Table I. Visible Absorption Maxima of Some Cobalt Complexes

	Maxima, nm	
Complex	Nujol mull	Soln
$\{[Co(en)_2(H_2O)OPO_3]_2Mo_5O_{15}\}$	508 ~375 sh[a]	
$[Co(en)_2(H_2O)OPO_3H]ClO_4 \cdot aq$	507 360	507 366
$[Co(en)_2PO_4] \cdot H_2O$	525 370	529 377
cis-$[Co(en)_2(H_2O)_2](ClO_4)_3$	490 ~355 sh	492 359

[a] sh shoulder.

P_2Mo_5 moiety. Optical absorption data are given in Table I. Energies of the first d–d bands are generally reliable indicators of the constitution of the first coordination sphere of the cobalt(III) ion.[9–11] The data in Table I thus support formula I as $[CoN_4(aq)$(monodentate phosphate)$]$ rather than a salt such as $[Co(en)_2(H_2O)_2]_2[P_2Mo_5O_{23}]$. The salt formulation is also ruled out by the hydrolytic dissolution of the complex at pH 6 to give $[Co(en)_2(PO_4)]$.

We conclude that the complex formed is indeed a neutral zwitterionic species. The interconversion of $[Co(en)_2PO_4]$ to *cis*-$[Co(en)_2(H_2O)(OPO_3H)]^+$ in aqueous solution occurs rapidly at pH 5,[5] and polymerization of molybdate is also rapid under these conditions. The resulting structure offers a number possibilities for isomerism, since both the *cis*-$[Co(en)_2(H_2O)(O-)]$ and $P_2Mo_5O_{23}$ moieties are chiral. It is mildly surprising, and somewhat disappointing, that the resulting zwitterion is insoluble. We presume that the approximately linear charge arrangement, 2+...4−...2+, leads to a staggered crystal packing with a lattice energy dominated by large electrostatic terms.

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Registry No. $\{[Co(en)_2(H_2O)OPO_3]_2Mo_5O_{15}\}$, 58933-78-1; $Na_6[P_2Mo_5O_{23}]$, 39475-33-7; $[Co(en)_2PO_4]$, 19169-67-6; Na_2MoO_4, 14666-91-2.

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Extension of Rate Correlations between Electrochemical and Chemical Electron-Transfer Processes to Heteronuclear Reactions

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Using an adiabatic theory of electron transfer that is expected to be applicable to outer-sphere reactions, Marcus[1] has shown that two relationships are expected to hold between the rates of such redox reactions in homogeneous solution and the corresponding reactions at inert-metal electrodes.

(a) The rate constants for an electrochemical exchange reaction k^s_{el} (measured at the standard potential $E°$) and the corresponding homogeneous self-exchange reaction k_{ex} are related by

$$\left(\frac{k_{ex}}{Z_{chem}}\right)^{1/2} \approx \left(\frac{k^s{}_{el}}{Z_{el}}\right)$$

where Z_{chem} and Z_{el} are the homogeneous and heterogeneous collision frequencies, respectively.

(b) When a series of reactants is reduced (or oxidized) electrochemically and chemically, the ratio of the rate constants for these two pathways will be constant for the conditions of a constant metal–solution potential difference and a given coreactant, respectively.

In deriving the above relations, it is assumed that the work terms associated with the approach of the reactants (and products) are negligible or constant. Correlation between electrochemical and chemical electron-transfer rates has chiefly been made using (a).[1–4] Comparison (b) has been used only on a limited basis to compare the electrochemical and chemical reduction rates of some cobalt(III)–pentaammine complexes.[5]

A practical limitation on the application of (a) is the relative scarcity of rate data for homogeneous self-exchange reactions which is apparently due to the difficulties of obtaining data for such reactions. Further, for many electron-transfer reactions followed by rapid chemical steps (e.g., aquation), self-exchange data cannot be obtained and standard potentials for the reactions are unknown or can only be estimated with insufficient precision. Comparison (b) can still be employed for such reactions, although the rate comparisons are relative rather than absolute and require the acquisition of kinetic data for a series of reactions with a common reductant or oxidant.

However, a correlation similar in form to (a) can also be derived enabling a comparison to be made of the absolute rates of outer-sphere electrochemical processes with those for the corresponding heteronuclear[6] homogeneous reactions (i.e., where a net chemical change occurs) as follows.

