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Effects of Reactant Ionic Charges and Nonlocal Dielectric Screening on Electron Transfer between Bis(terpyridine)cobalt(II) and Tris(phenanthroline)cobalt(III), Tris(bipyridine)cobalt(III), and Analogous, Electrically Neutral Sulfonated Cobalt(III) Complexes

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We have investigated interreactant work terms and solvent reorganization free enthalpies in outer-sphere electron-transfer reactions by comparing rate data for the oxidation of $[Co(terpy)_2]^{2+}$ by $[Co(phen)_3]^{3+}$ and $[Co(bpy)_3]^{3+}$ in water, ethylene glycol, and 72/28 w/w glycerol/water solution with analogous data for oxidation by the structurally similar, but electrically neutral, tris(phenanthroline-5-sulfonato)cobalt(III) and tris(bipyridine-5-sulfonato)cobalt(III) complexes. From continuum solvent models, it is found that the reactions are significantly diabatic. Due to negligible work terms and higher standard redox potentials the sulfonated complexes react 10^2–10^3 times faster than the unsubstituted complexes. Only the data for the phen and phen-SO_3^- complexes in water are quantitatively in line with solvent models based on a structureless continuum with bulk dielectric properties. The deviations from the crudest solvent models can, however, be understood by means of nonlocal electrostatic theory, which incorporates short-range dielectric and solvent structural effects in a continuum formalism. Values of the solvent polarization correlation length of 2–4 Å and about -10^{-2} Å K^{-1} for the temperature coefficient of this quantity are in line with the kinetic data for the other complexes and solvents.

Introduction

Recent developments in theoretical[1-22] and experimental[23-29] investigations of outer-sphere redox reactions have led to good experimental documentation of the physical events that induce electron transfer (ET) between mobile ions in a solvent. Direct determination of some of the fundamental quantities that appear in theoretical ET rate expressions has, however, been rather elusive. These quantities in particular are the interionic interaction and the ET distance as reflected in the transmission coefficient for diabatic reactions, the latter being the object of considerable current interest.[14,16,27-39]

The interionic interaction and the ET distance are obviously interrelated. ET between mobile reactants is thus nearly always assumed to occur at a contact distance between the reacting molecules. This is based on the fact that the Coulombic interaction, fully screened by the dielectric medium, depends weakly on the distance, while the electron exchange matrix element falls off rapidly with increasing ET distance. However, this assumption needs substantiation in the light of two kinds of recent observations. Electronic "tails" from reacting molecules, protruding into a polar medium, are strongly affected by the medium. This was first recognized in polaron theory.[40] In the context of ET reactions the appropriate polarization is, however, not the equilibrium polarization such as in polaron theory, but the instantaneous, nonequilibrium polarization at the moment of ET.[14,38,39] It has been shown recently that for ET processes in the "normal" free enthalpy range this leads to "swelling" of the electron cloud relative to equilibrium and therefore a weaker ET distance dependence than without incorporation of this effect.[14,38,39,41]

Secondly, for strongly charged reactant ions, interreactant

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repulsive forces could also lead to increased ET distances. This is not due solely to dielectric saturation but also to the fact that the solvent is not subjected to full dielectric polarization from the ionic fields at molecular distances, where the short-range spatial component of the dielectric permittivity function becomes important.[42-45] Repulsive forces would then be more pronounced than for bulk screening, and the ions might respond by "moving apart". We have recently shown that nonlocal dielectric effects are compatible with the interprotonic interaction in dibasic amines[44] and with the nonlinear Arrhenius behavior for the $[Ru(NH_3)_6]^{2+}/[Co(NH_3)_5(H_2O)]^{3+}$ ET reaction in mixed ethylene glycol/water solvents.[46]

In this work we investigate the interreactant repulsion and the electronic transmission coefficients for the reactions

$$[Co(terpy)_2]^{2+} + [Co(phen)_3]^{3+} \rightarrow [Co(terpy)_2]^{3+} + [Co(phen)_3]^{2+} \quad (1)$$

$$[Co(terpy)_2]^{2+} + [Co(phen\text{-}SO_3^-)_3] \rightarrow [Co(terpy)_2]^{3+} + [Co(phen\text{-}SO_3^-)_3]^- \quad (2)$$

$$[Co(terpy)_2]^{2+} + [Co(bpy)_3]^{3+} \rightarrow [Co(terpy)_2]^{3+} + [Co(bpy)_3]^{2+} \quad (3)$$

$$[Co(terpy)_2]^{2+} + [Co(bpy\text{-}SO_3^-)_3] \rightarrow [Co(terpy)_2]^{3+} + [Co(bpy\text{-}SO_3^-)_3]^- \quad (4)$$

in water, ethylene glycol, and mixed glycerol/water solvents. Terpy here stands for terpyridine, and phen and phen-SO_3^- stand for 1,10-phenanthroline and its 5-sulfonate derivative, while bpy and bpy-SO_3^- represent 2,2′-bipyridine and its 5-sulfonato derivative.

These reactions involve structurally very similar complexes expected to give almost identical molecular and solvent reorganization energies. However, only eq 1 and 3 involve strong interreactant repulsion. Previous analysis[15] has furthermore suggested that reactions 1 and 3 are significantly diabatic with electronic transmission coefficients of about 10^{-4}, so that ET distance variation would not be concealed by reaction adiabaticity. An outcome of the present investigations is that only reactions 1 and 2 in aqueous solution are adequately represented by the crudest bulk dielectric solvent models. In other cases solvent structural features are important, as described by the nonlocal dielectric formalism.

Experimental Section

Materials. Millipore water and commercial analytical grade reagents and organic solvents were used throughout. The glycerol contained 12–14% water.

$[Co(terpy)_2](ClO_4)_2 \cdot H_2O$, $[Co(phen)_3](ClO_4)_3 \cdot 2H_2O$, and $[Co(bpy)_3](ClO_4)_3 \cdot 3H_2O$ were prepared from AnalaR $CoCl_2 \cdot 6H_2O$ and the ligands by literature procedures and were checked spectrophotometrically.[47,48] phen-$SO_3H \cdot H_2O$ was prepared as cream-colored crystals by sulfonation of phen by ammonium acid sulfate, separated from the 3-isomer, and recrystallized from water. The method of Blair and Diehl[49] was used, except that it was found necessary to keep the temperature during the sulfonation at 365–370 °C for about 4 h in order to obtain significant amounts of the product. The yield was 5.52 g from 20 g of phen. Anal. Calcd for phen-$SO_3H \cdot H_2O$: C, 51.78; H, 3.63; N, 10.07; S, 11.51. Found: C, 51.31; H, 3.62; N, 10.03; S, 11.65.

Cream-colored crystals of bpy-SO_3H were prepared and recrystallized as described in ref 50. The yield was 7 g from 25 g of bipy. Anal. Calcd for bpy-SO_3H: C, 50.82; H, 3.42; N, 11.86; S, 13.57. Found: C, 49.72; H, 3.43; N, 11.56; S, 13.60.

