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Solvent, Ligand, and Ionic Charge Effects on Reaction Entropies for Simple Transition-Metal Redox Couples

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The dependence of the reaction entropies, ΔS°_{rc}, for simple M(III/II) redox couples (M = Ru, Fe, Os, Cr) upon the nature of the ligands and the solvent is examined with a view toward correlating ΔS°_{rc} with simple physical parameters. For couples containing ammine, ethylenediamine, polypyridine, cyclopentadiene, or pseudohalide ligands, ΔS°_{rc} in a given solvent is found to correlate well with $(Z_{ox}^2 - Z_{red}^2)$, where Z_{ox} and Z_{red} are the charge numbers of the oxidized and reduced forms, and with $1/r$, where r is the effective radius of the redox couple. This suggests that specific ligand–solute interactions do not provide a predominant contribution to ΔS°_{rc} for these systems, although this effect is probably important for aquo redox couples in water. The dependence of ΔS°_{rc} upon the solvent correlates reasonably well with the solvent "acceptor number" and other solvent polarity parameters. This is rationalized in terms of a contribution to ΔS°_{rc} arising from disruption of the surrounding solvent structure by the charged solute. The predictive as well as interpretative virtues of such semiempirical correlations of reaction entropies are pointed out.

Introduction

Relative entropies of simple inorganic ions in aqueous solution were widely measured and interpreted in the 1950s and 1960s in order to examine basic notions concerning ionic solvation.[1–7] Interest in this topic was revived in 1979 with the report by Weaver and co-workers that absolute measures of the entropy difference, ΔS°_{rc} $(=S^\circ_{red} - S^\circ_{ox})$, between the reduced and oxidized forms of a redox couple involving only electron transfer could readily be obtained from nonisothermal electrochemical measurements.[8] Besides their value for systematically determining entropic and enthalpic driving forces for redox processes, the virtue of individual ΔS°_{rc} values for unraveling structural changes accompanying electron transfer was emphasized.[8–10] Numerous papers dealing with reaction entropies have appeared since then.[9–26] These have been concerned with unraveling the details of solvent reorganization in connection with electron-transfer dynamics[14–16,24,28,29] or with the solvation of inorganic redox couples,[8–13,17–20,26–28] metalloproteins,[21–23] or other biological model compounds.[17,18,25] Although significant insights have been gained, some puzzles remain.

Paramount of these is the elucidation of the physical factors that are responsible for the observed marked sensitivity of ΔS°_{rc} to the nature of the ligands and the surrounding solvent, as well as to the charges carried by the redox couples.[8–13] It has been suggested that the large quantitative, and in some cases even qualitative, divergences seen between the experimental values of ΔS°_{rc} and the expectations of the Born dielectric continuum model are due chiefly to short-range, oxidation-state-dependent interactions between the coordinated ligands and the surrounding solvent molecules.[8–13]

This paper explores the ability of semiempirical relationships to rationalize the experimental data. The results suggest that a simpler interpretation may be valid, namely, that the ΔS°_{rc} values for a variety of structurally simple redox couples depend simply on the size and charge type of the redox couple once the specific nature of the solvent is included. Besides offering predictive power, it is suggested that these correlations and accompanying molecular interpretations can rationalize some of the more curious findings of earlier studies.

Experimental Section

The reaction entropies measured as part of this study were all obtained from the temperature dependence of the formal potential, E_f, by using a nonisothermal cell arrangement, essentially as described in ref 8 and 11. Thus values of E_f were measured with cyclic voltammetry with ca. 1–2 mM of either the reduced or oxidized form of the redox couple in solution. The nonisothermal cell for nonaqueous solvents featured a "double-junction" arrangment. This consisted of a fine-porosity glass frit separating the aqueous reference compartment containing the saturated calomel electrode (SCE), held at room temperature, from the thermal liquid junction located between the reference and working compartments, the latter having a variable

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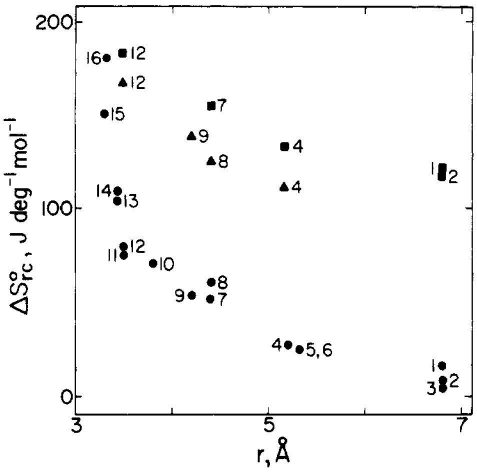

Figure 1. Reaction entropy, ΔS°_{rc}, vs. effective radius of reactant, r (Table II). Key to solvents: (●) water; (▲) dimethyl sulfoxide; (□) acetonitrile. Key to reactants: (1) $Cr(bpy)_3^{3+/2+}$; (2) $Fe(bpy)_3^{3+/2+}$; (3) $Ru(bpy)_3^{3+/2+}$; (4) *cis*-$Ru(NH_3)_2(bpy)_2^{3+/2+}$; (5) *cis*-$Ru(H_2O)_2(bpy)_2^{3+/2+}$; (6) *trans*-$Ru(H_2O)_2(bpy)_2^{3+/2+}$; (7) $Ru(NH_3)_4bpy^{3+/2+}$; (8) $Ru(NH_3)_4phen^{3+/2+}$; (9) $Ru(en)_3^{3+/2+}$; (10) $Ru(NH_3)_5py^{3+/2+}$; (11) $Ru(NH_3)_6^{3+/2+}$; (12) $Os(NH_3)_6^{3+/2+}$; (13) $Ru(NH_3)_5H_2O^{3+/2+}$; (14) $Ru(NH_3)_4(H_2O)_2^{3+/2+}$; (15) $Ru(H_2O)_6^{3+/2+}$; (16) $Fe(H_2O)_6^{3+/2+}$. Data were taken from Table I and ref 8, 9, 11, and 12.

temperature. This region between the "hot" and "cold" compartments was filled with the nonaqueous solvent and supporting electrolyte, a second frit separating this region from the working compartment itself.

