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SOLVENT EFFECTS ON THE KINETICS OF SIMPLE ELECTROCHEMICAL REACT--ETC(U)
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SOLVENT EFFECTS ON THE KINETICS OF SIMPLE ELECTROCHEMICAL REACTIONS

I. COMPARISON OF THE BEHAVIOR OF Co(III)/(II) TRIETHYLENEDIAMINE

AND AMMINE COUPLES WITH THE PREDICTIONS OF

DIELECTRIC CONTINUUM THEORY

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The electroreduction kinetics of $Co(en)_3^{3+}$ (en = ethylenediamine), $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5F^{2+}$ have been investigated at mercury electrodes in aqueous solution and six nonaqueous solvents in order to explore the influence of the solvent upon the electrode kinetics of such simple one-electron outer-sphere reactions where the composition of the reactant's coordination sphere remains		

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fixed. Substantial variations in the experimental rate parameters were observed as the solvent was altered; these reflect the influence of the outer-shell solvent upon the reorganization barrier to electron transfer. A simple phenomenological treatment of solvent effects upon the electrode kinetics of such simple redox reactions is given. It is pointed out that double-layer corrected rate constants k_{corr} can be evaluated at the same Galvani potential in different solvents with useful accuracy; these quantities can provide particular insight into the chemical influence of the solvent. The utility of separating such solvent effects into intrinsic and thermodynamic contributions is noted. The substantial decreases in k_{corr} seen when substituting several nonaqueous solvents for water were traced to increases in the outer-shell component of the intrinsic free energy barrier, $(\Delta G_i^\ddagger)_{\text{OS}}$. In contrast, small decreases in $(\Delta G_i^\ddagger)_{\text{OS}}$ are predicted by the dielectric continuum model under these circumstances. These discrepancies between theory and experiment are ascribed to contributions to $(\Delta G_i^\ddagger)_{\text{OS}}$ from extensive short-range reorientation of solvent molecules. Variations in the efficiency of electron tunneling within the transition state may also provide a contribution to the observed solvent effects.

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INTRODUCTION

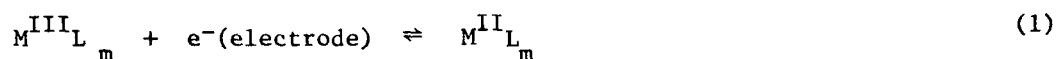
The nature of the solvent is expected to have profound influences upon the kinetics of electron transfer reactions.^{1,2} However, surprisingly little progress has been made in elucidating the underlying factors responsible for the substantial variations in electrochemical and homogeneous redox reactivity that are observed as the solvent is altered. The chief difficulty is that the origins of the observed solvent effects are frequently manifold, arising from alterations in the chemical nature of the reactant as well as from reactant-solvent interactions in both the ground reactant and transition states. The majority of studies of solvent substitution on the kinetics of electrochemical reactions have employed substitutionally labile cations where the observed effects can arise from changes in the composition of the coordination shell (inner-shell effect), as well as variations in the energy required to reorganize solvent molecules beyond the primary coordination shell (outer-shell contribution). Moreover, a number of the reactions studied up to now involve multi-electron and atom transfer [e.g. $\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}(\text{Hg})$] so that the charge and structure of the transition state is usually ill-defined.

For these reasons, it is preferable to select electrode reactions that involve only a single electron transfer for which both halves of the redox couple are stable in solution, and the reactant is substitutionally inert so that the composition of the coordination shell can be altered independently of the solvent, and maintained constant as the solvent is varied. For such systems it is thereby likely that the inner-shell contribution to the activation barrier arising from metal-ligand vibrations will remain approximately constant. The observed solvent dependence of the rate constants for outer-sphere reactions should then arise chiefly from variations in the outer-shell reorganization energy, enabling direct tests to be made of the conventional dielectric continuum model for solvent reorganization.^{1,2} Inner-shell effects can be studied separately

by varying the ligand composition in a given solvent.

Providing that both halves of the redox couple are kinetically or thermodynamically stable with respect to ligand dissociation, etc., the redox thermodynamics as well as the kinetics can be monitored. This enables experimental separations to be made between the so-called "intrinsic" and "thermodynamic" contributions to redox reactivity.³⁻⁵

Although suitable redox couples are not abundant, we have found that a number of transition-metal redox couples having the general form



where M is ruthenium, cobalt, iron, or chromium provide chemically reversible redox couples in a variety of nonaqueous solvents as well as in water when the ligands L are 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen)⁶, ammonia, or ethylenediamine (en)⁷. Of the couples studied in refs. 6 and 7, some were found to be unsuitable for kinetic scrutiny at mercury electrodes on account of immeasurably large standard rate constants [$Ru(NH_3)_6^{3+/2+}$, $Ru(en)_3^{3+/2+}$] or formal potentials that are situated beyond the anodic limit of mercury [$Fe(bpy)_3^{3+/2+}$]. However, $Co(en)_3^{3+/2+}$ was found to have the required combination of properties for the present purpose. Thus $Co(en)_3^{3+}$ is substitutionally inert, and although $Co(en)_3^{2+}$ is substitutionally labile it is sufficiently stable in the presence of a small excess of ethylenediamine to enable values of the formal potential E_f for the redox couple to be determined to a good approximation in a number of solvents using cyclic voltammetry.⁷ The reduction kinetics of $Co(en)_3^{3+}$ can also be conveniently measured as a function of electrode potential using d.c. and pulse polarographic techniques (*vide infra*). Furthermore, the values of E_f for this couple turn out to be quite close to the potentials of zero charge (p.z.c.) for mercury in a number of solvents so that the extent of the double-layer

corrections to the measured rate constants should be manageably small.

We have evaluated electrode kinetic parameters for the $\text{Co(en)}_3^{3+/2+}$ couple at mercury electrodes in water, dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N-methylformamide (NMF), formamide (F), propylene carbonate (PC), and acetonitrile (AN). These results are reported in the present article, and the solvent dependences of the rate parameters are compared with the predictions of the dielectric continuum model for outer-shell solvent effects as formulated by Marcus.¹ Rate-potential data are also given for the reduction of the structurally similar complexes $\text{Co(NH}_3)_6^{3+}$ and $\text{Co(NH}_3)_5\text{F}^{2+}$ in these solvents. Each of the three reactants studied here are expected to reduce via outer-sphere mechanisms on the basis of their behavior at the mercury-aqueous interface.^{8,9}

EXPERIMENTAL

Most nonaqueous 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 was typically $< 0.05\%$ as determined by Karl Fischer titration. Water was purified by distillation from alkaline permanganate followed by "pyrodistillation", which consisted of cycling a mixture of steam and oxygen through a silica tube network at 800°C for two days before collecting the distillate.

$\text{Co(en)}_3 \cdot (\text{ClO}_4)_3$, $\text{Co(NH}_3)_6 \cdot (\text{ClO}_4)_3$, and $\text{Co(NH}_3)_5\text{F} \cdot (\text{ClO}_4)_3$ were prepared as described in refs. 10, 11, and 12, respectively. Anhydrous lithium perchlorate was dried at $\sim 180^\circ\text{C}$ for several days. Tetraethylammonium perchlorate was recrystallized from water and dried in a vacuum oven at 80°C . All solutions were prepared in a dry box under a nitrogen atmosphere.