Table I. Half-Wave Potentials (V) and Reaction Entropies (J K^{-1}) for the Co(III)/Co(II) Couples and Free Enthalpies ΔG_0 (kJ), Enthalpies ΔH_0 (kJ), and Entropies ΔS_0 (J K^{-1}) of Reaction for Eq 1–4[a]

solvent	ligand	$E_{1/2}$	$\Delta S°$	ΔG_0	ΔH_0	ΔS_0
water	phen	0.155	103 ± 3	−10.9	−5	19 ± 6
	phen-SO_3^-	0.254	63 ± 3	−20.4	−26	−21 ± 5
	bpy	0.085	105 ± 6	−3.9	2	21 ± 7
	bpy-SO_3^-	0.273	65 ± 3	−22.3	−30	−19 ± 5
	terpy	0.042	84 ± 4			
ethylene glycol	phen	0.456	129 ± 7	−21.6	−18	14 ± 8
	phen-SO_3^-	0.480	115 ± 8	−24.0	−24	0 ± 8
	bpy	0.279	128 ± 7	−4.6	−0.7	13 ± 8
	terpy	0.231	115 ± 5			
glycerol/water 72/28 w/w	phen	0.150	110 ± 4	−1.7	7	29 ± 7
	phen-SO_3^-	0.211	90 ± 5	−7.6	−5	9 ± 7
	bpy	0.174	130 ± 4	−4.0	11	49 ± 7
	terpy	0.132	81 ± 6			

[a] In 0.05 mol dm^{-3} NaTS; temperature range 9–35 °C.

Tris Co(III) complexes of the sulfonated phen and bpy ligands were synthesized according to the following procedures modified from reported recipes for the unsubstituted complexes.[47,48]

$[Co(phen\text{-}SO_3^-)_3] \cdot 10H_2O$. A mixture of 7.19 mmol of phen-SO_3H, 7.19 mmol of NaOH, and 2.4 mmol of $CoCl_2 \cdot 6H_2O$ was dissolved in 200 mL of water and heated on a steam bath, and then 2.5 mL of 30% H_2O_2 and 2.5 mL of concentrated hydrochloric acid were added to the solution, which was then evaporated to a high-viscosity consistency. When this liquid was added dropwise and under stirring to cold methanol, yellow product crystals precipitated. The crystals could be purified by redissolution in hot water, evaporation, and renewed dropwise addition to cold methanol. the pH of an aqueous solution of the product was 5–7, indicating that the sulfonic acid groups were neutralized and the product contained no free acid. Anal. Calcd for $[Co(phen\text{-}SO_3^-)_3] \cdot 10H_2O$: C, 42.51; H, 4.07; N, 8.27; S, 9.46. Found: C, 42.94; H, 3.08; N, N, 8.29; S, 9.50.

$[Co(bpy\text{-}SO_3^-)_3] \cdot 9H_2O$. A mixture of 8.47 mmol of bpy-SO_3H, 8.47 mmol of NaOH, and 2.82 of mmol $CoCl_2 \cdot 6H_2O$ was dissolved in 15 mL of water, 3 mL of concentrated hydrochloric acid and 3 mL of 30% H_2O_2 were added, and the solution was evaporated to a small volume. Ethanol was added, the solution filtered, and the filtrate again evaporated to a small volume. Dropwise addition of this solution to cold ethanol caused precipitation of the product, which was subsequently washed with ethanol and ether. The aqueous solution again showed a practically neutral reaction, and none of the complexes gave any reaction for chloride or free ligand. Anal. Calcd for $[Co(bpy\text{-}SO_3^-)_3] \cdot 9H_2O$: C, 38.89; H, 4.25; N, 9.07; S, 10.38. Found: C, 39.08; H, 3.40; N, 9.08; S, 10.42.

Half-Wave Potentials. Half-wave potentials were measured by cyclic voltammetry using a potentiostat constructed in this department by Dr. C. E. Foverskov. The potentiostat was used along with a Hewlett-Packard 7004 B X-Y recorder and a three-electrode system mounted in a thermostated electrochemical cell. The working electrode was normally a V-10 Carbon Lorraine glassy-carbon disk, the area of which was 6.1 mm^2, mounted horizontally and fitted into a glass mantel. The counter electrode was a platinum wire melted into a glass pin, while a saturated calomel electrode (SCE), separated from the cell by a saturated potassium chloride salt bridge, was the reference electrode. It was ascertained that the reference electrode was thermally screened from the cell, and its temperature remained at ambient temperature (22 °C), varying by a few tenths of a degree only.

The solutions typically contained 4.0×10^{-3} mol dm^{-3} $CoCl_2 \cdot 6H_2O$, 2.0×10^{-2} mol dm^{-3} added free ligand, and 0.05 mol dm^{-3} sodium *p*-toluenesulfonate (NaTS) as bulk electrolyte. Well-defined cathodic and anodic peaks, independent of the sweep rate in the range 5–20 mV s^{-1}, were always obtained. The midpoint potentials, referred to the SCE and uncorrected for differences between the diffusion coefficients of the oxidized and reduced forms, are the potential values ($E_{1/2}$) reported. The temperature coefficients of both liquid-junction and thermocouple potentials between warm and cold regions for many metals are quite insignificant compared with the temperature variation of the half-wave potentials of many coordination compound redox couples, including those of the complexes considered here.[51,52] The fact that the same values of

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Table II. Rate Constants at 25 °C ($dm^3\ mol^{-1}\ s^{-1}$), Activation Enthalpies ($kJ\ mol^{-1}$), and Apparent Activation Entropies ($J\ K^{-1}\ mol^{-1}$) for Reactions 1–4[a]

ligand	k	ΔH_A	ΔS_A
phen	1.14×10^2	27 ± 2	−115 ± 10
phen-SO_3^-	1.20×10^4	20 ± 2	−100 ± 10
bpy	2.07×10	32 ± 2	−109 ± 10
bpy-SO_3^-	3.03×10^4	11 ± 1	−120 ± 10

[a] Aqueous solution with no added electrolyte. Initial concentration of $[Co(terpy)_2]^{2+}$: 7.5×10^{-5} mol dm^{-3} (1.13×10^{-5} mol dm^{-3} in the fourth row). Initial concentrations of the four Co(III) complexes in the order given in the table (mol dm^{-3}): 6.29×10^{-4}, 6.29×10^{-4}, 6.13×10^{-4}, 5.05×10^{-4}. $\mu^{1/2} = 0.057$ mol dm^{-3} for rows 1 and 3, 0.013 for row 2, and 0.0053 for row 4.

Table III. Rate Constants at 25 °C ($dm^3\ mol^{-1}\ s^{-1}$), Activation Enthalpies ($kJ\ mol^{-1}$), and Apparent Activation Entropies ($J\ K^{-1}\ mol^{-1}$) for Reactions 1–3[a]

ligand	k	ΔH_A	ΔS_A
phen	2.54×10	23 ± 2	−140 ± 10
phen-SO_3^-	2.85×10^3	7.5 ± 1	−154 ± 10
bpy	1.44×10	28 ± 4	−130 ± 10

[a] 80/20 w/w glycerol/water solvent with no added electrolyte. Initial concentration of $Co(terpy)_2^{2+}$: 7.5×10^{-5} mol dm^{-3}. Initial concentrations of the Co(III) complexes (mol dm^{-3}) in the order given in the table: 6.06×10^{-4}, 6.06×10^{-4}, 1.39×10^{-3}.

Table IV. Rate Constants at 25 °C ($dm^3\ mol^{-1}\ s^{-1}$), Activation Enthalpies ($kJ\ mol^{-1}$), and Apparent Activation Entropies ($J\ K^{-1}$) for Reactions 1–3[a]

ligand	k	ΔH_A	ΔS_A
phen	1.04×10	29 ± 2	−125 ± 10
phen-SO_3^-	6.93×10^2	17 ± 2	−135 ± 10
bpy	7.2	30 ± 3	−130 ± 10

[a] Ethylene glycol solvent with no added electrolyte. Initial concentration of $[Co(terpy)_2]^{2+}$: 7.5×10^{-5} mol dm^{-3}. Initial concentrations of the three Co(III) complexes in the order given in the table (mol dm^{-3}): 6.21×10^{-4}, 5.79×10^{-4}, 1.49×10^{-3}.

the half-wave potentials and their temperature coefficients were found for glassy-carbon and platinum electrodes was taken as evidence that this is most likely the case also for glassy carbon, and since the thermocouple potential is negligibly small for platinum (6 $\mu V\ K^{-1}$), it was also neglected for glassy carbon.

