is concluded to be lower than 1.8 eV for BzlCo(dmg)$_2$py and $CH_3Co(dmg)_2py$.

Recently, Halpern et al.[24] estimated the Co–C bond dissociation energy of $C_6H_5(CH_3)CHCo(dmg)_2py$ to be 19.9 kcal. This value is in a range of the estimated one in the present study.

In 1974, Seki et al.[25] studied the reductive cleavage of vitamin B_{12} and coenzyme B_{12}. They reported that the reduced vitamin B_{12} dissociates into vitamin B_{12r} and CN^-, whereas the reduced coenzyme B_{12} dissociates into B_{12s} and an organic radical. According to the present results, the difference in the dissociation reaction between the reduced vitamin B_{12} and coenzyme B_{12} is interpreted by the larger electron affinity of CN (3.8 eV)[23] and smaller one of the organic radical than that of vitamin B_{12r}. The dissociation energy of the Co–C bond in the coenzyme should be smaller than the electron affinity of vitamin B_{12r}.

Registry No. $[BzCo(dmg)_2py]^-$, 54388-32-8; $[ClCo(dmg)_2py]^-$, 79391-64-3; $[MeCo(dmg)_2py]^-$, 54388-33-9; $[MeCo(dmg)_2H_2O]^-$, 79391-65-4; $[MeCo(dmg)_2Im]^-$, 79391-66-5; $Co^{II}(dmg)_2$, 36451-49-7.

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Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99164

Electron Transfer between a Cobalt Clathrochelate and Ferrocene in Acetonitrile

DAN BORCHARDT, KARL POOL, and SCOT WHERLAND*

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The kinetics of electron transfer between the clathrochelate $Co(dmg)_3(BF)_2BF_4$ (dmg is the deprotonated dimethylglyoxime ligand) and ferrocene has been studied in acetonitrile as a function of concentration, temperature, and added n-Bu_4NBF_4. With no added electrolyte, the reaction is second order with a rate constant of $(1.6 \pm 0.1) \times 10^4$ M^{-1} s^{-1} (25 °C), a $\Delta H^‡$ of 8.4 kcal/mol, and a $\Delta S^‡$ of −11 cal/(mol deg). In the presence of 0.5 M n-Bu_4NBF_4 the rate constant is decreased by a factor of 1.8 and the activation parameters found are a $\Delta H^‡$ of 8.2 kcal/mol and $\Delta S^‡$ of −13 cal/(mol deg). The equilibrium constant measured for the reduction of the Co(III) complex by ferrocene at 25 °C and 0.05–0.5 M salt determined from pulse polarography measurements is 0.33. For 0.1 M electrolyte, ΔH° was found to be 5.0 kcal/mol and ΔS° to be 15 cal/(mol deg). From the above information and literature data, the Marcus theory was used to calculate an electron self-exchange rate constant for the cobalt complex of 1.1×10^2 M^{-1} s^{-1} ($\Delta H^‡ = 7.3$ kcal/mol; $\Delta S^‡ = -25$ cal/(mol deg)). This value is similar to the value of the self-exchange of $Co(phenanthroline)_3{}^{3+/2+}$. This system is a prototype for further detailed studies of nonaqueous electron transfer and theoretical analysis of the special case of electron transfer without the involvement of electrostatic work in precursor or successor complex formation.

The study of electron-transfer reactions has long been an active area of research. This activity has expanded during the last decade, with extensive experimental studies of bioinorganic systems[1,2] as well as classical inorganic[3,4] and some organometallic reactions.[5] Theoretical work has also been pursued, especially with reference to the distance dependence of electron-transfer efficiency and the quantum-mechanical details of the electron-transfer process.[6] There are also predictions[7,8] of the dependence of rate constants on the properties of solvents, although most studies have been done in aqueous solution.

