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TECHNICAL REPORT NO. 3

ENTROPIC AND ENTHALPIC CONTRIBUTIONS TO THE SOLVENT DEPENDENCE OF THE THERMODYNAMICS OF TRANSITION-METAL REDOX COUPLES

I. COUPLES CONTAINING AROMATIC LIGANDS

by

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Measurements of the formal potentials E_f for $Cr(bpy)_3^{3+/2+}$, $Fe(bpy)_3^{3+/2+}$, $Co(\ \ y)_3^{3+/2+}$, and $Co(phen)_3^{3+/2+}$ (where bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline) were evaluated as a function of temperature using cyclic voltammetry in eight solvents (water, dimethylsulfoxide, N-N-dimethylformamide, N-methylformamide, formamide, propylene carbonate, acetonitrile, and nitromethane) in order to unravel the various structural influences of the solvent

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upon the redox thermodynamics of such simple redox couples where the oxidized and reduced forms have identical structures and the composition of the coordination shell remains unchanged when the solvent is varied. The reaction entropies ΔS°_{rc} for each redox couple in each solvent were evaluated from the temperature dependence of E_f using a nonisothermal cell arrangement. Estimates of the free energy of transfer for each redox couple $\Delta(\Delta G^{\circ}_{rc})^{s-w}$ from water to each nonaqueous solvent were obtained from the difference in E_f relative to the corresponding differences for the ferricinium-ferrocene couple. The corresponding enthalpies of transfer $\Delta(\Delta H^{\circ}_{rc})^{s-w}$ were obtained by combining these values of ΔS°_{rc} and $\Delta(\Delta G^{\circ}_{rc})^{s-w}$. Substantially larger values of ΔS°_{rc} were found for all four redox couples in nonaqueous solvents compared to water, particularly in aprotic media where for a given couple $\Delta(\Delta S^{\circ}_{rc})^{s-w}$ $\sim$20-40 cal deg^{-1}mol^{-1}. Markedly larger values of ΔS°_{rc} in each solvent were found for the Co(III)/(II) couples compared with the low spin Cr(III)/(II) and Fe(III)/(II) couples. These entropic variations appear to reflect the ease by which solvent molecules are able to be oriented by the additional field around the oxidized compared to the reduced forms of the redox couple. Small negative values of $\Delta(\Delta G^{\circ}_{rc})^{s-w}$ were typically obtained as a result of partial compensation of the entropic terms by the corresponding enthalpic components. The utility of reaction entropy measurements for interpreting the dependence of electron transfer kinetics upon the nature of the solvent is pointed out.

Introduction

Variations in the solvent medium are generally expected to yield profound changes in the thermodynamics and kinetics of electron transfer reactions. The origins of the observed solvent effects are frequently manifold, arising from alterations in the chemical nature of the reacting species as well as the reactant-solvent interactions in both the ground reactant and transition states. This diversity of possible influences can severely hamper the fundamental understanding of the observed effects for both homogeneous and electrochemical redox reactions. Thus, the effects of solvent substitution upon the electrode kinetics of substitutionally labile cations can arise from changes in the composition of the coordination shell, which may often yield large variations in the inner-shell (metal-ligand reorganization) as well as the outer-shell (solvent reorganization) contribution[1] to the overall activation energy required for electron transfer. Also, the atom transfer reactions [e.g., $Cd^{2+} + 2e^- \rightleftharpoons Cd(Hg)$] that have been commonly employed to study solvent effects in electrode kinetics have the further disadvantage that the structure and location of the transition state is ill-defined. Consequently, the observed solvent dependence of the kinetics for such systems will inevitably contain a number of contributions that cannot be separated by experimental means. For these reasons, we have embarked on a systematic study of solvent effects upon the electrode kinetics and thermodynamics of redox couples involving *substitutionally inert* cations where the oxidized and reduced species are both stable in the solution phase and differ only by one electron. These couples have the general form

$$M^{III}L'_mL''_n + e^- \text{(metal electrode)} \rightleftharpoons M^{II}L'_mL''_n \tag{1}$$

where M is a transition metal, especially ruthenium, cobalt, iron, or chromium, and L' and L" are neutral or anionic ligands, especially saturated amines and aromatic chelates such as polypyridines. The use of these reactant systems allows the effects of varying the solvent to be investigated while keeping the composition of the inner coordination shell constant; the observed solvent effects upon the redox kinetics are then expected to be due entirely to variations in the outer-shell contributions. In addition, for a number of such redox couples it is possible to obtain accurate measurements of the formal electrode potentials E_f as well as electrochemical rate constants in a range of solvents which enables experimental separations to be made between the so-called "intrinsic" and "thermodynamic" contributions to redox reactivity.[2-4]

Although not an essential part of this approach, it is also instructive to obtain estimates of the changes in the standard Galvani metal-solution potential difference $\Delta(\phi_m^\circ)^{S_1-S_2}$ corresponding to the measured changes in E_f, $\Delta E_f^{S_1-S_2}$, for a given redox couple between pairs of solvents S_1 and S_2. This is because $-F\phi_m^\circ$ equals $(\bar{G}_{red}^\circ - \bar{G}_{ox}^\circ)$, where $\bar{G}_{red}^\circ$ and $\bar{G}_{ox}^\circ$ are the partial molal free energies of the reduced and oxidized species, respectively. For convenience, we shall term $(\bar{G}_{red}^\circ - \bar{G}_{ox}^\circ)$ the "reaction free energy" of the redox couple ΔG_{rc}°. The change in ΔG_{rc}° resulting from substituting solvent S_2 by solvent S_1 will be

$$\begin{aligned}\Delta(\Delta G_{rc}^\circ)^{S_1-S_2} &= -F\Delta(\phi_m^\circ)^{S_1-S_2} \\ &= -F[\Delta E_f^{S_1-S_2} - \Delta\phi_{lj}^{S_1-S_2}] \qquad (2)\end{aligned}$$

where $\Delta\phi_{lj}^{S_1-S_2}$ is the change in the liquid junction potential between the working and reference compartments which is brought about by substituting solvent S_1 by S_2.

The quantity $\Delta(\Delta G^\circ_{rc})^{S_1-S_2}$ is of fundamental interest for simple redox couples (eqn (1)) since it provides a measure of the relative changes in solvation energy of the reduced versus the oxidized forms as the solvent is varied: the correlation of values of $\Delta(\Delta G^\circ_{rc})^{S_1-S_2}$ for a series of solvents S_1 with their physical properties should provide valuable information on the variations in the reactant-solvent interactions (the "medium effect"[5] for a redox couple). Although the estimation of $\Delta\phi_{lj}^{S_1-S_2}$ and hence $\Delta(\Delta G^\circ_{rc})^{S_1-S_2}$ requires an extrathermodynamic assumption, there are a number of routes now available by which such transfer free energies can be obtained to a reasonable approximation (probably within 1-2 kcal mol^{-1} [5]). Recently, solvent effects upon the formal potentials for a number of substitutionally inert redox couples have been reported which demonstrate the importance of specific reactant-solvent interactions to the redox thermodynamics.[6-10]

In addition, in order to understand the solvent structural factors influencing $\Delta(\Delta G^\circ_{rc})^{S_1-S_2}$ it is desirable to evaluate the entropic and enthalpic components $\Delta(\bar{S}^\circ_{red} - \bar{S}^\circ_{ox})^{S_1-S_2}$ $[=\Delta(\Delta S^\circ_{rc})^{S_1-S_2}]$ and $\Delta(\bar{H}^\circ_{red} - \bar{H}^\circ_{ox})^{S_1-S_2}$ $[=\Delta(\Delta H^\circ_{rc})^{S_1-S_2}]$, respectively. Although the evaluation of these latter two quantities will also require some sort of extrathermodynamic assumption, we have recently pointed out that reliable *absolute* estimates of $(\bar{S}^\circ_{red} - \bar{S}^\circ_{ox})$ $[=\Delta S^\circ_{rc}]$ in a given solvent may be obtained from the temperature dependence of the formal potential for the redox couple using a nonisothermal cell arrangement.[11] These so-called "reaction entropies" are of particular interest since they are sensitive to the difference in the extent of solvent polarization ("ordering") in the vicinity of the solute induced by the reduced and oxidized forms of the redox couple.[11] Striking variations in ΔS°_{rc} have been observed in aqueous media by altering the nature of the ligands, even for couples of the same charge type and comparable size, which provides strong evidence of the sensitivity of the extent of solvent polarization to the net charge and ligand composition of transition-metal complexes.[11,12] Consequently, the evaluation of reaction entropies as a systematic function of the structure of the metal redox center, the ligands and the solvent should provide a valuable means of evaluating the role of reactant-solvent interactions in the reorganizational barrier to outer-sphere electron transfer. Indeed, we have shown that there is a close parallel between the magnitude of the free energy barrier to outer-sphere electron exchange of a number of transition metal redox couples in aqueous solution and the corresponding reaction entropies.[13]