Values for the formal reaction entropies, ΔS°_{el}, for the redox reactions

$$Co(III) + e^- \rightleftarrows Co(II) \tag{5}$$

were calculated from the equation

$$F(dE_{1/2}/dT) = \Delta S^\circ_{el} \tag{6}$$

Combination of $E_{1/2}$ and ΔS°_{el} for the phen, bpy, phen-SO_3^-, and bpy-SO_3^- complexes with the values for the $[Co(terpy)_2]^{2+/3+}$ couple then provides the enthalpies and entropies for the homogeneous electron-transfer processes (1)–(4).

Magnetic Susceptibilities. Magnetic susceptibilities were obtained by the Faraday method[86] for the temperature range 5.4–298 K and were provided by Dr. Erik Pedersen, Chemistry Department I, The H. C. Ørsted Institute, University of Copenhagen.

Kinetic Measurements. The reactions were followed by monitoring $[Co(terpy)_2]^{2+}$ spectrophotometrically at its maximum absorption wavelength of 505 nm. At this wavelength its molar extinction coefficient, $\epsilon_m = 1.4 \times 10^3$ dm^3 mol^{-1} cm^{-1},[47,53] is much larger than those of all the other cobalt complexes. In most cases the spectral changes were followed by stopped-flow techniques with a Durrum-Gibson instrument with Teflon drive syringes and with a tape puncher for direct data processing. At the temperatures in question (20–40 °C) the mixing chamber ensures effective mixing even for the most viscous solutions. In some cases a Beckman 24 spectrophotometer was used for the slowest reactions where, however, great care was required to ensure complete mixing for the more viscous solvents.

Co(III) was usually present in 8- or 9-fold excess. As the rate constant for the strongly charged unsubstituted complexes turned out to be rather sensitive to the ionic strength, it was not possible to check the reaction order systematically with respect to Co(III) for these complexes, although variation of the Co(III)/Co(II) concentration ratio from 6 to 12 at constant ionic strength (NaTS) did not give any variation in the rate constant. The rate constants are therefore compared for given small (i.e. about 6×10^{-4} mol dm^{-3} concentrations of Co(III).

Solutions of $[Co(bpy\text{-}SO_3^-)_3]$ decomposed slowly, liberating the ligand. Decomposition did not occur when small amounts of free ligand were added (even a small fraction per mole of Co(III)). In order to avoid possible ionic strength effects, rate constants were obtained for different concentrations of added free ligand and extrapolated to zero free ligand concentration.

Reactions 1, 2, and 4 can straightway be regarded as completely irreversible for all the solvents. From the half-wave potentials for the $[Co(bpy)_3]^{2+/3+}$ and $[Co(terpy)_2]^{2+/3+}$ couples the equilibrium constants for reaction 3 are found to be 5.3, 6.5, and 5.2 for water, ethylene glycol and 72/28 w/w glycerol/water, respectively, at 25 °C and in the presence of 0.05 mol dm^{-3} NaTS. For the concentrations of Co(II) and Co(III) used in the kinetic runs (Tables II–IV), these values then show that the equilibrium mixtures of reaction 3 represent from 97 to 99% conversion, so that for all practical purposes this reaction can also be regarded as essentially irreversible.

The absorbance-time data were fitted to the equation

$$\ln [(D - D_\infty)/(D_0 - D_\infty)] = k_2[Co(III)]t \tag{7}$$

where D, D_0, and D_∞ are the absorbance at time t, zero, and infinity, respectively, [Co(III)] is the concentration of Co(III), and k_2 is the second-order rate constant. Accurate fits of this equation were always obtained for over 90% of the reaction.

Results

Electrochemical Data. Table I summarizes the half-wave potentials and formal reaction entropies of the Co(III)/Co(II) couples and the free enthalpies, enthalpies, and entropies for reactions 1–4. The values refer to 0.05 mol dm^{-3} NaTS, but are independent of the NaTS concentration in the range 0.05–0.15 mol dm^{-3} for all the solvents. The most important observations are as follows:

(A) The half-wave potentials of the unsubstituted complexes in aqueous solution agree well with those of previous reports.[53,54] The half-wave potentials are shifted by 2–300 mV toward more positive values in the organic solvents, which is understandable in view of the weaker ionic solvation in these solvents, but the effect only leads to small changes in the equilibrium constants and reaction enthalpies of reactions 1–4. Small equilibrium constant shifts were also found previously[55] for reaction 3 in a number of other solvents.

(B) The half-wave potentials are substantially more positive for the sulfonato derivatives than for the unsubstituted complexes. This difference is largest for water, amounting to 99 and 188 mV at 25 °C for the phen and bpy systems, respectively. It is 36 and 61 mV for phen and phen-SO_3^- in ethylene glycol and 72/28 w/w glycerol/water. Significant redox potential shifts on sulfonation of phen in the 5-position have also been observed for the $[Fe(phen)_3]^{2+/3+}$ couple[48] and are accompanied by notable modifications in the ligand dissociation and electron-transfer properties of these complexes.[56,57] The shifts are compatible with electron attraction to the electronegative $-SO_3^-$ group dominating over "mesomeric" electron donation from this otherwise electron-rich substituent to the rings.

(C) The formal reaction entropies of the phen and bpy couples in water agree with those of a previous report[52]. These values are shifted by 15–20 $J\ K^{-1}$ in a positive direction in the organic solvents, again in line with weaker ionic solvation, while the resulting entropies of reactions 1 and 3 are little affected.

(D) The formal reaction entropies for the sulfonated complexes in aqueous solution are significantly less positive than for the unsubstituted complexes. Less positive values are also found for

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the organic solvents, but the differences are here much smaller. Smaller numerical values than for the unsubstituted complexes are expected in view of the small charges on the complexes. Comparison with entropy changes when neutral ligand groups are substituted by anionic ligands in other transition-metal complexes[52] would, however, lead to the expectation of substantially larger entropy changes on such drastic charge variation as sulfonation in all the ligands. The observed small changes suggest that the negative charges on the sulfonato groups in this context could be regarded as partly localized on these groups, corresponding to significant positive charges in the central parts of the complex ions.

