

# Solvent Dynamics and Pressure Effects in the Kinetics of the Tris(bipyridine)cobalt(III/II) Electrode Reaction in Various Solvents

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**Abstract:** The volume of activation  $\Delta V_{el}^\ddagger$  for the  $\text{Co}(\text{bpy})_3^{3+/2+}$  electrode reaction in aqueous NaCl (0.2 mol  $\text{L}^{-1}$ ) is  $-8.6 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$  at 25.0 °C, as expected on theoretical grounds and by analogy with  $\text{Co}(\text{en})_3^{3+/2+}$  and  $\text{Co}(\text{phen})_3^{3+/2+}$ , and neither the rate constant  $k_{el}$  at various pressures nor  $\Delta V_{el}^\ddagger$  correlate with the corresponding mean diffusion coefficients  $D$  for the couple and the diffusional activation volume  $\Delta V_{diff}^\ddagger$ , respectively. In organic solvents, however,  $\Delta V_{el}^\ddagger$  is strongly positive ( $9.1 \pm 0.3$ ,  $10.2 \pm 0.7$ , and  $12.2 \pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$  for  $\text{CH}_3\text{CN}$ , acetone, and propylene carbonate, respectively, with 0.2 mol  $\text{L}^{-1}$   $[(\text{C}_4\text{H}_9)_4\text{N}]\text{ClO}_4$  at 25 °C) and correlates with  $\Delta V_{diff}^\ddagger$ , while  $k_{el}$  correlates with  $D$ . These results support the proposition of Murray et al. (*J. Am. Chem. Soc.* **1996**, *118*, 1743; **1997**, *119*, 10249) that solvent dynamics control the rate of the  $\text{Co}(\text{bpy})_3^{3+/2+}$  electrode reaction in organic solvents. In aqueous solution at near-ambient temperatures, solvent dynamical influences would not be revealed by pressure effects, but in any event the aqueous  $\text{Co}(\text{bpy})_3^{3+/2+}$  electrode reaction appears to be mechanistically different from the nonaqueous cases. For the reduction of  $\text{Co}(\text{bpy})_3^{3+}$  with  $\text{Co}(\text{sep})^{2+}$  in homogeneous aqueous solution, the rate constant is lower, and the volume of activation more negative, than can be accommodated by extended Marcus theory, suggesting nonadiabatic behavior. These observations are consistent with the view that, although the self-exchange and electrode reactions are generally adiabatic, cross reactions involving  $\text{Co}^{\text{III/II}}$  couples (and presumably others) become increasingly nonadiabatic as the driving potential is increased.

## Introduction

The question of the possible involvement of solvent dynamics (solvent friction) in the kinetics of electron transfer processes has been perceptively reviewed by Weaver<sup>1,2</sup> and continues to attract much theoretical interest.<sup>3–5</sup> Experimental evidence for solvent dynamical influences on the rate constants  $k_{el}$  of electrode reactions is nevertheless still limited and sometimes ambiguous.<sup>1,2,6–15</sup> In essence, if solvent dynamics are rate-controlling, one expects  $k_{el}$  to correlate inversely with the longitudinal relaxation time  $\tau_L$  (and hence with the viscosity

$\eta$ ) of the solvent. Such effects have been observed for electrode reactions of  $\text{Cr}(\text{EDTA})^{-2-}$  and  $\text{Fe}(\text{CN})_6^{3-/4-}$  in experiments in which  $\eta$  was adjusted by addition of dextrose or sucrose to the solvent (water or dimethyl sulfoxide).<sup>8–10</sup> Solvent friction has also been inferred in the reduction in aqueous acetone of  $(\text{NH}_3)_5\text{Co}^{3+}$  groups bound to Hg electrodes through thiophenecarboxylate ligands,<sup>11</sup> and in the redox kinetics of metallocene couples at Hg electrodes in various organic solvents.<sup>12,13</sup> Of particular interest is the recent observation by Murray and co-workers<sup>14,15</sup> that the rate constant  $k_{el}$  of the  $\text{Co}(\text{bpy})_3^{3+/2+}$  electrode reaction in Debye solvents is proportional to  $\tau_L^{-1}$  and  $\eta^{-1}$  and to the diffusion coefficient  $D$  of the complexes (which may be assumed to be the same for both the oxidized and reduced species); these correlations hold over a spectacular range of  $10^{11}$  in  $k_{el}$ .

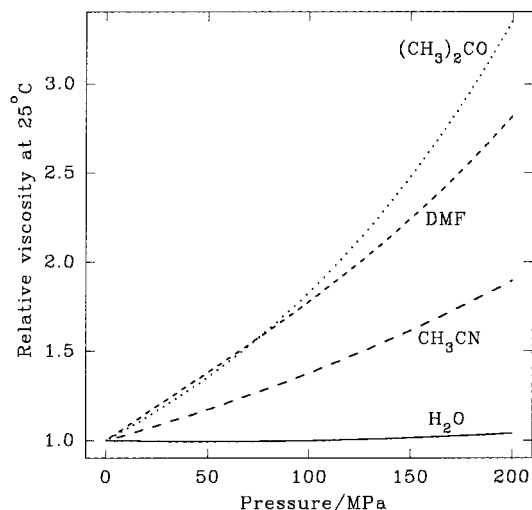
These tests for solvent dynamical effects all involve comparisons of  $k_{el}$  between chemically different solvents or mixtures. Since  $\eta$  is roughly exponentially dependent on pressure  $P$  over the first few hundred MPa for common solvents other than water (Figure 1), kinetic studies of electrode reactions at elevated pressures are potentially capable of revealing solvent dynamical behavior in nonaqueous systems without changing the solvent chemically.<sup>17</sup> In the case of water, pressure breaks up ice-like local structures in the liquid phase, so offsetting the normal increase of viscosity with rising pressure with the result that the  $\eta$  vs  $P$  plot at low temperatures passes through a shallow minimum around 50–100 MPa and at 25 °C is almost flat to

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(16) bpy = 2,2'-bipyridine; en = 1,2-diaminoethane; sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; DMF = *N,N'*-dimethylformamide; TBAP = tetrabutylammonium perchlorate.

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**Figure 1.** Pressure dependence of viscosity  $\eta$  for typical solvents at 25 °C, recalculated from refs 18 (water), 19 (acetonitrile and DMF), and 20 (acetone). Data for propylene carbonate are not available.