In the present paper, estimates of $\Delta(\Delta G^\circ_{rc})^{S_1-S_2}$, $\Delta(\Delta S^\circ_{rc})^{S_1-S_2}$, and $\Delta(\Delta H^\circ_{rc})^{S_1-S_2}$ for the transfer of $Fe(bpy)_3^{3+/2+}$, $Cr(bpy)_3^{3+/2+}$, $Co(bpy)_3^{3+/2+}$, and $Co(phen)_3^{3+/2+}$ (bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline) from water to seven nonaqueous solvents are reported on the basis of the solvent dependence of the formal potentials relative to those for the ferricinium-ferrocene couple, combined with the reaction entropies for these redox couples determined in each solvent. The nonaqueous solvents selected were dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N-methylformamide (NMF), formamide, propylene carbonate (PC), acetonitrile, and nitromethane. All these solvents have relatively good ionizing properties, yet they have widely varying basicities and degrees of "internal order" (i.e., bulk liquid structure arising from association between solvent molecules[14]), so that the possible influence of such factors upon the redox thermodynamics can be explored systematically. Polypyridine redox couples were selected for several reasons. The polypyridine ligands should provide an "insulating shield" around the central metal cation, and are not expected to interact strongly with the solvent so that dielectric continuum treatments may provide a reasonable description of the solute-solvent interactions. Indeed, these couples have been widely employed as inert outer-sphere reagents for homogeneous redox kinetics in aqueous media, and are anticipated to provide valuable model systems for investigating outer-shell solvent effects upon electrochemical as well as homogeneous electron transfer rates. Some measurements of the solvent dependence of E_f for $Fe(phen)_3^{3+/2+}$ and related couples[9] suggested that $\Delta(\Delta G^\circ_{rc})^{S_1-S_2}$ may be quite small for such systems. It is therefore of interest to ascertain if such behavior, if confirmed for the other couples, is found for the structurally more sensitive entropic component $\Delta(\Delta S^\circ_{rc})^{S_1-S_2}$, and also to test the ability of the conventional dielectric continuum treatments to predict the magnitudes of these thermodynamic quantities. The comparison between $Fe(bpy)_3^{3+/2+}$, $Cr(bpy)_3^{3+/2+}$, and $Co(bpy)_3^{3+/2+}$ is of particular interest for exploring the influence of the electronic structure of the metal center upon the redox thermodynamics. Thus the iron and chromium couples involve electron transfer into a t_{2g} orbital,[15] so that the charge should be extensively delocalized around the bipyridine rings via back bonding with the empty Π-orbitals on the ligand[16]. The cobalt couple involves the transition $t_{2g}^6 \rightarrow t_{2g}^5 e_g^2$[15] so that the added electron will be localized at the metal center and the cobalt-nitrogen bond distances will be substantially increased in the lower oxidation state.[16] Markedly larger values of ΔS°_{rc} have been seen in aqueous media for $Co(bpy)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ (both 22 e.u. for ionic strength $\mu = 0.05$ [11]) compared with those for the low spin couples $Fe(bpy)_3^{3+/2+}$, $Fe(phen)_3^{3+/2+}$, and $Ru(bpy)_3^{3+/2+}$ (2, 3, and 1 e.u., respectively, for $\mu = 0.05 - 0.1$ [11,12]); these effects have been attributed to differences in the extent of orientation of water molecules in the vicinity of the polypyridine rings.[11,12] It is therefore of interest to ascertain if such electronic structural effects upon S°_{rc} are obtained in other solvents.

A study of the dependence upon the solvent of the redox thermodynamics of transition-metal couples containing ammine and ethylenediamine ligands is reported in the following article.[17]

Experimental

Most solvents were Aldrich "Gold Label" grade and were used either following further drying with molecular sieves and vacuum distillation, or as received. The water content typically was $<0.05\%$ as determined by Karl Fischer titration. Water was purified by "pyrodistillation".[11] $Cr(bpy)_3(ClO_4)_3$ was prepared (cf. ref. 18) by electrolyzing an aqueous solution containing 50m<u>M</u> Cr^{3+} and 50m<u>M</u> $HClO_4$ over a stirred mercury pool held at -1100 mV. vs. a saturated calomel electrode (s.c.e.) to form Cr^{2+}. This solution was then transferred using a gas-tight syringe to a deoxygenated suspension of 2,2'-bipyridine in aqueous 10m<u>M</u> $HClO_4$. The resulting black suspension of $Cr(bpy)_3(ClO_4)_2$ was bubbled with oxygen for one hour to yield a yellow precipitate of $Cr(bpy)_3(ClO_4)_3$ which was filtered, washed with ethanol and water, and dried in a vacuum dessicator. $Co(bpy)_3(ClO_4)_2$, $Co(phen)_3(ClO_4)_2$, and $Fe(bpy)_3(ClO_4)_2$ were prepared using standard procedures.[15,19]

The formal potentials E_f for each redox couple were obtained using cyclic voltammetry by bisecting the cathodic- and anodic-going peak potentials. Either the oxidized or the reduced form of the redox couple was present in the bulk solution, as convenient, usually at a concentration of 1m<u>M</u>. Sweep rates in the range 50-200 mV sec^{-1} were typically employed;

reversible or quasi-reversible behavior was normally obtained using platinum, glassy carbon or mercury electrodes in that the cathodic-anodic peak separations were typically 60-80 mV. About 25 m<u>M</u> of bipyridine or phenanthroline was added (as appropriate) in order to inhibit dissociation of the reduced complexes in solution. The absence of significant dissociation was confirmed from the equality of the anodic and cathodic peak currents and the lack of a dependence of E_f upon the added ligand concentration. Anodic-cathodic cyclic voltammograms for the ferricinium-ferrocene couple using dissolved ferrocene yielded essentially reversible behavior as described in ref. 18. Ferricinium picrate was employed in aqueous media due to the limited solubility of ferrocene.[20] The derived values of E_f were usually reproducible to within 1-2 mV. [The actual values of E_f will generally differ slightly from the experimental estimates due to the inequality of the diffusion coefficients for the oxidized and reduced species.[11] However, this difference is generally small (2-3 mV) and, most importantly, is similar for all the systems studied here so that it generally cancels when differences in E_f are considered, as in the present work.] For some systems, particularly with $Co(bpy)_3^{3+/2+}$, larger peak separations (90-100 mV) were obtained, presumably resulting from slow electrode kinetics so that the derived values of E_f were known only approximately (±5-10 mV) under these circumstances. A conventional two-compartment cell was employed, with the reference compartment (in which was immersed a commercial s.c.e.) separated from the working compartment by means of a glass frit ("very fine" grade, Corning, Inc.). For most measurements, the working and reference compartments were filled with the same solution so that the solvent junction was formed between aqueous KCl and the solvent of interest at the fiber tip separating the reference compartment and the reference electrode itself. Values of the reaction entropy ΔS°_{rc} were obtained from the temperature derivative of E_f with the reference electrode held at room temperature. The thermal junction between the "hot" and "cold" regions of the electrolyte was formed within the reference compartment so that the solvent liquid junction was maintained at room temperature and therefore did not affect dE_f/dT. As explained in detail in ref. 11, such measurements yield ΔS°_{rc} directly since it is very likely that the thermal junction potentials are negligible, so that $\Delta S^\circ_{rc} = F(d\phi^\circ_m/dT) = F(dE_f/dT)$. Evidence in support of this assertion was obtained from the observation that the resulting values of ΔS°_{rc} were essentially independent of the ionic strength μ and composition of the electrolyte contained in the thermal junction region,[20] at least within the experimental reproducibility (±0.5-1 e.u.). The temperature of the working compartment was varied over as wide a range as practicable (usually 30-60 deg. C); the slopes $F(dE_f/dT)$ and hence ΔS°_{rc} were found to be nearly independent of temperature (within ±1 e.u.)