The sources of the complexes used were as follows. Samples of $[Ru(NH_3)_5py](PF_6)_3$ (py = pyridine), $[Ru(NH_3)_5pz](PF_6)_3$ (pz = pyrazine), and $[Ru(NH_3)_6](CF_3COO)_3$ were provided by Drs. Peter Lay and Roy Magnuson (Stanford). $[Ru(en)_3]Br_3$ and $[Ru(NH_3)_2(bpy)_2](ClO_4)_2$ were supplied by Dr. Gilbert Brown (Brookhaven), and $[Ru(NH_3)_4(phen)](CF_3COO)_3$ was supplied by Prof. Larry Bennett (San Diego State). $[Ru(NH_3)_5NCS](PF_6)_2$ was prepared as in ref 30, and $[Cr(bpy)_3](ClO_4)_3$ was prepared by Dr. Saeed Sahami as in ref 11. $[Ru(bpy)_3]Cl_3$ and ferrocene were purchased from G. F. Smith Co. and Aldrich, respectively.

Results and Discussion

Empirical Correlations. We consider here redox couples having the general form

$$M^{III}L'_mL''_n + e^- \rightleftharpoons M^{II}L'_mL''_n \quad (1)$$

where M = Ru, Fe, Os, and Cr and the ligands L′, L″ = OH_2, NH_3, ethylenediamine (en), pyridine (py), pyrazine (pz), 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), cyclopentadiene, NCS^-, Cl^-, and CN^-. The complexes were selected to be substitutionally inert (or at least thermodynamically stable) in both M^{III} and M^{II} oxidation states; this generally involved couples having a low-spin electron configuration. Such couples form especially tractable systems for interpreting reaction entropies, as well as other electron-transfer parameters, since they exhibit only small structural differences between the oxidized and reduced forms. In addition, with the exception of the couples containing aquo ligands, they can be examined in a variety of solvents besides water, with the inner-shell composition fixed.

We have noted previously that values of ΔS°_{rc} for couples containing aromatic ligands are substantially smaller than for those containing ammine or ethylenediamine groups.[11,12] Figure 1 contains values of ΔS°_{rc} for a number of M(III/II) couples containing polypyridines and/or ammine, ethylenediamine, or aquo ligands in water, dimethyl sulfoxide, and acetonitrile, plotted against the effective radius, r, of each couple. The ΔS°_{rc} values either were measured as part of the present work or were taken from previously published reports from this laboratory.[8,9,11,12] The former values are summarized in Table I; they refer to an ionic strength of 0.1. The effective radii used in Figure 1 are summarized for the various ligand compositions in Table II; these were estimated by using the

Table I. Reaction Entropies, ΔS°_{rc} (J K^{-1} mol^{-1}), and Formal Potentials, E_f, for Transition-Metal Redox Couples in Various Solvents

redox couple	solvent[a]	ΔS°_{rc}	E_f[b]
$Ru(NH_3)_6^{3+/2+}$	acetonitrile	185	−298
$Ru(NH_3)_6^{3+/2+}$	acetone[c]	200	−443
$Ru(en)_3^{3+/2+}$	formamide	90	−419
$Ru(NH_3)_5pz^{3+/2+}$	nitromethane	165	254
$Ru(NH_3)_5pz^{3+/2+}$	propylene carbonate	155	111
$Ru(NH_3)_4bpy^{3+/2+}$	acetonitrile	155	151
$Ru(NH_3)_4phen^{3+/2+}$	nitromethane	120	322
$Ru(NH_3)_4phen^{3+/2+}$	dimethyl sulfoxide	125	−185
$Ru(NH_3)_4phen^{3+/2+}$	propylene carbonate	150	120
$Ru(NH_3)_2(bpy)_2^{3+/2+}$	nitromethane	115	638
$Ru(NH_3)_2(bpy)_2^{3+/2+}$	acetonitrile	130	504
$Ru(NH_3)_2(bpy)_2^{3+/2+}$	dimethyl sulfoxide	110	273
$Ru(NH_3)_2(bpy)_2^{3+/2+}$	propylene carbonate	135	501
$Ru(bpy)_3^{3+/2+}$	acetonitrile	115	891
$Ru(bpy)_3^{2+/+}$	acetonitrile	70	−1718
$Ru(bpy)_3^{+/0}$	acetonitrile	25	−1916
$Cr(bpy)_3^{3+/2+}$	acetonitrile[d]	105	−573
$Cr(bpy)_3^{2+/+}$	acetonitrile[d]	65	−1092
$Cr(bpy)_3^{+/0}$	acetonitrile[d]	20	−1652
$Ru(NH_3)_5NCS^{2+/+}$	formamide[e]	80	−491
$Ru(NH_3)_5NCS^{2+/+}$	*N*-methylformamide[e]	105	−670
$Ru(NH_3)_5NCS^{2+/+}$	propylene carbonate[e]	140	−441
$Ru(NH_3)_5NCS^{2+/+}$	dimethyl sulfoxide[e]	109	−719
$Ru(NH_3)_5NCS^{2+/+}$	dimethylformamide[e]	140	−750

[a] 0.1 M KPF_6 used as supporting electrolyte unless otherwise noted. [b] Formal potential; mV vs. ferrocenium/ferrocene couple in same solvent and electrolyte. [c] 0.08 M KPF_6 supporting electrolyte. [d] 0.1 M tetraethylammonium perchlorate supporting electrolyte. [e] 0.1 M $LiClO_4$ supporting electrolyte; values determined by Dr. Saeed Sahami.

