was excluded from the average): -700×10^{-6}. The difference between the experimental value of -700×10^{-6} and the Pascal's constant value of -365×10^{-6} for H_2TPP equals -335×10^{-6} which could be used as a new "constitutive correction" for the porphyrin ring.

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Registry No. H_2-*p*-MeTPP, 14527-51-6; H_2-*o*-MeTPP, 37083-40-2; H_2-*i*-PrTPP, 38350-65-1; H_2TPP, 917-23-7.

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Correlations between Outer-Sphere Self-Exchange Rates and Reaction Entropies for Some Simple Redox Couples

Sir:

The free-energy barrier ΔG_λ^* to outer-sphere electron exchange between metal complexes consists of inner-shell ΔG_{in}^* and outer-shell ΔG_{out}^* contributions arising from the structural reorganization of the reactants and the surrounding solvent, respectively, that are required prior to electron transfer.[1] However, the interpretation of the observed reactivities in terms of theoretical models is limited by the lack of independent information on the nature and magnitude of these inner- and outer-shell terms. It is therefore worthwhile to search for experimental methods of providing estimates of such terms. One parameter that should yield information relevant to this question is the entropy difference $\Delta S_{\text{rc}}^\circ$ ($=\bar{S}_{\text{red}}^\circ - \bar{S}_{\text{ox}}^\circ$) between the two ions forming the redox couple. ($\Delta S_{\text{rc}}^\circ$ should not be confused with $\Delta S_{\text{ex}}^\circ$, the standard entropy change for the electron exchange reaction. The latter quantity is equal to zero since the reactants and products of exchange reactions are identical ($\Delta S_{\text{ex}}^\circ = \Delta S_{\text{rc}}^\circ - \Delta S_{\text{rc}}^\circ$).) The absolute ionic entropies $\bar{S}^\circ$ of aquo ions are very sensitive to both the size and charge of the ions, probably due to the effect of the ions upon the structure of the surrounding water.[2-4] Therefore $\Delta S_{\text{rc}}^\circ$ should be sensitive to the changes in solvent polarization that are required in order for electron transfer to occur and should become significantly larger as the difference in the effective radii $\Delta\bar{a}$ of the reduced and oxidized species increases.[5] Since large values of $\Delta\bar{a}$ are also associated with large inner-shell contributions to ΔG_λ^*, some of the factors that tend to increase ΔG_{in}^* are also expected to increase $\Delta S_{\text{rc}}^\circ$. ($\Delta G_{\text{in}}^*$ is primarily determined by differences between the radii of the reactants while ΔG_{out}^* is mainly determined by the actual sizes of the reactants.) Estimates of $\bar{S}^\circ$ for a number of aquo cations and complex anions have been available for some time,[6] but values of $\Delta S_{\text{rc}}^\circ$ for transition-metal redox couples of kinetic significance have been largely unavailable.[7] In addition, the existing data have been obtained by using a variety of methods and conditions so that intercomparisons are difficult. However, determinations of $\Delta S_{\text{rc}}^\circ$ have recently been made for a number of transition-metal redox couples in aqueous media by using a nonisothermal electrochemical cell arrangement.[2,8] In this communication, these and some values of $\Delta S_{\text{rc}}^\circ$ for additional redox couples that were obtained[9] by using the same method[2] are used to explore possible correlations between ΔG_λ^* and $\Delta S_{\text{rc}}^\circ$.

The interpretation of ΔG_λ^* is simplest for redox couples undergoing adiabatic electron transfer, for which the change in metal–ligand bond distances is not large. For such systems the inner-shell contribution ΔG_{in}^* is small and calculable, and the outer-sphere contribution ΔG_{out}^* can be obtained from ΔG_λ^*.[10] Although suitable systems are not abundant, Ru(III)/(II) couples containing ammine and/or polypyridine ligands provide such a class.[10] Estimates of ΔG_{out}^* for various $Ru(NH_3)_{2x}(bpy)_{3-x}{}^{3+/2+}$ couples where $x = 0$–3 have recently been made.[10] These are listed in Table I along with the corresponding values of ΔG_{out}^*(calcd) calculated by using the Marcus model which treats the surrounding solvent as a dielectric continuum.[10] The values of $\Delta S_{\text{rc}}^\circ$ for these ruthenium couples have also been determined[2,9] and are given in Table I[12] along with the corresponding values of $\Delta S_{\text{rc}}^\circ$(calcd) calculated by using the dielectric-continuum Born model.[13,14]