Consider the heteronuclear homogeneous reaction

$$A_1 + B_2 \rightarrow A_2 + B_1 \tag{1}$$

and the corresponding electrochemical reactions

$$A_1 + e^- \rightarrow A_2 \tag{2a}$$

$$B_2 - e^- \rightarrow B_1 \tag{2b}$$

For reactions 2a and 2b, respectively, the following equations may be written according to Marcus theory[1] at overpotentials where the quadratic potential term can be neglected and under conditions where the double-layer work terms are negligible

$$\ln k_A = \ln k^s{}_A - 0.5f(E - E^\circ{}_A) \tag{3a}$$

$$\ln k_B = \ln k^s{}_B + 0.5f(E - E^\circ{}_B) \tag{3b}$$

k_A and k_B are the rate constants for reactions 2a and 2b at potential E, $k^s{}_A$ and $k^s{}_B$ are the corresponding quantities measured at the standard potentials $E^\circ{}_A$ and $E^\circ{}_B$ for these reactions, and $f = F/RT$.

At an electrode potential where $\ln k_A = \ln k_B = \ln k^{el}{}_{AB}$, (3a) and (3b) may be combined to yield

$$\ln k^{el}{}_{AB} = 0.5(\ln k^s{}_A + \ln k^s{}_B + 0.5 \ln K_{AB}) \tag{4}$$

as $\ln K_{AB} = f(E^\circ{}_A - E^\circ{}_B)$, where K_{AB} is the equilibrium constant for reaction 1. However, Marcus has shown that the relation

$$\ln k^{chem}{}_{AB} = 0.5(\ln k_{AA} + \ln k_{BB} + \ln K_{AB}) \tag{5}$$

Table I. Comparison between Electrochemical and Chemical Rates for Some Heteronulcear Reactions[a,b]

Oxidant	Reductant	k^{el}_{AB},[c] cm s^{-1}	$(k^{chem}_{AB})_{calcd}$[d] M^{-1} s^{-1}	$(k^{chem}_{AB})_{obsd}$,[e] M^{-1} s^{-1}
$Co(NH_3)_6^{3+}$[7]	V^{2+}[8]	3×10^{-2}	0.9	3.7×10^{-3}[g,12]
	Eu^{2+}[9]	2.5×10^{-2}	0.65	2×10^{-2}[h,13]
	Cr^{2+}[9]	4×10^{-3}	1.6×10^{-2}	8×10^{-5}[g,12]
$Co(NH_3)_5H_2O^{3+}$[7]	V^{2+}[8]	0.11	12	0.5[12]
	Eu^{2+}[9]	9×10^{-2}	8	0.15[13]
	Cr^{2+}[9]	1.2×10^{-2}	0.15	$\leqslant 0.1$[14]
$Co(en)_3^{3+}$[10]	V^{2+}[8]	1.5×10^{-2}[h]	0.2	$\sim 2 \times 10^{-4}$[13]
	Eu^{2+}[9]	9×10^{-3}[h]	8×10^{-2}	$\sim 5 \times 10^{-3}$[h,13]
	Cr^{2+}[9]	1.2×10^{-3}[h]	1.5×10^{-3}	$\sim 2 \times 10^{-5}$[g,13]
$Co([14]dieneN_4)(NH_3)_2^{3+}$[2,i]	V^{2+}[8]	0.13[h]	17	9.8×10^{-2}[h,15]
	Cr^{2+}[9]	1.5×10^{-2}[h]	0.23	4×10^{-3}[g,15]
V^{3+}[8]	Eu^{2+}[9]	3.4×10^{-3}	1.2×10^{-2}	9×10^{-3}[f,16]
Cr^{3+}[9]	Eu^{2+}[9]	6.5×10^{-5}	4×10^{-6}	$\lesssim 1.7 \times 10^{-5}$[f,16]
Fe^{3+}[11]	V^{2+}[8]	~ 8	$\sim 6 \times 10^{4}$	1.8×10^{4}[17]
	Eu^{2+}[9]	~ 6	$\sim 4 \times 10^{4}$	3.4×10^{3}[18]
	Cr^{2+}[9]	~ 2	$\sim 4 \times 10^{3}$	$\sim 8 \times 10^{3}$[19]
$(2,2'\text{-bpy})_3Fe^{III}$[3]	Fe^{2+}[11]	2	4×10^{3}	2.7×10^{4}[g,20]

[a] All rates given are for acid-independent pathways and at 25 °C. Unless otherwise stated, ionic strength $\mu \approx 1$, perchlorate media. [b] Electrochemical rate data are from ref 2, 3, 7–11. The references given alongside each oxidant and reductant are the appropriate sources of rate-potential data. Where only standard rate constants were given without transfer coefficients α, Tafel lines were constructed over small potential ranges assuming that $\alpha = 0.5$. Chemical rate data are from ref 12–20. [c] k^{el}_{AB} is the electrochemical rate constant at the intersection of separate rate-potential plots for electrochemical reduction and oxidation of the listed oxidant and reductant, respectively. [d] $(k^{chem}_{AB})_{calcd}$ is the homogeneous heteronuclear rate constant estimated from k^{el}_{AB} using eq 7 and assuming[1] $Z_{chem} \approx 10^{11}$ M^{-1} s^{-1} and $Z_{el} \approx 10^{4}$ cm s^{-1}. [e] $(k^{chem}_{AB})_{obsd}$ is the observed homogeneous heteronuclear rate constant. [f] $\mu = 2.0$. [g] $\mu \approx 0.5$. [h] $\mu \approx 0.1$. [i] For terminology, see ref 2.