Other experimental details were essentially the same as described in ref. 11.

Results

Table I summarizes the formal potentials E_f obtained for $Cr(bpy)_3^{3+/2+}$, $Fe(bpy)_3^{3+/2+}$, $Co(bpy)_3^{3+/2+}$, and $Co(phen)_3^{3+/2+}$ in 0.1 $\underline{M}$ $LiClO_4$ in each solvent at 25°C quoted relative to the corresponding values of E_f for ferricinium/ferrocene (Fc^+/Fc), along with the corresponding reaction entropies ΔS°_{rc}. The formal potentials for Fc^+/Fc are also given in Table I, quoted versus an aqueous s.c.e. Estimates of the change in $(\bar{G}^\circ_{red} - \bar{G}^\circ_{ox})$ for the polypyridine redox couples resulting from substituting the various nonaqueous solvents for water, $\Delta(\Delta G^\circ_{rc})^{s-w}$, were obtained from the corresponding values of ΔE_f^{s-w} using eqn (2). A common extrathermodynamic approach for obtaining the required values of $\Delta\phi_{lj}^{s-w}$ has been to assume that $\Delta\phi_{lj}^{s-w}$ equals the measured values of ΔE_f^{s-w} for the Fc^+/Fc couple, $(\Delta E_f)_{Fc}^{s-w}$; i.e., that $\Delta(\Delta G^\circ_{rc})^{s-w}$ for the Fc^+/Fc couple, $\Delta(\Delta G^\circ_{rc})_{Fc}^{s-w}$, equals zero.[5] The validity of this "ferrocene assumption" has been questioned; on the balance of the presently available evidence[5] it appears that a more reliable extrathermodynamic method is the so-called "tetraphenylarsonium-tetraphenylborate" (TATB) assumption which is based on the assertion that the transfer free energies ΔG°_t for the Ph_4As^+ and Ph_4B^- ions are equal.[5] Nevertheless, the values of $(\Delta E_f)_{Fc}^{s-w}$ can still provide a straightforward route to the evaluation of $\Delta\Phi_{lj}^{s-w}$ and hence $\Delta(\Delta G^\circ_{rc})^{s-w}$ on the TATB scale if the appropriate values of $\Delta(\Delta G^\circ_{rc})_{Fc}^{s-w}$ on this scale are known. Fortunately, the required values of $\Delta(\Delta G^\circ_{rc})_{Fc}^{s-w}$ for most solvents can be easily obtained from the differences in the apparent values of ΔG°_t for a given ion that have been obtained using the ferrocene and TATB assumptions. Extensive data tabulations of ΔG°_t have been assembled for Ag^+ transfer,[5] from which the estimates of $\Delta(\Delta G^\circ_{rc})_{Fc}^{s-w}$ listed in Table I can be obtained. (See Notes to Table I for details). Since from eqn (2) we can write

$$F\Delta\phi_{1j}^{s-w} = F(\Delta E_f)_{Fc}^{s-w} + \Delta(\Delta G^\circ_{rc})_{Fc}^{s-w} \qquad (3)$$

the required values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ for a given redox couple can be obtained from

$$\Delta(\Delta G^\circ_{rc})^{s-w} = F(\Delta E_f)_{Fc}^{s-w} - F\Delta E_f^{s-w} + \Delta(\Delta G^\circ_{rc})_{Fc}^{s-w}$$

$$= -F\Delta(E_f^{Fc})^{s-w} + \Delta(\Delta G^\circ_{rc})_{Fc}^{s-w} \qquad (4)$$

where $\Delta(E_f^{Fc})^{s-w}$ is the change in the formal potential for the redox couple of interest (versus those for the Fc^+/Fc couple) resulting from substituting another solvent for water.

The appropriate values of $\Delta(E_f^{Fc})^{s-w}$ were obtained from the formal potentials listed in Table I, and inserted into eqn (4) along with the corresponding estimates of $\Delta(\Delta G^\circ_{rc})_{Fc}^{s-w}$ to yield values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ for the four $M^{III/II}$ polypyridine couples that are given in Table II. [The estimates of $\Delta(\Delta G^\circ_{rc})_{Fc}^{s-w}$ used in eqn (4) are also given in Table II, along with literature sources]. Values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ obtained by assuming that $\Delta(\Delta G^\circ_{rc})_{Fc}^{s-w} = 0$, i.e., by using the ferrocene rather than the TATB assumption, are listed in parentheses in Table II.

The corresponding variations in ΔS°_{rc} when changing from water to other solvents, $\Delta(\Delta S^\circ_{rc})^{s-w}$, were obtained directly from the values of ΔS°_{rc} given in Table I and are also listed in Table II. The corresponding enthalpies of transfer $\Delta(\Delta H^\circ_{rc})^{s-w}$ that are also given in Table II were obtained from the relation $\Delta(\Delta H^\circ_{rc})^{s-w} = \Delta(\Delta G^\circ_{rc})^{s-w} + T\Delta(\Delta S^\circ_{rc})^{s-w}$.

Formal potential measurements were also made at varying electrolyte concentrations in the range 0.025 - 0.2 M, and in tetraethylammonium perchlorate as well as lithium perchlorate electrolytes. However, the values of ΔS°_{rc} were found to be essentially independent of ionic strength

(1 e.u.). Also, the variations in E_f with ionic strength for the M(III)/(II) polypyridine couples were found to be approximately the same (within 2-3 mV) as those for the Fc^+/Fc couple; consequently the derived values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ are essentially independent of the electrolyte concentration, at least on the ferrocene scale.

Discussion

The data presented in Tables I and II exhibit three interesting features. Firstly, the values of ΔS°_{rc} are markedly larger in nonaqueous solvents compared to water, especially in aprotic media where $\Delta(\Delta S^\circ_{rc})^{s-w} \sim 20\text{-}40$ e.u. Secondly, there consistently is an approximate compensation between $\Delta(\Delta S^\circ_{rc})^{s-w}$ and $\Delta(\Delta H^\circ_{rc})^{s-w}$ so that the values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ are uniformly small and negative in the range 0 to -3 kcal mol^{-1} for all four polypyridine couples on the basis of the TATB assumption employed here. Thirdly, although the absolute values of ΔS°_{rc} for the Co(III)/(II) couples are 15-20 e.u. larger than for $Cr(bpy)_3^{3+/2+}$ and $Fe(bpy)_3^{3+/2+}$ (Table I), the values of $\Delta(\Delta S^\circ_{rc})^{s-w}$ in a given solvent are approximately the same for all four polypyridine couples (Table II).

The simplest theoretical treatment of such outer-shell solvent effects is to utilize the Born dielectric continuum theory. It is well known that this model yields estimates of solvation free energies and entropies for simple monatomic cations that are often in substantial disagreement with experiment, undoubtedly due in large part to the extensive short-range solvent order induced by such uncoordinated ions.[21] The Born model might be expected to be more applicable to the estimation of $\Delta(\Delta G^\circ_{rc})^{s-w}$ for the present systems since the polypyridine ligands should act to shield somewhat the solvent from the metal cation, and several complicating factors may cancel out in the measured difference of transfer free energies between the oxidized and reduced forms. The Born estimates of $\Delta(\Delta G^\circ_{rc})^{s-w}$ can be obtained from[21]

$$\Delta(\Delta G^\circ_{rc})^{s-w}_{Born} = \frac{e^2N}{2}\left(\frac{1}{\varepsilon_w} - \frac{1}{\varepsilon_s}\right)\left(\frac{Z^2_{ox}}{r_{ox}} - \frac{Z^2_{red}}{r_{red}}\right) \qquad (5)$$

where ε_w and ε_s are the (static) dielectric constants in water and the non-aqueous solvent, Z_{ox} and Z_{red} are the charges on the oxidized and reduced species, r_{ox} and r_{red} are the corresponding radii, e is the electronic charge, and N is Avogadro's Number. Calculations using radii appropriate for the M(III)/(II) polypyridines ($r_{ox} \approx 6.8$ Å[22]) yielded values of $\Delta(\Delta G^\circ_{rc})^{s-w}_{Born}$ for the various solvents here that lie in the range -1.5 to 1 kcal mol^{-1}. Bearing in mind that the experimental values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ are probably trustworthy only to within ca 1 kcal mol^{-1} due to the likely uncertainties in the TATB assumption,[5] the agreement can be considered to be reasonable.