Heterogeneous rate constants k_{app} as a function of electrode potential^o

were obtained for the reduction of Co(en)_3^{3+} , $\text{Co(NH}_3)_6^{3+}$, and $\text{Co(NH}_3)_5\text{F}^{2+}$ at a dropping mercury electrode (d.m.e.) by means of d.c. and normal pulse polarography, using a PAR 174 Polarographic Analyzer (Princeton Applied Research Corp.) coupled with a Hewlett-Packard 7045 X-Y recorder. The d.m.e. had a flow rate of 1.5 mg s^{-1} and a mechanically controlled drop time of 2 sec. Reactant concentrations between 0.5 and 1 mM were usually employed. The analyses of the polarographic waves utilized the methods due to Oldham and Parry.¹³ The reductions of $\text{Co(NH}_3)_6^{3+}$ and $\text{Co(NH}_3)_5\text{F}^{2+}$ are totally irreversible (i.e., no significant back reaction) since the products rapidly yield solvated Co(II) which cannot be reoxidized to Co(III) except at markedly more positive potentials.⁸ The greater stability of Co(en)_3^{2+} can result in significant anodic back reaction contributions to the polarographic reduction of Co(en)_3^{3+} in several solvents as evidenced by the presence of significant anodic current on the return scan of cathodic-anodic cyclic voltammograms. However, this unwanted complication was eliminated where necessary by adding a small ($\leq 5 \text{ mM}$) concentration of Ni^{2+} or Zn^{2+} . These cations preferentially complex the ethylenediamine released upon formation of Co(II) which acts to encourage dissociation of the remaining Co(en)_3^{2+} and therefore eliminate the anodic back reaction. Values of k_{app} for Co(en)_3^{3+} could therefore be determined at significant cathodic *underpotentials* as well as overpotentials which expedited the evaluation of rate parameters in media where the measured formal (i.e., "standard") rate constants k_{app}^f were fairly large ($> 10^{-2} \text{ cm sec}^{-1}$). The measured rate constants were generally reproducible to within ca 10-20%. Formal potentials for the $\text{Co(en)}_3^{3+/2+}$ couple were obtained in the same electrolytes using cathodic-anodic cyclic voltammetry; ca. 1 mM solutions of Co(en)_3^{3+} were employed that contained an excess of ethylenediamine to suppress

the dissociation of the Co(en)_3^{2+} product. Further details are given in ref. 7.

An aqueous saturated calomel electrode (s.c.e.) was used as the reference electrode, although for convenience electrode potentials are quoted here versus the formal potential for the ferricinium-ferrocene redox couple (Fc^+/Fc) determined in the same solvent and supporting electrolyte.^{6,14} The p.z.c. values for mercury in contact with the various nonaqueous electrolytes were determined using a streaming mercury electrode.

RESULTS

Table I summarizes rate-potential data for the one-electron reduction of Co(en)_3^{3+} in each solvent expressed as an apparent (experimental) cathodic rate constant k_{app}^{-800} measured at -800 mV versus the ferricinium-ferrocene (Fc^+/Fc) couple in the same electrolyte. Also listed are the apparent cathodic transfer coefficients α_{app} obtained from the experimental Tafel plots using $\alpha_{\text{app}} = -f^{-1}(\partial \ln k_{\text{app}} / \partial E)_{\mu}$ where $f = F/RT$, and μ denotes a given electrolyte composition. (The choice of -800 mV vs Fc^+/Fc minimized the extent of data extrapolation that was required, and provided a convenient basis for the kinetic analysis described below.) Since the Tafel plots were essentially linear over the ca 200 mV overpotential range that was typically accessible, a single value of k_{app} and α_{app} suffice to describe the rate parameters in a given electrolyte. Values of the apparent formal rate constants k_{app}^f for $\text{Co(en)}_3^{3+/2+}$ were determined by interpolation or extrapolation to the appropriate formal potential E_f in each electrolyte. In most cases the electrolyte composition μ was chosen to be 0.1 M lithium perchlorate or 0.1 M tetraethylammonium perchlorate (TEAP). These electrolytes probably exhibit negligible specific adsorption at the small to moderate negative electrode charge densities q^m where the kinetics were monitored in nonaqueous media,¹⁵ and

perchlorate anions have only a small tendency to form ion pairs with the cationic reactant.⁷ In aqueous media 0.1 M and 0.4 M potassium hexafluorophosphate were used as supporting electrolytes since the kinetics were measured at small positive values of q^m where perchlorate specific adsorption is quite noticeable. Hexafluorophosphate adsorption is sufficiently weak so that small positive values of the potential across the diffuse layer ϕ_d are obtained under these conditions.^{9,16,17}

The choice of these electrolytes therefore enabled the required diffuse-layer corrections to the cathodic rate parameters to be made with some confidence using the relation (e.g. ref. 9)

$$\ln k_{\text{corr}}^E = \ln k_{\text{app}}^E + f(Z_r - \alpha_{\text{corr}})\phi_d \quad (2)$$

where k_{corr}^E is the "double-layer corrected" rate constant corresponding to the measured value k_{app}^E at a given electrode potential E , Z_r is the charge on the reactant, and α_{corr} is the transfer coefficient after correction for double-layer effects. This last quantity can be obtained from α_{app} using

$$\alpha_{\text{corr}} = \frac{\alpha_{\text{app}} - Z_r (\partial\phi_d/\partial E)_\mu}{1 - (\partial\phi_d/\partial E)_\mu} \quad (3)$$

Eqns (2) and (3) involve the assumptions that the reaction site lies at the outer Helmholtz plane (o.H.p.) and that discreteness-of-charge effects are negligible.⁹ However, they have been shown^{8,9} to be approximately consistent with experimental kinetic data for Co(III) amine reduction in a wide range of aqueous supporting electrolytes when ϕ_d is calculated from double-layer compositional data using the Gouy-Chapman-Stern (GCS) theory.¹⁸ The required values of ϕ_d in aqueous media were obtained from the double-layer data i

ref. 16 (cf. refs. 9 and 17). The values of ϕ_d in nonaqueous media were determined as follows. Electrode charge-potential ($q^m - E$) plots were obtained by integrating the appropriate capacitance-potential curves taken from the literature (see footnote (c) to Table I for sources) along with the p.z.c. values determined in the present work. These p.z.c. values obtained in 0.1 M perchlorate media are (vs. Fc^+/Fc , values vs. s.c.e. given in parentheses): formamide, -729 mV (-448 mV); NMF, -732 mV (-335 mV); PC, -601 mV (-273 mV); AN, -622 mV (-250 mV); DMSO, -717 mV (-278 mV); DMF, -691 mV (-198 mV). The values of q^m at the required electrode potentials were then read off from these plots and inserted into the GCS expression¹⁸ to find the corresponding values of ϕ_d . Values of α_{corr} were also determined in a similar manner from the corresponding values of α_{app} (Table I) using eqn (3); they varied typically in the range ca 0.5-0.7. (Although the quantitative validity of these estimates of α_{corr} is questionable, this uncertainty has little influence upon the extent of the double-layer correction since $Z_r \gg \alpha_{corr}$.)

The resulting values of k_{corr}^{-800} and k_{corr}^f are also listed in Table I. In a given solvent, it was found that the corresponding values of k_{corr} determined in the various electrolytes, including 0.5 M $LiClO_4$ as well as 0.1 M $LiClO_4$ are typically in reasonable agreement (Table I), which supports the approximate validity of the double-layer corrections.