200 MPa. Consequently, for a given couple, if any pressure effects (retardations) on  $k_{el}$  observed in nonaqueous solutions are truly due to solvent dynamic effects, they will be conspicuously absent in water near 25 °C. Ordinarily, volumes of activation  $\Delta V_{el}^\ddagger$  ( $= -RT(\partial \ln k_{el}/\partial P)_T$ ) for cationic couples undergoing electron transfer at an electrode are expected (and found) to be moderately negative;<sup>21</sup> thus, as suggested previously in the context of self-exchange reactions,<sup>17</sup> the observation of a markedly *positive*  $\Delta V_{el}^\ddagger$  value for a *nonaqueous* solvent would constitute strong evidence for the incursion of solvent dynamics.

With these considerations and the observations of Murray et al.<sup>14,15</sup> in mind, we have measured volumes of activation  $\Delta V_{el}^\ddagger$  for the reduction of Co(bpy)<sub>3</sub><sup>3+</sup> at a Pt electrode in acetonitrile, acetone, propylene carbonate, and water, the choice of solvents being limited to these by the solubility and stability of the Co<sup>III</sup> and Co<sup>I</sup> complexes. The results broadly support the conclusion of Murray et al.<sup>14,15</sup> that solvent dynamics are dominant for this electrode reaction in the nonaqueous solvents, but also imply that in water the electrode reaction is mechanistically different. We have therefore also investigated the effects of pressure on the *chemical* reduction of Co(bpy)<sub>3</sub><sup>3+</sup> by Co(sep)<sup>2+</sup> in homogeneous aqueous solution. The results reinforce our interpretation of the electrochemical results for water, but also suggest that the cross reaction is not fully adiabatic.

## Experimental Section

**Materials.** [Co(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O was made by the method of Nyholm and Burstall<sup>22</sup> and checked for purity by CHN microanalyses and its UV–visible spectrum in water (absorbance maxima at 318, 307, and 222 nm; molar absorbances  $3.03 \times 10^4$ ,  $3.29 \times 10^4$ , and  $8.76 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>, respectively). [Co(sep)](ClO<sub>4</sub>)<sub>3</sub><sup>16</sup> was made by the method of Harrowfield et al.<sup>23</sup> (*Caution!* Perchlorate salts of Co<sup>III</sup> complexes containing organic ligands are potentially explosive.) Distilled water was further purified by passage through a Barnstead NANOpure train. Acetone and redistilled acetonitrile (BDH, Analytical

Grade) were dried by storage over freshly baked 4A molecular sieves. Propylene carbonate (Aldrich, Gold Label, sealed under N<sub>2</sub>) was used as received. DMF<sup>16</sup> (Burdick and Jackson, distilled in glass) was dried over molecular sieves and redistilled under reduced pressure. TBAP (Fluka) was either recrystallized from ethanol (AG grade) or used as received (Electrochemical grade, puriss.).

**Electrochemical Measurements.** Cyclic (CV) and alternating current (ACV) voltammograms were obtained with Pt wire working electrodes and analyzed as described previously.<sup>21,24</sup> Half-wave potentials  $E_{1/2}$  from the CVs were reproducible to within  $\pm 5$  mV. Glassy carbon working electrodes gave good CVs but distorted ACVs in initial aqueous studies and were not used further. ACV measurements were made at 25.2, 45.3, 85.3, and (at 3 °C) 159 Hz for solvent water; 25.2, 45.3, 85.3, and 149 Hz for propylene carbonate; and 45.3, 85.3, 159, and 258 Hz for acetone and acetonitrile. Measurements at ambient pressure were made using a glass-jacketed cell, thermostated with circulating water. Measurements at variable pressure were made in the apparatus previously described,<sup>21,24</sup> with the temperature controlled at  $25.0 \pm 0.1$  °C with water circulating through an external jacket. The supporting electrolyte was 0.2 mol L<sup>-1</sup> NaCl in aqueous solutions (in which solubility precluded the use of perchlorate media) and 0.2 mol L<sup>-1</sup> TBAP in the organic solvents. The Co complex was insufficiently soluble in CH<sub>3</sub>OH, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub>, and decomposed slowly in the course of measurements in the strong donor solvent DMF. The Ag/AgCl reference electrode used for aqueous solutions was unstable in organic solvents, in which a Ag/Ag<sup>+</sup>/TBAP electrode was employed for the kinetic experiments.

**Stopped-Flow Kinetics.** Aqueous [Co(sep)](ClO<sub>4</sub>)<sub>3</sub> was reduced to Co(sep)<sup>2+</sup> with amalgamated Zn for 4 h immediately prior to use, and this and the Co(bpy)<sub>3</sub><sup>3+</sup> solution were handled under Ar at all times. The ionic strength  $I$  of all solutions was adjusted to 0.2 mol L<sup>-1</sup> with LiClO<sub>4</sub> (pH  $\sim 6$ ). Kinetic measurements were made at 318 nm (relevant spectra are given in the Supporting Information, Figure S1) in a Hi-Tech SP-56 pressurizable stopped-flow system, with Co(sep)<sup>2+</sup> in  $> 10$ -fold excess over Co(bpy)<sub>3</sub><sup>3+</sup>; thus, the rate of spectrophotometric change was first order in [Co(bpy)<sub>3</sub><sup>3+</sup>]. A fragment of amalgamated zinc was placed in the reductant syringe to suppress any reoxidation of Co(sep)<sup>2+</sup>.<sup>25</sup>

## Results

Concentrations specified in this article are temperature and pressure independent, expressed as if at 22 °C and 0.1 MPa. Only those variable-pressure experiments in which the low-pressure measurements at the beginning and end of the pressure cycle agreed within the experimental uncertainty were accepted.