The comparison between the experimental and Born estimates of the reaction entropies is of greater interest since it enables the applicability of the Born model to be tested in a *single* solvent. The Born estimates of ΔS°_{rc} are given by

$$(\Delta S^\circ_{rc})_{Born} = \frac{e^2N}{2\varepsilon T}\left(\frac{d\ \ln\ \varepsilon}{d\ \ln\ T}\right)\left(\frac{Z^2_{ox}}{r_{ox}} - \frac{Z^2_{red}}{r_{red}}\right) \qquad (6)$$

Values of $(\Delta S^\circ_{rc})_{Born}$ calculated from eqn (6) for $r_{ox}=r_{red}=6.8$ Å are given for each solvent in Table I (see notes to Table I for sources of ε). The experimental values of ΔS°_{rc} are seen to be typically in marked disagreement with the corresponding Born predictions $(\Delta S^\circ_{rc})_{Born}$. A milder test of the Born model is to compare the observed solvent dependence of ΔS°_{rc}, $(\Delta S^\circ_{rc})^{s-w}$, with the corresponding differences in $(\Delta S^\circ_{rc})_{Born}$, $\Delta(\Delta S^\circ_{rc})^{s-w}_{Born}$.

Fig. 1 contains plots of $\Delta(\Delta S^{\circ}_{rc})^{s-w}$ against $\Delta(\Delta S^{\circ}_{rc})^{s-w}_{Born}$. It is seen that a rough correlation between these quantities is obtained, although there is considerable scatter and the average slope is somewhat larger than the predicted value of unity.

These comparisons suggest that a substantial part of the observed values of ΔS°_{rc} in the various solvents arise from extensive short-range polarization in the higher oxidation state which is partly dissipated upon reduction, this factor being superimposed upon the milder long-range cation-solvent interactions which are more likely to be described successfully by the Born dielectric continuum model. Thus typically $\Delta S^{\circ}_{rc} > (\Delta S^{\circ}_{rc})_{Born}$ (Table I), indicating that the enhancement of solvent polarization ("ordering") in the tripositive versus the dipositive oxidation states is in most cases greater than predicted from macroscopic dielectric considerations, probably as a result of dielectric saturation in the vicinity of the solute. The Born model also fails to account for the markedly larger values of ΔS°_{rc} seen for $Co(bpy)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ compared with $Cr(bpy)_3^{3+/2+}$ and $Fe(bpy)_3^{3+/2+}$ in each solvent.

In recent years there have been a number of attempts to provide more successful treatments of ion solvation, either by modifications to the Born model[23] or by the development of fundamentally new approaches.[24] However, most effort has been devoted to the utilization of these treatments for the estimation of solvation free energies in aqueous solution, and little attention has been paid to the estimation of solvation entropies, particularly in nonaqueous media.[25] It has been found that reasonable agreement with experimental solvation entropies for monatomic cations in various aprotic solvents can be obtained using a modified Born model where the first solvation layer was assumed to be dielectrically saturated.[25] Direct application of this approach to the present systems does indeed yield estimates of ΔS°_{rc} that are larger than $(\Delta S^{\circ}_{rc})_{Born}$ and in some cases closer to the experimental values. However, it is uncertain that the model is entirely appropriate to the present systems where the first solvation sphere is occupied by the coordinated ligands, and in any case it is unable to account for the observed variations of ΔS°_{rc} with the metal spin state or the small values of ΔS°_{rc} seen in hydrogen-bonded solvents. More sophisticated solvation treatments which take into account the molecular structure of the polar solvent[24] should ultimately yield accurate descriptions of the experimental results. However, these models in their present form are not entirely applicable to the present systems since neither chemical interactions between the complexes and their immediate environment nor dielectric saturation effects are fully taken into account.[24] Such effects should should provide an important influence upon the redox thermodynamic parameters considered here since these quantities reflect the *change* in solvent polarization resulting from decreasing the solute charge from +3 to +2. The remaining discussion will therefore be concerned with the utilization of more "intuitive chemical" approaches for rationalizing the experimental behavior.

The uniformly positive values of $\Delta(\Delta S^{\circ}_{rc})^{s-w}$ indicate that the increase of the metal oxidation state from +2 to +3 yields a relatively greater enhancement in the extent of solvent polarization ("ordering") in the vicinity of the complex for nonaqueous solvents compared with the same process in water. Such differences can be simply explained by the unusually high degree of internal order exhibited by liquid water. Thus the additional cationic charge carried by the oxidized compared to the reduced form of the redox couple will generate a greater degree of solvent polarization in the vicinity of the solute in solvents having a smaller degree of internal order due to the relative ease by which solvent molecules can be disturbed from their bulk orientation in response to the electric field. Indeed, Criss and Salomon[14,26] have pointed out that the ionic entropy $\bar{S}^\circ_+$ of a given univalent cation in various solvents generally becomes increasingly negative as the degree of internal order of the solvent decreases, suggesting that a major factor contributing to $\bar{S}^\circ_+$ is the extent to which the cation can induce additional solvent order within its vicinity. The decreases in $\bar{S}^\circ_+$ found for the transfer of a given cation from water to other solvents have been found to be determined predominantly by a characteristic "a" parameter for each solvent, the value of "a" becoming more negative as the internal order of the solvent decreases.[14,26] If the same factors that determine $\bar{S}^\circ_+$ also influence the values $\bar{S}^\circ_{ox}$ relative to $\bar{S}^\circ_{red}$ for the M(III)/(II) polypyridine couples, it would be expected that $\Delta(\Delta S^\circ_{rc})^{s-w}$ would be linearly related to -a. Such a plot is given in Fig. 2. It is seen that there is indeed an approximate correlation between the values of $\Delta(\Delta S^\circ_{rc})^{s-w}$ for all four polypyridine couples (closed symbols) and -a. Thus relatively small values of $\Delta(\Delta S^\circ_{rc})^{s-w}$ ($\lesssim 15$ e.u.) are observed in formamide and NMF that are expected to be polymerized to some extent via hydrogen bonding.[14] Larger values of $\Delta(\Delta S^\circ_{rc})^{s-w}$ (20-40 e.u.) are seen for the aprotic solvents PC, DMSO, DMF, and acetonitrile which are expected to have relatively small degrees of internal order, and have sizable dipole moments which should encourage additional solvent ordering around M(III) compared to the corresponding M(II) polypyridine complexes via ion-dipole interactions. Parallel, although smaller, variations in $\Delta(\Delta S^\circ_{rc})^{s-w}$ are also seen for the Fc^+/Fc couple (open symbols) in Fig. 2. We have noted elsewhere that these variations provide a major contribution to the apparent breakdown of the ferrocene assumption for estimating free energies of single ion transfer.[20]

There is also the possibility that the observed solvent dependence of ΔS°_{rc} may arise from variations in the ability of the solvents to engage in donor-acceptor interactions with the M(III) state to a greater extent than with M(II). If this factor does indeed provide a major contribution to ΔS°_{rc}, then a correlation between $\Delta(\Delta S^\circ_{rc})^{s-w}$ and the donicity of the solvents would be expected. Although it is difficult to formulate quantitative scales which reflect the electron donating abilities (or basicity) of solvents, *one such* measure which has proved useful is the so-called Donor Number (D.N.).[27] Fig. 3 contains plots of $\Delta(\Delta S^\circ_{rc})^{s-w}$ against the values of D.N. quoted in Ref. 27. In contrast to Figs. 1 and 2, it is seen that there is a complete failure of the values of D.N. for the various solvents to correlate with $\Delta(\Delta S^\circ_{rc})^{s-w}$.