It is seen that the values of k_{corr}^f as well as k_{corr}^{-800} vary markedly with the nature of the solvent, being substantially smaller in nonaqueous media, particularly DMSO and DMF, compared with the corresponding rate constants in water. In view of these marked solvent influences upon the electrode kinetics of $Co(en)_3^{3+/2+}$, it is of interest to ascertain if the structurally even simpler $Co(NH_3)_6^{3+/2+}$ couple exhibits similar behavior. The kinetic

parameters for $\text{Co}(\text{NH}_3)_6^{3+}$ reduction are summarized in Table II, along with those for $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ reduction. The latter exhibits similar rate parameters to $\text{Co}(\text{NH}_3)_6^{3+}$ reduction in aqueous media⁸ yet carries a smaller net charge so that the possible influence of varying Z_r upon the solvent effects can be assessed. Inspection of Table II reveals that the corresponding values of k_{corr}^{-800} for $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ reduction in most solvents are within a factor of three or so of each other, whereas those for $\text{Co}(\text{en})_3^{3+}$ reduction tend to be between five and tenfold smaller.

DISCUSSION

It is useful at the outset to summarize the phenomenological treatment which will be used to unravel the underlying factors responsible for the striking solvent effects presented in Tables I & II. This approach has also been described recently in connection with solvent isotope effects in electrode kinetics.¹⁹

Consider the generalized electrochemical reaction proceeding at a Galvani potential ϕ_m :



The free energies of the ground states I and II that are prior to, and following, electron transfer, respectively, can be expressed as²⁰

$$G_I^\circ = \bar{G}_{\text{ox}}^\circ + \mu_{e^-}^\circ - F\phi_m \quad (5)$$

$$G_{II}^\circ = \bar{G}_{\text{red}}^\circ \quad (6)$$

where $\bar{G}_{\text{ox}}^{\circ}$ and $\bar{G}_{\text{red}}^{\circ}$ are the free energies of the oxidized and reduced species, respectively, and $\mu_{e^-}^{\circ}$ is the chemical potential of the reacting electron. Since the overall free energy of reaction equals zero at the standard potential ϕ_m° , then

$$-F\phi_m^{\circ} = \bar{G}_{\text{red}}^{\circ} - \bar{G}_{\text{ox}}^{\circ} = \Delta G_{\text{rc}}^{\circ} \quad (7)$$

The alteration in the free energies of the ions forming the redox couple resulting from changing from water to a nonaqueous solvent $\Delta(\bar{G}_{\text{red}}^{\circ} - \bar{G}_{\text{ox}}^{\circ})^{s-w}$ [$= \Delta(\Delta G_{\text{rc}}^{\circ})^{s-w}$], will therefore be related to the corresponding variation in $\phi_m, \Delta(\phi_m^{\circ})^{s-w}$, by

$$-F\Delta(\phi_m^{\circ})^{s-w} = \Delta(\Delta G_{\text{rc}}^{\circ})^{s-w} \quad (8)$$

The corresponding relationship to eqn (8) for electrochemical kinetics can be derived by noting that the double-layer corrected free energy of activation $\Delta G_{\text{corr}}^{\ddagger}$ [$= G_{\text{corr}}^{\ddagger} - G_{\text{I}}^{\circ}$] can be separated into a potential-dependent ("electrical") part $(G_{\text{corr}}^{\ddagger} - G_{\text{I}}^{\circ})_e$ and a potential-independent ("chemical") part $(G_{\text{corr}}^{\ddagger} - G_{\text{I}}^{\circ})_c$.²⁰ The former component is related to the potential-dependent part of $(G_{\text{II}}^{\circ} - G_{\text{I}}^{\circ})$, $F\phi_m$ (eqns (5) and (6)) by^{19,20}

$$(G_{\text{corr}}^{\ddagger} - G_{\text{I}}^{\circ})_e = \alpha_{\text{corr}} F\phi_m \quad (9)$$

The double-layer corrected rate constant k_{corr} in a given solvent can be related to $\Delta G_{\text{corr}}^{\ddagger}$ by¹

$$k_{\text{corr}} = \kappa Z \exp(-\Delta G_{\text{corr}}^{\ddagger}/RT) \quad (10)$$

where κ is the transmission coefficient and Z is the electrochemical collision frequency. Since Z should be dependent only on the effective reactant mass,¹

it should be approximately solvent-independent. If κ is also solvent-independent (*vide infra*), the ratio of the double-layer corrected rate constant for a given reaction in water to that in another solvent at a fixed value of ϕ_m , $(k_w/k_s)_{\text{corr}}^{\phi_m}$, will be related to the corresponding free energies of activation $(\Delta G_{\text{corr}_w}^{\ddagger})^{\phi_m}$ and $(\Delta G_{\text{corr}_s}^{\ddagger})^{\phi_m}$ by

$$RT \ln(k_w/k_s)_{\text{corr}}^{\phi_m} = (\Delta G_{\text{corr}_s}^{\ddagger})^{\phi_m} - (\Delta G_{\text{corr}_w}^{\ddagger})^{\phi_m} \quad (11)$$

which in view of eqn (9) can be written as

$$RT \ln(k_w/k_s)_{\text{corr}}^{\phi_m} = \Delta(\Delta G_{\text{corr}_c}^{\ddagger})^{\text{s-w}} \quad (12)$$

where $\Delta(\Delta G_{\text{corr}_c}^{\ddagger})^{\text{s-w}}$ is the change in the chemical part of the activation free energy for a given reaction resulting from substituting a given nonaqueous solvent for water.

The evaluation of the quantities $\Delta(\Delta G_{\text{rc}}^{\circ})^{\text{s-w}}$ and $\Delta(\Delta G_{\text{corr}_c}^{\ddagger})^{\text{s-w}}$ in eqns (8) and (12), respectively, for a given electrode reaction is of fundamental interest since they provide a monitor of the purely chemical influences brought about by solvent substitution upon the thermodynamics⁶ and kinetics of electron transfer. Since neither absolute nor even relative values of ϕ_m in different solvents are strictly speaking thermodynamically accessible quantities, the evaluation of both $\Delta(\Delta G_{\text{rc}}^{\circ})^{\text{s-w}}$ and $\Delta(\Delta G_{\text{corr}_c}^{\ddagger})^{\text{s-w}}$ inevitably involves some sort of an extrathermodynamic procedure. The simplest of these involves the assumption that ϕ_m° for the ferricinium-ferrocene couple is independent of the solvent.²¹ If this assumption is correct, the values of k_{corr} evaluated at a fixed electrode potential (-800 mV) versus Fc^+/Fc given in Tables I & II can be inserted directly into eqn (12) to yield estimates of $\Delta(\Delta G_{\text{corr}_c}^{\ddagger})^{\text{s-w}}$. Likewise, values of the formal potential E_f for the

redox couple versus Fc^+/Fc in different solvents would then yield values of $\Delta(\Delta G_{\text{rc}}^\circ)^{\text{s-w}}$ using eqn (8). Actually, it is preferable to apply a correction to the electrode potentials employed in each of the various nonaqueous solvents in order to take into account the likely deficiencies of the ferrocene assumption and convert the free energies to the more reliable²¹ tetraphenylarsonium-tetraphenylborate (TATB) scale.⁶ Therefore the value of k_{corr} in each nonaqueous solvent that was inserted into eqn (12) was obtained at an electrode potential differing from -800 mV vs. Fc^+/Fc by an amount ΔE found from⁶