Magnetic Moments. The average magnetic moments of $[Co(phen\text{-}SO_3^-)_3]^-$ and $[Co(bpy\text{-}SO_3^-)_3]^-$ at 298 K were 5.62 and 4.56 μ_B, respectively. These measurements were based on microcrystalline samples and corrected for diamagnetism, and the bpy-SO_3^- complex also contained 2 mol of NaCl/mol of Co(II). The magnetic moments dropped to 4.03 and 3.72 μ_B at 5.4 K for the complexes of phen-SO_3^- and bpy-SO_3^-, respectively. These data suggest that the sulfonated Co(II) complexes behave as high-spin, approximately octahedral d^7 complexes with a $^4T_1$ ground state, although the different magnetic moments also suggest that there may be both some variation in the spin–orbit coupling constant and deviation from regular octahedral symmetry.[85]

Kinetics of Electron Transfer. Rate constants at 25 °C, activation enthalpies, ΔH_A, and apparent activation entropies, ΔS_A^{app}, of reactions 1–4, in aqueous solution are collected in Table II. The activation parameters are calculated from the expression[14]

$$k_2 = \frac{k_B T}{h} \exp(\Delta S_A^{app}/k_B) \exp(-\Delta H_A/k_B T) \qquad (8)$$

ΔS_A^{app} is related to the actual activation entropy, ΔS_A, by

$$\Delta S_A^{app} = \Delta S_A + k_B \ln (\kappa_e \Delta V) \qquad (9)$$

where ΔV is the reaction "zone", i.e. the (approximately spherical) region within which ET occurs, κ_e is the electronic transmission coefficient, k_B is Boltzmann's constant, T is the absolute temperature, and h is Planck's constant. Tables III and IV contain data for 72/28 w/w glycerol/water and ethylene glycol solvents. The sulfonated complexes were insoluble in methanol, ethanol, acetonitrile, and 1,4-dioxane, and the bpy-SO_3^- complex also in ethylene glycol. The kinetics deviate from that of simple second order for the reactions in methylformamide and tetrahydrofuran, due to decomposition processes involving the solvents.

The activation parameters for the unsubstituted complexes in aqueous 0.05 mol dm^{-3} perchlorate solution agree with reported values,[54] while the rate constant is higher for $[Co(phen)_3]^{3+}$ and lower for $[Co(bpy)_3]^{3+}$, in both cases by about 30%. Lower values of both k_2 and ΔH_A for $[Co(bpy)_3]^{3+}$ were reported in ref 55.

The most striking observation from Tables II–IV is the pronounced increase of the rate constants on sulfonation, amounting to a factor of about 10^2 for the phen complexes and well over 10^3 for the bpy complexes. A large rate increase is understandable in view of the more positive half-wave potentials and smaller electrostatic repulsion for the sulfonated complexes. We shall provide a quantitative frame for this in the next section.

The reduction of $[Co(bpy)_3]^{3+}$, but not of $[Co(phen)_3]^{3+}$, in 72/28 w/w glycerol/water displayed a tendency of upward curvature in the Arrhenius plot, giving a "high-temperature" and a "low-temperature" branch. This effect appears similar to the one observed previously for reduction of $[Co(NH_3)_5(H_2O)]^{3+}$ by $[Ru(NH_3)_6]^{3+}$, which was ascribed to temperature variation of the local solvent structural extension around the ions.[46] The transition region depended on the glycerol sample, ranging from a few degrees around 283 K to a few degrees around 303 K, reflecting the sensitive temperature variation of the viscosity (in which the structure extension is manifested) on the water content in this composition range.[58]

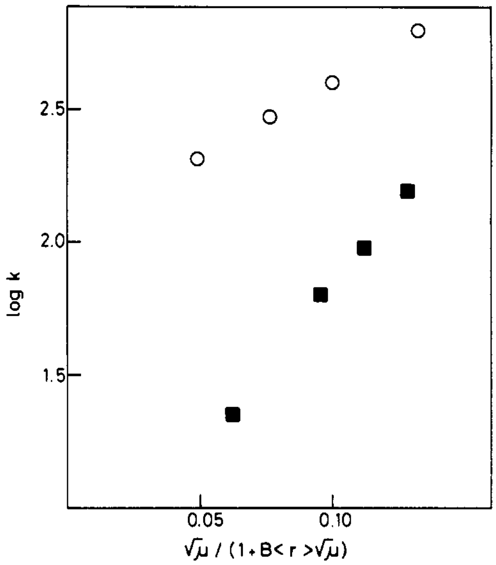

Figure 1. Plots of eq 9 for reactions 1 and 3 in water at 25 °C for initial [Co(III)] and [Co(II)] of 5.00 × 10^{-4} and 5.00 × 10^{-5} mol dm^{-3}, respectively: (○) reaction 1, $\langle r \rangle$ = 14 Å; (■) reaction 3, $\langle r \rangle$ = 10 Å.

The ionic strength (μ) dependence of the rate constants for the unsubstituted complexes displayed a rather variable behavior depending on the complex and electrolyte added. The rate constants were first referred to the approximate Debye–Hückel limiting law

$$\log k_2 = \log k_{2_0} + 2z_1z_2A\mu^{1/2}/(1 + B\langle r \rangle \mu^{1/2}) \qquad (10)$$

$$A = 1.82 \times 10^6(\epsilon_s T)^{-3/2} \qquad B = 5.03 \times 10^9(\epsilon_s T)^{-1/2} \qquad (11)$$

where k_{2_0} is the rate constant at zero ionic strength, z_1 and z_2 are the reactant ionic charges, ϵ_s is the static dielectric constant of the pure solvent, and $\langle r \rangle$ (in Å) represents an approximate ET distance (strictly speaking the distance from a reactant ion to the nearest counterion). For the ions here, $\langle r \rangle$ is then 10–14 Å. Equations 10 and 11 also rest on the assumption that work terms in the reactant and product states approximately cancel and that variations in the interreactant repulsion do not significantly modify the "effective" ET distance.

Equation 10 represents the data well for $[Co(bpy)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ in water and in the presence of small concentrations of NaTS (Figure 1). However, rather different values of the limiting slope emerge if the bulk dielectric constant and $\langle r \rangle$ = 14 Å are inserted in eq 11. The resulting values of $2Az_1z_2$ are 7.0 for $[Co(phen)_3]^{3+}$ and 12 for $[Co(bpy)_3]^{3+}$, while the formal charge product would give 6.2. The apparent charge product for $[Co(phen)_3]^{3+}$ is close to the expected value and in line with the value of 6.1 previously obtained for this process in potassium nitrate media and for $\langle r \rangle$ = 12 Å.[54] On the other hand, the large value for $[Co(bpy)_3]^{3+}$ is incompatible with the simplest structureless solvent models. Replacement of the bulk static dielectric constant by the lower "effective" value of $\epsilon_{eff} \approx 50$ gives an ionic product of 6.2 and is in line with other observations to which we shall return.

The ionic strength dependence was also reflected in a decrease of both the activation enthalpy and entropy (the latter to more negative values) with increasing ionic strength. The variation of ΔH_A amounted to about 30% when the concentration of added NaTS was varied from zero to 0.1 mol dm^{-3} for $[Co(bpy)_3]^{3+}$ and to about 33% for $[Co(phen)_3]^{3+}$ in the range from zero to 0.05 mol dm^{-3}. The relative variation of ΔS_A was larger, amounting to about 40% for both complexes. Rate constants extrapolated to zero ionic strength are smaller than the values in Table II by factors of 2 and 4, respectively, for the phen and bpy complex, while the extrapolated activation enthalpies are larger by 4–5 kJ. This observation is opposite to the expectations from the De-

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[58] J. Timmermans, "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions", Vol. 4, Interscience, New York, 1960.