For the Co(bpy)<sub>3</sub><sup>3+/2+</sup> electrode reaction in any solvent at each pressure and temperature, the mean reactant diffusion coefficient  $D$  was obtained from the averaged peak currents of multiple CV measurements, and the electrode rate constant  $k_{el}$  was calculated from the maximum in-phase and 90° out-of-phase alternating currents ( $I_x$  and  $I_y$ , respectively, at potential  $E_{max}$ ) of an ACV after correcting for the uncompensated resistance  $R_u$ .<sup>24</sup> Although  $k_{el}$  can, in principle, be obtained from the peak separation of CVs, such a procedure will give erroneous results if  $R_u$  is significant, which is generally the case for nonaqueous solvents.<sup>6,26,27</sup> In our ACV experiments, however,  $R_u$  was first obtained directly from the cell impedance, measured at a high frequency (typically 8 kHz) and a potential  $\geq 300$  mV away from  $E_{1/2}$  for Co(bpy)<sub>3</sub><sup>3+/2+</sup>, and was then specifically allowed for in the calculation of  $k_{el}$ .<sup>24</sup> The in-phase and 90° out-of-phase background currents  $I_{bx}$  and  $I_{by}$  were measured to obtain the total cell impedance, from which  $R_u$  was subtracted

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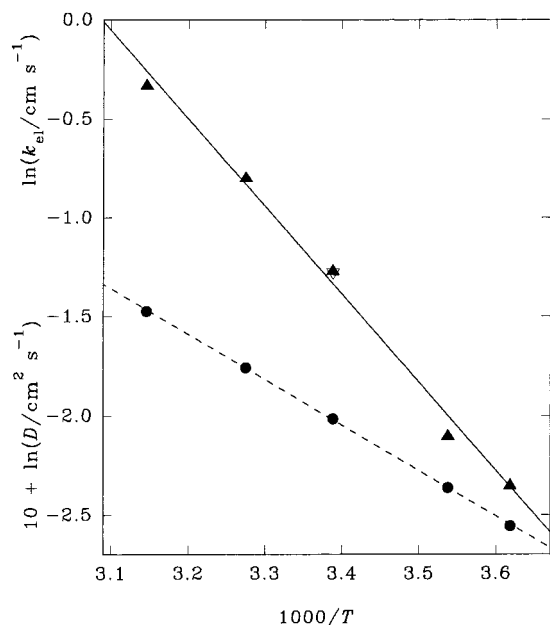
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**Figure 2.** Arrhenius plots showing the temperature dependences of the mean diffusion coefficient  $D$  (broken line) and the electrode reaction rate constant  $k_{el}$  (solid line) for  $\text{Co}(\text{bpy})_3^{3+/2+}$  at a Pt electrode in aqueous  $0.2 \text{ mol L}^{-1}$  NaCl.

to give the double-layer charging impedance  $Z_{dl}$ . This in turn was used to recalculate  $I_{bx}$  and  $I_{by}$  (phase shift  $\phi_Z$ ). The faradaic peak currents  $I_{fx}$  and  $I_{fy}$  were obtained by subtracting the recalculated  $I_{bx}$  and  $I_{by}$  from  $I_x$  and  $I_y$ , respectively, giving a phase angle  $\phi_f$ . Since the expression

$$E_{\max} = E_{1/2} + (RT/F) \ln\{\alpha/(1 - \alpha)\}$$

showed the transfer coefficient  $\alpha$  to be 0.5 in all cases, the simplified relation

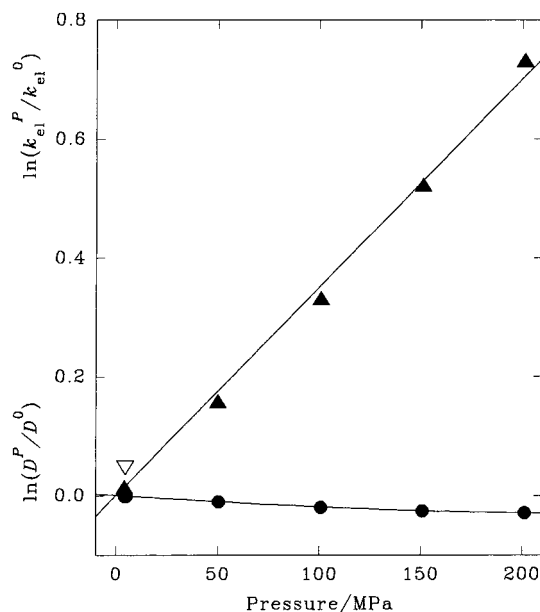
$$\cot \phi = 1 + (2D\omega)^{1/2}/k_{el}$$

where  $\phi$  is the corrected phase angle ( $=\phi_Z + \phi_f$ ) and  $\omega$  is the angular ac frequency, was used to calculate  $k_{el}$ .<sup>21,24</sup>

Although pressure-dependence parameters such as  $\Delta V_{el}^\ddagger$  appeared constant within experimental uncertainty over the pressure range 0–200 MPa, a small secondary dependence on pressure is expected, so that cited values should be regarded as valid at 100 MPa, the midpoint of the pressure range.

**The  $\text{Co}(\text{bpy})_3^{3+/2+}$  Electrode Reaction in Water.** Figure 2 shows the temperature dependences of  $\ln D$  (from CV data) and  $\ln k_{el}$  (from ACV measurements) for  $\text{Co}(\text{bpy})_3^{3+/2+}$  ( $1.0 \text{ mmol L}^{-1}$ ) in aqueous NaCl ( $0.2 \text{ mol L}^{-1}$ ) at a Pt electrode, 3.2–44.7 °C. The data<sup>28</sup> yield the respective Arrhenius activation energies  $E_{a(\text{diff})} = 19.1 \pm 0.1 \text{ kJ mol}^{-1}$  and  $E_{a(\text{el})} = 37.0 \pm 1.7 \text{ kJ mol}^{-1}$  (or, for the electrode reaction rate, the Eyring parameters  $\Delta H_{el}^\ddagger = 34.5 \pm 1.7 \text{ kJ mol}^{-1}$ ,  $\Delta S_{el}^\ddagger = -139 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$ ), with  $D^{298} = 6.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and  $k_{el}^{298} = 0.31 \text{ cm s}^{-1}$ .

Figure 3 shows the linear pressure dependences of  $\ln D$  and  $\ln k_{el}$  for  $\text{Co}(\text{bpy})_3^{3+/2+}$  in aqueous  $0.2 \text{ mol L}^{-1}$  NaCl at 25.0 °C. The corresponding parameters are given in Table 1. High-pressure CVs showed that  $E_{1/2}$  was also a linear function of pressure, 0–200 MPa,<sup>28</sup> giving the volume of reaction  $\Delta V_{\text{cell}}$  ( $= -F(\partial E_{1/2}/\partial P)_T$ , where  $F$  is the Faraday) relative to the Ag/AgCl electrode (Table 1) in good agreement with values reported



**Figure 3.** Pressure dependences of  $\ln D$  (●) and  $\ln k_{el}$  (▲, rising pressure; ▽, descending pressure) for  $\text{Co}(\text{bpy})_3^{3+/2+}$  at a Pt electrode in  $0.2 \text{ mol L}^{-1}$  aqueous NaCl at 25.0 °C.

