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

II. COUPLES CONTAINING AMMINE AND ETHYLENEDIAMINE LIGANDS

by

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The formal potentials E_f for $Ru(NH_3)_6^{3+/2+}$, $Ru(en)_3^{3+/2+}$, $Co(en)_3^{3+/2+}$, and $Co(sep)^{3+/2+}$ (where en = ethylenediamine, sep = sepulchrate) were evaluate using cyclic voltammetry as a function of temperature in eight solvents (wate dimethylsulfoxide, N,N-dimethylformamide, N-methylformamide, formamide, propylene carbonate, acetonitrile, and nitromethane). Estimates of the

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transfer free energy of each redox couple from water to the nonaqueous solvents $\Delta(\Delta G^{\circ}_{rc})^{s-w}$ were made from the solvent dependence of E_f at 25°C, and values of the reaction entropy ΔS°_{rc} of the redox couples in each solvent were obtained from the temperature dependence of E_f using a nonisothermal cell arrangement. The values of $\Delta(\Delta G^{\circ}_{rc})^{s-w}$ vary over a wide range, from about -4 to 8 kcal mol^{-1}. These variations arise predominantly from the enthalpic component $\Delta(\Delta H^{\circ}_{rc})^{s-w}$ and correlate broadly with the electron-donating ability of the solvent as given by the Donor Number, suggesting that solvent-solute donor-acceptor interactions involving amine hydrogens in the oxidized form of the couple provide a major influence upon the redox thermodynamics. However, substantial positive values of $\Delta(\Delta S^{\circ}_{rc})^{s-w}$ were also observed (ca. 5-10 cal deg^{-1}mol^{-1}) which failed to correlate with the solvent Donor Number, instead increasing as the "internal order" of the bulk solvent decreases. These behavioral differences between the enthalpic and entropic contributions to $\Delta(\Delta G^{\circ}_{rc})^{s-w}$ appear to result from the tendency of the entropic term to reflect the extent of additional solvent orientation induced by the oxidized form of the redox couple, rather than the strength of the solvent-solute interactions involved.

Introduction

We have been examining the solvent dependence of the thermodynamics of simple transition-metal redox couples as part of an experimental program exploring the role of the solvent in the kinetics and thermodynamics of outer-sphere electron transfer reactions. One-electron redox couples containing substitutionally inert complexes form especially tractable systems for this purpose since the influence of variations in the "outer-shell" solvent contributions can be assessed separately from the "inner-shell" (metal-ligand coordination shell) effects. Our general approach is to determine the formal potential E_f of each redox couple in a range of solvents having suitably varied chemical and physical properties. In addition, the temperature dependence of E_f is monitored in each solvent using a nonisothermal cell arrangement, yielding values of the "reaction entropy" of the redox couple ~~ΔS°_{rc}~~ [ΔS°_{rc} equals the difference ~~$(\bar{S}^\circ_{red} - \bar{S}^\circ_{ox})$~~ between the "absolute" ionic entropies of the reduced and oxidized forms[2]. These measurements yield estimates of the free energy, entropy, and enthalpy of transferring the redox couple from water to other solvents, ~~labeled~~ $\Delta(\Delta G^\circ_{rc})^{s-w}$, $\Delta(\Delta S^\circ_{rc})^{s-w}$, and $\Delta(\Delta H^\circ_{rc})^{s-w}$, respectively.[1]

In the preceeding article, estimates of $\Delta(\Delta G^\circ_{rc})^{s-w}$, $\Delta(\Delta S^\circ_{rc})^{s-w}$, and $\Delta(\Delta H^\circ_{rc})^{s-w}$ were reported for various M(III)/(II) couples containing only polypyridine ligands.[1] Although the free energies of transfer $\Delta(\Delta G^\circ_{rc})^{s-w}$ were generally close to zero, large positive values of $\Delta(\Delta S^\circ_{rc})^{s-w}$ were obtained that reflect the extensive changes in solvent structure that are brought about by electron transfer, even though the large aromatic ligands might be expected to shield the solvent from the metal redox center.

It is of interest to extend these measurements to structurally similar redox couples containing other types of uncharged ligands in order to explore the possibility that specific ligand-solvent interactions could play an important role in determining the redox thermodynamics. Couples containing ammine or ethylenediammine ligands form an especially tractable class of systems for this purpose. Thus a variety of substitutionally inert complexes containing only these ligands can be prepared as anhydrous crystalline solids that are stable and structurally well defined. They engage invariably in outer-sphere electron transfer pathways since coordinated ammine and ethylenediammine ligands have no lone pairs available and therefore cannot act as bridging groups. However, these ligands are considerably smaller and more polar than the polypyridines, containing relatively acidic amine hydrogens which might be expected to interact specifically with surrounding solvent molecules, especially those having strong electron donating capability. Indeed, a recent study[3] of the solvent effects upon the formal potential for the $Co(en)_3^{3+/2+}$ couple (en = ethylenediamine) has shown that E_f becomes marked more negative (relative to "reference solute" redox couples such as ferricinium/ferrocene) with increasing basicity of the solvent as measured by the so-called "Donor Number" D. N.[4] These apparently large positive changes in ΔG°_{rc} $(=\bar{G}^\circ_{red} - \bar{G}^\circ_{ox})$ were interpreted in terms of an increasing stabilization of the oxidized species $Co(en)_3^{3+}$ relative to the reduced form $Co(en)_3^{2+}$ resulting from donor-acceptor interactions between the solvent and the relatively more acidic amine hydrogens in the tripositive complex.[3]