Table V. Solvent Reorganization Energies (kJ) Calculated from the Conducting Sphere (cs) and Dielectric Ellipsoid (de) Models Using Bulk Dielectric Constants

solvent	ϵ_0	ϵ_s	E_s(cs)	E_s(de)	ϵ_s	$10^3\gamma_s$	n
water	1.766	78	50	75	78	−4.6	1.329
ethylene glycol	2.039	38	42	63	38	−4.9	1.42
72/78 glycerol/water	2.02	63	43	65	56	−5.0	1.428

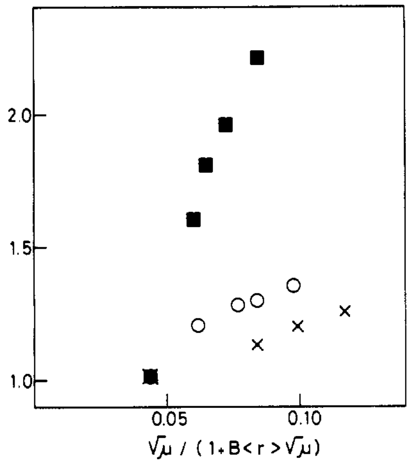

Figure 2. Plots of eq 10 for reaction 1 in ethylene glycol at 25 °C for initial concentrations of $[Co(phen)_3](ClO_4)_3$ and $[Co(terpy)_2](ClO_4)_2$ of 6.24×10^{-4} and 7.50×10^{-5} mol dm^{-3}, respectively: (■) $NaClO_4$ added; (○) NaTS added; (×) sodium fluoroacetate added. $\langle r \rangle = 14$ Å.

bye–Hückel limiting law (cf. ref 59 and 60). The Debye–Hückel interreactant interaction free enthalpy is thus

$$w_r^{\text{D-H}} \approx z_1 z_2 \exp(-B\langle r \rangle \mu^{1/2})/\epsilon_s\langle r \rangle \approx (z_1 z_2/\epsilon_s\langle r \rangle)/(1 + B\langle r \rangle \mu^{1/2}) \quad (12)$$

with the corresponding entropy and enthalpy

$$\Delta S_A^{\text{D-H}} = -\partial w_r^{\text{D-H}}/\partial T = w_r^{\text{D-H}}[\gamma_s - \tfrac{1}{2}B\langle r \rangle \mu^{1/2}(\gamma_s + 1/T)/(1 + B\langle r \rangle \mu^{1/2})] \quad (13)$$

$$\Delta H_A^{\text{D-H}} = w_r^{\text{D-H}} + T\Delta S_A^{\text{D-H}} \quad (14)$$

where $\gamma_s = \partial \ln \epsilon_s/\partial T$. Since $\gamma_s < 0$ (Table V[61,62]), both $\Delta H_A^{\text{D-H}}$ and $\Delta S_A^{\text{D-H}}$ thus increase with increasing ionic strength (cf. ref 58 and 59), and only if the dielectric constant is represented by a nonlocal function $\epsilon_{\text{eff}}(r)$, for which $\partial \ln \epsilon_{\text{eff}}/\partial T > 0$, can effects in the observed direction be expected.

Due to solubility problems the ionic strength variation in aqueous solution could not be investigated systematically by adding sodium perchlorate. Sodium trifluoroacetate gave a very weak ionic strength dependence for reduction of $[Co(phen)_3]^{3+}$ in aqueous solution, in fact less than a factor of 2 in the range from 1.6×10^{-2} to 7×10^{-2} mol dm^{-3}, whereas a factor of 7 would have been expected on the basis of eq 10. This indicates that the local solvent structure is sensitive to effects induced by specific properties of the added ions.

Figure 2 shows that the variation of the rate constant with ionic strength in ethylene glycol with added trifluoroacetate is again much smaller than expected from the formal charges. The variation is, however, also small when NaTS is added, although the limiting slope of eq 10 for $\langle r \rangle = 14$ Å and the bulk dielectric constant of ethylene glycol approaches 6 at the smallest ionic strengths. Weak ionic strength dependence would in fact be compatible with a larger electron-transfer distance in the nonaqueous solvent where the interreactant repulsion is also stronger, but this is unlikely in view of the much stronger variation of the rate when sodium perchlorate is added, which is possible for this solvent. In this case insertion of the bulk dielectric constant and the contact electron-transfer distance (14 Å) gives a limiting slope with a formal reactant charge product of 14, while a charge product of 6 is obtained for a nonlocal dielectric constant of 22–25. Rate constants extrapolated to zero ionic strength in NaTS would here be lower than in Table IV by an order of magnitude.

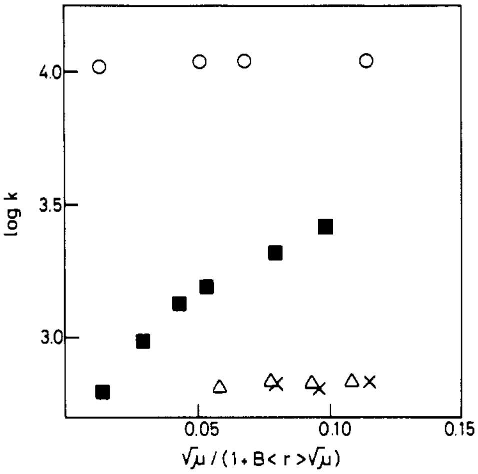

Figure 3. Plots of eq 10 for reaction 2 in water and ethylene glycol for initial concentrations of $[Co(phen\text{-}SO_3^-)_3]$ and $[Co(terpy)_2](ClO_4)_2$ of 5.00×10^{-4} and 5.00×10^{-5} mol dm^{-3}, respectively for water and 6.24×10^{-4} and 7.50×10^{-5} mol dm^{-3}, respectively, for ethylene glycol: (○) water, NaTS added; (■) ethylene glycol, $NaClO_4$ added; (△) ethylene glycol, NaTS added; (×) ethylene glycol, sodium trifluoroacetate added. $\langle r \rangle = 14$ Å.

The rate constants for reduction of $[Co(phen\text{-}SO_3^-)_3]$ were practically independent of the ionic strength for both water and ethylene glycol solutions, when NaTS or sodium trifluoroacetate were added in concentrations up to 0.05 mol dm^{-3} (Figure 3), as expected for an electrically neutral complex with uniform charge distribution. Specific ionic effects were observed when sodium perchlorate was added to ethylene glycol (Figure 3). The rate constant increased by a factor of 4 when sodium perchlorate was added up to 0.023 mol dm^{-3}. The variation is not linear, but gives a limiting slope corresponding to $z_1 z_2 = 4.4$ for $\langle r \rangle = 14$ Å and $\epsilon_{\text{eff}} = 38$. If the shorter range value of $\epsilon_{\text{eff}} = 22$ is used, then $z_1 z_2 = 1.9$ as for a positive charge slightly less than unity on the sulfonated complex. The effect is perhaps better viewed in terms of ion-pair formation between perchlorate and the $[Co(terpy)_2]^{2+/3+}$ ions, even though the half-wave potential of this couple was only shifted by −13 mV when 2.57×10^{-2} mol dm^{-3} $NaClO_4$ was added.

Discussion

Ionic Strength Variation and Nonlocal Solvent Properties. The kinetic data have suggested that ionic strength dependence and rate constant values for the phen/phen-SO_3^- complex couple in aqueous solution are well represented by a macroscopic spherical solute–solvent bulk electrostatic model. In all other cases such a crude structureless solvent description[1] fails. In order to gain insight into reasons for this we must therefore introduce a more detailed solvent representation.

In regard to such representations appropriate solvent features are dielectric saturation[44,63,64] and a nonlocal dielectric field response.[42–45,65] The former is caused by nonlinear polarization

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field dependence. A nonlocal dielectric polarization, commonly named spatial dispersion,[43,45,65] is still linear in the field but the dielectric permittivity, $\epsilon_{\mathrm{eff}}(r)$, depends on the distance from the field source. This is because the solvent is not fully polarized by the field at distances smaller than the local structure extension of the liquid. The two effects thus arise from quite different physical causes, but both provide distance dependence to the dielectric function ϵ_{eff}, with smaller values closer to the solute ions than in the bulk.