Table II. Equivalent Radii, r (Å), for Various Redox Couples

redox couple[a]	r[b]	redox couple[a]	r[b]
$M(NH_3)_6^{3+/2+}$	3.3	$Ru(NH_3)_2(L')_2^{3+/2+}$	5.6
$Ru(H_2O)_6^{3+/2+}$	3.2	$M(bpy)_3^{(n+1)+/n+}$	6.8
$Ru(en)_3^{3+/2+}$	3.8	$Fe(CN)_6^{3-/4-}$	4.4
$Ru(NH_3)_5L^{3+/2+}$	4.2	$Fe(CN)_4bpy^{-/2-}$	5.1
$Ru(NH_3)_4L'^{3+/2+}$	4.4	ferrocenium/ferrocene	3.8

[a] L = pyridine or pyrazine, L′ = 2,2′-bipyridine or 1,10-phenanthroline; M refers to either Ru, Os, Fe, or Cr. [b] Determined as outlined in ref 32.

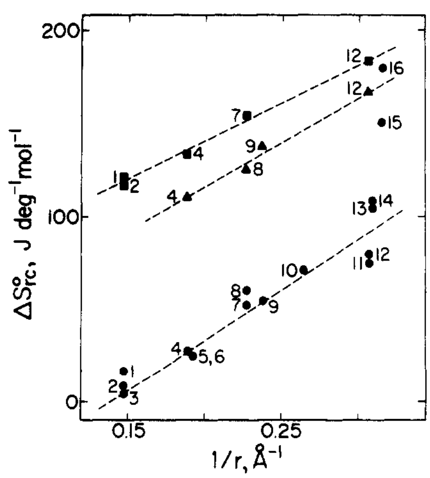

Figure 2. Reaction entropy, ΔS°_{rc}, vs. $1/r$. Keys to solvents and reactants are as shown in Figure 1.

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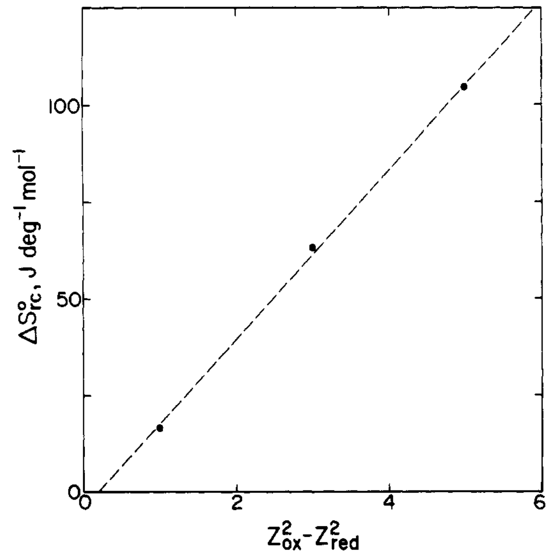

Figure 3. Reaction entropies for $Cr(bpy)_3^{(n+1)+/n+}$, with n = 2, 1, 0, in acetonitrile (Table I) vs. the difference in the square of the charge numbers for the oxidized and the reduced states, $(Z_{ox}^2 - Z_{red}^2)$.

procedure described in ref 32.

It is evident that there is a rough correlation between $\Delta S°_{rc}$ and r, although the plots are significantly nonlinear. Noticeably better linear correlations are found upon plotting $\Delta S°_{rc}$ against $1/r$ (Figure 2), with the exception of the points for the hexaaquo couples, which show large deviations on both plots. Similarly, linear relationships between $\Delta S°_{rc}$ and $1/r$ were obtained in solvents other than the three shown in Figure 2 but are ommitted for clarity.

Two types of data are available with which to examine the dependence of $\Delta S°_{rc}$ upon the charge type of a couple of a given solvent. First, a few complexes can form several sequential oxidation states in aprotic solvents. This enables values of $\Delta S°_{rc}$ to be obtained for two or more couples with successively varying charge numbers of the oxidized and reduced forms, Z_{ox} and Z_{red}, respectively. Figure 3 contains values of $\Delta S°_{rc}$ for $Cr(bpy)_3^{(n+1)/n+}$ in acetonitrile (for n = 2, 1, and 0) plotted against $(Z_{ox}^2 - Z_{red}^2)$. An excellent linear correlation is obtained. Almost identical results have been obtained for $Ru(bpy)_3^{(n+1)+/n+}$ in acetonitrile.[29] The corresponding plot for $Cr(bpy)_3^{(n+1)+/n+}$ in acetone yields a similar correlation, but with a significantly positive y intercept (22 J K^{-1} mol^{-1}). A similar linear dependence of $\Delta S°_{rc}$ upon $(Z_{ox}^2 - Z_{red}^2)$ has also been observed for metal dithiocarbamate couples carrying negative as well as positive charges in acetone.[34]

A second means of examining the charge dependence of $\Delta S°_{rc}$ involves successively substituting neutral ligands by charged groups. Figure 4 contains $\Delta S°_{rc}$ values for $Cr(bpy)_3^{3+/2+}$, $Ru(NH_3)_6^{3+/2+}$, $Ru(en)_3^{3+/2+}$, $Ru(NH_3)_5Cl^{2+/+}$, $Ru(NH_3)_5NCS^{2+/+}$, ferrocenium/ferrocene, $Fe(CN)_4bpy^{-/2-}$, and $Fe(CN)_6^{3-/4-}$ in aqueous solution, plotted against $(Z_{ox}^2 - Z_{red}^2)/r$. The data were taken from ref 3, 8, and 11. A reasonable straight line is again obtained, even though the chemical nature of the ligands varies substantially.[7] Since the radii for these couples vary only to a small extent in relation to the numerical alterations in the ionic charge, Figure 4 is insensitive to the choice of the radius function. Various authors have noted that the $\Delta S°_{rc}$ values for such "mixed-ligand" couples can be estimated approximately by linearly interpo-