should hold approximately between the rate constant k^{chem}_{AB} for the heteronuclear chemical reaction 1 and the rate constants k_{AA} and k_{BB} for the corresponding self-exchange reactions $A_1 + A_2 \rightleftharpoons A_2 + A_1$ and $B_1 + B_2 \rightleftharpoons B_2 + B_1$, respectively for small or moderate values of the "driving force" term $\ln K_{AB}$. By combining eq 4 and 5 and assuming that (correlation (a) above)

$$0.5 \ln \left(\frac{k_{AA}}{Z_{chem}}\right) = \ln \left(\frac{k^{s}_{A}}{Z_{el}}\right) \tag{6a}$$

$$0.5 \ln \left(\frac{k_{BB}}{Z_{chem}}\right) = \ln \left(\frac{k^{s}_{B}}{Z_{el}}\right) \tag{6b}$$

it follows that

$$0.5 \ln \left(\frac{k^{chem}_{AB}}{Z_{chem}}\right) = \ln \left(\frac{k^{el}_{AB}}{Z_{el}}\right) \tag{7}$$

Thus the rates of heteronuclear reactions can be correlated with electrochemical reaction rates in a similar way to the self-exchange reactions by assessing the electrochemical rate constant k^{el}_{AB} which is the rate constant at the intersection of the two rate–potential plots for the two electrochemical half-reactions which form the constituents of the heteronuclear reaction. It may be noted that correlation (a) is a special case of eq 7 for homonuclear[6] reactions; therefore either relation can be used equally in testing the underlying assumptions that are involved.[1] Note that no driving force term K_{AB} appears in eq 7 so that a direct correlation between the absolute rate constants for electrochemical and chemical electron-transfer reactions is possible for reactions where K_{AB} is unknown and/or where knowledge of the self-exchange rates (or the standard potential) of at least one of the constituent redox couples is unobtainable.

In Table I are listed corresponding values of k^{el}_{AB} and k^{chem}_{AB} for some representative electrochemical and chemical electron-transfer reactions that are expected to follow outer-sphere pathways. The values of the electrochemical "heteronuclear" rate constants k^{el}_{AB} were obtained by plotting the experimental Tafel lines of log (rate constant) vs. potential for the individual electrochemical reactions and reading off the rate constant at the intersection point as k^{el}_{AB}. In some cases short linear extrapolations of the Tafel lines to potentials beyond the range of the experimental data were required. Most data were obtained for the mercury–aqueous interface, except those for the Fe(III)–Fe(II) couples which were obtained using platinum electrodes.[3,11] For all of these systems, $(E - E°_{A})$, $(E - E°_{B})$, and $\ln K_{AB}$ were sufficiently small so that eq 3a, 3b, and 5 should hold to a good approximation. In no cases were double-layer corrections applied to the kinetic data; such effects were minimized by employing data gathered at high ionic strengths. Similarly, the homogeneous rate data in Table I are uncorrected for salt effects. Values of $(k^{chem}_{AB})_{calcd}$ were then calculated from k^{el}_{AB} using eq 7 for comparison with the observed values $(k^{chem}_{AB})_{obsd}$ and are listed in Table I.

It is seen that for the reactions not involving Co(III), a reasonably good correlation between $(k^{chem}_{AB})_{calcd}$ and $(k^{chem}_{AB})_{obsd}$ is obtained which mirrors the behavior found previously for some electrochemical and homogeneous self-exchange reactions.[1] However, for the reactions listed in Table I with Co(III) as the oxidant, the calculated values of k^{chem}_{AB} are up to 10^3 times larger than the values determined experimentally. It has been noted on a number of occasions that Marcus rate correlations often fail between Co(III)–Co(II) self-exchange and heteronuclear reactions involving cobalt as one of the reaction partners.[15,21–23] Discrepancies have also been seen between the experimental electrochemical and self-exchange rates and the predictions of correlation (a) for some of these cobalt systems.[2,24] At present, the most reasonable (i.e., least unsatisfactory) explanation for this behavior appears to be that the self-exchange reactions between Co(III) and Co(II) involve very small values of the transmission coefficient κ, presumably due to poor overlap of the donor and acceptor orbitals.[2,21,23] However, the present discrepancy (Table I) is between the rates of electrochemical and chemical reactions containing only one cobalt center. It is possible that if the latter reactions also proceed through nonadiabatic pathways, then the electrode could represent a more efficient electron donor (i.e., higher κ) than either Co(II) or the other homogeneous reducing agents listed in Table I. Alternatively, the apparently "anomalous" behavior of Co(III)–Co(II) in Table I could simply reflect differences in behavior between ammine and aquo complexes. Unfortunately, few kinetic data involving ammine complexes of metals other than cobalt appear to be available with which eq 7 could be further tested at the present time.