$$-F \Delta E = \Delta(\Delta G_{\text{rc}}^\circ)^{\text{s-w}}_{\text{Fc}} \quad (13)$$

where $\Delta(\Delta G_{\text{rc}}^\circ)^{\text{s-w}}_{\text{Fc}}$ is the value of $\Delta(\Delta G_{\text{rc}}^\circ)^{\text{s-w}}$ for the Fc^+/Fc couple in a given nonaqueous solvent on the TATB scale. [Literature estimates of $\Delta(\Delta G_{\text{rc}}^\circ)^{\text{s-w}}$ are given in Table II of ref. 6.] The resulting values of $\Delta(\Delta G_{\text{corr}}^\ddagger)^{\text{s-w}}_{\text{c}}$ for $\text{Co}(\text{en})_3^{3+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ reduction on the TATB scale are listed in Table III, along with the corresponding estimates of $\Delta(\Delta G_{\text{rc}}^\circ)^{\text{s-w}}$ for the $\text{Co}(\text{en})_3^{3+/2+}$ couple obtained using eqn (8) which are taken from Table II of ref. 7. (Although there are inevitable uncertainties in the use of such extra-thermodynamic procedures, the values of $\Delta(\Delta G_{\text{rc}}^\circ)^{\text{s-w}}$ given are probably accurate to about $\pm 3\text{-}5 \text{ kJ mol}^{-1}$,^{6,7} as are the values of $\Delta(\Delta G_{\text{rc}}^\ddagger)^{\text{s-w}}_{\text{c}}$ in Table III which are rounded off to the nearest 1 kJ mol^{-1} .)

It is seen that the values of $\Delta(\Delta G_{\text{rc}}^\ddagger)^{\text{s-w}}_{\text{c}}$ for $\text{Co}(\text{en})_3^{3+}$ reduction are uniformly positive and larger than the corresponding values of $\Delta(\Delta G_{\text{rc}}^\circ)^{\text{s-w}}$; i.e., the destabilization of the transition state for $\text{Co}(\text{en})_3^{3+}$ reduction relative to the bulk reactant when substituting nonaqueous for aqueous media is uniformly greater than that for the bulk product. Although values of

$\Delta(\Delta G_{rc}^{\circ})^{s-w}$ for $\text{Co}(\text{NH}_3)_6^{3+/2+}$ are unobtainable, they are likely to be closely similar to those for $\text{Co}(\text{en})_3^{3+/2+}$ so a similar result probably also applies to the ammine couple.

The values of $\Delta(\Delta G_{rc}^{\circ})^{s-w}$ for M(III)/(II) ammine and ethylenediamine couples are much larger than the dielectric continuum (Born) predictions; they have been interpreted in terms of donor-acceptor interactions between the ammine hydrogens and the solvent molecules.⁷ Thus $\Delta(\Delta G_{rc}^{\circ})^{s-w}$ has been shown to increase monotonically with increasing basicity of the solvent, suggesting that there are strong ligand-solvent interactions in the tri-positive (oxidized) state which are partly dissipated upon reduction as a consequence of the smaller charge of the product.⁷ At first sight, the even larger values of $\Delta(\Delta G_{corr}^{\ddagger})_c^{s-w}$ are surprising on this basis since the transition state is expected to have a solvent structure that is suitably intermediate between those for the reactant and product.

Solvent Dependence of Intrinsic Barriers

Further insight into the underlying factors which are responsible for these solvent effects can be obtained by separating $\Delta(\Delta G_{corr}^{\ddagger})_c^{s-w}$ into intrinsic and thermodynamic contributions.^{3-5,19} The double-layer corrected formal rate constant k_{corr}^f can be related directly to the so-called intrinsic free energy of activation ΔG_i^{\ddagger} by¹ (cf. eqn (10))

$$k_{corr}^f = \kappa Z \exp(-\Delta G_i^{\ddagger}/RT) \quad (14)$$

This intrinsic barrier ΔG_i^{\ddagger} (labeled $\lambda^{e1}/4$ in the Marcus treatment¹) forms the focus of attention of contemporary electron transfer theory.^{1,2} It is of particular interest since it represents the value of $\Delta G_{corr}^{\ddagger}$ when $G_I^{\circ} = G_{II}^{\circ}$, i.e. when the electrical and chemical parts of the overall free energy of reaction just cancel. The significance of the intrinsic barrier in the present context can be seen as follows.

In view of eqn (9), ΔG_i^\ddagger and $\Delta G_{\text{corr}}^\ddagger$ are related by

$$\Delta G_{\text{corr}}^\ddagger = \Delta G_i^\ddagger + \alpha_{\text{corr}} F(\phi_m - \phi_m^0) \quad (15)$$

Therefore from eqns (8) and (15) the alteration in ΔG_i^\ddagger , $\Delta(\Delta G_i^\ddagger)^{s-w}$, resulting from changing from water to another solvent is related to $\Delta(\Delta G_{\text{corr}}^\ddagger)^{s-w}$ and $\Delta(\Delta G_{\text{rc}}^\circ)^{s-w}$ by

$$\Delta(\Delta G_i^\ddagger)^{s-w} = RT \ln(k_w^f/k_s^f)_{\text{corr}} \quad (16a)$$

$$= \Delta(\Delta G_{\text{corr}}^\ddagger)^{s-w} - \alpha_{\text{corr}} \Delta(\Delta G_{\text{rc}}^\circ)^{s-w} \quad (16b)$$

The solvent dependence of the free energy barrier $\Delta(\Delta G_{\text{corr}}^\ddagger)^{s-w}$ is therefore equal to the sum of the "intrinsic" part $\Delta(\Delta G_i^\ddagger)^{s-w}$, and a "thermodynamic" part $\alpha_{\text{corr}} \Delta(\Delta G_{\text{rc}}^\circ)^{s-w}$. The latter is equal to the change in $\Delta G_{\text{corr}}^\ddagger$ expected for a hypothetical transition state having the properties of a stable species with a structure and charge appropriately intermediate between ox and red. Therefore nonzero values of $\Delta(\Delta G_i^\ddagger)^{s-w}$ signify that there are changes in G_{corr}^\ddagger resulting from solvent substitution that are not reflected in corresponding changes in $\bar{G}_{\text{ox}}^\circ$ and $\bar{G}_{\text{red}}^\circ$, i.e., are unique ("intrinsic") to the transition state.^{3-5,19}

Table IV contains values of $\Delta(\Delta G_i^\ddagger)^{s-w}$ for the $\text{Co(en)}_3^{3+/2+}$ couple obtained using eqn (16a) from the standard rate constants listed in Table I. As expected from eqn (16b) given that $\Delta(\Delta G_{\text{corr}}^\ddagger)^{s-w} > \Delta(\Delta G_{\text{rc}}^\circ)^{s-w}$ (Table III) it is seen that the values of $\Delta(\Delta G_i^\ddagger)^{s-w}$ are uniformly positive; they approach 5 kcal mol^{-1} for DMSO and DMF. As noted above, it is likely that the maintenance of a constant ligand composition around the reactant will keep the inner-shell contribution to the reorganization energy, and hence to ΔG_i^\ddagger , approximately constant as the surrounding solvent is varied. It is therefore

probable that any variations in $\Delta G_{\ddagger}^{\ddagger}$ resulting from altering the solvent are due to variations in the outer-shell contribution $(\Delta G_{\ddagger}^{\ddagger})_{OS}$.