Outer-sphere electron-transfer reactions, in which no bonds are made or broken, are the easiest to analyze mechanistically and theoretically, and the most complete theory has been developed for these reactions. The theoretical treatment most often applied to experimental data is that of Marcus as promulgated by Sutin.[7] In order to ensure that the reactions are limited to an outer-sphere pathway, it is sufficient to work with complexes that are substitution inert in the oxidation states used. It is also helpful if the complexes can be modified to change their size and structure so that aspects such as electrostatic interaction, solvation, electron-transfer distance, and ligand conjugation can be studied. The clathrochelates, ligands that form three-dimensional cages, are ideal for such studies.

The system chosen for this initial work involves the clathrochelate $Co(dmg)_3(BF)_2BF_4$, where dmg is the doubly deprotonated dimethyglyoxime ligand. This complex, initially synthesized by Rose and co-workers,[9] is formed by capping the N-bonded tris-chelate form of the tris(dimethylglyoxime)cobalt(III) ion with BF_3. This links the three free oxygen atoms on each of two opposite faces and forms a symmetric and stable complex. The Co–N bond is only 0.08 Å longer in the low-spin Co(II) complex than in the Co(III) complex.[10] The electron-transfer partner should have a similar electrochemical potential and should have well-known electron-transfer reactivity. The requirement for a similar potential arises from the need for a relatively low driving force. Highly exergonic reactions may be too rapid and also may deviate from theory because of the high-energy paths that are available to them.[11,12] Ferrocene meets these requirements well, and its electron-transfer reactivity has recently been carefully studied by Wahl and co-workers, who measured the electron

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self-exchange rate constant directly by an NMR line-broadening method as a function of solvent, temperature, and added electrolyte.[13,14]

This work is a study of the electron-transfer kinetics and thermodynamics of the reaction between $Co(dmg)_3(BF)_2BF_4$ and ferrocene as a function of concentration, temperature, and added electrolyte. It is the initial work in a project to study the reactivity of a variety of clathrochelates in a variety of solvents in order to test theories of electron-transfer reactivity and solvent influence.

Experimental Section

Complexes and Reagents. The cage complex $Co(dmg)_3(BF)_2BF_4$ was synthesized and recrystallized according to the literature.[15] Analyses for C, H, and N were done by the Canadian Microanalytical Service. Ferrocene was purchased from Aldrich and resublimed at atmospheric pressure. The electrolyte tetra-*n*-butylammonium tetrafluoroborate was made from the bromide salt (Aldrich) and fluorboric acid (Baker). The dried precipitate was recrystallized from warm ethyl acetate and pentane. Acetonitrile (Eastman) was distilled from P_2O_5 and stored over 4 Å molecular sieves.

Electrochemical measurements were made with a Princeton Applied Research Model 174A polarographic analyzer and a Model 303 cell assembly. An Ag/AgCl or $Ag/AgNO_3$ reference electrode and platinum working and counterelectrodes were used. All potentials are referenced to ferrocene by taking the potential of ferrocene to be 0.31 V vs. the saturated calomel electrode.[16] The electrode was preconditioned by electrolysis at −2 V in the $CH_3CN/n\text{-}Bu_4NBF_4$ electrolyte. All solutions were deoxygenated with nitrogen that had been passed through a vanadous solution to remove oxygen and then through acetonitrile and Drierite to equilibrate with the solvent. Thermostating was accomplished with a jacketed beaker placed around the cell and a Forma circulating bath. The polarographic analyzer was modified to provide *iR* compensation. Data were taken on an Omnigraphic Series 2000 XY recorder. Temerpatures were measured with a copper–constantan thermocouple calibrated vs. an NBS traceable thermometer and the voltages read with a Digitec Model 268 millivoltmeter. A calibration curve was prepared for the range 0–55 °C and fitted to a second-order polynomial to provide a calibration function.

