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Medium Effects on the Outer-Sphere Redox Reaction between $Co(terpy)_2^{2+}$ and $Co(bpy)_3^{3+}$ Complexes

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Rate constants with activation parameters and equilibrium constants are reported for the outer-sphere redox reaction between $Co(terpy)_2^{2+}$ and $Co(bpy)_3^{3+}$ measured in five protic and ten aprotic solvents. The lowest rate of electron transfer is measured in acetonitrile whereas the greatest occurs in acetophenone, a solvent with the smallest dielectric constant but the largest free energy of reaction of those solvents tested. There was a reasonably good linear correlation between the redox rate constants of the various solvents relative to water and the differences in the reciprocals of their dielectric constant if the solvents nitromethane, acetonitrile, and acetophenone are excluded. However, if the redox constants are adjusted for differences between the free energy of reaction in a given solvent and that in water, the corrected redox rate constant in acetophenone also conforms, leaving only nitromethane and acetonitrile as exceptions. The effect of ionic strength in acetophenone is briefly discussed as is the applicability of the Marcus theory.

Introduction

Redox reactions of transition-metal complexes proceeding by either an inner- or outer-sphere mechanism or both have been extensively studied in aqueous media. However, there have been relatively few studies made of these systems in nonaqueous solvents.[1] One exception is the Fe(II)–Fe(III) electron exchange which has been examined in several nonaqueous solvents,[2–5] mixed-solvent media,[6–9] ice,[10] and solid Me_2SO.[11] The predominant pathway for the electron exchange in the absence of bridging groups has been interpreted in terms of an inner-sphere mechanism. Examination of the literature shows there have been even fewer studies made on outer-sphere reactions in nonaqueous solvents. Although there have been some studies made on cobalt(II)–cobalt(III) polypyridyl systems,[12–14] due to the few solvents examined thus far, information relating to medium effects on outer-sphere redox rates between transition-metal complexes is quite limited. This study was undertaken to shed more light on those solvent properties which influence outer-sphere redox rates between transition-metal complexes.

The system selected for study was the electron transfer between tris(2,2′-bipyridyl)cobalt(III), $Co(bpy)_3^{3+}$, and bis(2,2′,2″-terpyridyl)cobalt(II), $Co(terpy)_2^{2+}$, which has been previously examined in aqueous media.[12] This work examines the redox rate of the $Co(bpy)_3^{3+}$–$Co(terpy)_2^{2+}$ system in a variety of protic and aprotic solvents[15] by using similar reactant concentrations and no added salts. However, a few kinetic measurements were made in acetophenone at different ionic strengths by varying the reactant concentrations. The usual form of an equation which relates a rate constant (k) with the dielectric constant (D) and ionic strength (μ) of the reaction solution is

$$\ln (k/k_0) = (e^2Z_AZ_B/krT)(1 - 1/D) + (e^2Z_AZ_B/DkT)(\beta/(1 + \beta r))$$

$$\beta^2 = 8\pi Ne^2\mu/1000DkT \qquad (1)$$

as reported in the literature,[1c] where Z_A and Z_B are the reactant charges, r is the radius of the activated complex, k_0 is the rate constant at zero ionic strength, and $D = 1$, with e, k, and N having their usual meaning. Since eq 1 is based on electrostatic interactions involving spherical reactants with the solvent regarded as a continuous dielectric, this study is made to test how well the equation holds in the various solvents examined here.

Experimental Section

Materials. The ligands bipyridine and terpyridine, obtained from G. F. Smith Chemical Co., were reagent grade and further purified by vacuum sublimation.[12,16] The cobalt complexes were prepared from literature methods and characterized by their spectra. These include $Co(bpy)_3(ClO_4)_3 \cdot 3H_2O$,[17,18] $Co(terpy)_2(ClO_4)_2 \cdot H_2O$,[13,19] $Co(terpy)_2(ClO_4)_3 \cdot H_2O$,[13,12b] and $Co(bpy)_3(ClO_4)_2$[17,20] with the references pertaining to their preparation and spectra, respectively.