The usual theoretical model for outer-shell reorganization treats the surrounding solvent as a uniform dielectric continuum, which according to Marcus^{1,22} yields the following expression for the intrinsic barrier:

$$(\Delta G_{\ddagger}^{\ddagger})_{OS} = \frac{e^2}{8} \left(\frac{1}{a} - \frac{1}{R_e} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (17)$$

where e is the electronic charge, ϵ_{op} and ϵ_s are the optical and static solvent dielectric constants, a is the radius of the (spherical) reactant, and R_e is twice the distance from the reacting species in the transition state to the electrode surface; i.e., the distance from the ion to its "image" in the metal. The $(1/R_e)$ term in eqn (17) therefore describes the stabilization of the transition state relative to the reactant ground state afforded by the presence of imaging interactions with the metal electrode.^{1,22} However, it has been pointed out that this term could overestimate the importance of image forces since eqn (17) ignores the screening effect of the surrounding ions.²³ It appears to be likely that the reaction sites for Co(III) amine reduction lie outside the primary inner layer of solvent molecules, and close to the outer Helmholtz plane⁸ (o.H.p.) where some diffuse-layer screening of the image interactions can be expected. Consequently, values of $(\Delta G_{\ddagger}^{\ddagger})_{OS}$ were calculated from eqn (17) for the various solvents in two ways. Either R_e was set equal to infinity (i.e., imaging was neglected) or taken as $2(a + L)$, where a is the reactant radius and L is the length of the solvent molecule L , since there is evidence that the thickness of the inner layer in some nonaqueous solvents roughly corresponds to L .²⁴ The value of L was taken as 3 Å for water,²⁵ and 6 Å for the nonaqueous solvents;²⁴ a was taken

to be 3.5 Å (appropriate for $\text{Co(en)}_3^{3+/2+}$ and $\text{Co(NH}_3)_6^{3+/2+}$ ²⁶).

Values of $\Delta(\Delta G_1^\ddagger)^{s-w}_{\text{calc}}$ obtained from the difference between the corresponding calculated values of $(\Delta G_1^\ddagger)_{\text{os}}$ in each nonaqueous solvent with that in water are also listed in Table IV, both for $R_e = \infty$ and $R_e = 2(a + l)$. It is seen that in both cases small negative values of $\Delta(\Delta G_1^\ddagger)^{s-w}$ are typically obtained, in contrast to the larger and positive experimental values obtained for $\text{Co(en)}_3^{3+/2+}$. (Similar results were also obtained using other plausible values of a and R_e). It is therefore concluded that the solvent dielectric continuum model is unable to account for the observed solvent dependence of the electrochemical kinetics of $\text{Co(en)}_3^{3+/2+}$.

Values of $\Delta(\Delta G_1^\ddagger)^{s-w}$ cannot be obtained for $\text{Co(NH}_3)_6^{3+/2+}$ since the formal potentials for this couple are unknown. However, the values of $\Delta(\Delta G_{\text{corr}}^\ddagger)^{s-w}$ for $\text{Co(NH}_3)_6^{3+}$ reduction are only marginally smaller than those for Co(en)_3^{3+} reduction (Table III), and consistently larger than the values of $\Delta(\Delta G_{\text{rc}}^\circ)^{s-w}$ for $\text{Co(en)}_3^{3+/2+}$ and other amine redox couples⁷ (including $\text{Ru(NH}_3)_6^{3+/2+}$). Therefore given that $t_{\text{corr}} \sim 0.5 - 0.7$,⁸ it follows from eqn (16b) that $\text{Co(NH}_3)_6^{3+/2+}$ as well as $\text{Co(en)}_3^{3+/2+}$ would likely yield values of $\Delta(\Delta G_1^\ddagger)^{s-w}$ which are in qualitative disagreement with the dielectric continuum predictions.

Two factors appear most likely to be responsible for these apparent discrepancies between theory and experiment. First, it seems feasible that the electron tunneling probability within the transition state (i.e., the transmission coefficient κ in eqns (10) and (14) could be substantially smaller in some nonaqueous solvents than in water as a result of the probable differences in inner-layer thickness that were noted above. Such a situation would render eqn (16a) invalid and yield values of $\Delta(\Delta G_1^\ddagger)^{s-w}$ that

are falsely large. If the distance D between the reaction plane and the electrode surface ($= 0.5 R_e$) is given roughly by $D = (a + L)$, D may well increase from 6.5 Å in water to around 8-9 Å in nonaqueous solvents of intermediate molecular weight such as those considered here. Although the question of whether outer-sphere electron transfer is commonly nonadiabatic ($\kappa \ll 1$) or adiabatic ($\kappa \approx 1$) has been the subject of extensive debate,²⁷ the likely dependences of κ upon the distance between and the nature of the redox centers are largely unsettled. However, recent electron tunneling calculations²⁸ for $\text{Fe}(\text{OH}_2)_6^{3+/2+}$ self-exchange in homogeneous solution indicate that κ falls rapidly as the internuclear distance increases above about 6 Å (e.g. $\kappa \sim 10^{-3}$ at 6.9 Å²⁸). Comparable results have been obtained with tunneling calculations performed for heterogeneous $\text{Fe}(\text{OH}_2)_6^{3+/2+}$ exchange.²⁹ If the reactant indeed does not penetrate the inner layer of solvent molecules in the transition state for electron transfer (i.e., outer-sphere electrode reaction pathways are followed^{30,31}), then the resulting increases in D when substituting nonaqueous solvents for water could be responsible for the smaller values of $k_{\text{corr}}^{\ddagger}$ in the former media via smaller values of κ rather than larger values of ΔG_1^{\ddagger} (eqn (14)).

Nevertheless, it seems likely that the observed behavior is at least partly due to variations in $(\Delta G_1^{\ddagger})_{\text{os}}$ arising from the more extensive changes in short-range solvent structure that may be necessary in order to surmount the Franck-Condon barrier in nonaqueous media. Although the likely contribution of such short-range reactant-solvent interactions has been widely recognized,² it is difficult to provide theoretical estimates of their contribution to $(\Delta G_1^{\ddagger})_{\text{os}}$. However, a valuable experimental monitor of the extent of solvent structural changes accompanying electron transfer can be obtained

from measurements of the so-called reaction entropy ΔS_{rc}° of individual redox couples.³² This quantity, which is most directly determined from the temperature derivative of the formal potential using a nonisothermal cell arrangement,³² is equal to the difference between the ionic entropies of the reduced and oxidized forms of the redox couple ($\bar{S}_{red}^\circ - \bar{S}_{ox}^\circ$). [Note that absolute values of ΔS_{rc}° are experimentally measurable to a useful accuracy ($\pm 2-3$ J deg⁻¹ mol⁻¹) whereas absolute values of ΔG_{rc}° are largely unknown.³²] The experimental values of ΔS_{rc}° for simple couples of the form in eqn (1) have been found to be sensitive both to the nature of the coordinated ligands^{32,33} and the surrounding solvent^{6,7,14,34} to a much greater extent than predicted by the dielectric continuum (Born) model. This illustrates the importance of short-range ligand-solvent interactions to the changes in solvent polarization ("ordering") brought about by electron transfer.