On the basis of Figs. 1-3, it therefore appears that the large changes in ΔS°_{rc} observed when the solvent is varied are primarily determined by the relative ability of the tripositive M(III) polypyridine complex compared to the corresponding M(II) species to disturb the bulk solvent structure and reorientate solvent molecules within its vicinity. The use of the macroscopic dielectric constant in the Born model presumes that such solvent polarization is minor. Nevertheless, it is interesting to note that at least qualitatively similar *variations* in ΔS°_{rc} with the nature of the solvent are predicted by the "a" parameter, and the simple Born treatment, inasmuch as the corresponding plots in Figs. 2 and 1 have similar shapes. This similarity reflects the interrelationship between the internal order of solvents and their macroscopic dielectric properties, and suggests that both these factors play a major role in determining the alterations in the degree of solvent ordering induced by M(III) vs. M(II) polypyridines as the solvent is varied. In contrast, the almost complete lack of a correlation between $\Delta(\Delta S^\circ_{rc})^{s-w}$ and the solvent Donor Number suggests that the changes in relative solvent polarization on the nature of solvent only depend to a minor extent, if at all, on the ability of the solvent to coordinate to the cationic solute. Although there may well be substantial variations in solvent polarization in the vicinity of the M(III) polypyridine complexes as the solvent is altered arising from variations in the solvent coordinative abilities, if present they appear to be largely compensated by similar changes for the corresponding M(II) complexes.

Nevertheless, the apparent sensitivity of ΔS°_{rc} to the symmetry of the orbital occupied by the reducing electron suggests that the extent of solvent polarization in the oxidized state relative to the corresponding reduced form in a given solvent is indeed sensitive to local, and presumably short-range, solvation factors. The strikingly smaller values of ΔS°_{rc} (1-4 e.u.) seen in aqueous solution for $Cr(bpy)_3^{3+/2+}$, $Fe(bpy)_3^{3+/2+}$ (Table I), $Fe(phen)_3^{3+/2+}$, and $Ru(bpy)_3^{3+/2+}$ [11,12] compared with the values for $Co(bpy)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ (22 e.u.) probably arise from the delocalization of the reducing t_{2g} electron around the aromatic rings for the Fe(III)/(II), Ru(III)/(II), and Cr(III)/(II) couples; this delocalization will be largely absent for the Co(III)/(II) couples which involve the electronic transition $t_{2g}^6 \rightarrow t_{2g}^5 e_g^2$. As noted previously,[11,12] this electron delocalization may influence ΔS°_{rc} by inducing an increase in solvent polarization in the vicinity of the aromatic rings in the reduced state compared with the oxidized form which will counteract the normal entropy increase resulting from the decrease in solvent polarization close to the metal redox center. Evidence supporting this contention includes the negative value of ΔS°_{rc} (-5 e.u.) found for Fc^+/Fc in aqueous solution.[12,20] The structure of Fc^+/Fc differs from the polypyridine couples in that the compact "sandwich" structure of the former couple should prevent the close approach of solvent molecules to the metal redox center that can occur along the channels formed by the more open polypyridine rings. Therefore the only major factor contributing to ΔS°_{rc} for the Fc^+/Fc couple is presumed to be the additional solvent polarization in the reduced state arising from the delocalization of the added ligand around the cyclopentadienyl rings, yielding a negative value of ΔS°_{rc}.[12]

As noted above, the values of ΔS°_{rc} for $Co(bpy)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ compared with those for $Cr(bpy)_3^{3+/2+}$ and $Fe(bpy)_3^{3+/2+}$ are also consistently 15-20 e.u. larger not only in water, but also in all seven nonaqueous solvents (Table I). This simple result is surprising; the tendency of the various solvents to be oriented by the delocalized electron might be expected to be dependent to some extent upon solvent properties such as the extent of internal order or the ability to act as an electron acceptor. However, the behavioral simplicity may be misleading in that it could arise from a fortuitous cancellation between several effects. Thus the degree of internal order of several of the solvents used here vary roughly with their expected tendency to act as electron acceptors as measured by the so-called "acceptor number".[27] The extent of solvent orientation induced near the aromatic ligands could remain similar when changing, for example, from water to DMF since both the degree of internal order and electron accepting ability of the solvent are thereby diminished.

The approximate compensation between corresponding values of $T\Delta(\Delta S^\circ_{rc})^{s-w}$ and $\Delta(\Delta H^\circ_{rc})^{s-w}$ yielding markedly smaller values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ (Table II) has often been observed for entropic and enthalpic quantities in electrolyte solutions.[28] Such a compensation is expected since the (entropically unfavorable) orientation of solvent molecules as a result of ion-dipole interactions, for example, would necessarily yield favorable enthalpic changes. Although $\Delta(\Delta G^\circ_{rc})^{s-w}$ is frequently close to zero, the values are typically negative (at least on the TATB scale) so that the entropic factors appear to provide the predominant influence upon the free energies of transfer.

Measurements of reaction entropies for the $Fe(phen)_3^{3+/2+}$ and related redox couples involving methyl substitution around the phenanthroline ring have been previously compared in acetonitrile and water.[29] The value of ΔS°_{rc} given for $Fe(phen)_3^{3+/2+}$ in acetonitrile (25 e.u., $\mu=0.1$[29]) is close to our value for $Fe(bpy)_3^{3+/2+}$ in this solvent (23 e.u., Table I). However, the value of ΔS°_{rc} reported in ref. 29 for $Fe(phen)_3^{3+/2+}$ in water (-20.5 e.u.) is markedly different to our previous determinations for $Fe(phen)_3^{3+/2+}$ and $Fe(bpy)_3^{3+/2+}$ (3 and 2 e.u., respectively, $\mu=0.05$ [11]). Since values of ΔS°_{rc} close to zero have also been given earlier for these and other low-spin M(III)/(II) polypyridine couples in aqueous solution,[30] the disparate value for $Fe(phen)_3^{3+/2+}$ quoted in ref. 29 is presumably in error. One possible source of this discrepancy is the confusion that can be caused by the indiscriminate use of alternative entropy scales without clearly identifying which scales are being employed. As pointed out in ref. 11, the values of ΔS°_{rc} obtained from a non-isothermal cell arrangement as employed here differ markedly from the frequently quoted "reaction entropies" ΔS°_H that actually refer to the overall entropy change for an electrochemical cell containing a hydrogen reference electrode; it can be shown that[12] $\Delta S^\circ_{rc} = \Delta S^\circ_H + 20.5$ e.u. Some, but not all, of the "reaction entropies" quoted in ref. 29 are actually values of ΔS°_H rather than ΔS°_{rc}.