It is seen that the increasing values of ΔG_{out}^* that are observed as the smaller ammonia ligands replace bipyridine in the ruthenium coordination sphere are also associated with markedly increasing values of $\Delta S_{\text{rc}}^\circ$. This is not surprising since greater changes in solvent polarization are required for electron transfer as the effective radii of the reactants decrease.[1,10] The dielectric-continuum estimates of ΔG_{out}^*(calcd) and $\Delta S_{\text{rc}}^\circ$(calcd) are seen to be in broad agreement with the corresponding experimental parameters. However, it is interesting to note that there is substantially better agreement between ΔG_{out}^* and ΔG_{out}^*(calcd) than between $\Delta S_{\text{rc}}^\circ$ and $\Delta S_{\text{rc}}^\circ$(calcd). This behavior may be related to the fact that ΔG_{out}^*(calcd) is mainly determined by the optical dielectric constant ϵ_{op}[1] rather than by the static dielectric constant ϵ_s. The latter determines the value of $\Delta S_{\text{rc}}^\circ$(calcd).[13] It is known that ϵ_{op} is much less sensitive to solvent structure than is ϵ_s, so that any breakdown in the validity of the dielectric continuum model of ion–solvent interactions caused by alteration in solvent structure in the vicinity of the solute is likely to affect ΔG_{out}^* to a much smaller extent than $\Delta S_{\text{rc}}^\circ$.

Most other outer-sphere exchange reactions involve significant changes in metal–ligand bond distances so that the

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(6) (a) Powell, R. E.; Latimer, W. M. *J. Chem. Phys.* **1951**, *19*, 1139. (b) Cobble, J. W. *Ibid.* **1953**, *21*, 1446.
(7) It should be noted that neither $\bar{S}^\circ$ nor $\Delta S_{\text{rc}}^\circ$ can be obtained without resort to at least one extrathermodynamic assumption.[2,4]
(8) With this approach, values of $\Delta S_{\text{rc}}^\circ$ can be obtained that are probably trustworthy to 1–2 cal $\text{deg}^{-1}\ \text{mol}^{-1}$.
(9) Yee, E. L.; Weaver, M. J., to be submitted for publication.
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(11) The effective or equivalent radius, a, of a reactant is taken as equal to half of the cube root of the product of the diameters along the three L–M–L axes.[10]
(12) Although the values of $\Delta S_{\text{rc}}^\circ$ quoted in Tables I and II were obtained at ionic strength $\mu = 0.1$ M, they were found to be essentially independent of μ over the range $0 < \mu < 0.2$ M. For $\mu > 0.2$ M, gradual decreases of $\Delta S_{\text{rc}}^\circ$ with increasing μ are observed,[2] presumably arising from an increasing extent of ion pairing.
(13) Noyes, R. M. *J. Am. Chem. Soc.* **1962**, *84*, 513.
(14) Calculated from the formula[13] $\Delta S_{\text{rc}}^\circ = 9.65(Z_{\text{ox}}^2/\bar{a}_{\text{ox}} - Z_{\text{red}}^2/\bar{a}_{\text{red}})$ cal $\text{deg}^{-1}\ \text{mol}^{-1}$, where Z_{ox} and Z_{red} are the charges on and $\bar{a}_{\text{ox}}$ and $\bar{a}_{\text{red}}$ are the equivalent radii of the oxidized and reduced species, respectively.