Significantly, the values of ΔS_{rc}° for $\text{Co}(\text{en})_3^{3+/2+}$ (and also $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and $\text{Ru}(\text{en})_3^{3+/2+}$) have been found to be substantially (up to 100 J deg⁻¹ mol⁻¹) larger in nonaqueous media, particularly DMSO and DMF, compared to the corresponding quantity in water. These variations in ΔS_{rc}° , $\Delta(\Delta S_{rc}^\circ)^{S-W}$, have been found to increase as the extent of "internal order"³⁵ of the bulk solvent decreases;^{6,7,14} i.e., when going from highly structured solvents, especially water, to polar yet more weakly associated liquids, especially PC, DMF, and DMSO. This trend can be understood in terms of the smaller resistance of the latter solvents to orientation around the solute in the higher oxidation state, the orientation partially dissipated in the reduced state so that $\bar{S}_{ox}^\circ \approx \bar{S}_{red}^\circ$.

Such sensitivities of ΔS_{rc}° to the solvent medium might be expected to be reflected also in variations in the outer-shell part of the intrinsic barrier.¹⁹ Thus the formation of the transition state for $\text{Co}(\text{en})_3^{3+}$ reduction

in DMSO, for example, is expected to involve a much greater decrease in solvent polarization than the corresponding process in water in view of the large positive value of $\Delta(\Delta S_{rc}^{\circ})^{S-W}$ for DMSO ($63 \text{ J deg}^{-1} \text{ mol}^{-1}$).⁷ This difference will not affect the intrinsic barrier if $\Delta(\Delta G_{corr}^{\ddagger})^{S-W} = \alpha_{corr} \Delta(\Delta G_{rc}^{\circ})^{S-W}$ (eqn (16b)); i.e., when the solvent effect upon the transition-state stability is that expected for (hypothetical) stable cation with a structure identical to that of the transition state but having the charge $(Z_r - \alpha_{corr})$. However, in actuality the transition state is reached via the reorganization of nuclear coordinates *while the reactant charge remains fixed*, electron transfer occurring rapidly ($\sim 10^{-16}$ sec) once the transition state is formed.³⁶ The required solvent reorientation will therefore be unaided by a concomitant variation in the reactant charge so that these solvent structural changes should involve an additional component of the activation energy which will contribute to the intrinsic barrier. Generally, therefore, the presence of greater differences in the extent of solvent polarization between the oxidized and reduced halves of the redox couple would be expected to yield larger values of $\Delta(\Delta G_{rc}^{\ddagger})^{S-W}$. However, the likely magnitude of the effect is difficult to assess.

Fig. 1 is a plot of $\Delta(\Delta G_{rc}^{\ddagger})^{S-W}$ for the $\text{Co(en)}_3^{3+/2+}$ couple (Table IV) against the corresponding values of ΔS_{rc}° in each solvent, taken from ref. 7. It is seen that there is a roughly linear correlation between $\Delta(\Delta G_{rc}^{\ddagger})^{S-W}$ and ΔS_{rc}° , suggesting that there is indeed a contribution to ΔG_{rc}^{\ddagger} arising from specific short-range solvent polarization not considered in the dielectric continuum treatment. Thus ΔG_{rc}^{\ddagger} as well as ΔS_{rc}° increases as the extent of association between bulk solvent molecules decreases, such as the extent of hydrogen bonding in the sequence water, formamide, NMF, and DMF.^{6,7} The progressively greater decreases in the extent of solvent polarization

attend the formation of Co(en)_3^{2+} from Co(en)_3^{3+} in this sequence also appear to require that additional energy be expended to reach the required degree of *nonequilibrium* solvent polarization in the transition state. A similar correlation between ΔS_{rc}^{\ddagger} and ΔG_i^{\ddagger} has been demonstrated for a series of outer-sphere electron transfer processes in homogeneous aqueous media, including reactions where the reorganization of outer-shell solvent provides the dominant contribution to ΔG_i^{\ddagger} .³⁷

Other kinetic data for simple outer-sphere redox processes involving substitutionally inert reactants in nonaqueous solvents are sparse, both at electrodes and in homogeneous solution. However, we have recently pointed out⁶ that the rate constant k_{ex} for the homogeneous self-exchange of $\text{Fe(phen)}_3^{3+/2+}$ and related couples are 1-2 orders of magnitude smaller in acetonitrile than in water.^{38,39} The dielectric continuum model predicts that k_{ex} should be closely similar in these solvents. Interestingly, this decrease in k_{ex} is again accompanied by a substantial increase in ΔS_{rc}^{\ddagger} .⁶ The variations of k_{ex} for the ferricinium/ferrocene couple between different nonaqueous solvents have also been reported to differ from the dielectric continuum predictions.⁴⁰

It should be noted that the likely limitations of the conventional dielectric continuum model in describing both the thermodynamics of outer-shell solvation and the outer-shell contribution to the reorganization energy for electron transfer has frequently been noted.^{2,41,42} Indeed, theoretical models of solvation have recently been developed which take into account the spatial dispersion of the surrounding solvent structure.^{2,41,42} In principle, these models allow the various short-range vibrational and reorientational motions of the solvent to be treated, although they still

do not consider the existence of specific interactions between the coordinated ligands and the nearest-neighbor solvent molecules. Such interactions are indicated from the redox thermodynamic measurements to be important for the present reactants.⁷

CONCLUSIONS

The foregoing demonstrates that the chemical nature of the solvent can play an important role in determining the "intrinsic" as well as the "thermodynamic" part of the free energy barrier to heterogeneous electron transfer, even when the solvent is excluded from the reactant's coordination sphere. These results, if confirmed for other reactions and solvents, cast doubt on the validity of the uniform dielectric continuum model for estimating the outer-shell contribution to the reorganization barrier. The breakdown of this model may be most serious for weakly associated yet polar solvents where especially large changes in short-range solvent polarization accompany electron transfer. Since it is conventional to utilize dielectric continuum estimates of $(\Delta G_1^\ddagger)_{os}$ in order to extract the inner-shell contribution $(\Delta G_1^\ddagger)_{is}$ from experimental rate constants, the estimates of $(\Delta G_1^\ddagger)_{is}$ thus obtained could well be seriously in error. Fortunately, most of the comparisons between experimental and theoretical estimates of $(\Delta G_1^\ddagger)_{is}$ have involved reactions in aqueous media, where the short-range solvent effects may well be smaller than in other solvents. However, we have shown from a study of solvent isotope effects that short-range solvation may influence $(\Delta G_1^\ddagger)_{os}$ substantially in aqueous media for reactants that engage in strong hydrogen-bonding interactions with surrounding water molecules.¹⁹ Unfortunately, these conclusions are clouded by the uncertainty

to what extent the observed reactivity differences between the various solvents are due to variations in the efficiency of electron tunneling rather than in the height of the Franck-Condon barrier. In principle, such distinctions could be made by careful studies of the temperature dependence of the electrochemical rate constants.^{31,43,44}

It is hoped that experimental studies of solvent effects upon both electrochemical and homogeneous reactivities for a variety of simple redox reactions will stimulate the further development of increasingly realistic theories describing outer-shell solvent reorganization. Detailed comparisons between experiment and theory, particularly utilizing the recently developed structural solvation models^{2,41,42} should be most enlightening and a valuable aid to the elucidation of the role of short-range solvent structure in electron-transfer processes.

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TABLE I. Solvent dependence of electrochemical kinetic parameters for the $\text{Co(en)}_3^{3+/2+}$ couple at mercury electrodes at 25°C.