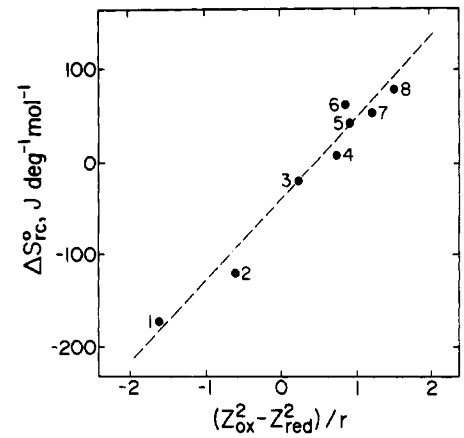

Figure 4. Reaction entropy in water vs. $(Z_{ox}^2 - Z_{red}^2)/r$. Key to redox couples: (1) $Fe(CN)_6^{3-/4-}$; (2) $Fe(CN)_4bpy^{-/2-}$; (3) ferrocenium/ferrocene; (4) $Cr(bpy)_3^{3+/2+}$; (5) $Ru(NH_3)_5Cl^{2+/+}$; (6) $Ru(NH_3)_5NCS^{2+/+}$; (7) $Ru(en)_3^{3+/2+}$; (8) $Ru(NH_3)_6^{3+/2+}$. Data were taken from ref 3, 8, and 13 and Tables I and II.

lating the values for the appropriate pure-ligand couples.[3a,9,33] It has therefore been suggested that each ligand provides a roughly additive contribution to the measured $\Delta S°_{rc}$.[9,33] However, the foregoing demonstrates that reaction entropies in a given solvent can be correlated simply to the charge and effective radius of the complexes, even for structurally diverse couples.

The plots presented in Figures 2–4 have functional forms that are reminiscent of the simple Born expression for the reaction entropy:[12]

$$\Delta S°_{rc} = \frac{e^2N}{2\epsilon rT}\left(\frac{\mathrm{d}\ln\epsilon}{\mathrm{d}T}\right)(Z_{ox}^2 - Z_{red}^2) \quad (2)$$

where e is the electronic charge, N is the Avogadro number, and ϵ is the static dielectric constant of the solvent. However, eq 2 commonly yields estimates of $\Delta S°_{rc}$ that are in marked quantitative, or even qualitative, disagreement with experiment.[8,9,11-13] This is the case for the data presented in Figures 2–4. For example, the slope of the "best fit" straight line in Figure 4, 83.5 J K^{-1} mol^{-1} Å, is substantially larger than the predicted value from eq 2, 39.5 J K^{-1} mol^{-1} Å. Similarly, the plot in Figure 3 has a slope, 22 J K^{-1} mol^{-1}, that is considerably larger than the Born estimate, 11.2 J K^{-1} mol^{-1}. In addition, eq 2 predicts that these plots should have zero intercepts. Although this is approximately the case for $Cr(bpy)_3^{(n+1)+/n+}$ in acetonitrile, as noted above a substantial positive y intercept (22 J K^{-1} mol^{-1}) is found in acetone, whereas the data in Figure 4, obtained in water, yield a large negative y intercept, −40 J K^{-1} mol^{-1}. It is therefore clear that the experimental values of $\Delta S°_{rc}$ contain a solvent-dependent yet charge-independent component that is not described by simple electrostatic models.

One might expect that such a contribution could be associated with short-range donor–acceptor interactions between the redox couple and surrounding solvent molecules. Since most redox couples considered here are likely to act as "electron acceptors" in view of their positive charge, the solvent dependence of $\Delta S°_{rc}$ for such couples might be anticipated to correlate with the "electron-donating" ability of the solvent. However, we have shown that no such correlation is observed.[11-13] This is illustrated in Figure 5 which contains representative plots of $\Delta S°_{rc}$ for $Ru(NH_3)_6^{3+/2+}$ and ferrocenium/ferrocene against the solvent "donor number", DN.[35] However, plots of $\Delta S°_{rc}$ for a number of cationic redox couples against the solvent "acceptor number", AN,[35] show reasonably

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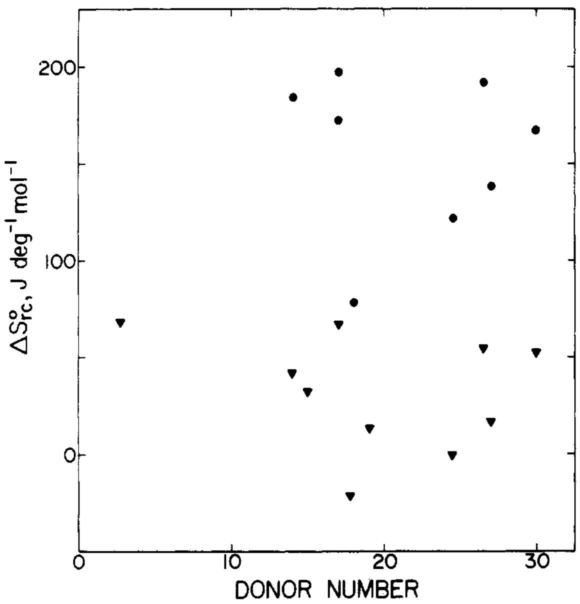

Figure 5. Reaction entropies vs. solvent donor number.[35] Redox couples: (●) $Ru(NH_3)_6^{3+/2+}$; (▼) ferrocenium/ferrocene. Solvents (with donor numbers): nitromethane (2.7); acetonitrile (14); propylene carbonate (15); acetone (17); water (18); methanol (19); formamide (24); dimethylformamide (26.6); *N*-methylformamide (27); dimethyl sulfoxide (30). Data were taken from ref 8, 12, 13, and 27b and Table I.