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Table I. Comparison between Activation Free Energies for Some Ruthenium(III)–Ruthenium(II) Self-Exchange Reactions and the Reaction Entropies for Corresponding Redox Couples at 25 °C

exchange reacn	$\bar{a}$,[a] Å	ΔG_{out}^*,[b] kcal mol^{-1}	ΔG_{out}^*(calcd),[c] kcal mol^{-1}	$\Delta S_{rc}°$,[d] cal deg^{-1} mol^{-1}	$\Delta S_{rc}°$ (calcd),[e] cal deg^{-1} mol^{-1}
$Ru(bpy)_3^{3+/2+}$	6.8	3.4	3.3	1	7.0
$Ru(NH_3)_2(bpy)_2^{3+/2+}$	5.6	4.0	4.0	6.5	8.6
$Ru(NH_3)_4(bpy)^{3+/2+}$	4.4	5.1	5.1	12.5	10.9
$Ru(NH_3)_5(py)^{3+/2+}$	3.8	5.8	5.9	17	12.6
$Ru(NH_3)_6^{3+/2+}$	3.3	7.3	6.8	18.5	14.6

[a] Equivalent radius of reacting cation,[11] taken from ref 10. [b] Outer-shell (solvent) contribution to the activation free energy for the self-exchange reaction. Obtained from $\Delta G_{out}^* = RT(\ln Z - \ln k_{ex}) - \Delta G_{in}^* - w_r$, where Z is the collision frequency for the particular pair of reactants, k_{ex} is the observed rate constant, ΔG_{in}^* is the inner-shell contribution, and w_r is the electrostatic work required to form the collision complex from the separated reactants. Data taken from Table IV of ref 10. See also footnote 15. [c] Outer-shell contribution calculated from Marcus' theory;[1] taken from Table IV of ref 10. [d] Reaction entropy of redox couple, taken from ref 2 and 9 (obtained at ionic strength $\mu = 0.1$ M). [e] Reaction entropy of redox couple, calculated from the Born model[13] noting that $\Delta\bar{a} = (\bar{a}_{red} - \bar{a}_{ox}) \approx 0$.[14]

Table II. Comparison between Kinetic Parameters for Selected Outer-Sphere Self-Exchange Reactions and Reaction Entropies for Corresponding Redox Couples at 25 °C

exchange reacn	k_{ex},[a] M^{-1} s^{-1}	$\Delta G_\lambda^‡$,[b] kcal mol^{-1}	$\Delta S_{rc}°$,[c] cal deg^{-1} mol^{-1}
$Cr(OH_2)_6^{3+/2+}$	~2 × 10^{-7} (1.0)[16]	~24	50
$V(OH_2)_6^{3+/2+}$	1.5 × 10^{-2} (2.0)[18]	17.4	37
$Fe(OH_2)_6^{3+/2+}$	4 (0.55)[19]	13.8	43
$Ru(OH_2)_6^{3+/2+}$	~60 (1.0)[5]	~12	36
$Ru(NH_3)_6^{3+/2+}$	3 × 10^3 (0.1)[10]	8.2	18.5
$Ru(en)_3^{3+/2+}$	3 × 10^3 (0.1)[10]	8.9	13
$Ru(bpy)_3^{3+/2+}$	4 × 10^8 (0.1)[20]	3.4	1[9]
$Co(en)_3^{3+/2+}$	8 × 10^{-5} (1.0)[21]	20.4	38
$Co(sep)^{3+/2+}$ [d]	5 (0.2)[22]	14.4	19
$Co(bpy)_3^{3+/2+}$	~20 (0.1)[23]	13.4	22

[a] Rate constant for acid-independent self-exchange pathway, obtained from indicated data sources. Ionic strengths are given in parentheses. [b] Free energy of reorganization for the self-exchange reaction, corrected for the electrostatic work required to form the collision complex. See footnote 15 for details of calculation. [c] Reaction entropy of redox couple, obtained at (or extrapolated to) ionic strength $\mu = 0.1$ M. Data from ref 2, unless otherwise indicated. [d] sep = sepulchrate.

inner-shell reorganization energy ΔG_{in}^* forms a sizable component of ΔG_λ^*. This is particularly true of $M(OH_2)_6^{3+/2+}$ reactions, and some reactions of this type are listed in Table II. This table also includes values of k_{ex}, ΔG_λ^*, and $\Delta S_{rc}°$ for a number of other 3+/2+ redox couples containing ammine, ethylenediamine, or bipyridine ligands.[15] Complexes containing the first two ligands, in particular, form an interesting comparison with the aquo complexes since all three ligands are of comparable size so that the outer-shell terms ΔG_{out}^* should be similar. These data are also presented in Figure 1 as a plot of $\Delta S_{rc}°$ vs. ΔG_λ^*.