**Table 1.** Characteristics of  $\text{Co}(\text{bpy})_3^{3+/2+}$  at a Pt Wire Electrode<sup>a</sup>

	solvent			
	$\text{H}_2\text{O}^b$	$\text{CH}_3\text{CN}^c$	$(\text{CH}_3)_2\text{CO}^c$	propylene carbonate <sup>c</sup>
$E_{1/2}/\text{mV}$	(125) <sup>d</sup>	4 <sup>e,f</sup>	0 <sup>e</sup>	-52 <sup>e</sup>
$\Delta V_{\text{cell}}$	(26.8 ± 0.9) <sup>d</sup>	15.9 ± 0.4 <sup>e</sup>	12.3 ± 1.0 <sup>e</sup>	14.0 ± 0.4 <sup>e</sup>
$k_{el}^0/\text{cm s}^{-1}$	0.172	0.198	0.070	0.0160
$D^0/10^{-6} \text{ cm}^2 \text{ s}^{-1}$	6.06	10.6	9.41	1.40
$\Delta V_{el}^\ddagger/\text{cm}^3 \text{ mol}^{-1}$	-8.6 ± 0.4	9.1 ± 0.3	10.2 ± 0.7	12.2 ± 0.9
$\Delta V_{\text{diff}}^\ddagger/\text{cm}^3 \text{ mol}^{-1}$	0.37 ± 0.03	8.8 ± 0.1	11.1 ± 0.1	15.6 ± 0.4
$RT(\partial \ln \eta/\partial P)/\text{cm}^3 \text{ mol}^{-1}$	0.5 <sup>g</sup>	8.2 <sup>g</sup>	13.2 <sup>h</sup>	
$\Delta V_{\text{SD}}^\ddagger/\text{cal}/\text{cm}^3 \text{ mol}^{-1}$	1.5 <sup>g</sup>	8.8 <sup>g</sup>	13.1 <sup>h</sup>	

<sup>a</sup> 1.0 mmol L<sup>-1</sup> Co; 25.0 °C; transfer coefficient  $\alpha = 0.5$  in all cases. <sup>b</sup> 0.20 mol L<sup>-1</sup> NaCl. <sup>c</sup> 0.20 mol L<sup>-1</sup> Bu<sub>4</sub>NClO<sub>4</sub>. <sup>d</sup> Reference electrode Ag/AgCl/(4 mol L<sup>-1</sup> KCl). <sup>e</sup> Reference electrode Ag/(0.013 mol L<sup>-1</sup> AgClO<sub>4</sub>-0.20 mol L<sup>-1</sup> Bu<sub>4</sub>NClO<sub>4</sub>-CH<sub>3</sub>CN). <sup>f</sup> -85 ± 10 mV vs Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub><sup>+/0</sup>. <sup>g</sup> Calculated for midrange pressure of 100 MPa. <sup>h</sup> 30 °C, 0–100 MPa.

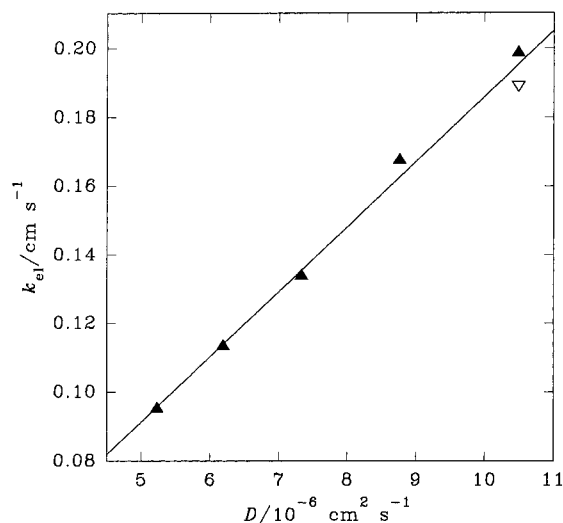
by other workers.<sup>29</sup> At  $3.0 \pm 0.1$  °C, ACV measurements over the range 0.1–201 MPa again showed an accurately linear dependence of  $\ln k_{el}$  on  $P$ ,<sup>28</sup> giving  $\Delta V_{el}^\ddagger = -9.1 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ . Thus, the temperature dependence of  $\Delta V_{el}^\ddagger$  (cf. Table 1) is not significant in view of the standard deviations cited.

**The  $\text{Co}(\text{bpy})_3^{3+/2+}$  Electrode Reaction in Organic Solvents.** The choice of solvents was limited to acetonitrile, acetone, and propylene carbonate by insufficient solubility of  $\text{Co}(\text{bpy})_3^{3+}$  salts in methanol, dichloromethane, chloroform, etc., and by the tendency of the transiently formed  $\text{Co}(\text{bpy})_3^{2+}$  to decompose in strong donor solvents such as DMF. The CV for reduction of  $\text{Co}(\text{bpy})_3^{3+}$  in acetonitrile ( $0.3 \text{ mol L}^{-1}$  TBAP) showed redox waves with  $E_{1/2} = 618$  and  $-655$  mV vs Ag/AgCl, corresponding to the  $\text{Co}(\text{bpy})_3^{3+/2+}$  and  $\text{Co}(\text{bpy})_3^{2+/+}$  couples, but decomposition of the transient  $\text{Co}^{\text{I}}$  species was evident at scan rates  $< 50 \text{ mV s}^{-1}$ . Uncompensated resistance was relatively high and increased with rising pressure (Table S1<sup>28</sup>), as expected for organic solvents, but was specifically corrected for in each experiment and at all temperatures and pressures when calculating  $k_{el}$ .<sup>21</sup> This is an important point, because the pressure and