Electrolyte	k_{app}^{-800} cm.s^{-1}	a	k_{app}^b	k_{corr}^{-800} cm.s^{-1}	c	$-E_f^d$	k_{app}^e	k_{corr}^f
	cm.s^{-1}			cm.s^{-1}	mV. vs. Fc/Fc ⁺		cm.s^{-1}	cm.s^{-1}
Water	$\sim 100^j$		0.95	~ 50		565	3×10^{-2}	3×10^{-2}
	$\sim 30^j$		0.85	~ 30		580	5×10^{-2}	2.5×10^{-2}
Formamide	3×10^{-3}	h	1.0	1×10^{-3}		813	4.5×10^{-3}	1.3×10^{-3}
	2×10^{-3}	h	1.0			806	2.5×10^{-3}	
	3.5×10^{-3}	h	0.95	1.5×10^{-3}		800	3.5×10^{-3}	1.6×10^{-3}
NMF	3.5×10^{-5}	h	0.95	1.5×10^{-5}		945	7×10^{-3}	6.5×10^{-4}
	2.5×10^{-5}	h	0.85			943	4×10^{-3}	
PC	4×10^{-2}	h	0.7	1.1×10^{-3}		632	4.5×10^{-3}	3×10^{-4}
	2×10^{-2}	h	0.6			633	4.5×10^{-3}	
AN	0.35	i	0.7	4×10^{-3}		590	1.0×10^{-3}	1.3×10^{-3}
	0.25 ^j	i	0.7					
DMSO	3×10^{-6}	h	0.85	2.5×10^{-7}		1040	8.5×10^{-3}	8×10^{-6}
	2×10^{-6}	h	0.8	2×10^{-7}				
	1.0×10^{-6}	h	0.8	4×10^{-7}		1015	1.4×10^{-3}	2×10^{-5}
DMF	5×10^{-6}	h	0.95	7×10^{-7}		968	3×10^{-3}	1×10^{-5}
	5×10^{-6}	h	0.95	8.5×10^{-7}		970	4×10^{-3}	

Notes to Table 1

^a Apparent (experimental) rate constant for Co(en)_3^{3+} reduction in solvent and electrolyte indicated, measured at -800 mV. vs. formal potential for ferricinium-ferrocene couple (Fc^+/Fc) in same media.

^b Apparent cathodic transfer coefficient in solvent and electrolyte indicated, obtained from $\alpha_{\text{app}} = -(RT/F)(\partial \ln k_{\text{app}}/\partial E)_H$.

^c Double-layer corrected rate constant at -800 mV. vs. Fc^+/Fc , obtained from corresponding value of k_{app}^{-800} using eqn (2) assuming that $Z_r = 3$ and $\alpha_I \approx 0.6-0.7$ (see text). Sources of electrode capacitance data used to estimate $q^m - E$ curves and hence values of ϕ_d employed in eqn (2): Water, ref. 16; formamide, ref. 24; NMF, ref. 15b; AN, R. Payne, J. Phys. Chem., 71, 1548(1967); PC, DMSO, DMF, R. Payne, ref. 15a.

^d Formal potential for $\text{Co(en)}_3^{3+/2+}$ couple against Fc^+/Fc , determined in stated media using cyclic voltammetry (see text and references 11 and 12).

^e Apparent "formal" rate constant (i.e. measured at E_f) in stated media.

^f Double-layer corrected formal rate constant, obtained from corresponding value of k_{app}^f using eqn (2) assuming that $Z_r = 3$ and $\alpha_{\text{corr}} \approx 0.6-0.7$ (see text).

^g Solution contained $\sim 2 \text{ mM } \text{H}^+$

^h Solution contained $\sim 5 \text{ mM } \text{Ni}^{2+}$

ⁱ Solution contained $\sim 5 \text{ mM } \text{Zn}^{2+}$

^j Extrapolated value

TABLE II. Solvent dependence of electrochemical kinetic parameters for the one-electron reduction of $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ at mercury electrodes at 25°C.

Solvent ^d	Electrolyte	$\text{Co}(\text{NH}_3)_6^{3+}$ reduction			$\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ reduction		
		$k_{\text{app}}^{-800\text{a}}$ cm.s ⁻¹	$\alpha_{\text{app}}^{\text{b}}$	$k_{\text{corr}}^{-800\text{c}}$ cm.s ⁻¹	$k_{\text{app}}^{-800\text{a}}$ cm.s ⁻¹	$\alpha_{\text{app}}^{\text{b}}$	$k_{\text{corr}}^{-800\text{c}}$ cm.s ⁻¹
Water	0.1M KPF_6	5	0.65	~5	3	0.58	~3
Formamide	0.1M LiClO_4	5×10^{-3}	0.95	1.5×10^{-3}	3.5×10^{-3}	0.76	2×10^{-3}
NMF	0.1M LiClO_4	2×10^{-4}	0.90	9×10^{-5}	1.2×10^{-4}	0.66	7×10^{-5}
PC	0.1M LiClO_4	0.3	0.65	8×10^{-3}	2×10^{-2}	0.66	2.5×10^{-3}
DMSO	0.1M LiClO_4	1.5×10^{-5}	1.0	1.5×10^{-6}	7×10^{-6}	0.66	1.7×10^{-6}
DMF	0.1M LiClO_4	1.1×10^{-4}	0.9	1.5×10^{-5}	3.5×10^{-5}	0.7	1.0×10^{-5}

Notes to Table II

- ^a Apparent (experimental) rate constant in solvent and electrolyte indicated, measured at -800 mV. vs. formal potential for ferricinium-ferrocene couple in same media.
- ^b Apparent transfer coefficient in solvent and electrolyte indicated, obtained from $\alpha_{app} = (-RT/F)(\partial \ln k_{app} / \partial E)_u$.
- ^c Double-layer corrected rate constant corresponding to quoted value of k_{app}^{-800} ; obtained using eqn (2) assuming that $Z_r = 3$ for $\text{Co}(\text{NH}_3)_6^{3+}$ and $Z_r = 2$ for $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ reduction, respectively. (For further details, see text and footnote (c) to Table I).
- ^d Kinetic data were not obtained in acetonitrile due to insufficient reactant solubility in this solvent.

TABLE III. Estimates of the variations in the potential-independent free energy of activation $\Delta(\Delta G_{\text{corr}}^\ddagger)_c^{s-w}$ for $\text{Co}(\text{en})_3^{3+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ reduction resulting from substituting various nonaqueous solvents for water.

Solvent	$\Delta(\Delta G_{\text{corr}}^\ddagger)_c^{s-w}$, kJ mol ⁻¹ ^a		$\Delta(\Delta G_{\text{rc}}^0)_c^{s-w}$ kJ mol ⁻¹
	$\text{Co}(\text{en})_3^{3+}$ red ⁿ	$\text{Co}(\text{NH}_3)_6^{3+}$ red ⁿ	$\text{Co}(\text{en})_3^{3+/2+}$
Formamide	23	17	15
NMF	31	23	26
PC	23	13	-4
AN	17	---	-15
DMSO	42	29	33
DMF	33	25	24

Notes to Table III

- ^a Change in potential-independent part of free energy of activation (on TATB scale) resulting from altering solvent from water to solvent indicated. Obtained from rate data in Table I using eqn (12); values of k_{corr} evaluated at -800 mV. vs. Fc^+/Fc in water and at potentials of $(-800 + \Delta E)$ mV. vs. Fc^+/Fc in each aqueous solvent, where ΔE is given by eqn (13) (see text). [Resulting values of $\Delta(\Delta G_{\text{corr}}^\ddagger)_c^{\text{s-w}}$ are rounded off to nearest 1 kJ mol^{-1} .]
- ^b Change in free energy of $\text{Co}(\text{en})_3^{3+/2+}$ couple (on TATB scale) when solvent altered from water to solvent indicated at ionic strength $\mu = 0.1$, obtained from eqn (8). Taken from ref. 7, and rounded off to nearest 1 kJ mol^{-1} .