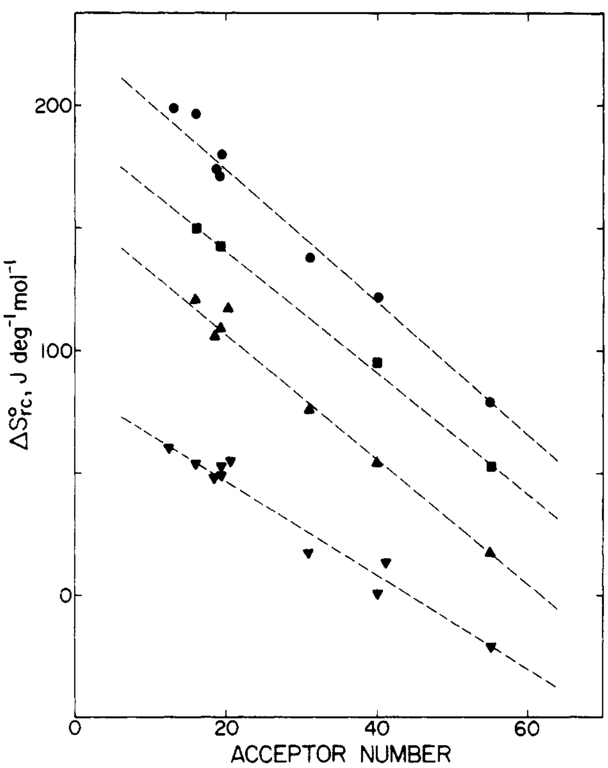

Figure 6. Reaction entropies vs. solvent acceptor number.[35] Key to redox couples: (●) $Ru(NH_3)_6^{3+/2+}$; (□) $Ru(en)_3^{3+/2+}$; (▲) $Cr(bpy)_3^{3+/2+}$; (▼) ferrocenium/ferrocene. Solvents (with acceptor numbers): acetone (12.5); dimethylformamide (16); propylene carbonate (18.3); dimethyl sulfoxide (19.3); acetonitrile (19.3); nitromethane (20.5); *N*-methylformamide (31); formamide (40); methanol (41); water (55). Data were taken from ref 8, 11–13, and 27b and Table I.

linear correlations (Figure 6). Inasmuch as the acceptor number scale partly reflects the solvent polarity,[36a] similar correlations can also be anticipated with solvent polarity scales, such as π, E_T, and Z.[36,37] Although these latter quantities

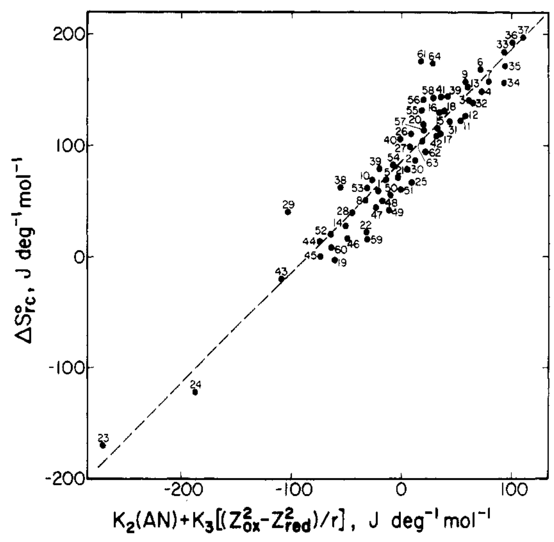

Figure 7. Fit of $\Delta S°_{rc}$ values to the function $K_2(AN) + K_3[(Z_{ox}^2 - Z_{red}^2)/r]$. K_2, K_3, and *y* intercept K_1 were obtained by linear least-squares analysis. Key to redox couples and solvents: (1) $Ru(en)_3^{3+/2+}$, H_2O; (2) $Ru(en)_3^{3+/2+}$, FA; (3) $Ru(en)_3^{3+/2+}$, Me_2SO; (4) $Ru(en)_3^{3+/2+}$, DMF; (5) $Ru(NH_3)_5py^{3+/2+}$, H_2O; (6) $Ru(NH_3)_5pz^{3+/2+}$, NM; (7) $Ru(NH_3)_5pz^{3+/2+}$, PC; (8) $Ru(NH_3)_4bpy^{3+/2+}$, H_2O; (9) $Ru(NH_3)_4bpy^{3+/2+}$, AN; (10) $Ru(NH_3)_4phen^{3+/2+}$, H_2O; ferrocenium/ferrocene, NM; (11) $Ru(NH_3)_4phen^{3+/2+}$, NM; (12) $Ru(NH_3)_4phen^{3+/2+}$, Me_2SO; (13) $Ru(NH_3)_4phen^{3+/2+}$, PC; (14) $Ru(NH_3)_2(bpy)_2^{3+/2+}$, H_2O; *cis*-$Ru(bpy)_2(H_2O)_2^{3+/2+}$, H_2O; *trans*-$Ru(bpy)_2(H_2O)_2^{3+/2+}$; (15) $Ru(NH_3)_2(bpy)_2^{3+/2+}$, NM; (16) $Ru(NH_3)_2(bpy)_2^{3+/2+}$, AN; (17) $Ru(NH_3)_2(bpy)_2^{3+/2+}$, Me_2SO; $Fe(phen)_3^{3+/2+}$, H_2O; (18) $Ru(NH_3)_2(bpy)_2^{3+/2+}$, PC; $Ru(NH_3)_5NCS^{2+/+}$, DMF; (19) $Ru(bpy)_3^{3+/2+}$, H_2O; (20) $Ru(bpy)_3^{3+/2+}$, AN; (21) $Ru(bpy)_3^{2+/+}$, AN; (22) $Ru(bpy)_3^{+/0}$, AN; (23) $Fe(CN)_6^{3-/4-}$, H_2O; (24) $Fe(CN)_4bpy^{-/2-}$, H_2O; (25) $Os(NH_3)_6^{3+/2+}$, H_2O; (26) $Ru(NH_3)_5H_2O^{3+/2+}$, H_2O; (27) $Ru(NH_3)_4(H_2O)_2^{3+/2+}$, H_2O; (28) $Ru(NH_3)_5Cl^{2+/+}$, H_2O; (29) $Ru(NH_3)_4Cl_2^{+/0}$, H_2O; (30–37) $Ru(NH_3)_6^{3+/2+}$, with solvents (30) H_2O, (31) FA, (32) NMF, (33) AN, (34) Me_2SO, (35) PC, (36) DMF, and (37) acetone; (38–42) $Ru(NH_3)_5NCS^{2+/+}$, with solvents (38) H_2O, (39) FA, (40) NMF, (41) PC, and (42) Me_2SO; (43–50) ferrocenium/ferrocene, with solvents (43) H_2O, (44) methanol, (45) FA, (46) NMF, (47) AN, (48) Me_2SO, (49) PC, and (50) DMF; (51) Fc^+/Fc, acetone; $Cr(bpy)_3^{2+/+}$, AN; (52–58) $Cr(bpy)_3^{3+/2+}$, with solvents (52) H_2O, (53) FA, (54) NMF, (55) NM, (56) AN, (57) PC, and (58) DMF; (59) $Cr(bpy)^{+/0}$, AN; (60–64) $Fe(bpy)_3^{3+/2+}$, with solvents (60) H_2O, (61) NM, (62) AN, (63) PC, and (64) DMF. Solvent abbreviations: AN = acetonitrile; Me_2SO = dimethyl sulfoxide; DMF = dimethylformamide; FA = formamide; NMF = *N*-methylformamide; NM = nitromethane. Data were taken from ref 3, 8, 9, 11–13, and 27b and Tables I and II.