In view of the large geometric size of the reactant ions we shall disregard dielectric saturation[44] and base our discussion on nonlocal dielectric effects. This theory constitutes a rather powerful frame for incorporation of solvent structural effects clearly going beyond the crudest structureless models, which are otherwise almost exclusively applied to electron-transfer systems. It furthermore turns out from the literature on nonlocal dielectrics[42,45,65] that the simplest solute representation (conducting spheres) leads to analytical expressions for solvent reorganization and work terms of comparable transparency to those for the structureless model.

Nonlocal dielectric effects are suitably based on a representation of $\epsilon_{\mathrm{eff}}(r)$ in simple form[43,45,65]

$$\epsilon_{\mathrm{eff}}(r) = \epsilon_s/[1 + ((\epsilon_s/\epsilon_i) - 1)\exp(-r/\Lambda)] \tag{15}$$

ϵ_i is a "short-range" dielectric constant corresponding solely to electronic and molecular polarization and Λ is a "correlation length", i.e. a measure of the local structure extension in the solvent. Equation 15 is empirical, but approaches the correct limiting values; i.e., $\epsilon_{\mathrm{eff}}(r \rightarrow \infty) = \epsilon_s$ and $\epsilon_{\mathrm{eff}}(r \rightarrow 0) = \epsilon_i$. Since the local structure dissipates with increasing temperature, $\mathrm{d}\Lambda/\mathrm{d}T < 0$. This means that $\mathrm{d}\epsilon_{\mathrm{eff}}/\mathrm{d}T$ can be positive, whereas $\mathrm{d}\epsilon_s/\mathrm{d}T$ is normally negative. As an illustration, taking for water $\epsilon_s/\epsilon_i = 16$ and $\Lambda = 5.6$ Å, corresponding to the extension of two water molecules, eq 14 gives $\epsilon_{\mathrm{eff}} = 15$ for $r = 7$ Å and $\epsilon_{\mathrm{eff}} = 35$ for $r = 14$ Å. Nonlocality is thus a conceivable reason that kinetic quantities and their temperature dependence can be different from those based on bulk solvent properties.

Reduction of the triply charged $[\mathrm{Co(phen)_3}]^{3+}$ ion in aqueous solutions of NaTS now follows the Debye–Hückel limiting law, nonlocal effects apparently being of little importance. For ethylene glycol solution this behavior is, on the other hand, displayed at best only for much smaller NaTS concentrations (Figure 3), the rate constant becoming almost independent of [NaTS] at concentrations higher than 10^{-2} mol dm^{-3}. Approach to limiting values is expected from both ion-pair formation and when nonlinear terms in the Poisson–Boltzmann equation are important.[64]

$[\mathrm{Co(bpy)_3}]^{3+}$ behaves differently in aqueous NaTS (Figure 2). Although a linear Debye–Hückel plot is obtained, the charge product is only compatible with the formal value, if ϵ_{eff} is lower than the bulk value, a nonlocal value of about 50 representing the best fit. For $\langle r\rangle = 14$ Å this corresponds to correlation lengths of 4 and 8 Å for $\epsilon_i = 5$ and 20, respectively. Nonlocal effects are also compatible with the ionic strength variation when $\mathrm{NaClO_4}$ is added to ethylene glycol solution, but is probably here in reality obscured by ion pairing.

There seems to be no obvious explanation for the very small effect of sodium trifluoroacetate in either water or ethylene glycol. The half-wave potentials are shifted negatively by 20–25 mV, but this could only account for a rate decrease of a factor of 2. Sodium trifluoroacetate is known from infrared spectroscopic data[66] as a solvent "structure-maker". This could lead to a lower dielectric constant around the ions with concomitant stronger interreactant repulsion.

Elements of Electron-Transfer Theory in Nonlocal Dielectric Solvents. In order to illuminate the charge effects on sulfonation of the phen and bpy complexes and possible dielectric nonlocality, we rewrite the rate constant, eq 8, in such a way that the explicit dependence of the activation parameters on the molecular and solvent properties becomes apparent. We use the following expression for the observed activation free enthalpy, ΔG_A, which has emerged from recent formulations of ET theory, in ref 15 and 67–69 in particular:

$$\begin{gathered} k_2 = \frac{\omega_{\mathrm{eff}}}{2\pi}\kappa_e \Delta V \exp(-\Delta\tilde{G}_A/k_B T) \\ \Delta G_A = \Delta\tilde{G}_A - k_B T \ln\left[\frac{\hbar\omega_{\mathrm{eff}}}{k_B T}\Delta V \kappa_e\right] \end{gathered} \tag{16}$$

$\Delta\tilde{G}_A$ is the real activation free enthalpy, ω_{eff} is the "effective" vibrational frequency representing a weighted average of all the classical nuclear modes shifted during the reaction,[72,73] and $\hbar = h/2\pi$. This form is useful for outer-sphere processes involving mobile reactant and product molecules around ambient temperatures. It is valid when the electronic transmission coefficient falls off rapidly with increasing r. This ensures that only a narrow interval, δr, around a particular value $\langle r^*\rangle$ represents the range of ET distances. It is also a implicit assumption that intermolecular motion is slow compared with all other solvent and molecular modes.[70,71]

Several terms contribute to ΔG_A[15]

$$\begin{aligned} \Delta G_A(\theta) = \theta\Delta G_0 + U_r(\langle r^*\rangle) + \theta[U_p(\langle r^*\rangle) - U_r(\langle r^*\rangle)] + \\ \Delta G_A{}^{\mathrm{out}} + \Delta G_A{}^{\mathrm{in}} - k_B T \ln\left[\frac{\hbar\omega_{\mathrm{eff}}}{k_B T}\kappa_e \Delta V\right] \end{aligned} \tag{17}$$

ΔG_0 is the free enthalpy of reaction, $U_r(\langle r^*\rangle)$ and $U_p(\langle r^*\rangle)$ are the free enthalpies (work terms[1]) of bringing the reactants and products from infinity to the separation $\langle r^*\rangle$, $\Delta G_A{}^{\mathrm{out}}$ and $\Delta G_A{}^{\mathrm{in}}$ are contributions from reorganization of the solvent and molecular structure, respectively, and θ is the "symmetry" factor.

We now invoke particular representations for these terms. ω_{eff} receives a significant contribution from low-frequency metal–ligand stretching modes and varies only insignificantly with the solvent. It is assigned the value of 5×10^{13} s^{-1}. For spherically symmetric reactants ΔV has the form $\Delta V \approx 4\pi\langle r\rangle^2\delta r$. If the r dependence of κ_e is exponential with an orbital exponent of 1–2 Å^{-1}, the reaction zone is about 1 dm^3 mol^{-1}, which is the value used in the following calculations.

The work terms $U_r(\langle r^*\rangle)$ and $U_p(\langle r^*\rangle)$ will be represented as electrostatic free enthalpies of interaction between spherical charges. We do, however, incorporate a nonlocal dielectric function $\epsilon_{\mathrm{eff}}(\langle r^*\rangle)$, giving[43,74]

$$\begin{gathered} U_r(\langle r^*\rangle) = \frac{z_1 z_2}{\epsilon_s\langle r^*\rangle}[1 + ((\epsilon_s/\epsilon_i) - 1)\zeta\exp(-\langle r^*\rangle/\Lambda)] \\ \zeta = \frac{\Lambda^2}{2a^2}\left[\cosh\left(\frac{2a}{\Lambda}\right) - 1\right] \end{gathered} \tag{18}$$

where we have used eq 14 for $\epsilon_{\mathrm{eff}}(\langle r^*\rangle)$ and ζ incorporates the finite ionic radii a.