The evaluation of the entropic and enthalpic components to such free energies of transfer would clearly be of value for providing a deeper insight as to their origin. As for the M(III)/(II) polypyridine couples,[1] it is also of interest to compare the behavior of ammine and ethylenediamine redox couples having the same charge type and ligand composition, but differing in the electronic state of the central metal cation. The range of possible metal couples is limited in view of the relative instability and lability of ammine complexes with divalent oxidation states such as Co(II) and Cr(II). However, a number of Ru(III)/(II) amine couples, including $\mathrm{Ru(NH_3)_6^{3+/2+}}$ and $\mathrm{Ru(en)_3^{3+/2+}}$, are substitutionally inert in the divalent as well as trivalent oxidation states so that their redox thermodynamics may be studied in a range of solvents in the absence of added ligand. Although $\mathrm{Co(en)_3^{2+}}$ is labile, it is sufficiently stable in a range of solvents in the presence of small concentrations of free ethylenediamine so that $\mathrm{Co(en)_3^{3+/2+}}$ provides a suitably reversible couple *(vide infra)*. The comparison between the behavior of $\mathrm{Co(en)_3^{3+/2+}}$, $\mathrm{Ru(en)_3^{3+/2+}}$, and $\mathrm{Ru(NH_3)_6^{3+/2+}}$ is of particular interest since the reduction of Co(III) involves the electronic conversion $t_{2g}^6 \rightarrow t_{2g}^5 e_g^2$, whereas the reduction of Ru(III) involves the transformation $t_{2g}^5 \rightarrow t_{2g}^6$; these differences are reflected in a markedly greater expansion of the cobalt center upon reduction.[5]

In the present paper, measurements of the formal potentials and their temperature derivatives are reported for $\mathrm{Co(en)_3^{3+/2+}}$, $\mathrm{Ru(NH_3)_6^{3+/2+}}$, and $\mathrm{Ru(en)_3^{3+/2+}}$ in water, dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N-methylformamide (NMF), formamide, propylene carbonate (PC), acetonitrile, and nitromethane, and are used to obtain estimates of $\Delta(\Delta G^\circ_{rc})^{s-w}$, $\Delta(\Delta S^\circ_{rc})^{s-w}$, and $\Delta(\Delta H^\circ_{rc})^{s-w}$ for each redox couple. Experimental data are also given for the capped trisethylenediamine ("sepulchrate") couple $\mathrm{Co(sep)^{3+/2+}}$.[6,7] The sepulchrate system provides an interesting comparison to the trisethylenediamine and hexaammine couples since it is structurally rigid[6,7] and contains only one hydrogen coordinated to each amine nitrogen, compared to two and three hydrogens, respectively, for the latter two couples.

Experimental

The sources and purification of the solvents was as described in the preceding article.[1] $Co(en)_3(ClO_4)_3$ was prepared as described in ref. 8. $Ru(NH_3)_6(ClO_4)_3$ was recrystallized from the chloride salt (Matthey Bishop, Inc.). Samples of $Ru(en)_3Br_3$ were kindly supplied by Dr. Gilbert Brown, and $Co(sep)(ClO_4)_3$ was kindly provided by Prof. John Endicott. The formal potentials E_f were obtained using cyclic voltammetry by bisecting the cathodic and anodic peak potentials. $Ru(NH_3)_6^{3+/2+}$, $Ru(en)_3^{3+/2+}$, and $Co(sep)^{3+/2+}$ all yielded essentially reversible behavior (peak separations 60-70 mV) as expected from the substitution inertness of both oxidation states and the rapidity of their electron exchange. Since $Co(en)_3^{2+}$ is substitutionally labile, this species can dissociate in the absence of added ligand. However, it was found that only small concentrations of ethylenediammine (2-10m<u>M</u>) were required in order to prevent the dissociation of $Co(en)_3^{2+}$ produced in the cathodic segment of the cyclic voltammogram since equal cathodic and anodic peak currents were then obtained together with peak potential separations that were typically in the range ca. 60-90 mV. Measurements of E_f for $Ru(NH_3)_6^{3+/2+}$, $Ru(en)_3^{3+/2+}$, and $Co(sep)^{3+/2+}$ in acetonitrile and nitromethane were precluded by solubility restrictions; in addition, $Ru(en)_3^{3+/2+}$ yielded irreproducible and ill-defined cyclic voltammograms in several solvents which restricted further the useful data that could be obtained for this couple. Values of E_f were typically reproducible to within 2 mV. Measurements of E_f as a function of temperature employed nonisothermal cells as described in detail in refs. 1 and 2. Other experimental aspects were also essentially as given in refs. 1 and 2.

Results

In Table I are summarized the formal potentials E_f obtained for $Ru(NH_3)_6^{3+/2+}$, $Ru(en)_3^{3+/2+}$, $Co(en)_3^{3+/2+}$, and $Co(sep)^{3+/2+}$ in 0.1M $LiClO_4$ in each solvent at 25°C quoted relative to E_f for the ferricinium/ferrocene (Fc^+/Fc) couple in the same solution, along with the corresponding reaction entropies ΔS°_{rc}. The latter values were obtained from the temperature dependence of E_f using $\Delta S^\circ_{rc} = F(dE_f/dT)$.[1,2] Estimates of the change in $(\bar{G}^\circ_{red} - \bar{G}^\circ_{ox})$ for amine redox couples resulting from substituting the various nonaqueous solvents for water, $\Delta(\Delta G^\circ_{rc})^{s-w}$, were obtained from eqn (1) [eqn (4) of ref (1)]:

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

where $\Delta(E_f^{Fc})^{s-w}$ is the variation in E_f (relative to Fc^+/Fc) for a given redox couple resulting from changing from water to a given nonaqueous solvent and $\Delta(\Delta G^\circ_{rc})^{s-w}_{Fc}$ is the corresponding variation in ΔG°_{rc} for the Fc^+/Fc couple between the same two solvents. The use of the "ferrocene assumption" is tantamount to the assertion that $\Delta(\Delta G^\circ_{rc})^{s-w}_{Fc} = 0$.[1,9] Although this approach has often been followed, we prefer[1] instead to compute values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ based on the "tetraphenylarsonium-tetraphenylborate" (TATB) scale in view of its more likely validity.[9] Therefore the values of $\Delta(E_f^{Fc})^{s-w}$ obtained from the formal potentials in Table I were inserted into eqn (1) along with the corresponding estimates of $\Delta(\Delta G^\circ_{rc})^{s-w}_{Fc}$ on the TATB scale that are listed in Table II of ref. 1 (see this source for details) to yield the resulting estimates of $\Delta(\Delta G^\circ_{rc})^{s-w}$ for the various amine redox couples given in Table II. Estimates of $\Delta(\Delta G^\circ_{rc})$ based on the ferrocene scale [i.e., by assuming that $\Delta(\Delta G^\circ_{rc})^{s-w}_{Fc} = 0$] are listed in parentheses in Table II.

The corresponding variations in ΔS°_{rc} for a given amine redox couple, $(\Delta S^\circ_{rc})^{s-w}$, were obtained directly from the differences between the appropriate values of ΔS°_{rc} given in Table I, and are also listed in Table II along with the corresponding enthalpies of transfer $\Delta(\Delta H^\circ_{rc})^{s-w}$ that were obtained from the relation $\Delta(\Delta H^\circ_{rc})^{s-w} = \Delta(\Delta G^\circ_{rc})^{s-w} + T\Delta(\Delta S^\circ_{rc})^{s-w}$.

The values of the formal potentials E_f relative to Fc^+/Fc for all four amine couples were typically found to be approximately independent (within 5 mV or so) of the ionic strength μ in the range $\mu = 0.025 - 0.2$. The values of ΔS°_{rc} were also found to be essentially independent (±1 e.u.) of ionic strength within this range.

Discussion

Inspection of the data presented in Tables I and II reveals that substantial changes in the redox thermodynamics of ammine and ethylenediamine redox couples occur when the solvent is varied. Two main features are apparent. Firstly, the values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ vary over a wide range, from ca. -4 kcal mol^{-1} in nitromethane to around 8 kcal mol^{-1} in DMSO, the values being usually within ca. 0.5-1 kcal mol^{-1} for all four amine couples in a given solvent. Even larger variations in $\Delta(\Delta H^\circ_{rc})^{s-w}$ are seen (ca. -1.5 to 15 kcal mol^{-1}). The solvent sensitivity of $\Delta(\Delta G^\circ_{rc})^{s-w}$ contrasts with the behavior of the M(III)/(II) polypyridine couples, where the values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ were typically small and negative.[1] Secondly, the values of ΔS°_{rc} are uniformly and markedly larger in nonaqueous media compared with water, especially in aprotic solvents where $\Delta(\Delta S^\circ_{rc})^{s-w}$ approaches 30 e.u. Broadly similar values of $\Delta(\Delta S^\circ_{rc})^{s-w}$ have also been observed for the polypyridine couples[1], so that the differences in $\Delta(\Delta G^\circ_{rc})^{s-w}$ between the saturated amine and polypyridine couples are chiefly due to the enthalpic component $\Delta(\Delta H^\circ_{rc})^{s-w}$.

However, the values of ΔS°_{rc} in a given solvent are, as before,[1,2] sensitive to the nature of both the metal and the coordinated ligands.

It is instructive to compare the experimental values of $\Delta(\Delta G^\circ_{rc})^{s-w}$, ΔS°_{rc}, and $\Delta(\Delta S^\circ_{rc})^{s-w}$ with the corresponding predicted values from the dielectric continuum Born model $\Delta(\Delta G^\circ_{rc})^{s-w}_{Born}$, $(\Delta S^\circ_{rc})_{Born}$, and $\Delta(\Delta S^\circ_{rc})^{s-w}_{Born}$. These latter quantities can be obtained from[1]

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

and

$$(\Delta S^\circ_{rc})_{Born} = \frac{e^2N}{2\varepsilon T}\left(\frac{d\ \ln\ \varepsilon}{d\ \ln\ T}\right)\left(\frac{Z^2_{ox}}{r_{ox}} - \frac{Z^2_{red}}{r_{red}}\right) \qquad (3)$$

where ε is the dielectric constant in the appropriate 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. Values of $\Delta(\Delta G^\circ_{rc})^{s-w}_{Born}$ and $(\Delta S^\circ_{rc})_{Born}$ calculated from eqns (2) and (3) for $Z_{ox} = 3$, $Z_{red} = 2$, and $r_{ox} = r_{red} = 3.5$ Å (appropriate for the small amine couples[11]) are given in Tables II and I, respectively. (The literature sources of the dielectric constant data used here are given in Table I of ref. 1.)