Kinetic Measurements. Kinetic measurements were made on a Dionex stopped-flow spectrophotometer (D-110) with a dual-detector accessory (D-117). The signal used was log (I_{450}/I_{600}), where the two wavelengths were isolated with interference filters. The signal was primarily from the increase in absorbance due to the formation of the reduced cobalt complex (ϵ = 5450 M^{-1} cm^{-1} at 460 nm).[17] There is little change in absorbance at 600 nm. The signal from the stopped-flow spectrophotometer was stored to 10-bit precision by a Physical Data Model 514A Transient Digitizer. Typically, the dual-time-base feature was used to automatically obtain 1900 points in the first 4–7 half-lives and the remaining 148 points over a much longer period. The data could be viewed on a Hewlett-Packard Model 1304A Display and transferred to the microcomputer system for data analysis and plotting.

The microcomputer was a Cromemeco Z-2W system with 64K of random access memory and two 8-in. floppy-disk drives. All programs were written in Fortran, and plots were produced on a Hewlett-Packard Model 7225A digital plotter.

Table I. Interpolated Values of $E_{1/2}$'s for $Fe(cp)_2$ and $Co(dmg)_3(BF)_2BF_4$ vs. Temperature[a]

$E_{1/2}$, mV			
$Fe(cp)_2$	$Co(dmg)_3$-$(BF)_2BF_4$	T, °C	$\Delta E_{1/2}$, mV ($E_{1/2}$(Co) − $E_{1/2}$(Fe))
622.5	578.4	0	−44.1
626.3	585.3	5.0	−41.0
630.0	592.3	10.0	−37.7
633.8	599.2	15.0	−34.6
637.5	606.1	20.0	−31.4
641.3	613.1	25.0	−28.2

[a] $[Co(dmg)_3(BF)_2BF_4]$ = 1 mM; $[Fe(cp)_2]$ = 1 mM; $[n\text{-}Bu_4NBF_4]$ = 0.1 M.

Data treatment was by least-squares analysis. In some cases, linear least-squares analysis was adequate, provided that the proper weighting factors were used. In more complex cases, nonlinear least-squares fitting was required and the GRADLS routine of Bevington[18] was used. Data were fit to the first-order equation

$$\ln (S_\infty - S_t) = \ln S_0 - kt \qquad (1)$$

where S_t, S_∞, and S_0 are the signal at time t, at the end, and at time zero of the reaction, respectively, and k is the pseudo-first-order rate constant, by treating S_∞ as a nonlinear parameter and weighting ln $(S_\infty - S_t)$ by $(S_\infty - S_t)^2$. For a reaction that follows an approach to equilibrium rate law, pseudo first order in the forward direction and second order with equal concentrations of the two reactants in the reverse direction, the equation used is

$$S_t = A(E - 1)/(1 - P + E) + S_0 \qquad (2a)$$

$$E = \exp (k(2 - P)t/P) \qquad (2b)$$

where P is the fractional completion, A is the amplitude of the signal change observed, and k is the pseudo-first-order constant in the forward direction. The data were fit by fixing P as predicted from the equilibrium constant and the ratio of reactant concentrations and finding the best fit values of A, k, and S_0. Various initial guesses of these values were used to ensure that the best fit had been found.

All reactions were run with a minimum of a 10-fold excess of ferrocene and usually with a cobalt concentration of 0.06 mM. Runs were typically done in triplicate on one filling of the stopped-flow syringes.

Conductivity experiments were run in a thermostated Freas cell with a cell constant of 0.355 cm^{-1}. Cell resistance was measured with an Industrial Instruments conductivity bridge. Data were fit by a recursive technique to eq 3,[19] where α^* = 0.713, β^* = 227.13, $\delta(f)$

$$1/\Lambda S(z) = 1/\Lambda^0 + c\Lambda(y\pm)^2 S(z) K_{\text{assoc}}/(\Lambda^0)^2 \qquad (3a)$$

$$z = \delta(\Lambda)(\Lambda c)^{1/2}(\Lambda^0)^{-3/2} \qquad (3b)$$

$$(\Lambda) = \alpha^*\Lambda^0 + \beta^* \qquad (3c)$$

$$S(z) = 1 + z + z^2/2 + z^3/8 + \ldots \qquad (3d)$$

$$\log (y\pm) = -\delta(f)(\alpha c)^{1/2} \qquad (3e)$$

$$\alpha = \Lambda S(z)\Lambda^0 \qquad (3f)$$

= 1.585 for a 1:1 electrolyte in CH_3CN, Λ is the observed molar conductance, and Λ^0 is the extrapolated value at infinite dilution.