The solvent activation free enthalpy is, in the absence of spatial and vibrational frequency dispersion

$$\begin{gathered} \Delta G_A{}^{\mathrm{out}} = \theta(1-\theta)E_s{}^{\mathrm{cl}} \qquad E_s{}^{\mathrm{cl}} = \frac{c}{8\pi}\int \mathrm{d}\vec{r}[\vec{\mathcal{E}}_i(\vec{r}) - \vec{\mathcal{E}}_f(\vec{r})]^2 \\ c = \epsilon_0{}^{-1} - \epsilon_s{}^{-1} \end{gathered} \tag{19}$$

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where $\vec{\mathcal{E}}_i$ and $\vec{\mathcal{E}}_f$ are the reactant and product ionic vacuum fields at point $\vec{r}$, and ϵ_0 is the optical dielectric constant. While frequency dispersion can be disregarded for many organic solvents, water possesses a high-frequency "tail".[75-77] This is of some importance for aqua and ammine complexes,[15] but can be neglected for the large ions in question here. Values of the space integral in eq 19 for the two most frequently encountered solute ionic models, i.e. a pair of conducting spheres[1] and a spherical ellipsoid with a low (e.g. about 3) internal dielectric constant,[78-80] are given in Table V. Distinction between these two models, however, turns out to be of minor importance here.

E_s is also affected by dielectric nonlocality. For a pair of conducting spheres of radius a, E_s thus becomes[43,74]

$$E_s = E_s^{\mathrm{nl}} = e^2 c\left[\frac{1}{a}\varphi\left(\frac{2a}{\Lambda}\right) - \frac{1}{\langle r^*\rangle}(1 - \zeta \exp(-\langle r^*\rangle/\Lambda))\right]$$

$$\varphi(x) = 1 - \frac{1}{x}(1 - e^{-x}) \qquad (20)$$

We notice that $E_s^{\mathrm{nl}} \rightarrow E_s^{\mathrm{cl}}$ for $\langle r^*\rangle \rightarrow \infty$ or $\Lambda \rightarrow 0$. For $a = 7$ Å and $\langle r^*\rangle = 14$ Å, E_s^{nl} calculated by eq 20 for water would take the quite small values of 23 and 16 kJ for $\Lambda = 5.6$ and 8 Å, respectively, compared with the values in Table V for structureless media.

Within the harmonic approximation, the contribution from the metal–ligand stretching modes is finally[4,15,80]

$$\Delta G_A^{\mathrm{in}} = \sum_m \{\tanh\,[\beta\hbar\omega_i^m(1-\theta)/2] \times \tanh\,(\beta\hbar\omega_i^m\theta/2)\}/\{(\beta\hbar\omega_\alpha^m/2)\tanh\,[\beta\hbar\omega_i^m(1-\theta)/2] + (\beta\hbar\omega_i^m/2)\tanh\,(\beta\hbar\omega_i^m\theta/2)\}E_{rm}$$

$$E_{rm} = {}^1\!/_2\omega_i^m\omega_f^m(\Delta Q_m)^2 \qquad \beta = (k_B T)^{-1} \qquad (21)$$

where ω_i^m and ω_f^m are vibrational frequencies for the mth mode in the initial and final state, and ΔQ_m (mass weighted) equilibrium coordinate shifts. This equation incorporates nuclear tunneling. For the appropriate metal–ligand stretching frequencies of $[Co(bpy)_3]^{2+}$ and $[Co(bpy)_3]^{3+}$ at 228 and 266 cm^{-1} and at 370 cm^{-1}, respectively,[81] it is, however, a good approximation to replace eq 20 by its high-temperature limit

$$\Delta G_A^{\mathrm{in}} \approx \theta(1-\theta)E_r \qquad E_r = \sum_m E_{rm} \qquad (22)$$

The repulsion and reorganization energies can now be associated with the activation enthalpies and entropies in eq 8. Formally $\Delta S_A = -(\partial\Delta G_A/\partial T)$; then, for a structureless dielectric

$$\Delta S_A^{\mathrm{app}} \sim \theta\Delta S_0 + \gamma_s U_r + \theta\gamma_s(U_p - U_r) + k_B \ln\left[\kappa_c\Delta V\frac{\hbar\omega_{\mathrm{eff}}}{k_B T}\right]$$

$$\gamma_s = \mathrm{d}\,\frac{\ln\epsilon_s}{\mathrm{d}T} \qquad (23)$$

where we have disregarded temperature dependence of E_s and ΔG_A^{in}. The activation entropy is thus composed of the reaction entropy, ΔS_0, the temperature dependence of the dielectric constant, and the electronic transmission coefficient. The activation enthalpy becomes

$$\Delta H_A = \Delta G_A + T\Delta S_A^{\mathrm{app}} = \theta\Delta H_0 + U_r(1 + \gamma_s T) + \theta(1 + \gamma_s T)(U_p - U_r) + \theta(1-\theta)(E_s + E_r) \qquad (24)$$

Nonlocal dielectric effects modify eq 23 and 24 due to temperature dependence of the polarization correlation length. From eq 15 and 18–20, disregarding at first the temperature dependence of E_s^{nl} compared with that of the nonlocal work terms (cf. the following section)

$$\Delta S_A^{\mathrm{app}} = \theta\Delta S_0 + \xi U_r + \theta\xi(U_p - U_r) + k_B \ln\left[\kappa_e\frac{\hbar\omega_{\mathrm{eff}}}{k_B T}\Delta V\right] \qquad (25)$$

$$\xi = \gamma_s\left[1 - \frac{\Lambda^2}{2a^2}\exp(-\langle r^*\rangle/\Lambda)\left(\cosh\frac{2a}{\Lambda} - 1\right)\right] - (\mathrm{d}\ln\Lambda/\mathrm{d}T)\exp(-\langle r^*\rangle/\Lambda)\frac{\Lambda}{2a}\left(\frac{\epsilon_s}{\epsilon_i} - 1\right) \times \left[\frac{\Lambda}{2a}\left(\frac{\langle r^*\rangle}{\Lambda} + 2\right)\left(\cosh\frac{2a}{\Lambda} - 1\right) - \sinh\frac{2a}{\Lambda}\right] \qquad (26)$$

$$\Delta H_A = \theta\Delta H_0 + U_r + U_r^\circ\xi T + \theta(1 + \xi T)(U_p - U_r) + \theta(1-\theta)(E_s + E_r) \qquad (27)$$

where U_r and E_s are given by eq 18–20 and $U_r^\circ = z_1 z_2/\epsilon_s\langle r^*\rangle$.

Relation to the Co(II)/Co(III) Systems. We can now reconsider the kinetic data in Tables II–IV in terms of the formalism summarized in eq 16–27. From reported EXAFS data for the metal–ligand bond lengths in solution,[82] crystallographic data for analogous complexes of iron,[83,84] and the ligand geometry, radii of 7 Å were taken for all the complexes, giving the values of E_s in Table V. It is then convenient to consider water and the organic solvents separately.