We have recently observed that there is a consistent correlation between the reaction entropies of a number of redox couples and the (coulombic work-corrected) free energy of reorganization $\Delta G^\ddagger_{ex}$ for the corresponding homogeneous outer-sphere self-exchange reactions in aqueous media.[13] (In view of the close relationship between the energetics of homogeneous and electrochemical exchange processes,[1,31,32] a similar correlation is expected between ΔS°_{rc} and the standard electrochemical free energy of activation for the redox couples). These correlations are of particular interest for couples where the contribution to $\Delta G^\ddagger_{ex}$ from inner-shell reorganization (changes in metal-ligand bond distances and associated stereochemical differences between the oxidized and reduced forms) is small or constant, since the changes in $\Delta G^\ddagger_{ex}$ will then be determined only by the energy required to reorganize the surrounding solvent in order for electron transfer to occur.[1] It has been noted[13] that the substantially larger values (up to ca. 4 kcal mol^{-1}) of $\Delta G^\ddagger_{ex}$ resulting from the stepwise replacement of ammine for bipyridine ligands in $Ru(bpy)_3^{3+/2+}$ are paralleled by progressive increases in ΔS°_{rc} (up to ca. 18 e.u.). Since the inner-shell contributions to $\Delta G^\ddagger_{ex}$ are small for these systems,[13] the increases in both $\Delta G^\ddagger_{ex}$ and ΔS°_{rc} chiefly reflect the greater changes in solvent polarization in the vicinity of the smaller ammine ligands which need to occur in order to induce electron transfer. Such relationships should also provide a valuable means of unraveling the dependence of $\Delta G^\ddagger_{ex}$ for a given redox couple on the nature of the solvent, particularly since the inner-shell contribution to $\Delta G^\ddagger_{ex}$ should remain constant if the ligands remain unchanged. In view of the unexpectedly large increases in ΔS°_{rc} for the M(III)/(II) polypyridine couples in changing from water to nonaqueous media, it is of interest to ascertain if parallel increases in $\Delta G^\ddagger_{ex}$ for such low-spin polypyridine couples (and hence decreases in the rate constant k_{ex} for homogeneous self-exchange) also occur. The available data, although limited, do indeed bear out this expectation to some extent. Thus the values of k_{ex} for $Fe(phen)_3^{3+/2+}$ and related couples appear to be typically 1-2 orders of magnitude smaller in acetonitrile than in water.[33,34] These reactivity differences are not predicted by the conventional dielectric continuum model of electron transfer. Thus inserting the relevant dielectric constants into the usual expression for the outer-shell barrier to homogeneous self-exchange[35] (and assuming that the distance between the reacting centers in the transition state is twice the reactant radius of 6.8 Å[22]) yields the prediction that k_{ex} should be very similar in water and acetonitrile (about 20% larger in the latter solvent). On the basis of the above interpretation of the substantially (ca. 20 e.u.) larger values of ΔS°_{rc} for M(III)/(II) polypyridine couples in acetonitrile compared to aqueous media (Table II), it seems likely that the observed decreases in k_{ex} arise from the greater changes in short-range solvent polarization around the polypyridine complexes that are apparently required in order to induce electron transfer in acetonitrile.

Such differences suggest that substantial short-range solvent influences upon the magnitude of the outer-shell contribution to the reorganization barrier to outer-sphere electron transfer may often be expected; measurements of reaction entropies as a function of the solvent may well provide a valuable independent probe for detecting such effects. This approach is utilized for exploring the solvent dependence of the electrode kinetics of simple redox couples in a forthcoming article.[36]

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TABLE I. Formal Potentials and Reaction Entropies for M(III)/(II) Polypyridine and Ferricinium/Ferrocene Redox Couples in Various Solvents.

Solvent	$(\Delta S^o_{rc})_{Born}$[d]	$Cr(bpy)_3^{3+/2+}$		$Fe(bpy)_3^{3+/2+}$		$Co(bpy)_3^{3+/2+}$		$Co(phen)_3^{3+/2+}$		Fc^+/Fc	
		E_f^{Fc}[a]	ΔS^o_{rc}[b]	E_f^{Fc}[a]	ΔS^o_{rc}[b]	E_f^{Fc}[a]	ΔS^o_{rc}[b]	E_f^{Fc}[a]	ΔS^o_{rc}[b]	E_f[c]	ΔS^o_{rc}[b]
Water	7.1	-607	4	718	2	-57	22	18	22	127	-5
Formamide	3.7	-627	14	g	f	-86	28	-35	28	281	0
N-Methylformamide	5.6	-675	1[illegible]	f	f	-127	37.5	-72	34	397	4
Propylene Carbonate	7.2	-648	27	657	25	-92	46	-22	43	328	11
Acetonitrile	13.7	-650	29	670	23	-72	43	-15	42	342	11.5
Dimethylsulfoxide	9.1	~-690	f	g	f	h	h	-105	47.5	[illegible]	[illegible]
Dimethylformamide	15.9	-697	34	624	41.5	h	h	-85	48.5	[illegible]	[illegible]
Nitromethane	14.0	-600	32	727	42	-22	56	43	57.5	[illegible]	[illegible]

Notes for Table I

[a] Formal potential for redox couple in solvent given in far left column, using $0.1\underline{M}$ $LiClO_4$ as supporting electrolyte; quoted in mV. versus E_f for ferricinium/ferrocene couple in same electrolyte. Obtained using cyclic voltammetry (see text).

[b] Reaction entropy of redox couple in listed solvent obtained from temperature dependence of E_f using nonisothermal cell arrangement (see text for details). Units are cal. deg^{-1} mol^{-1}.

[c] Formal potential for ferricinium-ferrocene couple in $0.1\underline{M}$ $LiClO_4$, mV. versus s.c.e. immersed in same electrolyte unless otherwise noted.

[d] Reaction entropy for $M(bpy)_3^{3+/2+}$ couples (cal. deg^{-1} mol^{-1}) calculated from the Born model for each solvent (eqn. 5) using the radius $r = 6.8\mathring{A}$[22] and following literature sources for dielectric constants: formamide, DMF, NMF - S. J. Bass, W. I. Nathan, R. M. Meighan, R. H. Cole, J. Phys. Chem., 68, 509(1964); DMSO, acetonitrile - G. J. Janz, R. P. T. Tomkins, "Nonaqueous Electrolyte Handbook", Vol. I, Academic Press, N. Y., London, 1972; propylene carbonate - R. Payne, I. E. Theodorou, J. Phys. Chem., 76, 2892(1972); methanol - P. G. Sears, R. R. Holmes, L. R. Dawson, J. Electrochem. Soc., 102, 145(1955); nitromethane - C. P. Smyth, W. S. Walls, J. Chem. Phys., 3, 557(1935).

[e] Using cell arrangement s.c.e. $|0.1\underline{M}$ $LiClO_4(aq)||0.1\underline{M}$ $LiClO_4(solvent)|$Pt, C, Hg.

[f] Erratic Voltammetric behavior precluded measurement of ΔS^{o}_{rc}.

[g] Electrooxidation of background precluded determination of E_f.

[h] Highly irreversible behavior (cathodic-anodic peak separation $\gtrsim$(120mV.) precluded determination of E_f and ΔS^{o}_{rc}.

TABLE II. Free Energies (A), Enthalpies (B), and Entropies (C) of Transfer of M(III)/(II) Polypyridine Redox Couples from Water to Various Solvents, Calculated from Data in Table I (Free Energies and Enthalpies in kcal. mol^{-1}; Entropies in cal. deg^{-1} mol^{-1}).

Solvent	$Cr(bpy)_3^{3+/2+}$			$Fe(bpy)_3^{3+/2+}$			$Co(bpy)_3^{3+/2+}$			$Co(phen)_3^{3+/2+}$			Fc^+/Fc^* $-\Delta(\Delta G^o_{rc})^{s-w}_{Fc}$
	A	B	C	A	B	C	A	B	C	A	B	C	
Formamide	(0.5) -1.0	2.0	10				(0.6) -0.9	2.7	6	(1.2) -0.3	2.0	6	1.5
N-Methylformamide	(1.6) -0.4	4.1	15				(1.6) -0.4	4.3	15.5	(2.1) 0.1	3.7	12	2.0
Propylene Carbonate	(1.0) -1.0	5.9	23	(1.4) -0.6	6.3	23	(0.8) -1.2	6.0	24	(0.9) -1.1	5.2	21	2.0
Acetonitrile	(0.6) -2.9	4.6	25	(1.1) -2.4	3.9	21	(0.3) -3.2	3.1	21	(0.8) -2.7	3.3	20	3.5
Dimethylsulfoxide	(1.9) -0.6									(2.8) 0.3		25.5	2.5
Dimethylformamide	(2.0) -1.0	8.0	30	(2.4) -0.6	11.2	39.5				(2.4) -0.6	7.0	26.5	3.0
Nitromethane	(-0.2) -1.7	6.7	28	(-0.2) -1.7	10.3	40	(-0.8) -2.3	7.9	34	(-0.6) -2.1	8.5	35.5	1.5

Notes to Table II

A = Free energy of transfer of redox couple $\Delta(\Delta G^{o}_{rc})^{s-w}$ (kcal. mol^{-1}) from water to nonaqueous solvent listed. Obtained from formal potentials E_{f}^{Fc} for each redox couple versus Fc^{+}/Fc given in Table I using eqn.(4). Values in parentheses obtained by assuming that $\Delta(\Delta G^{o}_{rc})^{s-w}_{Fc} = 0$ (i.e. using ferrocene assumption); lower values obtained using estimates of $\Delta(\Delta G^{o}_{rc})^{s-w}_{Fc}$ given in far right-hand column (i.e. using TATB assumption - see text).