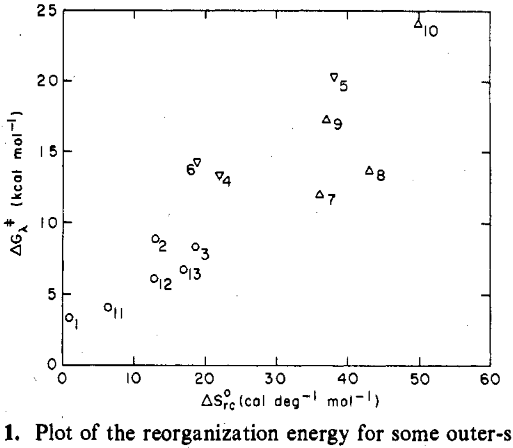

Figure 1. Plot of the reorganization energy for some outer-sphere self-exchange reactions (calculated according to footnote 15) vs. the reaction entropy $\Delta S_{rc}°$ for the redox couples. Key to symbols: (1) $Ru(bpy)_3^{3+/2+}$, (2) $Ru(en)_3^{3+/2+}$, (3) $Ru(NH_3)_6^{3+/2+}$, (4) $Co(bpy)_3^{3+/2+}$, (5) $Co(en)_3^{3+/2+}$, (6) $Co(sep)^{3+/2+}$, (7) $Ru(OH_2)_6^{3+/2+}$, (8) $Fe(OH_2)_6^{3+/2+}$, (9) $V(OH_2)_6^{3+/2+}$, (10) $Cr(OH_2)_6^{3+/2+}$, (11) $Ru(NH_3)_2(bpy)_2^{3+/2+}$, (12) $Ru(NH_3)_4(bpy)^{3+,2+}$, (13) $Ru(NH_3)_5(py)^{3+/2+}$.

Inspection of Table II and Figure 1 reveals that there is a general tendency of $\Delta S_{rc}°$ to increase along with ΔG_λ^*, although not surprisingly there is a considerable scatter in the individual points. For the aquo couples, the increasing values of $\Delta S_{rc}°$ as well as of ΔG_λ^* are broadly compatible with the conventional explanation which ascribes the latter changes to increasing values of the inner-shell contribution ΔG_{in}^*. Thus the $Cr(OH_2)_6^{3+/2+}$ exchange reaction involves transfer of an antibonding ϵ_g electron which is expected to require substantially larger changes in $\Delta\bar{a}$ than the $Ru(OH_2)_6^{3+/2+}$, $Fe(OH_2)_6^{3+/2+}$, and $V(OH_2)_6^{3+/2+}$ exchange reactions which involve transfer of a nonbonding t_{2g} electron. Indeed, the $Cr(OH_2)_6^{3+/2+}$ reaction exhibits the largest values of both ΔG_λ^* and $\Delta S_{rc}°$. However, substantial differences in ΔG_λ^*, which do not correlate in any simple way with $\Delta S_{rc}°$, are observed between the $Ru(OH_2)_6^{3+/2+}$, $Fe(OH_2)_6^{3+/2+}$, and $V(OH_2)_6^{3+/2+}$ reactions. Of these aquo couples, $\Delta\bar{a}$ has been directly determined by using crystallographic data only for $Fe(OH_2)_6^{3+/2+}$; the substantial value of 0.14 Å was obtained.[24] This value of $\Delta\bar{a}$ leads to a calculated value of k_{ex} that is in good agreement with the measured value for the $Fe(OH_2)_6^{3+/2+}$ system.[25] The slightly larger $\Delta\bar{a}$ value expected for $V(OH_2)_6^{3+/2+}$ on the basis of structural data[26] is consistent with its slower exchange rate[28] but is not reflected in $\Delta S_{rc}°$