Water. The bulk dielectric constant gives a negative enthalpy contribution of −2.4 kJ to U_r for the unsubstituted complexes. Addition of the enthalpy contribution from the half-wave potential difference then provides the following intramolecular reorganization energies, where the first, second, and third figures refer to values calculated from the conducting sphere, dielectric ellipsoid, and "nonlocal" conducting sphere models, respectively, where $\epsilon_i = 5$ and $\Lambda = 5.6$ Å in the latter model: for $[Co(phen)_3]^{3+}$, 79, 54, and 106 kJ; for $[Co(bpy)_3]^{3+}$, 85, 60, and 112 kJ. The resulting θ values are 0.48–0.49, i.e. almost as for symmetric reactions. E_r values for the two complexes are thus very close, and the large values are in line with observed significant equilibrium coordinate shifts.[82]

By means of the reaction entropies in Table I and γ_s in Table V the activation entropies (J K^{-1}) take the numerical forms $\Delta S_A = -25 + k_B \ln \kappa_e$ and $\Delta S_A = -24 + k_B \ln \kappa_e$ for the phen and bpy complexes, respectively. Comparison with the experimental values of ΔS_A in Table II then provides the practically coinciding values of κ_e of $(2 \pm 1) \times 10^{-5}$ and $(4 \pm 2) \times 10^{-5}$ for the two complexes. They are also small enough that it can be concluded that reactions 1 and 3 are likely to be strongly diabatic. This conclusion agrees with previous analysis[15,69] based on the same formalism but emphasizing comparison of rate data for symmetric electron-exchange reactions of the Co(II)/Co(III) couples with those of analogous other systems.

Using the same approach and values of ϵ_s and γ_s for the sulfonated complexes we obtain E_r values of 69, 44, and 100 kJ for the phen-SO_3^- complex based on the conducting sphere, dielectric ellipsoid, and nonlocal conducting sphere models. These values correspond to $\theta = 0.4$ due to the large negative enthalpy of reaction. The transmission coefficient becomes $\kappa_e = (5 \pm 3) \times 10^{-6}$. This slightly smaller value compared with those for the unsub-

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stituted complexes may reflect electronic localization at the electronegative $-SO_3^-$ substituents. The extracted parameter differences are, however, too small for real significance to be assigned to them. The data for the phen and phen-SO_3^- complexes in aqueous solution are thus within a factor of 2 or so in the rate constant, consistent with a single set of reorganization energies, small and close-lying electronic transmission coefficients, macroscopic electrostatic interreactant repulsion, and ions at van der Waals contact. There is no indication that the high charges on the unsubstituted complexes should push the ions apart, and nonlocal dielectric effects appear to be unimportant.

Sulfonation of bpy induces more pronounced modifications. Both the transmission coefficient and the molecular reorganization energy are smaller than for the unsubstituted complexes and the phen-SO_3^- complex. The former is about 5×10^{-7} and the latter is 40 and 15 kJ, respectively, for the conducting sphere and dielectric ellipsoid models. Analysis of these values requires that we invoke also temperature dependence of E_s^{nl} as in the next section, but the accuracy of the data for the bpy-SO_3^- complex is lower than for the other complexes due to the extrapolation procedure involved and hardly warrants such a detailed analysis. It is notable that an effective dielectric constant of 52, i.e. close to the value obtained from the ionic strength dependence of the rate constant rather than the bulk value, gives a rate ratio for the bpy-SO_3^- and bpy complexes similar to the experimental value of this ratio.

Ethylene Glycol and Glycerol/Water. The molecular parameters for the charged complexes in ethylene glycol, based on the structureless dielectric solvent models, differ significantly from the values for aqueous solution. The transmission coefficients are about 10^{-3} for both the phen and bpy complex, i.e. a factor of 50 higher than for aqueous solution. E_r values for the phen complex are 140 and 115 kJ for the conducting sphere and dielectric ellipsoid models and 110 and 85 kJ for the bpy complex, i.e. in both cases notably higher than for aqueous solution. A higher transmission coefficient might be expected for a less polar solvent,[14,38,39,41] but both this and the large E_r values more likely reveal that the solvent is not well represented by the structureless models.

Nonlocal electrostatic effects can account for the apparent differences and are in line with ionic strength effects. Moreover, nonlocality effects only in the work terms give an effect in the observed direction, whereas nonlocal solvent reorganization terms give opposite effects (cf. below). By invoking nonlocal work terms, we can obtain E_r values coinciding with those for aqueous solution, provided that certain values can be assigned to Λ and $d \ln \Lambda/dT$. For the bpy complex $\Lambda \lesssim 2$ Å or $\epsilon_{eff} \gtrsim 35$ (for $\epsilon_i = 5$) and $d \ln \Lambda/dT \gtrsim -4 \times 10^{-3}$ K^{-1}, account for the effects, but Λ and $d \ln \Lambda/dT$ cannot be obtained independently. The values for the phen complex are $\Lambda \lesssim 3.5$ Å or $\epsilon_{eff} \gtrsim 26$ and $d \ln \Lambda/dT \gtrsim -2 \times 10^{-3}$ K^{-1}. Larger values of Λ can only account for the effects for "unphysical", i.e. positive $d \ln \Lambda/dT$. These effects also modify the transmission coefficient. The limiting values for Λ and $d \ln \Lambda/dT$ indicated thus give values of κ_e around 10^{-4}, i.e. close to the values for aqueous solution.

Nonlocal dielectric effects for the unsubstituted complexes seem to be less important for the glycerol/water solution. κ_e is close to the values for aqueous solution, namely $(2 \pm 1) \times 10^{-5}$ and $(5 \pm 3) \times 10^{-5}$ for the phen and bpy complexes. So is E_r for the bpy complex, 80 and 55 kJ having been calculated by the conducting sphere and dielectric ellipsoid model. E_r values for the phen complex are slightly smaller, i.e. 60 and 35 kJ, but could be brought within this range by a minor correction for nonlocal dielectric effects.

If we consider next the phen-SO_3^- complex, relatively large negative activation entropies and small activation enthalpies give molecular parameters in the opposite direction compared with those for the unsubstituted complexes, i.e. small values of both κ_e and E_r. This effect is furthermore by far the largest for the glycerol/water solution. Using the structureless solvent models, we thus obtain κ_e values of 10^{-7} and 10^{-8} for ethylene glycol and glycerol/water, respectively. E_r becomes 60 and 40 for ethylene glycol with the two models, while E_r even virtually vanishes for glycerol/water solution.

The most likely reason for this is that the solvent structure around the phen-SO_3^- complex differs in the aqueous and nonaqueous solutions, forming a kind of rigid, possibly hydrogen-bonded network in the latter. Since work terms are now absent, we can accommodate this in terms of nonlocal solvent reorganization free enthalpies, E_s^{nl} (eq 20). As $d \ln \Lambda/dT < 0$, this means that $dE_s^{nl}/dT > 0$, giving an additional negative activation entropy contribution. In qualitative terms this accounts for both the "anomalously" small κ_e and for the small ΔH_A value compared with that in aqueous solution. Using eq 20 and its temperature derivative, and assuming that κ_e and E_r should have approximately the same values as for aqueous solution, i.e. 10^{-6}–10^{-5} and $E_r \approx 80$ kJ (for the conducting sphere model), we can estimate the limits of Λ and $d \ln \Lambda/dT$, which will reproduce the experimental values of ΔH_A and ΔS_A for the two solvents. These values are $\Lambda \approx 2$ Å for both solvents, but a somewhat larger $|d \ln \Lambda/dT|$ for glycerol/water than for ethylene glycol, viz. $d \ln \Lambda/dt \approx -3 \times 10^{-3}$ K^{-1} and -10^{-3} K^{-1}, respectively.

Nonlocal dielectric theory thus seems to be able to account for most of the solvent effects observed but also indicates that the solvent structure parameter values are rather system specific and must reveal local features.

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Registry No. $[Co(terpy)_2]^{2+}$, 18308-16-2; $[Co(phen)_3]^{2+}$, 18581-79-8; $[Co(bpy)_3]^{3+}$, 19052-39-2; $[Co(phen\text{-}SO_3^-)_3]$, 99747-69-0; $[Co(bpy\text{-}SO_3^-)_3]$,, 99747-70-3.