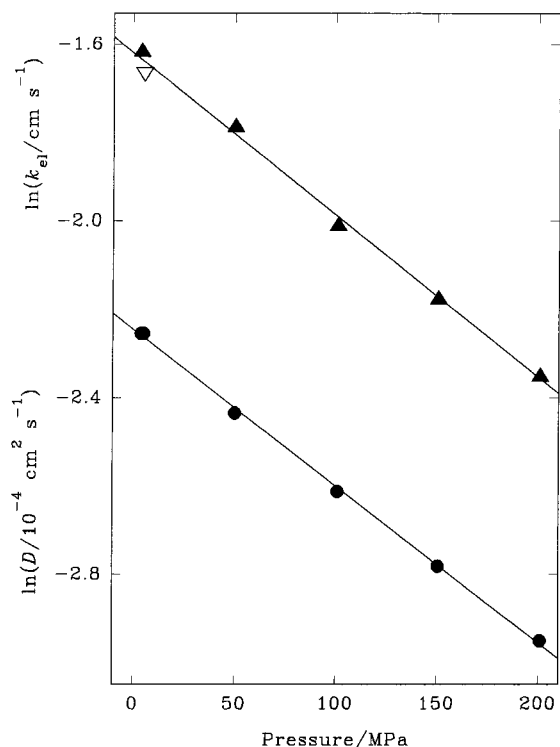
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**Figure 4.** Dependence of  $k_{el}$  on  $D$  for  $\text{Co}(\text{bpy})_3^{3+/2+}$  at a Pt electrode in acetonitrile containing  $0.2 \text{ mol L}^{-1}$  TBAP at  $25.0 \text{ }^\circ\text{C}$ .



**Figure 5.** Pressure dependences of  $\ln D$  (●) and  $\ln k_{el}$  (▲, rising pressure; ▽, descending pressure) for  $\text{Co}(\text{bpy})_3^{3+/2+}$  at a Pt electrode in acetonitrile containing  $0.2 \text{ mol L}^{-1}$  TBAP at  $25.0 \text{ }^\circ\text{C}$ .

temperature dependences of disregarded  $R_u$  could account (at least qualitatively) for those observed for  $k_{el}$  (in other words, concealed  $R_u$  could mimic solvent dynamical effects).<sup>1</sup>

Figure 4 shows that  $k_{el}$  is directly proportional to  $D$  over the pressure range 0–201 MPa for  $\text{Co}(\text{bpy})_3^{3+/2+}$  in acetonitrile (slope  $1.89 \times 10^4 \text{ cm}^{-1}$ , negligible intercept). The pressure dependences of  $\ln k_{el}$  and  $\ln D$  for  $\text{Co}(\text{bpy})_3^{3+/2+}$  in acetonitrile are shown in Figure 5; these and the corresponding plots for acetone and propylene carbonate<sup>28</sup> are linear within the experimental uncertainty. The derived parameters are summarized in Table 1, together with cell reaction volumes  $\Delta V_{cell}$  relative to the Ag/Ag<sup>+</sup> electrode obtained from the linear pressure dependences of  $E_{1/2}$  over the range 0.1–200 MPa.<sup>28</sup> For aceto-

nitrile as solvent,  $\Delta V_{cell}$  is in good agreement with the published value.<sup>29</sup>

**Reduction of  $\text{Co}(\text{bpy})_3^{3+}$  in Homogeneous Aqueous Solution.** For stopped-flow kinetic measurements, the choice of a suitable reductant for  $\text{Co}(\text{bpy})_3^{3+}$  is severely limited by the need for the reductant to be substitutionally inert and also for the reduction to be fast enough (implying a high  $\Delta E_{1/2}$  for the cross reaction) to be substantially complete before the incursion of a secondary process with rate constant  $k_{sec} = 2.4 \text{ s}^{-1}$  at  $24.8 \text{ }^\circ\text{C}$ . These criteria are met by the cage complex  $\text{Co}(\text{sep})^{2+}$  ( $\Delta E_{1/2} = 660 \text{ mV}$ , from ref 21 and Table 1). With  $\text{Co}(\text{sep})^{2+}$  as the reductant,  $k_{sec}$  was independent of  $[\text{Co}(\text{sep})^{2+}]$  ( $0.67\text{--}2.0 \text{ mmol L}^{-1}$ ). Thus, the secondary process was evidently aquation of the newly formed  $\text{Co}(\text{bpy})_3^{2+}$ , for which Farina et al.<sup>30</sup> reported a rate constant of  $0.7 \text{ s}^{-1}$  at  $18 \text{ }^\circ\text{C}$  and pH 5 in the presence of terpyridine. The secondary process showed a stronger temperature dependence<sup>28</sup> ( $\Delta H_{sec}^\ddagger = 59.1 \pm 1.3 \text{ kJ mol}^{-1}$ ,  $\Delta S_{sec}^\ddagger = -40 \pm 4 \text{ J K}^{-1} \text{ mol}^{-1}$ ) than the initial reduction step ( $\Delta H_{12}^\ddagger \sim 4 \text{ kJ mol}^{-1}$ , not accurately measurable). Thus, by lowering the temperature to  $5.9 \pm 0.2 \text{ }^\circ\text{C}$ , satisfactory separation of the faster initial electron-transfer step (pseudo-first-order rate constant  $k_{obs} = 34$  to  $145 \text{ s}^{-1}$  for  $[\text{Co}(\text{sep})^{2+}] = 0.4$  to  $2.0 \text{ mmol L}^{-1}$ ) from the subsequent aquation was obtained. For the cross reaction,  $k_{obs}$  was first order in  $[\text{Co}(\text{sep})^{2+}]$  as well as  $[\text{Co}(\text{bpy})_3^{3+}]$ ,<sup>28</sup> giving the second-order rate constant  $k_{12} = (8.0 \pm 0.3) \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$  at  $5.9 \text{ }^\circ\text{C}$  and  $I = 0.2 \text{ mol L}^{-1}$ .

Although the temperature dependence of  $k_{12}$  was not accurately measurable,  $\ln k_{12}$  gave satisfactory linear plots against pressure  $P$  up to 150 MPa at  $5.3\text{--}6.0 \text{ }^\circ\text{C}$ . Independent runs gave  $\Delta V_{12}^\ddagger = -9.9 \pm 0.7, -10.9 \pm 0.9, -9.7 \pm 0.4$ ,<sup>28</sup> and  $-9.5 \pm 0.4$ <sup>28</sup>  $\text{cm}^3 \text{ mol}^{-1}$  at 5.3, 5.9, 5.9, and 5.6  $^\circ\text{C}$ , respectively; the weighted mean is  $-9.7 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$  at  $5.6 \pm 0.3 \text{ }^\circ\text{C}$  and  $I = 0.2 \text{ mol L}^{-1}$ .

