ are estimated to be 0.046, 0.069, and 0.021, respectively. While the tridentate ligands are very bulky, the *meso*-$Co(bzo_3$-[12]hexaeneN₃)₂²⁺ complex has a somewhat more open structure than the *rac* isomer[53] (approximately parallel, but staggered rather than eclipsed phenyl rings on the opposite ligands), and the effective sizes may be quite different. The metal-to-ligand

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(51) If the excited-state distortion involves one or more nuclear coordinates, which are not used in describing the reaction coordinate, then there will be many values of $q_j$ for which eq 6 is satisfied. The coordinates $q_j$ will define a potential energy surface (or curve for a single coordinate) orthogonal to the classical nuclear reaction coordinate ($q_c$). In this situation, simultaneous satisfaction of conditions (5) and (6) can be described in terms of $q_c$ and the value of $q_j$ which gives the least value of $E_e(r_e^\ddagger, q_n^\ddagger)$. The value of $E^\ddagger$ so constructed is necessarily greater than $E^*$.

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charge-transfer (MLCT) absorptions of the Co(bzo$_3$[12]hexae-neN$_3$)$_2$$^{2+}$ complexes occur at relatively low energies ($\lambda_{max}$ = 570 and 550 nm, respectively), and the comparisons may be complicated by inter- or intramolecular MLCT perturbations.

Similarly, the much larger value of $\beta$ estimated for Co(Me$_4$-[14]tetraeneN$_4$)(NH$_3$)$_2$$^{3+}$ than for Co([14]aneN$_4$)(NH$_3$)$_2$$^{3+}$ is very likely a consequence of the low-energy $\pi^*$ acceptor system of the tetraene ligand and the resulting MLCT perturbations. It seems likely that charge-transfer perturbations contribute to donor–acceptor electronic coupling (i.e., $H_{RP}$) in most experimental systems and that it is very difficult to design experiments which provide information about charge-transfer independent contributions to $H_{RP}$. Nevertheless, neither charge-transfer perturbations nor variations in size can contribute significantly to the variations of $\beta_{ab}$ in Figure 2.

## Conclusions

In this study we have documented some systematic deviations from predictions of the Marcus square-root relation of a series of Co(III)–Co(II) electron-transfer reactions. The magnitudes of the discrepancies have been found to correlate with the mismatch of the energies of the lowest energy ligand field excited states of the reactant and product Co(III) and Co(II) species. This effect appears to be qualitatively consistent with either (or both) (a) a larger value of the one-electron exchange integral when the reactants and products are electronically degenerate (i.e., a "pure" electronic effect) or (b) a modulation in the electronic wave function by the variations in nuclear coordinates across the reaction trajectory (i.e., a vibronic effect). A vibronic effect is likely to be manifested, at least partly, by changes in enthalpies of activation.

Self-exchange electron transfer-reactions define the electronically degenerate limit in which electron-transfer behavior becomes relatively adiabatic. Our experimental probes necessarily provide only relative information and do not permit any inference about the degree to which the self-exchange reactions themselves might be nonadiabatic.

The effects that we have investigated do appear to be electronic in origin, and the magnitude of their kinetic manifestations can be altered by simple electronic perturbations. Despite the contributions of these electronic effects to electron-transfer reactivity patterns, it is important to bear in mind that the dominant factors in these reactions are clearly those associated with nuclear reorganization and that these factors do seem to be adequately treated by using various quantum, semiclassical, or classical models. Indeed, it is only the systematic deviations from predictions of such models that permit the identification of electronic factors.

The major conclusion of this study, that electron-transfer reactions tend to become less adiabatic as the electronic structures of reactants and products become more dissimilar, has been demonstrated for a somewhat unique set of reactions: i.e., these involving Co(III) oxidants and Co(II) reductants. An approximate selection rule governing the adiabaticity of these reactions can be given an "electronic" or a "vibronic" formulation. Thus, mismatched electronic excited states of reactants and products will lead to retardation of electron-transfer rates (a) when at least one of the electron-density functions in the exchange integral (e.g., $\rho^{III}$ or $\rho^{II}$ in eq 3) is very small (as when the oxidized species of the reactants and products both have filled redox orbitals) and (b) the first coordination sphere nuclear reorganization contributions are large and when the electronic wave functions for the redox orbitals of both the oxidant and reductant contain significant contributions from distorted electronic excited states. Further study may permit a more precise statement of the electronic selection rules governing electron-transfer processes.

# Stereochemistry of Allyl Sulfones. On the Structure of Metalated Allyl Sulfones and Their Stereochemistry of Alkylation
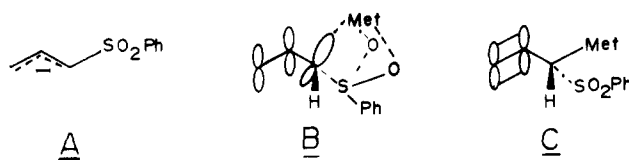
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**Abstract:** Stereochemical studies involving alkylation of metalated allyl sulfones are probed to address the question of the structure of these important synthetic intermediates. In contrast to recent conclusions, both experimental and theoretical, declaring sulfone-stabilized carbanions planar, the diastereoselectivity of these alkylations questions such conclusions even though the additional allylic conjugation would have been anticipated to provide a further driving force for planarity. A model to rationalize the seemingly contrasteric highly diastereoselective alkylations in which the sulfone-stabilized allylic carbanion exists as a somewhat pyramidalized organometallic emerges. The preferred conformations of the cyclohexenyl allylic sulfones place the sulfone moiety in an axial orientation and, in at least one acyclic case, the C–S bond parallel to the p-orbitals. An electronic stabilization is proposed to account for this conformation. In addition, the stereochemistry of the palladium-catalyzed allylic alkylation with arylsulfinate places this nucleophile into the class of heteroatom nucleophiles that proceed with predominant net retention of configuration.

The question of the nature of a carbanion stabilized by a sulfone group continues to be a major controversy. While evidence has accumulated to suggest that such carbanions behave asymmetrically,[1] recent experimental[2a] and theoretical[2b] work has pronounced them planar. Intuition would lead one to predict that conjugating a sulfone stabilized carbanion with a double bond as in the case of carbanions derived from allylsulfones should indeed assure their planarity as in A. We wish to record evidence that

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questions the validity of such conclusions for metalated allyl sulfones. Structures such as B or C differ only in the degree of