Potentials were measured vs. a Ag/AgCl(s) (0.1 M $(CH_3CH_2)_4NCl$ in CH_3CN) reference electrode by pulse polarography, and $E_{1/2}$ values were determined from the plot of the data as

$$\ln ((i_d - i)/i) = (nF/RT)(E - E_{1/2})$$

where i is the current at applied potential E and i_d is the diffusion-limited current, n is 1, F is the Faraday constant, and R is the gas constant. Weighting factors for the plot were σ^{-2}, where

$$\sigma_i = 0.01((2/(i_d - i)^2) + (1/i^2))^{1/2} \qquad (4)$$

This method of obtaining $E_{1/2}$ was much more precise than is possible from treatment of cyclic voltammetry data.

Results

The cobalt is stable as a solid. In solution it is quite sensitive to the presence of amines or hydroxide, which cause immediate darkening and decomposition. The analysis gave 26.44% C, 3.13% H, and 15.12% N, in agreement with the theoretical values for $C_{12}H_{18}N_6O_8B_3F_6Co$ of 26.32% C, 3.31% H, and 15.35% N.

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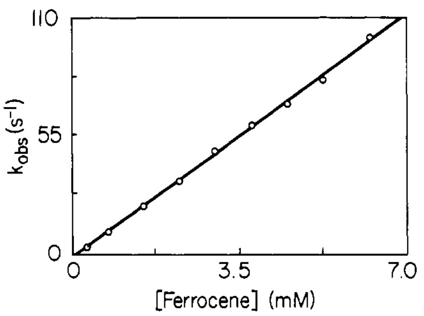

Figure 1. Dependence of k_{obsd} on the ferrocene concentration (25 °C; $[Co(dmg)_3(BF)_2BF_4]$ = 3.8 × 10^{-5} M; slope of best-fit line 1.62 × 10^4 M^{-1} s^{-1}; intercept −1.15 s^{-1}).

Cyclic voltammetry of the cobalt complex gave two quasi-reversible reduction waves separated by 1.1 V. The difference in potential between ferrocene and the Co(II)/Co(III) couple as a function of temperature is given in Table I. These data are interpolated from data for the potential of each complex vs. temperatures given in Supplementary Table 1. With use of the data from 0 to 25 °C and the equation

$$\Delta E_{1/2} = -\Delta H^\circ/nF + T\Delta S^\circ/nF \qquad (5)$$

ΔH° is 5.0 kcal/mol and ΔS° is 15 cal/(mol deg) for the reaction

$$\mathrm{Fe(II)} + \mathrm{Co(III)} \rightarrow \mathrm{Fe(III)} + \mathrm{Co(II)} \qquad (6)$$

in CH_3CN with 0.1 M n-Bu_4NBF_4, where the complexes are represented by their central metal ions. The point taken at 30 °C falls below the line for the other points. At 25 °C, the potential difference between the two complexes was found to be independent of ionic strength from 0.05 to 0.5 M (n-Bu_4NBF_4). However, the potentials of the individual complexes vs. the Ag/AgCl reference electrode changed by 37 mV in this range, decreasing monotonically but nonlinearly with salt concentration.

Data from conductivity experiments on the cobalt complex as the tetrafluoroborate salt over the concentration range 0.1–10.0 mM at 25 °C were fitted to the equation given in the Experimental Section. The precision of the data did not warrant a more complex analysis. The result of the fitting gave an equilibrium constant for ion association of 10.5 M^{-1} when it, Λ^0, $y\pm$, and $S(z)$ were treated as adjustable parameters.