Comparison of $\Delta(\Delta G^\circ_{rc})^{s-w}_{Born}$ with the corresponding experimental values $\Delta(\Delta G^\circ_{rc})^{s-w}$ (Table II) reveals, not unexpectedly, that the Born predictions are frequently in large and even qualitative disagreement with experiment. In particular, large positive values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ (ca. 5 - 8.5 kcal mol^{-1}) are observed for all four amine couples in the strongly basic solvents DMSO and DMF (D.N. = 29.8 and 26.6, respectively[4]) in contrast to the negative values of $\Delta(\Delta G^\circ_{rc})^{s-w}_{Born}$ predicted for these solvents (Table II). Nevertheless for the other five, less basic, nonaqueous solvents the values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ and $\Delta(\Delta G^\circ_{rc})^{s-w}_{Born}$ agree at least qualitatively and are indeed in close agreement for the weakly basic solvents propylene carbonate, acetonitrile, and nitromethane (D.N. = 15.1, 14.1 and 2.7, respectively[4]) for which negative values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ are observed (Table II). [Although these transfer free energies naturally rely upon the choice of water as the reference solvent, water also appears to be a relatively weak electron donor (D.N. ≈18 [4]).] These considerations therefore suggest that long-range solvation influences may provide an important part of the *additional* solvation energy for the oxidized versus the reduced forms of these redox couples, at least in solvents of low basicity where short-range solvent-solute interactions of the donor-acceptor type should be relatively weak.

However, if donor-acceptor interactions are instead providing the predominant contribution to the solvent-dependent redox thermodynamics of $Co(en)_3^{3+/2+}$, as suggested by Mayer et al[3], as well as for the other amine couples considered here, a linear correlation between the experimental values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ or $\Delta(\Delta H^\circ_{rc})^{s-w}$ and the solvent Donor Number (or a related measure of the solvent basicity) would be expected. Fig. 1 consists of such plots for $Co(en)_3^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$. [Similar plots were obtained for $Ru(en)_3^{3+/2+}$ and Co(s[illegible])$^{3+/2+}$ but are omitted for clarity.] It is seen that there is indeed a reasonably linear correlation for both $\Delta(\Delta G^\circ_{rc})^{s-w}$ and $\Delta(\Delta H^\circ_{rc})^{s-w}$ with the solvent D.N. for both couples in the six nonaqueous solvents for which Donor Numbers are available, although the values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ and $\Delta(\Delta H^\circ_{rc})^{s-w}$ in nitromethane are decidedly less negative than expected. A related plot of E_f for $Co(en)_3^{3+/2+}$ [measured versus the "reference solute" couple bisbiphenylchromium (I/0)] against D.N. for a number of nonaqueous solvents has previously shown by Mayer et al. to be approximately linear[3]. This result provided the chief basis for their assertion that donor-acceptor interactions between the solvent and the acidic amine hydrogens on $Co(en)_3^{3+}$ provided the prevailing contribution to the solvent influence upon the redox thermodynamics of $Co(en)_3^{3+/2+}$. Although the present data do not entirely contradict this conclusion, they suggest instead that such short-range interactions may be of predominant importance only with the more highly basic solvents. Nevertheless, the uniformly large positive values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ obtained in DMSO and DMF for the four amine couples in comparison with the small and negative corresponding values for the polypyridine couples that have no electron acceptor sites provides strong evidence for the importance of donor-acceptor interactions to the redox thermodynamics for the former systems.

However, the comparable values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ obtained for $Ru(NH_3)_6^{3+/2+}$, $Ru(en)_3^{3+/2+}$ and $Co(en)_3^{3+/2+}$, and $Co(sep)^{3+/2+}$ couples that contain eighteen, twelve, and six amine hydrogens, respectively, is somewhat surprising on this basis. One plausible explanation is that there is only one solvent molecule strongly coordinated to each amine center anyway as a consequence of electrostatic and steric limitations. Another surprising result is the apparent insensitivity of $\Delta(\Delta G^\circ_{rc})^{s-w}$ to the electronic structure of the metal center in the reduced state. For example, $Ru(en)_3^{3+/2+}$ and $Co(en)_3^{3+/2+}$ yield comparable values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ in both DMSO and DMF (Table II). This behavioral simplicity may well have some utility in that values of ΔE_f^{Fc} could presumably be predicted with some confidence for redox couples for which measurements of E_f are impractical [e.g. $Co(NH_3)_6^{3+/2+}$].

One inevitable difficulty in interpreting such experimental estimates of $\Delta(\Delta G^\circ_{rc})^{s-w}$ lies in the uncertainties inherent in the extrathermodynamic assumption required for their evaluation. Thus the values of $\Delta(\Delta G^\circ_{rc})^{s-w}$ based on the ferrocene scale (given in parentheses in Table II) are up to 3.5 kcal mol^{-1} larger than those based on the TATB scale; the former values are uniformly positive except in nitromethane (Table II) so that it would be concluded that the Born model is noticeably less successful for predicting $\Delta(\Delta G^\circ_{rc})^{s-w}$ if the ferrocene rather than the TATB scale had been employed. However, the available evidence suggests that the TATB scale provides estimates of single-ion transfer energies [and hence values of $\Delta(\Delta G^\circ_{rc})^{s-w}$] that are trustworthy at least to within 1-2 kcal mol^{-1} [9].