## Discussion

The rate constant  $k$  for an electron-transfer reaction can be expressed in terms of a free energy of activation  $\Delta G^*$  (comprising internal and solvent reorganizational components,  $\Delta G_{IR}^*$  and  $\Delta G_{SR}^*$ , respectively), the equilibrium constant  $K_{prec}$  for assembly of a precursor complex, the electronic frequency factor (transmission coefficient)  $\kappa$ , and a nuclear frequency factor  $\nu_n$ .<sup>31</sup>

$$k = K_{prec} \kappa \nu_n \exp(-\Delta G^*/RT) \quad (1)$$

If the electron-transfer step is fully adiabatic,  $\kappa = 1$ . Solvent properties can influence  $k$  not only energetically through the contribution  $\Delta G_{SR}^*$  to the height of the activation barrier, but also dynamically through  $\nu_n$  by reducing the barrier crossing frequency, if the solvent and transition-state motions are significantly coupled. In the simplest treatment,<sup>1,2,7,12–15,32</sup> which assumes adiabatic electron transfer and a low  $\Delta G_{IR}^*$ , we can write

$$\nu_n = \tau_L^{-1} (\Delta G_{SR}^*/4\pi RT)^{1/2} \quad (2)$$

and, if  $V_M$  is the hard-sphere effective volume and  $\epsilon_0$  and  $\epsilon_{op}$  are respectively the static and optical dielectric constants of the solvent,

$$\tau_L^{-1} = (\epsilon_0/\epsilon_{op})RT/3V_M\eta \quad (3)$$

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For our purposes,  $\epsilon_{\text{op}}$  may be taken to be the square of the refractive index  $n$  of the solvent. The experimental volume of activation  $\Delta V_{\text{obs}}^\ddagger$  is given by

$$\Delta V_{\text{obs}}^\ddagger = \Delta V_{\text{SD}}^\ddagger + (\Delta V_{\text{IR}}^\ddagger + \Delta V_{\text{SR}}^\ddagger + \Delta V_{\text{COUL}}^\ddagger + \Delta V_{\text{DH}}^\ddagger) \quad (4)$$

where the sum in parentheses is the volume of activation associated with *barrier height* ( $\Delta V_{\text{COUL}}^\ddagger$  representing the pressure dependence of the Coulombic work terms, i.e., of  $K_{\text{prec}}$ , and  $\Delta V_{\text{DH}}^\ddagger$  the pressure effect on the Debye–Hückel activity coefficients) and  $\Delta V_{\text{SD}}^\ddagger$  is due to *barrier crossing* (solvent dynamics). From eqs 2 and 3, we have

$$\Delta V_{\text{SD}}^\ddagger = -RT(\partial \ln v_{\text{n}}/\partial P)_T = RT[(\partial \ln \eta/\partial P)_T - (\partial \ln \epsilon_0/\partial P)_T + 2(\partial \ln n/\partial P)_T - \Delta V_{\text{SR}}^\ddagger/2\Delta G_{\text{SR}}^*] \quad (5)$$

The last three terms in eq 5 are small for typical solvents and tend to cancel each other, so that the calculated<sup>18–20,33</sup>  $\Delta V_{\text{SD}}^\ddagger$  is determined almost entirely by  $(\partial \ln \eta/\partial P)_T$  as shown in Table 1. Values of  $RT(\partial \ln \eta/\partial P)_T$  calculated using literature data<sup>18–20</sup> (Table 1) are close to the electrochemically measured activation volumes for diffusion of  $\text{Co}(\text{bpy})_3^{3+/2+}$  ( $\Delta V_{\text{diff}}^\ddagger = -RT(\partial \ln D/\partial P)_T$ ), as expected from the Stokes–Einstein relation ( $D = k_{\text{B}}T/6\pi a\eta$ , where  $a$  is the effective radius of the diffusing particle). We note that the Arrhenius activation energy for diffusion of  $\text{Co}(\text{bpy})_3^{3+/2+}$  in water ( $E_{\text{a(diff)}} = -RT(\partial \ln D/\partial T)_P = 19.1 \text{ kJ mol}^{-1}$ , from Figure 2) is similar to that for viscous flow of water ( $16.8 \text{ kJ mol}^{-1}$  at  $25 \text{ }^\circ\text{C}$ , calculated from the data of ref 18).

Equations 1–5 apply to both bimolecular self-exchange reactions and the corresponding reactions at an electrode. For the latter, however, the free energy of activation  $\Delta G_{\text{el}}^*$  was predicted by Marcus<sup>34</sup> to be *one-half* that for homogeneous self-exchange ( $\Delta G_{\text{ex}}^*$ ). This relationship is difficult to demonstrate directly through  $k_{\text{el}}$  and  $k_{\text{ex}}$  because the preexponential factor in eq 1 for  $k_{\text{el}}$  is very sensitive to the nature of the electrode surface. However, because electrode surfaces are not significantly affected by pressures in the 0–200 MPa range, a remarkably precise relationship exists between the corresponding *volumes* of activation  $\Delta V_{\text{el}}^\ddagger$  and  $\Delta V_{\text{ex}}^\ddagger$  for a wide variety of transition-metal complex couples in aqueous solution:<sup>21,24,35</sup>

$$\Delta V_{\text{el}}^\ddagger = (0.50 \pm 0.02)\Delta V_{\text{ex}}^\ddagger \quad (6)$$

We call eq 6 the “fifty-percent rule”. For aqueous solutions around  $25 \text{ }^\circ\text{C}$ ,  $\Delta V_{\text{SD}}^\ddagger$  is predicted to be negligible, and so eq 6 can be expected to hold for such systems regardless of whether solvent dynamics are important. In other words,  $\Delta V_{\text{el}}^\ddagger$  gives the pressure dependence of  $\Delta G^*$  unambiguously for aqueous systems at near-ambient temperatures. Furthermore, the theory that has been developed<sup>36</sup> for  $\Delta V_{\text{ex}}^\ddagger$  can be directly applied to  $\Delta V_{\text{el}}^\ddagger$  for aqueous systems, in particular,  $\Delta V_{\text{el}}^\ddagger$  for cationic couples can be expected to be *negative* ( $-2$  to  $-6 \text{ cm}^3 \text{ mol}^{-1}$ ) and, in the case of tris-bidentate  $\text{Co}^{\text{III/II}}$  complexes such as  $\text{Co}(\text{bpy})_3^{3+/2+}$  where  $\text{Co}^{\text{II}}$  is high spin, quite strongly so (near  $-9 \text{ cm}^3 \text{ mol}^{-1}$ ).<sup>21</sup> In *nonaqueous* systems, however, the incursion of solvent dynamics should in general lead to *positive*

experimental  $\Delta V_{\text{el}}^\ddagger$  values, since  $\Delta V_{\text{SD}}^\ddagger$  for organic solvents is predicted to be on the order of  $+10 \text{ cm}^3 \text{ mol}^{-1}$  (Table 1).