All solvents were purified by methods described in the literature.[21] Acetonitrile, benzonitrile, glycerol, and nitromethane were spectroquality solvents from Matheson, Coleman, and Bell while acetic anhydride (RG), *N*-methylformamide (chromatographic), and sulfolane (technical) were solvents of other grades (as indicated) which were obtained from the same source. Acetone (AR), acetophenone (BA), and nitrobenzene (AR) were obtained from Baker Chemical

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[15] The following abbreviations for the solvents (Figure 1) are employed: NMF = *N*-methylformamide, FA = formamide, EC = ethylene carbonate, PC = propylene carbonate, SU = sulfolane, GL = glycerol, AN = acetonitrile, NM = nitromethane, NB = nitrobenzene, MA = methanol, BN = benzonitrile, AC = acetone, AA = acetic anhydride, AP = acetophenone.

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Table I. Rate Constants, Activation Parameters, and Free-Energy Drives of $Co(terpy)_2^{2+}$–$Co(bpy)_3^{3+}$ Reaction in Various Solvents (T = 25 °C, μ = 0.0027 M (Except Where Noted)

solvent	ϵ	k_u, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	K	$\Delta G°$,[f] kcal/mol
N-methylformamide	182.4	11.5	5.3	−36	5.9[e]	−1.05
formamide[a]	109.5	18.5	12.2	−12	3.6[e]	−0.76
ethylene carbonate[a]	89.6[b]	9.6[d]	3.1	−44	3.1	−0.70
water	78.5	9.9	5.0	−37	5.4[e]	−1.00
propylene carbonate	64.4	10.0	5.7	−35	3.5[e]	−0.74
sulfolane	43.3[c]	3.3[d]	12.2	−15	3.3	−0.71
glycerol	42.5	9.2	5.5	−36	6.4	−1.10
acetonitrile	37.5	1.0	7.0	−35	6.9	−1.14
nitromethane[a]	36.2	1.7	7.0	−34	6.2	−1.08
nitrobenzene	34.8	10.1	8.1	−27	4.6	−0.90
methanol	32.7	7.6	8.9	−24	7.1	−1.16
benzonitrile	25.2	19.2	8.2	−25	5.6	−1.02
acetone	20.7	10.7	11.7	−15	6.2	−1.08
acetic anhydride	20.1	9.1	10.8	−18	6.2	−1.08
acetophenone	17.4	86.8	8.6	−21	43.0	−2.23

[a] μ = 0.0046 M. [b] 40 °C. [c] 30 °C. [d] Extrapolated to 25 °C. [e] Averaged from spectral and kinetic measurements. [f] $\Delta G° = -RT \ln K$.

Co. and both formamide and propylene carbonate from Eastman Organic Chemicals. Water was deionized and triply distilled prior to use. The water content never exceeded 0.05% in any nonaqueous solvent as determined by the Karl Fischer method. The solvent selection for this study was limited by the solubility of the cobalt complexes and by the absence of any interaction which would interfere with the redox reaction of the metal complexes.

Kinetics. The redox rates in all solvents were measured on the Cary 14 recording spectrophotometer which was fitted with a thermostated jacket mounted in the sample compartment. The temperature inside the reaction vessel (1-cm spectral cell) was measured by a copper-constantan thermocouple and maintained to within ±0.02° of the selected value via a Haake Model FE circulator. A Teflon wand was used to mix the reactant solutions.

Prior to all kinetic runs, each reactant was examined in the various solvents to check that there would be no exchange with coordinated ligands and no redox reactions occurring with the solvent during the reaction period. Freshly prepared solutions were used in all the kinetic measurements and pseudo-first-order kinetics were maintained by keeping the oxidant in ample excess. Rates were measured at the $Co(terpy)_2^{2+}$ band (505 nm). All measurements were made at three or more temperatures over a temperature range of 5-50° with the actual temperatures being such that they always exceeded the freezing point of a given solvent. The rate constants obtained are the average of two or more kinetic runs. In each solvent, logarithmic plots of absorbance differences vs. time were linear to greater than 90% of the reaction. The ionic strength, which was derived solely from the concentration of the reaction components, was maintained at 0.0027 M (unless otherwise noted) by keeping the reactant concentrations similar in the different solvents. A few kinetic measurements were made in acetophenone at different ionic strengths by varying the reactant concentrations. All data were subjected to an error analysis with the errors in k being ±10%, in ΔH^* (±1 kcal/mol), and in ΔS^* (±3 eu).