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(15) Obtained by using $\Delta G_\lambda^* = RT(\ln Z - \ln k_{ex}) - w_r$, where Z is the collision frequency for the particular pair of reactants and w_r is the electrostatic work required to form the collision complex.[10] If the preequilibrium rather than the collision model is used, then Z should be replaced by $(8\pi N\bar{a}^3/3000)\nu_n$, where ν_n is the appropriate nuclear frequency.[10]

(16) Estimated from rates of outer-sphere cross reactions having small driving forces involving $Cr(OH_2)_6^{3+/2+}$ by using the Marcus cross relation.[17]

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(26) From ref 27, for six-coordinate $V^{3+/2+}$, the difference in ionic radii is 0.15 Å; for six-coordinate $Fe^{3+/2+}$, this difference is 0.14 Å, in good agreement with $\Delta\bar{a}$ for $Fe(OH_2)_6^{3+/2+}$.[24]

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for this couple. One factor complicating the interpretation of the results for the aquo redox couples is the lack of information concerning the coordination numbers of many of the ions of interest. Thus one possible explanation for the vanadium results is that the reduction of V(III) to V(II) is accompanied by an increase in the number of bound water molecules (including those held by hydrogen bonding). Such a change is sterically reasonable in view of the large ionic radius of V^{2+} (~0.8 Å[27]) and would result in an additional contribution to ΔG_λ^* and a smaller value of $\Delta S_{rc}°$, as is observed. Similarly, Cr(II) is highly Jahn–Teller distorted and the water molecules in the axial positions of the hydrated ion are very weakly held. As a consequence, the reduction of Cr(III) to Cr(II) will be accompanied by a decrease in the number of bound water molecules and this could in part be responsible for the large values of both ΔG_λ^* and $\Delta S_{rc}°$. A more detailed discussion of these effects must await the results of EXAFS studies which are currently in progress.[29] Fortunately calculations of the electronic coupling matrix elements indicate that corrections for nonadiabaticity are not large for the aquo redox couples considered.

The data in Table II and Figure 1 reveal that a dependence of ΔG_λ^* upon $\Delta S_{rc}°$ is also obtained for nonaquo redox couples. Thus both ΔG_λ^* and $\Delta S_{rc}°$ are markedly larger for $Co(en)_3^{3+/2+}$ than for $Ru(en)_3^{3+/2+}$; similar differences are also seen between $Co(bpy)_3^{3+/2+}$ and $Ru(bpy)_3^{3+/2+}$. It is likely that the larger values of $\Delta S_{rc}°$ for the cobalt couples are related to their larger $\Delta\bar{a}$ values;[30,31] the latter also account for the larger values of ΔG_{in}^* and hence of ΔG_λ^* for these systems.[32] Since the cobalt(III) complexes are low-spin $^1A_1$ while the cobalt(II) complexes are high-spin $^4T_1$, $\Delta S_{rc}°$ for the cobalt couples contains a small entropy contribution (3 cal deg^{-1} mol^{-1}) arising from the spin multiplicity change accompanying the electron transfer. A similar contribution is not present in the ruthenium systems since the ruthenium(III) and ruthenium(II) complexes are all low spin, and consequently no spin multiplicity change accompanies the electron transfer. Another consequence of the spin multiplicity change in the cobalt system is nonadiabaticity (that is, κ, the probability of electron transfer within the activated complex, is <1; nonadiabaticity increases the apparent value of ΔG_λ^* since ΔG_λ^* includes a term $-RT \ln \kappa$). It has been estimated[32] that κ for the $Co(NH_3)_6^{3+/2+}$ exchange reaction is $\sim 10^{-4}$. If a similar factor applies to the $Co(en)_3^{3+,2+}$ exchange reaction, ΔG_λ^* for the ethylenediamine couple should be decreased by about 5 kcal mol^{-1}. Although this correction is appreciable (and reduces the scatter in Figure 1), substantial differences between the cobalt and ruthenium systems remain even after corrections for spin multiplicity.