Turning now to the entropy data, as might be anticipated the values of $(\Delta S^\circ_{rc})_{Born}$ are generally in poor agreement with the experimental quantities (Table I). Also, plots of $\Delta(\Delta S^\circ_{rc})^{s-w}$ versus $\Delta(\Delta S^\circ_{rc})^{s-w}_{Born}$ for the three small amine couples exhibit considerable scatter. In view of the reasonable correlations obtained between $\Delta(\Delta G^\circ_{rc})^{s-w}$ and $\Delta(\Delta H^\circ_{rc})^{s-w}$ with the solvent Donor Number (Fig. 1) it is of interest to ascertain if a similar relationship exists between $\Delta(\Delta S^\circ_{rc})^{s-w}$ for each redox couple and D. N. Such plots are given for the four amine couples in Fig. 2. It is seen that in contrast to Fig. 1, there is little if any correlation between $\Delta(\Delta S^\circ_{rc})^{s-w}$ and D. N. Thus solvents of relatively low basicity such as propylene carbonate and nitromethane give rise to values of $\Delta(\Delta S^\circ_{rc})^{s-w}$ that are comparable to, or even larger than, those obtained in the strongly donating solvents DMSO and DMF. Also, if such donor-acceptor interactions were important it would be expected that the values of $\Delta(\Delta S^\circ_{rc})^{s-w}$ in a given solvent would be greater for couples containing likely electron acceptor sites compared to couples of similar size and charge type not containing such ligand sites. In fact the opposite appears to be the case. For example, the values of $\Delta(\Delta S^\circ_{rc})^{s-w}$ in each nonaqueous solvent reported here and in ref. 1 increase in the sequence $Co(en)_3^{3+/2+} < Co(sep)^{3+/2+} < Co(bpy)_3^{3+/2+} \approx Co(phen)_3^{3+/2+}$ even though $Co(en)_3^{3+/2+}$ and $Co(sep)^{3+/2+}$ contain a total of twelve and six amine hydrogens, respectively, and the last two couples contain no amine hydrogens or other clearly identifiable acceptor sites.

A more successful correlation than Fig. 2 is obtained by plotting the experimental values of $\Delta(\Delta S^\circ_{rc})^{s-w}$ for each couple against -a for each nonaqueous solvent (Fig. 3), where "a" is an empirical parameter[12,13] which provides a measure of the degree of "internal order" (the extent of association between solvent molecules in the bulk liquid[12]). It is seen that $\Delta(\Delta S^\circ_{rc})^{s-w}$ increases almost uniformly with increasing solvent internal order. These plots have similar shapes to those for the polypyridine redox couples (Fig. 2 of ref. 1), although the present plots are significantly less linear and have smaller slopes. The success of this correlation suggests that the values of ΔS°_{rc} are at least partly determined by the ease by which surrounding solvent molecules are able to reorientate away from their bulk structure in response to the enhanced electric field around the oxidized versus the reduced forms of the redox couple.[1]

These results therefore argue against the predominant importance of solvent-solute donor-acceptor interactions in determining the degree of this additional solvent polarization. Although at first sight surprising, this conclusion is quite compatible with the apparent sensitivity of the free energy term $\Delta(\Delta G^\circ_{rc})^{s-w}$ to solvent basicity since the entropic terms ΔS°_{rc} and hence $\Delta(\Delta S^\circ_{rc})^{s-w}$ should respond to the *extent* of solvent ordering induced, rather than the *strength* of the donor-acceptor interactions themselves. Provided that such enthalpic-based interactions are sufficiently strong to ensure that the solvent molecules in contact with the amine ligands are strongly oriented, variations in the strength of the donor-acceptor interactions may have only a relatively minor influence upon the extent of this orientation. Indeed, the markedly larger experimental values of ΔS°_{rc} in a given solvent compared to the Born predictions (Table I) suggest that there commonly is extensive additional short-range solvent polarization induced by the oxidized form of the redox couple, most likely involving oriented solvent molecules in the first solvation sphere.

Nevertheless, some influence of solvent donicity upon ΔS°_{rc} for couples containing electron acceptor sites might often be expected. Indeed, a comparison of the plots of $\Delta(\Delta S^\circ_{rc})^{s-w}$ versus D. N. for the saturated amine couples (Fig. 2) with the corresponding plots for the polypyridine couples (Fig. 3 of ref. 1) reveals that the values of $\Delta(\Delta S^\circ_{rc})^{s-w}$ for the former systems tend to increase more (or decrease less) with increasing D. N. in comparison with those for the latter systems. Further, a number of aquo redox couples of the form $M(OH_2)_6^{3+/2+}$ exhibit values of ΔS°_{rc} that are markedly (20-30 e.u.) larger than for structurally similar ammine redox couples $M(NH_3)_6^{3+/2+}$ in aqueous solution.[2] These differences are most likely due, at least in part,[14] to the greater extent of hydrogen bonding between the more acidic hydrogens on the aquo ligands with surrounding oriented water molecules.[2]

It is apparent from the above considerations that a number of molecular factors can contribute towards the thermodynamics of outer-shell solvation even for the archetypically simple one-electron redox couples considered here. Nevertheless, an encouraging overall feature of these results is that the dependence of the redox thermodynamic parameters upon the nature of the central metal, the coordinated ligands, and the surrounding solvents fall into clear patterns which should allow predictions of the solvent-dependent behavior of structurally related redox couples to be made with some confidence. It is clearly desirable to expand our knowledge of redox thermodynamics and kinetics beyond the confines of aqueous media, particularly as the present results along with numerous prior data demonstrate the atypical and even unique solvating properties of water in comparison with other ionizing solvents. A parallel study of the solvent dependence of the electrode kinetics of ammine and ethylenediamine complexes at mercury electrodes will be reported elsewhere.[15]

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TABLE I. Formal Potentials and Reaction Entropies for [illegible](III)/(II) Amine and [illegible]ediamine [illegible] Complexes in Various Solvents.