Equilibrium Measurements. Two different methods were used to evaluate equilibrium constants in nonaqueous solvents with the spectrophotometric technique being the principal one employed. In this method, equal concentrations of reactants were used such that, after mixing, the resulting ionic strength would be equal to that of the relevant kinetic experiment. Prior to mixing, the absorbances of both the reactants and products were determined in each solvent. The reactants were then mixed, and the equilibrium reaction followed at 505 nm until there was no detectable change in absorbance. The fraction of reactants converted to products was calculated from the spectroscopic data from which concentration quotients were obtained. Since the charges on both the reactants and products are identical, the ratio of activity coefficients is unity according to the Debye–Hückel theory and consequently, the equilibrium constant, K, was taken as the concentration quotient obtained for each solvent.

The second method involved the measurement of the reaction rates in both directions under the same experimental conditions. This method was limited to the solvents formamide, *N*-methylformamide, water, and propylene carbonate due to the insolubility of both $Co(terpy)_2^{3+}$ and $Co(bpy)_3^{2+}$ in the other solvents where one of these species had to be present in large excess to ensure that the reverse reaction went to completion. A third method was employed to estimate the equilibrium constant in water, our reference solvent. The method consisted of measuring the redox potentials of the Co(II) and Co(III) tris(bipyridyl) and bis(terpyridyl) complexes as described elsewhere.[12] All these methods yielded equilibrium constants which were in good agreement with each other.

Results

Both bipyridine and terpyridine are multidentate ligands which strongly coordinate to metal ions and are not expected to be displaced by any solvents used in this study as confirmed by the spectroscopic measurements. Since both complexes are substitution inert, the mechanism of electron transfer is believed to be outer sphere in all solvents. The insolubility of the cobalt complexes restricted this study to solvents having a dielectric constant greater than 17.

The redox rate for the reaction $Co(bpy)_3^{3+} + Co(terpy)_2^{2+} \rightarrow Co(bpy)_3^{2+} + Co(terpy)_2^{3+}$ in all solvents can be expressed as $-d[Red]/dt = k_{12}[Ox][Red]$. All rates were within the range of measurement on the Cary 14 spectrophotometer by excluding salts and keeping the concentration of reactants low. Previous studies of this system in aqueous salt solutions were made on the stopped flow due to the accelerated rate at high ionic strength.[12] In Table I are contained the second-order rate constants and activation parameters in the various solvents, listed in order of decreasing dielectric constant. The slowest electron transfer is found in acetonitrile whereas the fastest is in acetophenone, the solvent with the smallest dielectric constant. The latter result can be attributed to the relatively large free energy of reaction in this solvent which apparently offsets the greater electrostatic repulsion expected between these reactant cations upon formation of the activated complex. With the exception of acetophenone, the free energies of reaction in the various solvents are similar (see Table I). The negative entropy of activation, ΔS^*, found in all solvents is consistent with reactions involving an activated complex of greater charge than either reactant and solvated more than the individual reactants.

Rate constants and activation parameters of the protic solvent group, *N*-methylformamide, formamide, water, glycerol, and methanol are quite similar with the exception of formamide. In this solvent, the electron transfer is fastest despite the relatively large enthalpy of activation and low free energy of reaction, which is offset by a favorable entropy of activation for the reaction. Although the redox rate constants in the aprotic aromatic solvents, nitrobenzene, benzonitrile, and acetophenone parallel their free energy of reaction, there were no trends found in the other solvent groups with the nonaromatic solvents exhibiting nearly a reverse trend between their rate constants and free energy of reaction.