The differences in $\Delta S_{rc}°$ for $Fe(OH_2)_6^{3+/2+}$, $Ru(OH_2)_6^{3+/2+}$, and $Ru(NH_3)_6^{3+/2+}$ have recently been used to provide an estimate of $\Delta\bar{a} \approx 0.1$ Å for $Ru(OH_2)_6^{3+/2+}$.[5] The accuracy of this estimate depends upon the extent to which $\Delta S_{rc}°$ for the aquo couples differs from similar ammine couples due to the hydrogen-bonding ability of the aquo ligands.[2] Taking $\Delta\bar{a}$ for the $Fe(OH_2)_6^{3+/2+}$ couple as 0.14 Å, the empirical entropy correlation of Powell and Latimer[6a] predicts that $\Delta S_{rc}°$ should only be ca. 10 cal deg^{-1} mol^{-1} lower for an analogous aquo couple for which $\Delta\bar{a} = 0$. However, $\Delta S_{rc}°$ for the $Ru(NH_3)_6^{2+,3+}$ couple ($\Delta\bar{a} = 0.04$ Å[32]) is 25 cal deg^{-1} mol^{-1} smaller than for $Fe(OH_2)_6^{3+/2+}$ (Table II). Most likely, therefore, hydrogen-bonding effects do contribute to $\Delta S_{rc}°$ for the aquo couples.

Despite the complexities, there appears to be a consistent correlation between ΔG_λ^* and $\Delta S_{rc}°$ for the outer-sphere exchange reactions considered here. The apparent simplicity of this correlation is somewhat deceiving since a number of factors contribute to $\Delta S_{rc}°$ that may not always affect ΔG_λ^* in a similar way. Nevertheless, on the basis of the present survey the correlation seems well worth pursuing further, both as a means of estimating $\Delta\bar{a}$ and hence ΔG_{in}^* and as a means of gaining further clues as to the nature of the solvent rearrangement process required for the electron transfer.[33]

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Registry No. $Cr(OH_2)_6^{3+}$, 14873-01-9; $Cr(OH_2)_6^{2+}$, 20574-26-9; $V(OH_2)_6^{3+}$, 21374-21-0; $V(OH_2)_6^{2+}$, 15696-18-1; $Fe(OH_2)_6^{3+}$, 15377-81-8; $Fe(OH_2)_6^{2+}$, 15365-81-8; $Ru(OH_2)_6^{3+}$, 30251-72-0; $Ru(OH_2)_6^{2+}$, 30251-71-9; $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(en)_3^{3+}$, 21393-87-3; $Ru(en)_3^{2+}$, 21393-86-2; $Ru(bpy)_3^{3+}$, 18955-01-6; $Ru(bpy)_3^{2+}$, 15158-62-0; $Co(en)_3^{3+}$, 14878-41-2; $Co(en)_3^{2+}$, 23523-25-3; $Co(sep)^{3+}$, 72496-77-6; $Co(sep)^{2+}$, 63218-22-4; $Co(bpy)_3^{3+}$, 19052-39-2; $Co(bpy)_3^{2+}$, 15878-95-2; $Ru(NH_3)_2(bpy)_2^{3+}$, 55266-15-4; $Ru(NH_3)_2(bpy)_2^{2+}$, 56993-98-7; $Ru(NH_3)_4(bpy)^{3+}$, 69799-61-7; $Ru(NH_3)_4(bpy)^{2+}$, 54194-87-5; $Ru(NH_3)_5(py)^{3+}$, 33291-25-7; $Ru(NH_3)_5(py)^{2+}$, 21360-09-8.

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On the Study of a Mixed-Valence Hemin Dimer

Sir:

Hematins such as μ-oxo-bis[(tetraphenylporphinato)iron(III)] [$(TPPFe)_2O$] are antiferromagnetically coupled oxo-bridged dimers containing high-spin iron(III).[1] The similar, but not isoelectronic, nitrido-bridged dimer $(TPPFe)_2N$ is a mixed-valence iron(III,IV) system which behaves as a simple one electron per dimer paramagnet.[1-4] Interest in these systems has been stimulated by the electron-transfer role of hemes in the biological electron-transport chain.[1]

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