Solvent	$(\Delta S^{o}_{rc})_{Born}$ ^{d}	$Ru(NH_3)_6^{3+/2+}$		$Ru(en)_3^{3+/2+}$		$Co(en)_3^{3+/2+}$		$Co(sep)^{3+/2+}$		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}
Water	14.0	-305	19	-187	13	-587	37	-667	19	127
Formamide	7.2	-553	29	g	g	-813	42	-897	34	281
N-Methylformamide	13.4	-707	33	g	g	-945	46	-996	40	397
Propylene Carbonate	14.0	-373^{h}	41^{h}	g	g	-633^{i}	50^{i}	-888	48	328
Acetonitrile	26.5	f	f	f	f	-589^{i}	47^{i}	f	f	342
Dimethylsulfoxide	17.8	-781^{h}	40^{h}	-594	33	-1039	52	-1112	44	439
Dimethylformamide	31.0	-739^{h}	46^{h}	-596	36	-970^{i}	51^{i}	g	g	493
Nitromethane	27.1	f	f	f	f	-488^{i}	4[illegible]^{i}	f	f	147^{e}

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 unless otherwise noted; quoted in mV. versus 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;[1,2] 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 calculated from the Born model for each solvent (eqn. (3)) using radius r = 3.5Å (appropriate for the small amine couples[11]) and the appropriate dielectric constant data (sources given in Notes to Table I of reference 1); units are cal. deg^{-1} mol^{-1}.

[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] Insolubility of solute precluded measurement of E_f.

[g] Erratic voltammetric behavior precluded measurement of E_f.

[h] Obtained in $25m\underline{M}$ $LiClO_4$.

[i] Obtained in $0.1\underline{M}$ tetraethylammonium perchlorate.

TABLE II. Free Energies (A), Enthalpies (B), and Entropies (C), of Transfer [illegible] Ammine and Ethylenediamine 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	$Ru(NH_3)_6^{3+/2+}$			$Ru(en)_3^{3+/2+}$			$Co(en)_3^{3+/2+}$			$Co(sep)^{3+/2+}$			$\Delta(\Delta G^o_{rc})^{s-w}_{Born}$ *
	A	B	C	A	B	C	A	B	C	A	B	C	
Formamide	(5.7) 4.2	7.2	10				(5.2) 3.7	5.2	5	(5.3) 3.8	8.3	15	0.85
N-Methylformamide	(9.3) 7.3	11.5	14				(8.3) 6.3	9.0	9	(7.6) 5.6	11.9	21	1.7
Propylene Carbonate	(1.6) -0.4	6.2	22				(1.1) -0.9	3.0	13	(5.1) 3.1	11.8	29	-0.6
Acetonitrile							(0.0) -3.5	-0.5	10				-3.2
Dimethylsulfoxide	(11.0) 8.5	14.8	21	(9.4) 6.9	12.9	20	(10.4) 7.9	12.4	15	(10.3) 7.8	15.3	25	-2.0
Dimethylformamide	(10.0) 7.0	15.1	27	(9.4) 6.4	13.3	23	(8.8) 5.8	10.0	14				-3.4
Nitromethane							(-2.3) -3.8	-1.4	8				-3.4

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.(1). 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 Table II of reference 1 (i.e. using TATB assumption - see reference 1 for details).

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.

*Free energy of transfer of redox couple (kcal. mol^{-1}) calculated from the Born model for each solvent (eqn.(2)) using radius $r = 3.5Å$ (appropriate for the small amine couples) and the appropriate dielectric constant data (sources given in Note to Table I of reference 1).

Notes to Figures

Fig. 1.

Plots of the variation in the free energy of reaction, $\Delta(\Delta G^\circ_{rc})^{s-w}$, and the enthalpy of reaction, $\Delta(\Delta H^\circ_{rc})^{s-w}$, for $Co(en)_3^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$ when changing from water to various nonaqueous solvents against the "Donor Number" for each solvent[4]: Closed symbols: $\Delta(\Delta G^\circ_{rc})^{s-w}$. Open symbols: $\Delta(\Delta H^\circ_{rc})^{s-w}$. Redox couples: ●,○, $Co(en)_3^{3+/2+}$; ■,□, $Ru(NH_3)_6^{3+/2+}$. Solvents in this and subsequent figures: 1, formamide; 2, N-methylformamide; 3, propylene carbonate; 4, dimethylsulfoxide; 5, dimethylformamide; 6, acetonitrile; 7, nitromethane. The straight lines are drawn between adjacent points for a given redox couple in the various solvents.