Kinetic studies were performed under a variety of conditions. The concentration dependence over the range 0.30–6.23 mM ferrocene with no added electrolyte is depicted in Figure 1. For the three lowest concentrations, the approach to equilibrium rate law was used, as the reaction proceeded to less than 95% completion. The data at the higher concentrations gave the same rate constant whether a simple first-order rate law or the approach to equilibrium rate law was used. The second-order rate constant derived from the slope of the line in Figure 1 is (1.6 ± 0.1) × 10^4 M^{-1} s^{-1}. Figure 2 shows the dependence of the rate constant on added electrolyte with the observed rate constant decreasing by a factor of 1.8 in the range 0–0.5 M n-Bu_4NBF_4.

The temperature dependence was performed at the two extremes of salt concentration, and the results are shown in Figure 3 as an Eyring plot. The activation parameters calculated from the least-squares fits to the data are ΔH^*_{12} of 8.4 kcal/mol and a ΔS^*_{12} of −11 cal/(mol deg) with no added salt and a ΔH^*_{12} of 8.2 kcal/mol and a ΔS^*_{12} of −13 cal/(mol deg) with 0.5 M n-Bu_4NBF_4 added.

All reaction conditions and rate constants are listed in Supplementary Table 2 as the mean and standard deviation of the multiple determinations performed for each experimental condition.

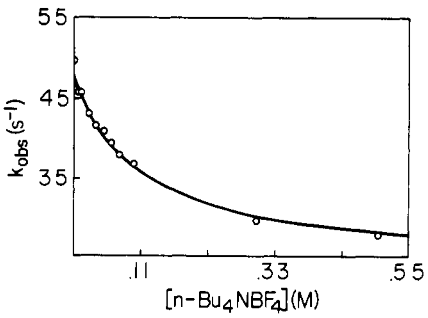

Figure 2. Dependence of k_{obsd} on added n-Bu_4NBF_4 (25 °C; $[Co(dmg)_3(BF)_2BF_4]$ = 3.0 × 10^{-5} M; [ferrocene] = 3.0 × 10^{-3} M; best fit to eq 10 k_1 = 1.6 × 10^4 M^{-1} s^{-1}, k_2 = 8.0 × 10^3 M^{-1} s^{-1}, and K_{assoc} = 9 M^{-1}).

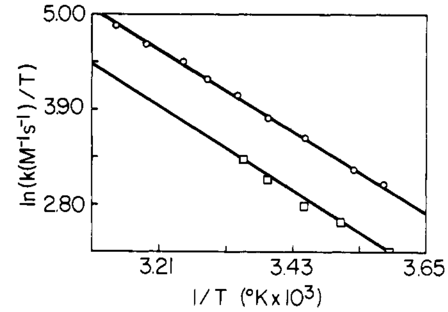

Figure 3. Eyring plot of the temperature dependences ([ferrocene], 3.0 × 10^{-3} M): (□) 0.5 M n-Bu_4NBF_4, $[Co(dmg)_3(BF)_2BF_4]$ = 3.1 × 10^{-5} M; (○) no added electrolyte, $[Co(dmg)_3(BF)_2BF_4]$ = 2.9 × 10^{-3} M.

Discussion

The available data may be analyzed within the Marcus theory formalism to give the electron self-exchange rate constant and its activation parameters for the complex. The self-exchange rate constant is calculated by using eq 7, where