Comparison of Figures 3 and 5 immediately shows that, qualitatively at least, these predictions are fulfilled for the  $\text{Co}(\text{bpy})_3^{3+/2+}$  couple. The value of  $\Delta V_{\text{el}}^\ddagger$  for water (Table 1) is closely similar to those for  $\text{Co}(\text{en})_3^{3+/2+}$  and  $\text{Co}(\text{phen})_3^{3+/2+}$  ( $-8.3 \pm 0.5$  and  $-9.1 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$ , respectively).<sup>21</sup> In acetonitrile, acetone, and propylene carbonate, however,  $\Delta V_{\text{el}}^\ddagger$  is almost as strongly positive as  $\Delta V_{\text{diff}}^\ddagger$  (Table 1), implying rate control by solvent dynamics. This inference is supported by the strong linear correlation between  $k_{\text{el}}$  and  $D$  at various pressures for each organic solvent (shown for acetonitrile in Figure 4). Murray and co-workers<sup>14,15</sup> reported such a correlation over a wide numerical range using different solvents at atmospheric pressure; Figure 4 shows that a very tight correlation can be obtained without changing the chemical identity of the solvent, using pressure to vary the solvent viscosity. Application of eq 4 to the nonaqueous systems indicates that the barrier-height part of  $\Delta V_{\text{el}}^\ddagger$  (that in parentheses) is on the order of 0 to  $-3 \text{ cm}^3 \text{ mol}^{-1}$ .

For water as solvent,  $k_{\text{el}}$  increases with increasing pressure, whereas  $D$  remains essentially constant (Figure 3). Qualitatively, this is as expected, because, in water at near-ambient temperatures, solvent friction (if present at all) will not be revealed by varying the pressure, as noted above. The magnitude of  $\Delta V_{\text{el}}^\ddagger$  in water, however, implies that the barrier-height contribution is about  $-9 \text{ cm}^3 \text{ mol}^{-1}$ , that is, much more negative than for the organic solvents. Thus, there may be a mechanistic change on going from water to nonaqueous solvents. Furthermore, the Arrhenius activation energy for the  $\text{Co}(\text{bpy})_3^{3+/2+}$  electrode reaction in aqueous NaCl ( $37 \text{ kJ mol}^{-1}$ ) is twice as large as that for diffusion of the complexes or for viscous flow of water (Figure 2). This is further evidence for a relatively large activation contribution to the electron-transfer kinetics in water, regardless of any influence of solvent dynamics.

The inferred mechanistic difference may be due to ion pairing between the highly charged Co complexes and the anion of the supporting electrolyte. Such ion association is probably inconsequential in  $0.2 \text{ mol L}^{-1}$  aqueous NaCl, but will almost inevitably be important in organic solvents. Its impact on the self-exchange parameters  $k_{\text{ex}}$  and  $\Delta V_{\text{ex}}^\ddagger$  is hard to predict; cation–cation reactions often show mild retardation ascribable to ion pairing,<sup>37</sup> whereas anion–anion electron transfers can be dramatically catalyzed by cations even in water.<sup>38</sup> Counterion effects are more difficult to interpret for electrode reactions because of the probable modification of the double layer, and therefore we have not pursued this question in the present study. Pyati and Murray,<sup>14</sup> however, concluded that ion pairing was not a major factor in their study of the  $\text{Co}(\text{bpy})_3^{3+/2+}$  electrode reaction in a wide range of solvents. Thus, the origin of the inferred mechanistic change between water and organic solvents remains an open question.

It might be argued that  $\Delta V_{\text{el}}^\ddagger$  for  $\text{Co}(\text{bpy})_3^{3+/2+}$  in aqueous NaCl is in some way anomalous, although its consistency with  $\Delta V_{\text{el}}^\ddagger$  for  $\text{Co}(\text{en})_3^{3+/2+}$  and  $\text{Co}(\text{phen})_3^{3+/2+}$  suggests otherwise. For the latter two couples,<sup>21</sup> the measured  $\Delta V_{\text{el}}^\ddagger$  values were authenticated through  $\Delta V_{\text{ex}}^\ddagger$  by conformity with the fifty-percent rule, but no  $\Delta V_{\text{ex}}^\ddagger$  is available for  $\text{Co}(\text{bpy})_3^{3+/2+}$ . As an alternative, we have attempted to estimate  $\Delta V_{\text{ex}}^\ddagger$  from the cross-reaction of  $\text{Co}(\text{bpy})_3^{3+}$  with  $\text{Co}(\text{sep})^{2+}$  in aqueous  $\text{LiClO}_4$ . The Marcus cross relation for rate constants of adiabatic, outer-sphere, bimolecular electron-transfer reactions<sup>31</sup>

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$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}W \quad (7)$$

$$\ln f = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/Z_{11}/Z_{22}) + (w_{11} + w_{22})/RT]}$$

$$W = \exp[(w_{11} + w_{22} - w_{12} - w_{21})/2RT]$$

leads to a corresponding relation in volumes of activation:<sup>25,39</sup>

$$\Delta V_{12}^\ddagger = [(\Delta V_{11}^\ddagger + \Delta V_{22}^\ddagger + \Delta V_{12})/2] + C \quad (8)$$

in which the subscripts 11 and 22 refer to self-exchange reactions of reactants **1** and **2**, and 12 and 21 refer to the cross reaction of **1** with **2** and its reverse, respectively,  $k_{ij}$  are rate constants,  $K_{12}$  is the equilibrium constant ( $=\exp(F\Delta E_{1/2}/RT)$ ), and  $\Delta V_{12}$  is the reaction volume ( $=\Delta V_{\text{cell}(2)} - \Delta V_{\text{cell}(1)}$ ). The symbols  $w$  refer to the Coulombic work required to bring the reactants together.  $Z_{ij}$  are the frequency factors (preexponential part of eq 1). For self-exchange reactions and for cross reactions that are symmetrical with respect to the charges on the reactants,  $W \sim 1$  if the reactant radii are comparable, and the term  $C$  is then  $-(RT/2)(\partial \ln f/\partial P)_T$  (see Grace et al.<sup>39</sup> for further development). For small  $\Delta E_{1/2}$  ( $<200$  mV),  $f \sim 1$  and  $C \sim 0$ .