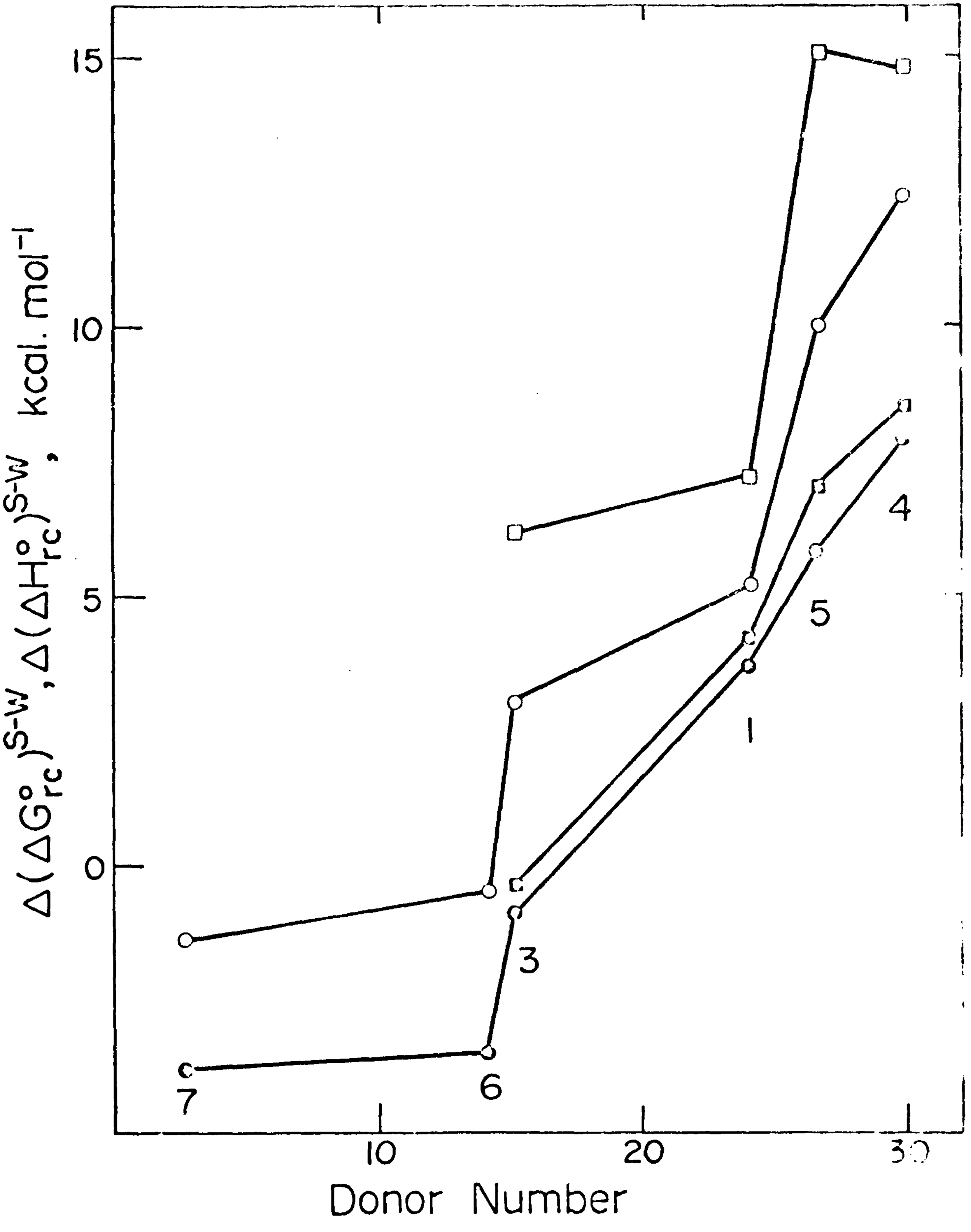
Fig. 2.

Plots of $\Delta(\Delta S^\circ_{rc})^{s-w}$ for each amine redox couple against the "Donor Number" for the various nonaqueous solvents.[4] Key to redox couples as in notes for Fig. 3; key to solvents as in notes to Fig. 1.

Fig. 3.

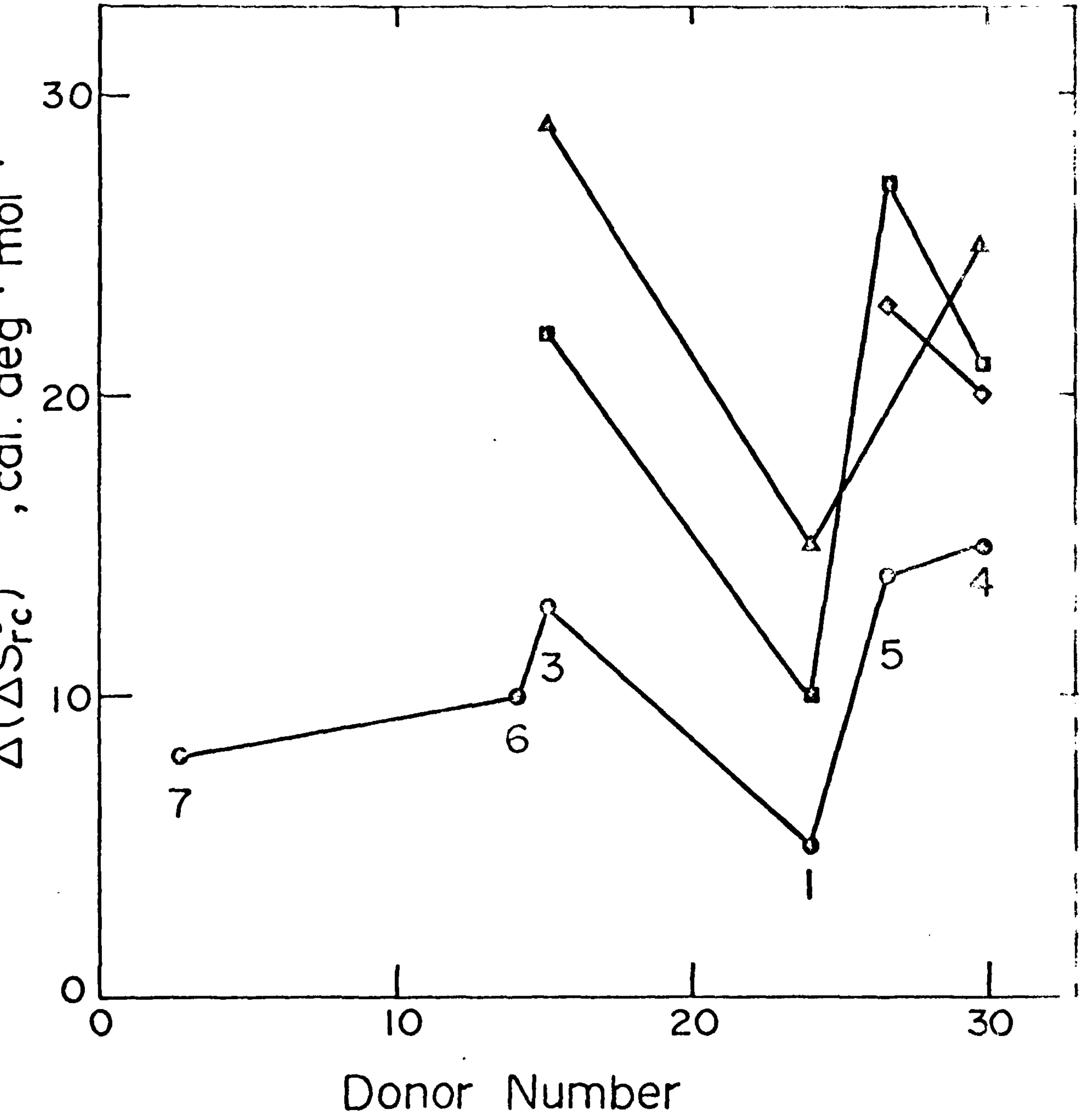
Plots of $\Delta(\Delta S^\circ_{rc})^{s-w}$ for each amine redox couple against -a, where "a" is a parameter related to the degree of "internal order" of each solvent.[12,13] Redox couples: ●, $Co(en)_3^{3+/2+}$; ■, $Ru(NH_3)_6^{3+/2+}$; ◆, $Ru(en)_3^{3+/2+}$; ▲, $Co(sep)^{3+/2+}$. Key to solvents as in notes to Fig. 1.