also yield rough correlations with $\Delta S°_{rc}$, decidedly better linear correlations were obtained between $\Delta S°_{rc}$ and AN. The acceptor number appears to reflect a combination of the electrophilicity and polarity of the solvent.[36a]

The success of these various solute charge, size, and solvent polarity correlations shown in Figures 2–4 and 6 suggests that the modification of eq 2 by the addition of a charge-independent component along with adjustment of the charge-dependent slope provides a satisfactory description of the experimental data. This led us to test the ability of all the available reaction entropy data for couples of the form in eq 1 to fit the combined semiempirical relationship

$$\Delta S°_{rc} = K_1 + K_2(AN) + K_3(Z_{ox}^2 - Z_{red}^2)/r \quad (3)$$

(36) (a) Abboud, J. L M.; Kamlet, M. J.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485. (b) Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.
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The constants K_1, K_2, and K_3 were adjusted so as to yield the single "best fit" correlation given in Figure 7. The resulting straight line shown yields a reasonably good fit to eq 3, with $K_1 = 91.5$ J K^{-1} mol^{-1}, $K_2 = -2.43$ J K^{-1} mol^{-1}, and $K_3 = 86.6$ J K^{-1} mol^{-1} Å.

Clearly, better fits could be obtained by using more complex multiparametric relations, such as allowing K_3 to be solvent dependent. Nevertheless, a major virtue of eq 3 is its mathematical simplicity as well as its physical significance.

Molecular Interpretation. Although one must be careful when interpreting such semiempirical correlations on a molecular basis, aside from the predictive usefulness of eq 3 useful insights into the likely factors influencing reaction entropies can be gleaned from these results.

The surprisingly close correspondence observed between ΔS°_{rc} and the dielectric continuum function $(Z_{ox}^2 - Z_{red}^2)/r$ in a given solvent suggests that the reaction entropies are determined in part by nonspecific electrostatic interactions with the surrounding solvent. The observation that such a unified functional relationship is maintained even for structurally different ligands indicates that short-range ligand–solvent interactions do not provide a predominant contribution to ΔS°_{rc} for these systems. (An exception is aquo couples in water; vide infra). The ionic charge–radius dependence, as described by the coefficient K_3 (86.6 J K^{-1} mol^{-1} Å), tends to be larger than the Born predictions. These range from 20.5 J K^{-1} mol^{-1} Å in formamide to 87 J K^{-1} mol^{-1} Å in dimethylformamide. One might expect the use of a single value of K_3 in different solvents to be an oversimplification. Nevertheless, the approximately parallel ΔS°_{rc}–AN plots for different redox couples in Figure 6 show that K_3 is nearly solvent independent. Broadly speaking, the underestimation of K_3 by the Born model is consistent with partial dielectric saturation in the vicinity of the solute, since ΔS°_{rc} will increase as the effective dielectric constant, ϵ_{eff}, decreases (eq 2).[38] On this basis, it is not surprising that K_3 and hence ϵ_{eff} are less strongly solvent dependent than is ϵ. Although more sophisticated treatments along these lines have been pursued,[38] further such development for the systems considered here seems superfluous at present.