As will be discussed in detail elsewhere,[25] the relative success of the Marcus correlation (a) (and therefore also eq 7) found for some systems here and in ref 1 and 2 may be misleading inasmuch as a quite different result would probably be obtained if a comparison could be made between rate constants that were corrected for the free energy of the approach of the reactants and products. Thus the measured entropies of activation for the homogeneous reactions listed in Table I are uniformly large and negative[12–20] which probably arises chiefly from solvent ordering attending the approach of the multicharged cationic reactants, whereas the corresponding entropic term for the electrode reactions is probably small.[25,26] Consequently, comparison between the (few available) enthalpies of activation for the corresponding electrochemical and homogeneous self-exchange systems indicates that the former values are substantially greater than half of the latter values, in contradiction to the reasoning behind correlation (a) above.[1] Therefore it is likely that the relative success of correlation (a)[1,2] and eq 7 is due to the unfavorable activation entropy for the chemical systems effectively compensating for the additional activation enthalpy in the electrochemical systems which may arise because the reactant is unable to penetrate the solvent layer adjacent to the electrode surface.[1] The relative importance of these effects may well vary with the size and structure of the reactants, as well as the charge carried by the reactants.

The discrepancies notwithstanding, there do appear to be similar trends exhibited by $(k^{\mathrm{chem}}{}_{\mathrm{AB}})_{\mathrm{calcd}}$ and $(k^{\mathrm{chem}}{}_{\mathrm{AB}})_{\mathrm{obsd}}$ for a series of related heteronuclear reactions. This correlation may therefore be utilized with some confidence to estimate approximate outer-sphere rates for either electrochemical or chemical reactions given rate data for either of these reaction types that is known to refer to an outer-sphere pathway. For example, the electroreduction of $Cr(OH_2)_5F^{2+}$ (in addition to $Cr(OH_2)_5SO_4^{+}$ and $Cr(OH_2)_6^{3+}$) proceeds by an outer-sphere mechanism at a mercury electrode,[27,28] and the electrochemical rate data[9,27,28] can be inserted into eq 7 to yield a calculated rate constant for the outer-sphere homogeneous reaction between $Cr(OH_2)_5F^{2+}$ and Cr^{2+} of 10^{-9} M^{-1} s^{-1}, markedly slower than the inner-sphere rate constant observed to be 2.6×10^{-3} M^{-1} s^{-1} for this reaction involving bridging by F^-.[29] This example illustrates one exploitable aspect of eq 7 in using electrochemical rate data to estimate outer-sphere rates for homogeneous reactions in that rate measurements of reactions with very small second-order rate constants ($<10^{-4}$ M^{-1} s^{-1}) are difficult and often impossible to obtain due to chemical instability of the reactants, competing reactions such as acid-dependent pathways, etc. However, the rate measurements for the corresponding heterogeneous electrochemical reactions are easily performed with measurement times in the subsecond region (thus minimizing any influence of following chemical reactions) and acid-dependent pathways are usually unimportant,[30] probably due to the ineffectiveness of hydroxyl as a bridging group at electrode surfaces.

It is also anticipated that eq 7 will prove to be useful in extending the Marcus correlation between electrochemical and chemical reactivities to a greater variety of redox processes than have hitherto been considered, e.g., to metal ion–nonmetal and bioinorganic reactions. A number of such applications await the further acquisition of good-quality electrochemical rate data.

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Oxygen- and Nitrogen-Bonded Borane Cations of Betaines and Amino Acid Esters

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In the few years since the initial elucidation[1] of the first borane cation $H_2B(NH_3)_2^+$ in the "diammoniate of diborane" many structural classes of cations have been discovered,[2] but few of these have functional substitution. It is of interest then to report a newly defined class of cations derived from betaines $(CH_3)_3NBH_2O_2C(CH_2)_nN(CH_3)_3^+$ and to extend the known amino acid ester derived cations[3] to the series $(CH_3)_3NBH_2N(CH_3)_2(CH_2)_nCO_2C_2H_5^+$. Comparison of the physical and chemical properties of the series provides insight into potential chemical transformations of the ester function.

The first member of ω-dimethylamino acid ester derived cations, namely, $(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2C_2H_5^+$, was characterized as a water-stable species[3d] that hydrolyzes in dilute base to form a novel five-membered heterocycle $H_2\overline{BN(CH_3)_2CH_2CO_2}$.[3b] Extension of the series to n = 2–4 is now reported (Table I). Of these cations, only one, where n = 2, forms a crystalline hexafluorophosphate salt; the others remain as viscous oils (and, in our experience, are essentially