B = Enthalpy of transfer of redox couple $\Delta(\Delta H^{o}_{rc})^{s-w}$ (kcal. mol^{-1}) from water to nonaqueous solvent listed. Obtained from corresponding free energies (TATB scale) and entropies of transfer using $\Delta(\Delta H^{o}_{rc})^{s-w} = \Delta(\Delta G^{o}_{rc})^{s-w} + T\Delta(\Delta S^{o}_{rc})^{s-w}$.

C = Entropy of transfer of redox couple $\Delta(\Delta S^{o}_{rc})^{s-w}$ (cal. deg^{-1} mol^{-1}) from water to nonaqueous solvent listed. Obtained from differences between appropriate values of ΔS^{o}_{rc} listed for each solvent in Table I.

*Estimates of free energy of transfer for ferricinium-ferrocene couple (kcal. mol^{-1}) from water to nonaqueous solvent listed. Obtained from difference in apparent values of transfer free energy ΔG^{o}_{t} of Ag^{+} from water to nonaqueous solvents using ferrocene and TATB assumptions. ΔG^{o}_{t} data for most solvents taken from compilation in Table 12.VI of reference 5; for nitromethane taken from R. Alexander, A. J. Parker, J. H. Sharp, W. E. Waghorne, J. Am. Chem. Soc., 94, 1148(1972); value given for N-methylformamide is estimated. Most values of $\Delta(\Delta G^{o}_{rc})^{s-w}_{Fc}$ quoted are probably accurate to within ca. ± 1 kcal. mol^{-1}.

Notes to Figures

Fig. 1.

Plots of $\Delta(\Delta S^{\circ}_{rc})^{s-w}$ for each polypyridine redox couple against the corresponding Born estimates $\Delta(\Delta S^{\circ}_{rc})^{s-w}_{Born}$ obtained from the values of $(\Delta S^{\circ}_{rc})_{Born}$ calculated for water and the appropriate nonaqueous solvent using eqn (6) (see text). Key to this and subsequent figures -- Redox couples: ● $Cr(bpy)_3^{3+/2+}$, ■ $Fe(bpy)_3^{3+/2+}$, ▲ $Co(bpy)_3^{3+/2+}$, ▼ $Co(phen)_3^{3+/2+}$, ○ Ferricinium/ferrocene. Solvents: 1, formamide; 2, N-methylformamide; 3, propylene carbonate; 4, dimethylsulfoxide; 5, dimethylformamide; 6, acetonitrile; 7, nitromethane.

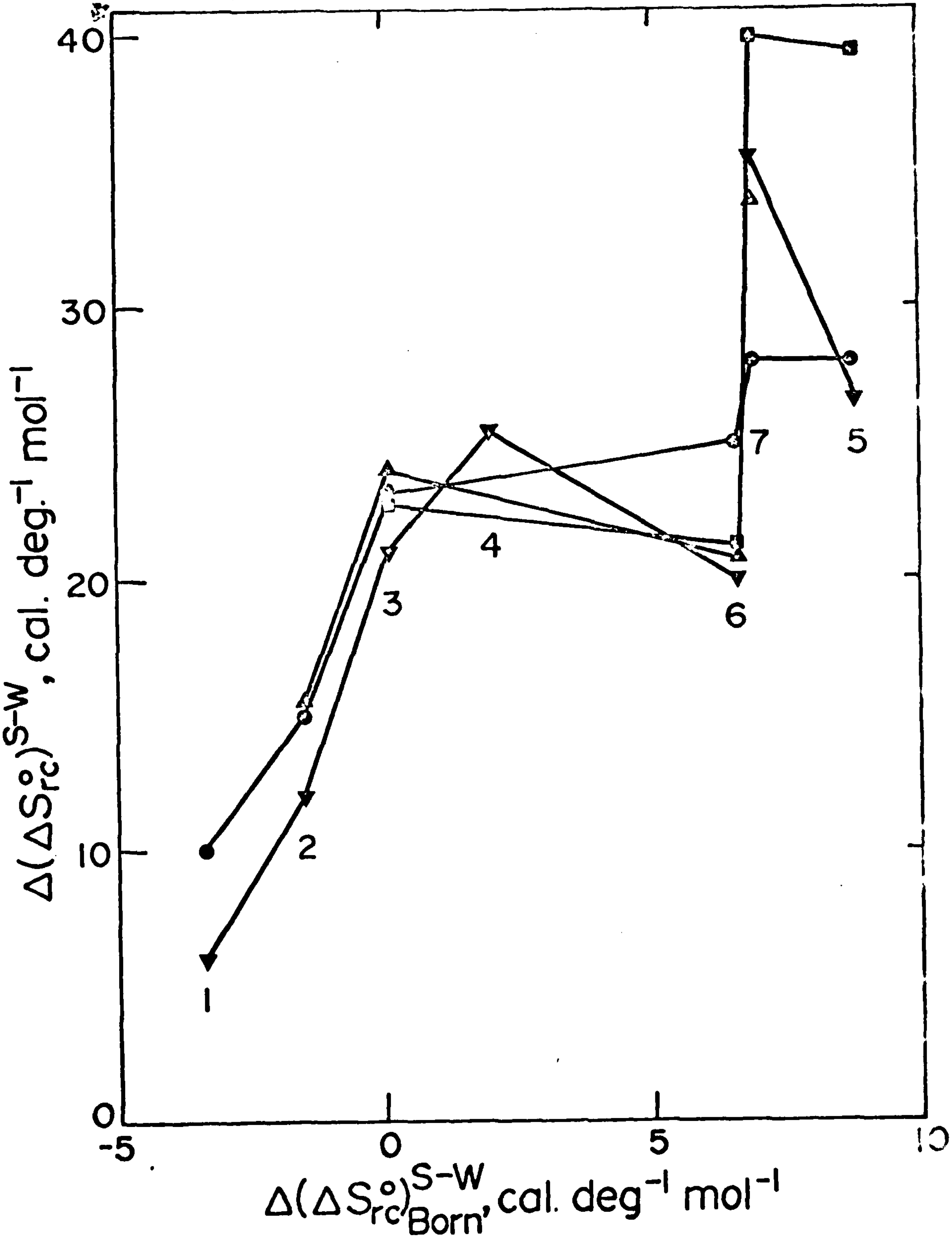
Fig. 2

Plots of the variation in the reaction entropy $\Delta(\Delta S^{\circ}_{rc})^{s-w}$ for a given polypyridine redox couple when changing from water to various nonaqueous solvents against -a, where "a" is a parameter related to the degree of "internal order" of each solvent.[14,26] Values of $\Delta(\Delta S^{\circ}_{rc})^{s-w}$ taken from Table II. The straight lines are drawn between adjacent points for a given redox couple in the various solvents. Key to redox couples and solvents as in notes to Fig. 1.

Fig. 3

Plots of $\Delta(\Delta S^{\circ}_{rc})^{s-w}$ for each polypyridine redox couple against the "Donor Number" for the various nonaqueous solvents.[27] Key to redox couples and solvents as in notes to Fig. 1.