As noted above, Figure 6 indicates that specific intermolecular interactions rather than dielectric properties are primarily responsible for the changes in the reaction entropy as the solvent is varied. The correlation between ΔS°_{rc} and solvent AN in Figure 6, together with the absence of such a correlation with the solvent DN (Figure 5), suggests that such interactions might involve solvent molecules as electron acceptors and the metal complexes as donors. Although this is reasonable for complexes containing electron-rich ligands such as bipyridine or cyclopentadiene, such behavior is implausible for couples such as $Ru(NH_3)_6^{3+/2+}$, which act instead as electron acceptors.[12,39]

As an alternative to *solvent–ligand* interactions, this observed solvent dependence may well predominantly reflect changes in *solvent–solvent* interactions. This accounts for the otherwise surprising insensitivity of the ΔS°_{rc}–AN correlations to the nature of the redox couple (Figure 6). The dependence of ΔS°_{rc} upon the solvent AN can be rationalized on this basis provided that solvents with high AN values are also associated with a high degree of "internal order" (i.e. exhibit strong intermolecular interactions). Thus such highly structured solvents should experience a loss of order in the vicinity of the charged solute, at substantial entropic gain, when disrupted by the nonspecific ion–solvent dipole interactions that are invoked above in connection with the ionic charge and size dependencies of ΔS°_{rc}. (Such "solvent structure breaking" is commonly assigned to a region beyond the solvent layer in contact with the solute ligands.[41]) This entropy of disruption will be greater with ions of higher charge, yielding a *negative* contribution to ΔS°_{rc} for cationic couples. This contribution will be largest in hydrogen-bonded solvents such as water and the smallest in aprotic media having low "internal order" such as acetone or acetonitrile. Although quantitative measures of solvent internal order are lacking, examination of the available semiquantitative scales[42] reveals that a rough correlation with the solvent acceptor properties[35] is indeed evident.

In particular, this negative contribution to ΔS°_{rc} provides a simple rationalization of the small or even negative ΔS°_{rc} values observed in water for cationic couples containing large aromatic ligands. Explanations for this surprising behavior have previously been sought in terms of short-range "hydrophobic" interactions between the aromatic ligands and surrounding water molecules.[21b] The success of the above correlations (Figures 2 and 6) suggests instead that the small ΔS°_{rc} values for these couples reflect simply their relatively large size, so that the negative contribution to ΔS°_{rc} from solvent "structure breaking" largely offsets the solvent polarization term, which is proportional to $1/r$. One suspects that the negative ΔS°_{rc} values are observed for cationic metalloprotein couples[21] in water might also represent merely size effects rather than hydrophobic interactions. (However, this is not to deny the overall importance of hydrophobic interactions to ionic solvation).

There are two difficulties with this argument, however, that suggest that other factors are likely to be at least partly responsible for the solvent dependence of ΔS°_{rc}. First, the solvent disruption entropy is expected to yield a contribution to ΔS°_{rc} for anionic couples of a sign opposite to that for cationic couples. Nevertheless, a single, albeit only approximate, correlation having a negative y intercept is observed between ΔS°_{rc} and $(Z_{ox}^2 - Z_{red}^2)/r$ in water (Figure 4), even though two anionic couples are included in this plot. Second, although this solvent disruption effect is predicted to be small for solvents with relatively low solvent polarity, such as acetone, it still predicts that negative y intercepts of ΔS°_{rc} vs. $(Z_{ox}^2 - Z_{red}^2)/r$ plots will be obtained in such cases. This contrasts, for example, with the positive y intercept that is obtained for $Cr(bpy)_3^{(n+1)+/n+}$ in this solvent. [More generally, the values of K_1 and K_2 quoted above indicate that positive y intercepts for such plots are expected for solvents with acceptor numbers below about 35, i.e. when $K_1 > K_2$(AN).]

One factor that can account for these results is the likelihood that the structurally disrupted polar solvent in the vicinity of the solute may tend to orient in a specific direction even in the absence of an ionic charge. Evidence in favor of this possibility is provided by a statistical–mechanical and semiempirical analysis, which shows that the minimum solvation energy for hydrated ions occurs at a fractional positive charge rather than for $Z = 0$.[43] This infers that the water molecules in the "structurally disrupted" region have a tendency to orient preferentially with the electropositive hydrogens pointing toward the solute in the absence of an ionic charge. This may be associated with the stronger tendency of water to act as an electron acceptor toward the solute than as a donor. The effect would yield smaller values of ΔS°_{rc} ($=S^{\circ}_{red} - S^{\circ}_{ox}$) for cationic couples and larger ΔS°_{rc} values for anionic couples since

(38) For example, see: Abraham, M. J.; Liszi, J. *J. Chem. Soc., Faraday Trans 1* **1978**, *74*, 2858.
(39) The electron-accepting tendencies of ruthenium(III) ammines have been demonstrated convincingly by solvatochromic experiments, which show that such complexes are selectively solvated by strongly electron-donating solvents in mixed-solvent media.[40]
(40) Curtis, T.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.
(41) Frank, H. S.; Wen, W.-Y. *Discuss. Faraday Soc.* **1957**, *24*, 133.
(42) Criss, C. M. *J. Phys. Chem.* **1974**, *78*, 1000.
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it would subtract from, and add to, the charge-induced polarization effect in the former and latter cases, respectively. This is at least qualitatively in accordance with the negative y intercept of the ΔS°_{rc} vs. $(Z_{ox}^2 - Z_{red}^2)/r$ plot for water (Figure 4).

This effect can also account for the positive y intercept of such plots found in solvents such as acetone that have low acceptor numbers.[34] Such solvents would tend to orient with their positive ends away from the solute, leading to an effect opposite to that found in water. This would yield *larger* ΔS°_{rc} values for cationic couples, again in accordance with the experimental results in acetone. This notion also provides an explanation for the positive value of K_1 (eq 3) in Figure 7 (91.5 J K^{-1} mol^{-1}), since K_1 constitutes the y intercept expected for a ΔS°_{rc} vs. $(Z_{ox}^2 - Z_{red}^2)/r$ plot in a (hypothetical) solvent for which AN = 0.