Since the redox reactions in the various solvents are believed to be outer sphere, an attempt was made to examine the kinetic results in terms of the Marcus theory where there has been great success.[22] According to the Marcus theory, the free energy of activation (ΔG_{12}^*) is related to the work term (w_{12}), solvent reorganization free energy (λ), and free energy of reaction ($\Delta G_{12}°$) as $\Delta G_{12}^* = w_{12} + \lambda/4 + \Delta G_{12}°/2$. With use of the appropriate expression involving the experimental redox rate constants for ΔG_{12}^* and correction of this term by adjusting for differences in the free energy of reaction in the different solvents (bring $\Delta G_{12}°/2$ on the same side as ΔG_{12}^*), the rate constants showed a *linear correlation* with the work term, w_{12} (note eq 1 and Figure 1), in all solvents except

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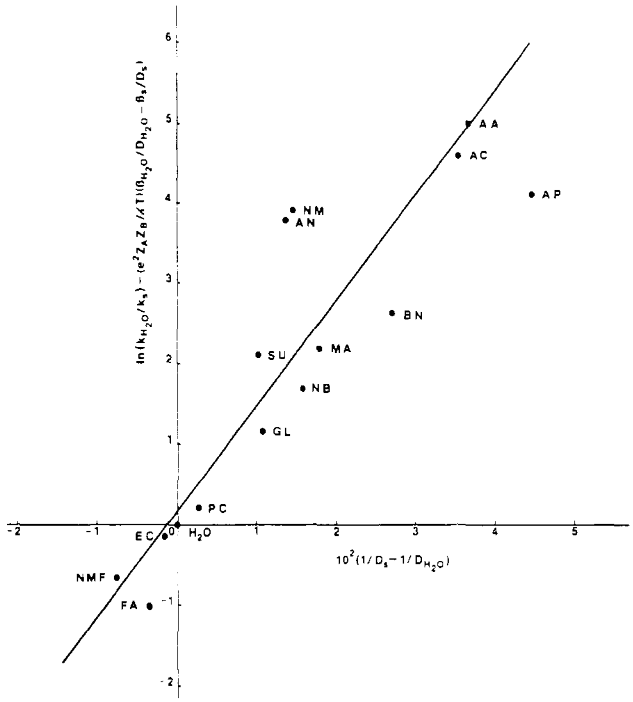

Figure 1. Plot of $\ln(k_{H_2O}/k_s) - (e^2Z_AZ_B/kT)(\beta_{H_2O}/D_{H_2O} - \beta_s/D_s)$ vs. $1/D_s - 1/D_{H_2O}$ for the $Co(terpy)_2^{2+}$–$Co(bpy)_3^{3+}$ redox reaction in various solvents.

nitromethane and acetonitrile. This result is quite surprising and unexpected since it suggests that the solvent reorganization free energy (λ) does not vary significantly in most of the solvents tested here. However, it should be noted that in redox studies of other systems, the contribution of the solvent reorganization free energy to the free energy of activation was smaller than predicted by the Marcus theory.[23]

Solvent properties such as donor and acceptor number, viscosity, Z value, Y value, and other empirical parameters discussed in the literature[1c,13,24] were examined, but no trend could be found. In fact, the results show that large differences in solvent viscosity have little effect on the redox rate since similar rate constants are obtained in acetone and glycerol (viscosities are 0.3 and 945 cp, respectively. However, Figure 1 shows that, for most of the solvents, a reasonable good linear relationship is obtained between the redox rate constants in the solvents relative to that in water and differences in the reciprocals of their dielectric constant (D_s) and water (D_{H_2O}) by utilizing eq 1 (see Discussion). The large deviation from linearity of the redox rate constants measured in nitromethane and acetonitrile compared to water results from the relatively slow redox rates found in these solvents while the reverse is true in the case of acetophenone. In the past, lower rates were found in nitromethane and acetonitrile relative to water for the Fe(II)–Fe(III) redox system[3,8] when these solvents did not interfere with the redox reaction.[1c,25] Similar results were found in acetonitrile relative to water with some Fe(II)–Fe(III) polypyridyl systems although the comparison is questionable due to the different anions present.[1d] It has already been noted that both these solvents have relatively high dielectric constants and are often poor solvents for ionic reactants since they cannot effectively solvate anions.[26,27] Therefore, the possibility exists that, since the source of reactants are their perchlorate salts, the interaction of the perchlorate anion with either reactant or both in acetonitrile and nitromethane interferes with the electron-transfer process and that the interference may be energy related rather than entropy related when these solvents are compared with others having similar entropies of activation (see Table I).