Fig 1



40
30
20
10
0
-5
0
5
10
1
2
3
4
5
6
7
$\Delta(\Delta S^{\circ}_{rc})^{S-W}$, cal. deg.$^{-1}$ mol^{-1}
$\Delta(\Delta S^{\circ}_{rc})^{S-W}_{Born}$, cal. deg^{-1} mol^{-1}

Fig 6

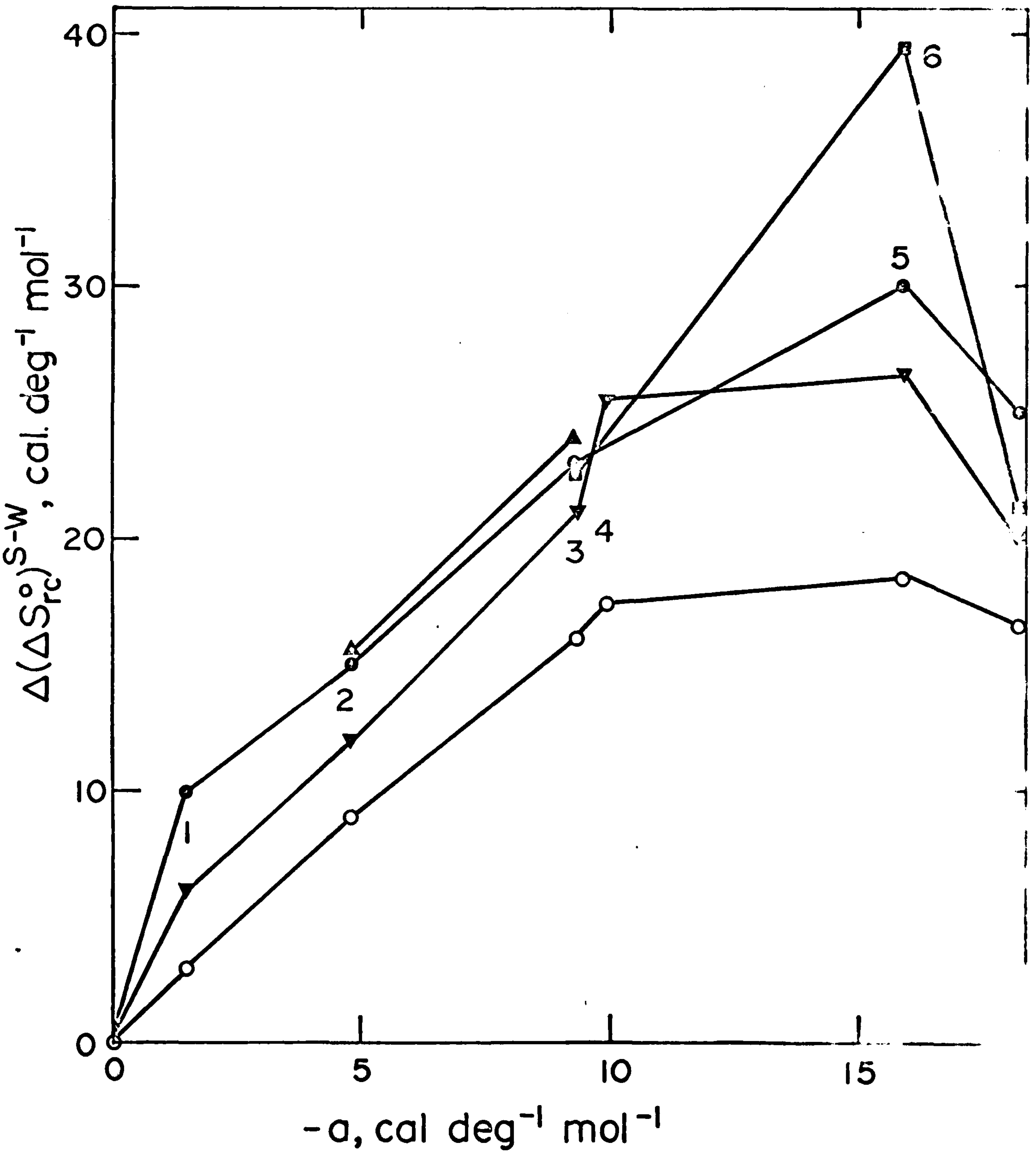
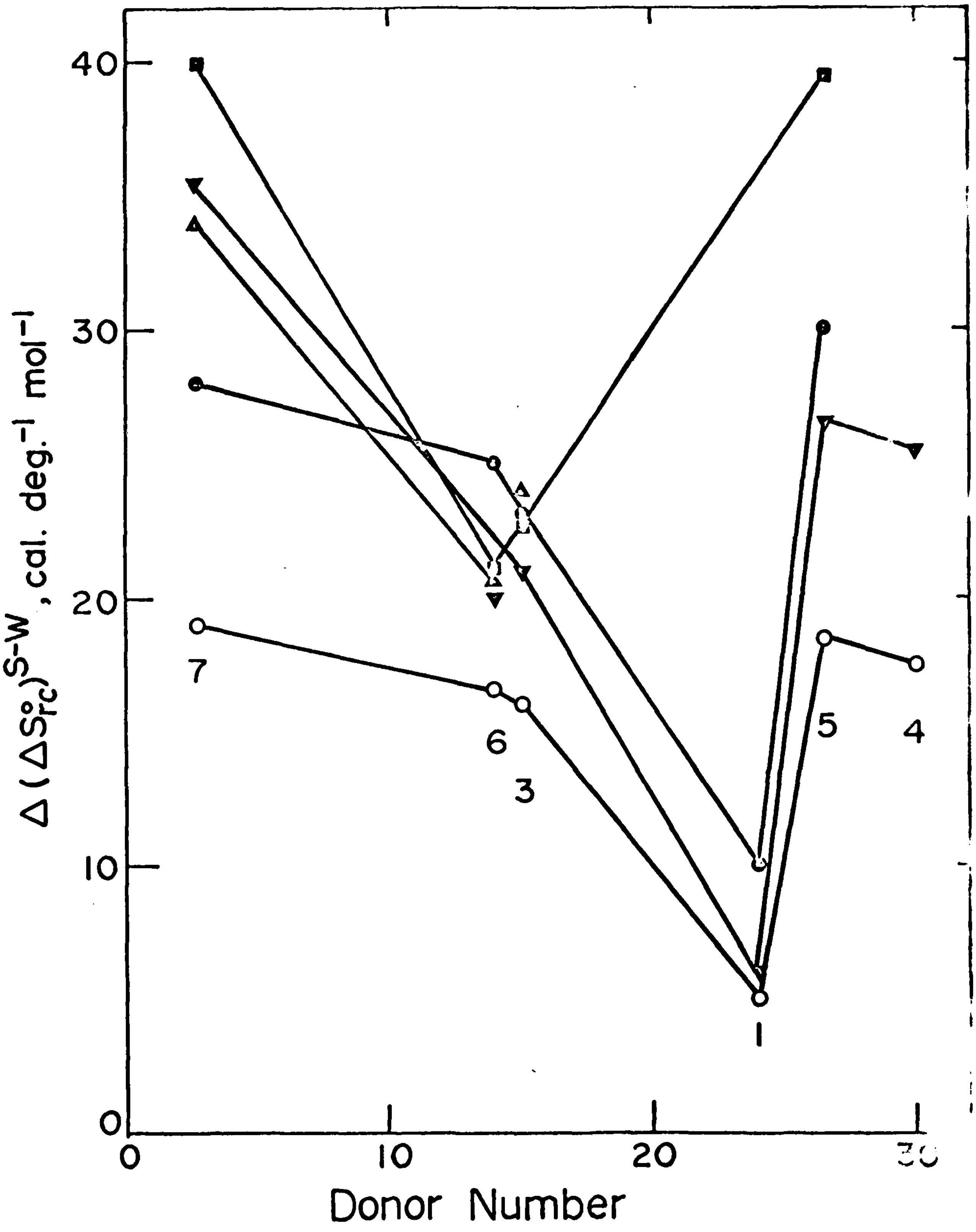

40
30
20
10
0
0
5
10
15
$\Delta(\Delta S^{\circ}_{rc})^{S-W}$, cal. deg^{-1} mol^{-1}
−a, cal deg^{-1} mol^{-1}
1
2
3
4
5
6

Fig 3


40
30
20
10
0
0
10
20
30
Donor Number
$\Delta(\Delta S^{\circ}_{rc})^{S\text{-}W}$, cal. deg.$^{-1}$ mol^{-1}
7
6
3
1
5
4

DATE
ILMED

8