For the reduction of Co(bpy)<sub>3</sub><sup>3+</sup> (reactant **1**), the choice of reductant (reactant **2**) and reaction conditions was limited by the tendency of most complex-ion reductants as well as the product Co(bpy)<sub>3</sub><sup>2+</sup> to lose ligands, even at neutral pH, on the time scale of the stopped-flow measurements. Furthermore, application of eq 8 requires that  $\Delta V_{22}^\ddagger$  be known. The only practical cationic option was the cage complex Co(sep)<sup>2+</sup>,<sup>40</sup> for which the cross relation 7 is unfortunately not closely obeyed ( $k_{12}(\text{calc}) = 4.0 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$  at 5.9 °C and  $I \sim 0.2 \text{ mol L}^{-1}$ , cf.  $k_{12}(\text{obsd}) = 8.0 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ ). Thus, eq 8 can be expected to generate a  $\Delta V_{12}^\ddagger$  value that is a few  $\text{cm}^3 \text{ mol}^{-1}$  too negative.<sup>25</sup> In addition, there are the inevitable mismatches of temperature, media, etc., with data from different sources. With  $\Delta V_{12}^\ddagger = -9.7 \text{ cm}^3 \text{ mol}^{-1}$  from this study, and parameters for the closest matching conditions from the literature,<sup>21,29,40,41</sup> eqs 6 and 8 predict  $\Delta V_{\text{el}}^\ddagger$  for Co(bpy)<sub>3</sub><sup>3+/2+</sup> =  $-12.4 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$  at 5.9 °C, cf. the observed  $-9.1 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$  at 3.0 °C (both at  $I = 0.2 \text{ mol L}^{-1}$ ). Although the agreement is not close, the estimate of  $\Delta V_{\text{el}}^\ddagger$  from the cross relation does at least confirm a strongly negative value for the Co(bpy)<sub>3</sub><sup>3+/2+</sup> electrode reaction in water, in contrast to the positive values found for organic solvents.

The apparent failure of eqs 7 and 8 for Co(bpy)<sub>3</sub><sup>3+/2+</sup>/Co(sep)<sup>2+</sup> reaction in water, like that for the Fe(H<sub>2</sub>O)<sub>6</sub><sup>3+/2+</sup>/Ru(en)<sub>3</sub><sup>2+</sup> reaction ( $\Delta E_{1/2} = 534$  mV),<sup>25</sup> may be taken as evidence for increasing nonadiabaticity as one goes to higher driving forces. Nonadiabatic electron transfer would give slower rate constants ( $\kappa \ll$

1) and more negative volumes of activation<sup>42</sup> than expected. Endicott and Ramasami<sup>43</sup> have presented data on the kinetics of reductions of a variety of Co<sup>III</sup> complexes by Co(sep)<sup>2+</sup> that indicate that the cross reactions are in general nonadiabatic but that  $\kappa \rightarrow 1$  as  $\Delta E_{1/2} \rightarrow 0$ ; in other words, self-exchange (and electrode) reactions are adiabatic but kinetic parameters for cross reactions with high  $\Delta E_{1/2}$  may deviate from the predictions of eqs 7 and 8. Our observations<sup>25,36,39,42</sup> are certainly consistent with this view (our early suggestion,<sup>42</sup> that the Co(en)<sub>3</sub><sup>3+/2+</sup> and Co(phen)<sub>3</sub><sup>3+/2+</sup> self-exchange reactions might be nonadiabatic, has proved to be incorrect<sup>36</sup>). Significantly, Fürholz and Haim<sup>44</sup> have proposed that cross reactions of the Co(bpy)<sub>3</sub><sup>3+/2+</sup> couple may be “mildly nonadiabatic.”

## Conclusions

Within the limitations and approximations implicit in the theory underlying eqs 2–5, pressure effects on electrode reaction rates and reactant diffusion coefficients can provide strong evidence for the incursion of solvent dynamics in nonaqueous systems without changing the chemical identity of the solvent. For the Co(bpy)<sub>3</sub><sup>3+/2+</sup> electrode reaction, solvent dynamics are found to be important in nonaqueous solvents. This is somewhat surprising, since  $\Delta G_{\text{IR}}^\ddagger$  is expected to be substantial for Co(bpy)<sub>3</sub><sup>3+/2+</sup> self-exchange reactions, in which case solvent dynamics should not be dominant and, indeed, eq 2 should not be valid.<sup>1,2,6,7,32,45</sup> For an electrode reaction, however, the fifty-percent rule<sup>21,24,25</sup> predicts that the activation free energy barrier height is only one-half that for the corresponding self-exchange reaction, and besides we have presented here evidence that suggests a difference in mechanism for the Co(bpy)<sub>3</sub><sup>3+/2+</sup> electrode reaction between organic solvents and the aqueous systems on which expectations are typically based. Finally, although the Co(bpy)<sub>3</sub><sup>3+/2+</sup> electrode reaction in water behaves much as do its analogues Co(en)<sub>3</sub><sup>3+/2+</sup> and Co(phen)<sub>3</sub><sup>3+/2+</sup>, for which adiabaticity in self-exchange reactions has been inferred,<sup>36</sup> the reduction of Co(bpy)<sub>3</sub><sup>3+</sup> by Co(sep)<sup>2+</sup> and other cross reactions with a high driving potential appears to be nonadiabatic, leading to failure of eqs 7 and 8.

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**Supporting Information Available:** Figures and tables of spectral changes and pressure and [Co(sep)<sup>2+</sup>] dependences of rate constants for the Co(bpy)<sub>3</sub><sup>3+/2+</sup>/Co(sep)<sup>2+</sup> reaction; temperature dependence of the decomposition of Co(bpy)<sub>3</sub><sup>2+</sup> in water; pressure dependences of  $k_{\text{el}}$ ,  $R_u$ ,  $D$ , and  $\Delta E_{1/2}$  for the Co(bpy)<sub>3</sub><sup>3+/2+</sup> electrode reaction in various solvents (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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