Due to the unexpectedly large redox rate in acetophenone, ionic strength studies were made in this solvent. Moreover, since the dielectric constant of acetophenone is the smallest of those examined, ion association would be enhanced relative to the other solvents. The redox rate constants obtained at 25 °C and different ionic strength are 87 (0.0027 M), 57 (0.0014 M), and 40 $M^{-1}\ s^{-1}$ (0.0007 M) with the ionic strength range limited by the insolubility of the reactants in this solvent and by our inability to monitor the redox reaction at lower reactant concentrations.[28] The redox rate in acetophenone increases with ionic strength as predicted from eq 1.

Discussion

Permittivity Dependence. For ion–ion reactions, electrostatic interactions generally make the greatest contribution to the activation free energy. The solvent parameter widely used as a measure of the electrostatic interactions between solute and solvent is the dielectric constant. With water as the reference solvent, an expression can be easily derived from eq 1 which relates the redox rate constant in water (k_{H_2O}) to that of other solvents (k_s). This expression is

$$\ln(k_{H_2O}/k_s) - (e^2Z_AZ_B/kT)(\beta_{H_2O}/D_{H_2O} - \beta_s/D_s) = e^2Z_AZ_B/kTr(1/D_s - 1/D_{H_2O}) \quad (2)$$

where it is assumed that $1 >> \beta r$ and all terms have been previously defined. A plot of the left side of eq 2 vs. $1/D_s - 1/D_{H_2O}$ is linear provided Z_AZ_B/r remains similar in all solvents. Figure 1 represents a linear least-squares plot of the data which shows that, for most of the solvents, a reasonable linear correlation is obtained with the exceptions of nitromethane, acetonitrile, and acetophenone. On the basis of reactant charges of 2+ and 3+, respectively, an r value of 25 Å is obtained from the slope of the line in Figure 1. Although this experimental result for r should not be taken as its precise value, it does suggest that the electron transfer may be a long-range process. If the reactant radii are assumed to be 7 Å, a value reported in the literature for these type complexes,[29] there would be ample space between the reactants to fit solvent molecules and/or perchlorate anions which are present as the counterions of the reactants in solution. In fact, Wahl and co-workers[1d] point out in their redox studies with metal complexes containing similar type ligands that there is sufficient space between the coordinated ligands of each reactant to accommodate anions and/or solvent molecules. For these reasons, ion association is especially attractive in those solvents with lower dielectric constants. If ion association occurs in any of the solvents examined here, our results suggest that the reactant charges and the separation between reactants in the activated complex both decrease in such a manner that their ratio Z_AZ_B/r remains fairly constant in most of the solvents. Finally, if the redox rate constants are corrected for differences in the free energy of reaction between a given solvent and water, only the rate constant in acetophenone undergoes a significant change, with the adjusted value being well defined by the line shown in Figure 1 leaving only nitromethane and acetonitrile as the exceptions.

Ionic Strength Studies in Acetophenone. With use of eq 1

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and the redox rate constants from ionic strength studies in acetophenone, we find the product of the reactant charges to be approximately 4 when an *r* value of 25 Å is assumed and even less when smaller values of *r* are used. These results suggest either that more extensive ion association has occurred in acetophenone relative to the other solvents or that the radius of the activated complex is larger. The latter could occur if acetophenone molecules are between the reactants in the activated complex. In either case, the Z_AZ_B/r ratio would decrease. The smaller Z_AZ_B/r ratio obtained from ionic strength studies relative to that in Figure 1 is consistent with the low position of acetophenone. However, at this point, some mention should be made of the low ionization potential of acetophenone which is less than that of any solvent examined here.[30] A solvent with a relatively low ionization potential could promote removal of an electron from the oxidant (ionization) and thus facilitate the electron transfer.[6c] Using similar arguments, we could find no explanation for the relatively low redox rates in nitromethane and acetonitrile.