$$k_{12} = (Kk_{11}k_{22}f)^{1/2} \qquad (7a)$$

$$\ln f = (\ln K)^2/(4 \ln (k_{11}k_{22}/Z^2)) \qquad (7b)$$

k_{11} and k_{22} are the self-exchange rate constants for the cobalt complex and ferrocene, respectively, K is the equilibrium constant for the cross reaction, and k_{12} is its rate constant. Z is a collision frequency term, taken as 10^{11} s^{-1}. In acetonitrile at 25 °C with 0.1 M n-Bu_4NBF_4, k_{12} is 1.2 × 10^4 M^{-1} s^{-1}, K is 0.33, k_{22} is 4.1 × 10^6 M^{-1} s^{-1}[14] (interpolated from data on PF_6^-) and k_{11} is calculated to be 1.1 × 10^2 M^{-1} s^{-1}. For the condition of no added electrolyte k_{12} is 1.6 × 10^4 M^{-1} s^{-1}, k_{22} is 5.2 × 10^6 M^{-1} s^{-1}[14] (from a fit to the salt dependence), and K is assumed to have the same value as it does in the range 0.05–0.5 M n-Bu_4NBF_4, giving a k_{11} value of 1.5 × 10^2 M^{-1} s^{-1}. Similarly, the values of ΔH^*_{11} and ΔS^*_{11} can be calculated from eq 8,[12] where h is Planck's constant, and the known values

$$\Delta H^*_{12} = \left(\frac{\Delta H^*_{11} + \Delta H^*_{22}}{2}\right)(1 - 4(\alpha^*)^2) + \frac{\Delta H^\circ}{2}(1 + 2\alpha^*) \qquad (8a)$$

$$\Delta S^*_{12} = \left(\frac{\Delta S^*_{11} + \Delta S^*_{22}}{2}\right)(1 - 4(\alpha^*)^2) + \frac{\Delta S^\circ}{2}(1 + 2\alpha^*) \qquad (8b)$$

$$\alpha^* = \Delta G^\circ/(4(\Delta G^*_{11} + \Delta G^*_{22})) \qquad (8c)$$

$$\Delta S^* = \Delta S^{*} - R \ln (hZ/kT) + (R/2) \qquad (8d)$$

$$\Delta H^* = \Delta H^{*} + RT/2 \qquad (8e)$$

of $\Delta H^{\ddagger}_{22}$ of 4.4 kcal/mol, $\Delta S^{\ddagger}_{22}$ of −13 cal/(mol deg) (measured at less than 5 mM BF_4^-),[14] ΔH°_{12} of 5.0 kcal/mol, ΔS°_{12} of 15 cal/(mol deg), $\Delta H^{\ddagger}_{12}$ of 8.4 kcal/mol, and $\Delta S^{\ddagger}_{12}$ of −12 cal/(mol deg) were used. The last two values are interpolated for 0.1 M $n\text{-}Bu_4NBF_4$ from the two temperature dependencies measured, and the ΔH°_{12} and ΔS°_{12} values are measured at 0.1 M salt. These parameters lead to a calculated value for $\Delta H^{\ddagger}_{11}$ of 7.3 kcal/mol and for $\Delta S^{\ddagger}_{11}$ of −25 cal/(mol deg).

The value of the self-exchange rate constant can be compared to that of another diimine complex of cobalt, $Co(phen)_3^{3+}$ (phen = 1,10-phenanthroline), for which the self-exchange rate constant is 45 $M^{-1}\ s^{-1}$ ($\Delta H^{\ddagger}_{11}$ = 5.1 kcal/mol; $\Delta S^{\ddagger}_{11}$ = −34 cal/(mol deg)) in water with 0.1 M KNO_3[20] and 1.1 $M^{-1}\ s^{-1}$ ($\Delta H^{\ddagger}_{11}$ = 7.2 kcal/mol; $\Delta S^{\ddagger}_{11}$ = −34 cal/(mol deg)) in 1:1 water–propanol with 0.02 M KNO_3.[21] The difference between these two measured values can be accounted for by considering the greater electrostatic work required to form the precursor complex in the lower dielectric and lower ionic strength of the second medium.[2] Such considerations raise the self-exchange value to over 100 $M^{-1}\ s^{-1}$ when the rate constant is extrapolated to infinite ionic strength. Thus, the self-exchange of $Co(dmg)_3(BF)_2^{+/0}$ is similar to that of $Co(phen)_3^{3+/2+}$ when work terms are compensated for in the latter system. Another cobalt complex of a cage ligand shows much different behavior. Cobalt sepulchrate is derived from $Co(1,2\text{-ethanediamine})_3^{3+}$ by capping it with formaldehyde and ammonia. The self-exchange rate constant for the cage system is 5 orders of magnitude higher than that of its simple precursor.[22]