TABLE IV. Experimental estimates of the variations in the intrinsic barrier $\Delta(\Delta G_1^\ddagger)^{s-w}$ for $\text{Co(en)}_3^{3+/2+}$ resulting from substituting various nonaqueous solvents for water. Comparison with predicted variations $\Delta(\Delta G_1^\ddagger)^{s-w}_{\text{calc}}$ from dielectric continuum theory.

Solvent	$\Delta(\Delta G_1^\ddagger)^{s-w}$ kJ mol ⁻¹ ^a	$\Delta(\Delta G_1^\ddagger)^{s-w}_{\text{calc}}$ kJ mol ⁻¹	
		$R_e = -a^c$	$R_e = 2(a+l)^d$
Water	---	27.0 ^c	20.0 ^c
Formamide	7.5	-4.0	-1.0
NMF	9.5	-3.5	-1.0
PC	11.5	-3.5	-1.0
AN	7.5	-1.0	1.0
DMSO	20.5	-5.5	-2.5
DMF	19.5	-4.0	-1.0

Notes to Table IV

^aObtained from values of k_{corr}^S listed in Table I using eq. (16).

^bDifference between dielectric continuum estimate of the outer-shell energy barrier $(\Delta G_{1,OS}^{\ddagger})_{\text{DC}}$ calculated from eqn (17) in given nonaqueous solvent and that in water. Values of ϵ_{op} for each solvent obtained from refractive indices n_{op} in "Handbook of Chemistry and Physics", CRC Press, Cleveland, Ohio, 1963, $\epsilon_{\text{op}} = n_{\text{op}}^2$. Values of ϵ_{S} for nonaqueous solvents and literature sources are as follows: Formamide 108.7, NMF 182, DMF 36.7 [S. I. Bass, w. I. Nathan, J. Phys. Chem., **68**, 2779 (1964)]; R. H. Cole, J. Phys. Chem., **68**, 509 (1964); DMSO 36.7, AN 39 [J. G. Lund, J. Phys. Chem., **68**, 2463 (1964)]; Tomkins, "Nonaqueous Electrolyte Handbook", Vol. 1, Academic Press, New York, 1967, PC 64.9 [R. Payne, I. E. Theodorou, J. Phys. Chem., **76**, 2897 (1972)].

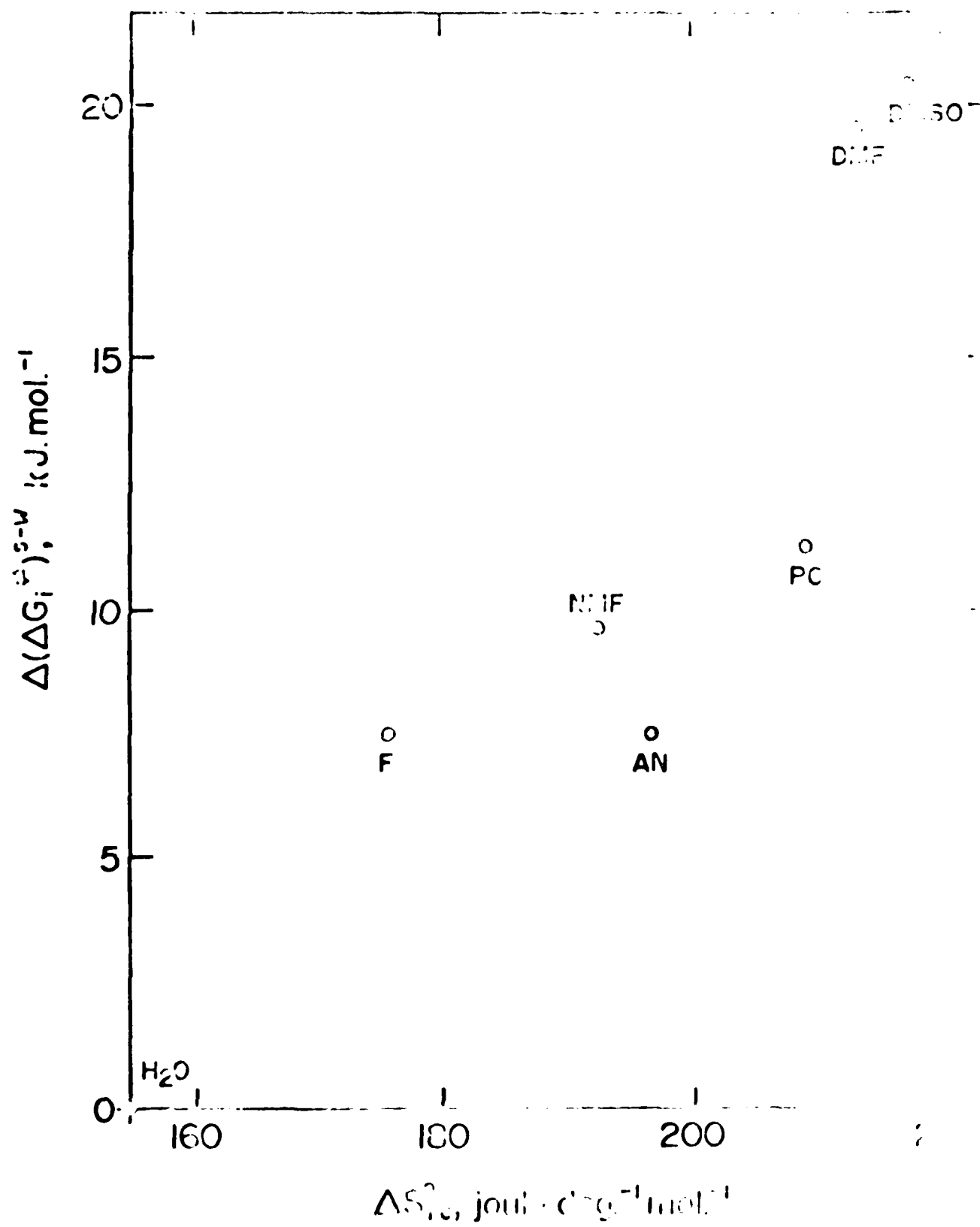
^cCalculated assuming that $a = 3.5\text{\AA}$, $R_e = \infty$ in eqn (17) (see text).

^dCalculated from eqn (17) assuming that $a = 3.5\text{\AA}$, $R_e = 2(a+1)$, where $a = 3.5\text{\AA}$ in water and 6\AA in nonaqueous solvents (see text).

^eAbsolute values of $(\Delta G_{1,OS}^{\ddagger})_{\text{DC}}$ in water, calculated from eqn (17).

FIGURE CAPTION

The variation in the intrinsic free energy of activation for $\text{Co(en)}^{3+/2+}$ resulting from substituting various nonaqueous solvents for water, $\Delta(\Delta G_i^\ddagger)^{S-W}$, plotted against the corresponding reaction entropies ΔS_{rc}° . Values of $\Delta(\Delta G_i^\ddagger)^{S-W}$ obtained from formal rate constants k_{corr}^f given in Table I using eqn (16a). Values of ΔS_{rc}° (determined at $\mu = 0.1$) taken from Table I of ref. 7.



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