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Registry No. $Co(terpy)_2^{2+}$, 18308-16-2; $Co(bpy)_3^{3+}$, 19052-39-2.

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Notes

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Nonaiodononaborane(9), B_9I_9. A Stable Boron Iodide Cluster[1]

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Simple boron halides such as boron trihalides, BX_3, and diboron tetrahalides, B_2X_4 (X = F, Cl, Br, I) are well-known compounds, and several are familiar Lewis acid reagents in chemical synthesis.[2] Much less common are neutral boron halide clusters with polyhedral geometries and the general formulation B_nX_n. These have also been referred to as boron subhalides and include only B_4Cl_4, B_8Cl_8, B_9Cl_9, and B_9Br_9 as well-characterized species.[3] Mass spectral evidence for B_7, B_{10}, B_{11}, and B_{12} chlorides has also been reported.[4]

For both classes of boron halides, formal electron deficiency exists. Boron trihalides, of course, are two electrons short of the octet at the central borons while B_nX_n clusters are formally species with $2n$ skeletal electron counts, two electrons shy of the $2n + 2$ closed-shell configurations.[5] A variety of evidence supports halogen back-donation in simple boron halides as a major stabilizing factor.[6] The general trend of π-bonding significance is believed to be B–F > B–Cl > B–Br > B–I, although Lappert has reported MO calculations that predicted an exactly opposite trend for BX_3.[7] Nonetheless the majority of experimental data support optimal stabilization of BX_3 and B_2X_4 species for X = F and minimal stabilization for X = I, as evidenced by the relative instability of both BI_3 and B_2I_4. Lipscomb has performed ab initio SCF calculations on the tetrahedral clusters B_4H_4, B_4F_4, and B_4Cl_4 and has concluded that indeed the extent of π bonding is significantly greater for B_4F_4 compared to B_4Cl_4.[8] While similar calculations for larger clusters are not yet available, the lack of any literature report of a boron iodide cluster does seem to support the premise that iodine substituents alone may not be capable of stabilizing an electron-deficient boron cage. Literature reports on attempts at synthesizing neutral boron iodide clusters are meager. Schumb reported the room-temperature decomposition of B_2I_4 to give a nonvolatile black polymeric solid with the composition $(BI)_n$.[9] This poorly characterized solid decomposed in solvents such as CS_2, CCl_4, and water while yielding free iodine upon pyrolysis at 125 °C. Recently, Massey obtained mass spectral evidence for clusters of composition $B_9Cl_{9-n}I_n$ (n = 1–6) from the reaction of iodine with a $B_{10}Cl_{10}/B_{11}Cl_{11}$ mixture at 130 °C.[10] However, none was isolated, and furthermore no periodinated clusters were observed.

We recently reported the first stable boron halide radicals $B_9X_9^{-}\cdot$ (X = Cl, Br, I) and have demonstrated the redox relationships $B_9X_9 \rightleftharpoons B_9X_9^{-}\cdot \rightleftharpoons B_9X_9^{2-}$ (X = Cl, Br).[11] We have now successfully extended this to prepare the first boron iodide cluster, B_9I_9. Excess thallic trifluoroacetate reacted with either $(n\text{-}Bu_4N)_2B_9I_9$ or $(n\text{-}Bu_4N)B_9I_9$ in CH_2Cl_2, yielding a red-purple suspension. After solvent removal and CCl_4 extraction, a dark brown microcrystalline solid can be isolated in about 30% yield. Positive identification of the product as B_9I_9 is based on the following data.

(1) Elemental analysis confirmed the formulation as $(BI)_n$.

(2) The infrared spectrum of the compound is simple and contains only one strong, broad band in the cage and B–I vibration region. This is remarkably similar to the spectra of B_9Cl_9 and B_9Br_9 (Figure 1) except for shifting of all the absorption bands to lower frequencies. Similar trends have already been noted for the polyhedral borane derivatives $B_nX_n^{2-}$

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