Fig. 1



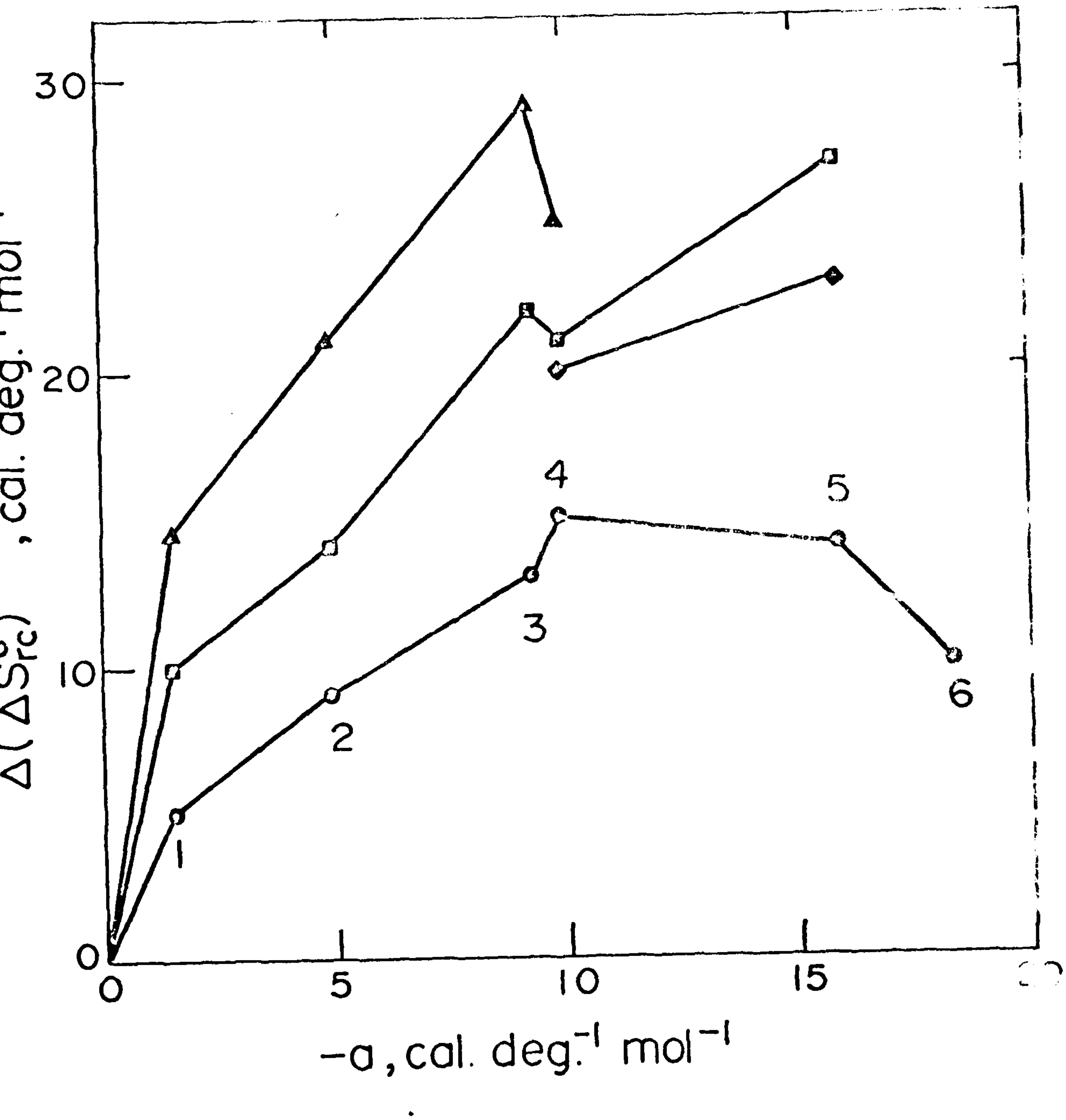
$\Delta(\Delta G^o_{rc})^{S-W}, \Delta(\Delta H^o_{rc})^{S-W}$, kcal. mol^{-1}
15
10
5
0
10
20
30
Donor Number
7
6
3
1
5
4

Fig 2.



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

Fig 5



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

DATE
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– 8