Deviations from Empirical Correlations. The above semiempirical correlations suggest that specific ligand–solvent interactions do not provide a major contribution to the reaction entropies of these couples. However, large deviations from these correlations occur for a few systems. Such discrepancies indicate that additional factors can have an important influence upon ΔS°_{rc} in some cases. Most prominently, couples containing aquo ligands, such as $Ru(OH)_2)_6^{3+/2+}$ and $Fe(OH_2)_6^{3+/2+}$ in water, exhibit values of ΔS°_{rc} that are ca. 50–100 J K^{-1} mol^{-1} larger than expected from these correlations (Figure 2). Thus $Ru(OH_2)_6^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$ are closely similar in size, yet ΔS°_{rc} for the former is 80 J K^{-1} mol^{-1} larger. This effect is incipient in the larger ΔS°_{rc} for $Ru(NH_3)_5OH_2^{3+/2+}$ and $Ru(NH_3)_4(OH_2)_2^{3+/2+}$ relative to that for $Ru(NH_3)_6^{3+/2+}$ (Figure 2). On the basis of the present results, it is evident that it is the aquo couples that behave anomalously.

We have suggested that an important positive contribution to ΔS°_{rc} for aquo couples arises from hydrogen bonding between the aquo ligands and surrounding water molecules.[8] Such hydrogen bonding is expected to be more extensive in the trivalent state as a result of the greater acidity of the aquo ligand hydrogens[44] combined with the field-assisted orientation of surrounding water molecules. The resulting greater solvent orientation in the trivalent relative to the divalent oxidation state will therefore yield a positive contribution to ΔS°_{rc}. The even larger value of ΔS°_{rc} for $Cr(OH_2)_6^{3+/2+}$ (205 J K^{-1} mol^{-1}) relative to those for $Fe(OH_2)_6^{3+/2+}$ (180 J K^{-1} mol^{-1}) and $Ru(OH_2)_6^{3+/2+}$ (155 J K^{-1} mol^{-1}) can be understood in terms of the greater changes in electron density on the aquo ligand hydrogens resulting from the transfer of an antibonding (e_g) electron in the first-named couple. These arguments are nicely consistent with the linear correlation observed between ΔS°_{rc} and the solvent deuterium isotope effect upon E_f for aquo couples.[45] The unimportance of such ligand–solvent hydrogen bonding for ammine couples in water is supported by the virtual absence of a solvent isotope effect upon E_f for these systems.[45]

The other important class of structurally simple systems exhibiting large deviations from the above correlations are Co(III/II) couples featuring high-spin Co(II). Although the variety of these couples exhibiting chemical reversibility is necessarily limited in view of the substitutional lability of high-spin Co(II), they exhibit variations in ΔS°_{rc} with solute charge,[46] size, and the solvent similar to those for the low-spin couples considered here.[11,12] However, reaction entropies for the Co(III/II) couples tend to be about 80 J K^{-1} mol^{-1} greater than for low-spin couples containing the same ligands.[12,13] This difference could arise from the change of spin multiplicity involved with the Co(III/II) couple; such spin-equilibrium effects can yield substantial positive contributions to ΔS°_{rc}.[17]

Conclusions

The foregoing demonstrates that reaction entropies for a large number of low-spin M(III/II) couples containing a variety of saturated and unsaturated ligands can be rationalized quantitatively on a unified, relatively straightforward, basis. Particularly significant is the commonality of behavior thus exposed for ligands as chemically different as ammonia and polypyridines. The former, but not the latter, have been noted as engaging in donor–acceptor interactions with the surrounding solvent as evidenced by the sensitivity of the reaction free energies for ammine couples to the solvent donor number.[12] The lack of a need to include this factor to account for the reaction entropies for these couples indicates that ΔS°_{rc} tends to be determined by longer range solute–solvent interactions. The only clear-cut exception to this rule known at present is provided by aquo redox couples in aqueous solution.

The $1/r$ dependence of ΔS°_{rc} observed for the present couples appears to account at least partially for the approximate inverse correlation observed between the reaction entropy and the logarithm of the self-exchange rate constant for a number of outer-sphere couples since the intrinsic solvent reorganization energy is also predicted[47] to depend on $1/r$. However, the present findings concerning the shortcomings of the dielectric continuum model hint that a more molecular approach would be useful for understanding not only the thermodynamics of solvent reorganization but also the nonequilibrium solvent polarization process associated with electron-transfer dynamics.[29,48]

While inevitably oversimplified, the present approach appears to provide useful interpretative as well as predictive power. This may well prove useful for estimating reaction entropies that cannot be obtained experimentally. It may also be feasible to extend such semiempirical treatments to structurally more complicated redox couples, such as macrocycles and biological systems. Further measurements for such systems, utilizing a range of structurally diverse solvents besides water, would be extremely valuable in this regard.

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Registry No. $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(en)_3^{3+}$, 21393-87-3; $Ru(NH_3)_5pz^{3+}$, 38139-16-1; $Ru(NH_3)_4bpy^{3+}$, 69799-61-7; $Ru(NH_3)_4phen^{3+}$, 69799-62-8; $Ru(NH_3)_2(bpy)_2^{3+}$, 55266-15-4; $Ru(bpy)_3^{3+}$, 18955-01-6; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(bpy)_3^{+}$, 56977-24-3; $Cr(bpy)_3^{3+}$, 15276-15-0; $Cr(bpy)_3^{2+}$, 17632-84-7; $Cr(bpy)_3^{+}$, 34424-07-2; $Ru(NH_3)_5NCS^{2+}$, 44819-58-1; $Os(NH_3)_6^{3+}$, 48016-91-7; $Ru(H_2O)_6^{3+}$, 30251-72-0; $Ru(NH_3)_5py^{3+}$, 33291-25-7; $Ru(NH_3)_2(phen)_2^{3+}$, 92055-47-5; $Fe(bpy)_3^{3+}$, 18661-69-3; $Fe(CN)_6^{3-}$, 13408-62-3; $Fe(CN)_4bpy^{-}$, 22337-23-1; ferrocenium, 12125-80-3.

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