The activation parameters calculated for the self-exchange of $Co(dmg)_3(BF)_2^{+/0}$ resemble those for $Co(phen)_3^{3+/2+}$ more than they do those for ferrocene. It is much more difficult, however, to predict the activation parameters[2] for the $Co(phen)_3^{3+/2+}$ in the absence of work terms than it is to predict the rate constant. It has been suggested[23] that the large magnitude and negative sign of the entropies of activation observed for many self-exchange reactions between 2+ and 3+ metal ions and complexes arise from the work terms for the formation of the precursor complexes. The observation of similarly unfavorable entropies of activation in the case of the cobalt complex and to a lesser extent with ferrocene indicates that, at least in these cases, the work terms are not the origin of the entropy barrier since they are zero. Remaining possibilities include outer-sphere contributions from nonelectrostatic interactions, solvation, and orientation effects. Inner-sphere reorganization is expected to contribute primarily to the enthalpy of activation. Contributions from nonadiabatic pathways are also possible, as well as other deviations from the assumptions of the Marcus theory,[12] but these should be minimized in the reaction under discussion because of its small driving force.

Another question that arises concerns the origin of the dependence on salt concentration. There is no electrostatic work required to form the precursor complex or dissociate the successor complex; thus some other factor must be involved. Another consideration, especially since a solvent of much lower dielectric constant than that of water is being used, is extensive ion pairing. In this case, the cobalt complex could exist in free form or as an ion pair and the two species could react independently, at different rates (see eq 9).

$$Co^+ + BF_4^- \xrightleftharpoons{K_{assoc}} Co{\cdot}BF_4 \tag{9a}$$

$$Co^+ + Fe \xrightarrow{k_1} Co + Fe^+ \tag{9b}$$

$$CoBF_4 + Fe \xrightarrow{k_2} Co + Fe^+ + BF_4^- \tag{9c}$$

The rate law, with the assumption that the Co(III) complex is always in equilibrium with the ion pair, is given in eq 10. The data were fit to this rate law to give the solid line in Figure 2.

$$d[Co]/dt = (k_1 + k_2K_{assoc}[BF_4^-])([Co^+]_T[Fe])/(1 + K_{assoc}[BF_4^-]) \tag{10}$$

The parameters are $1.6 \times 10^4\ M^{-1}\ s^{-1}$ for k_1, $8.0 \times 10^3\ M^{-1}\ s^{-1}$ for k_2, and 9 M^{-1} for K_{assoc}. This ion-pairing equilibrium constant agrees with the value derived from the conductivity experiments, but the value from the conductivity is quite poorly defined. The ion-pairing model, with the addition of the ion pairing by ferricenium, would also predict a change in the equilibrium constant if the Co(III) and Fe(III) ion-pairing constants differed appreciably. The observation that the equilibrium constant, as derived from the measured $E_{1/2}$ values, does not change in the concentration range from 0.05 to 0.5 M thus indicates that the ion-pairing constants do not differ. Both ions have the same charge, but ferricenium is significantly smaller; thus it should bind ions more tightly. However, the difference in the pairing might not be measurable given its low value in both cases. The self-exchange behavior of ferrocene shows a similar response to added electrolyte.[14] The self-exchange rate constant decreased by a factor of 2 when the ion pair formed, and the ion-pairing constants derived from a fit to the kinetic data were in the range 10–20 M^{-1} for PF_6^- and ClO_4^-.

Other explanations for the salt dependence of the ferrocene and cobalt rate constants are that ion pairs are not extensively formed but the activity coefficients of the reactants decrease with added electrolyte or that the dielectric behavior of the solvent is a function of added electrolyte.[24] These arguments cannot be further supported or refuted from the available data.

A remaining concern is the nonlinearity of the dependence of $\Delta E_{1/2}$ on temperature above 25 °C. This behavior indicates that either ΔH°, ΔS°, or both change abruptly. The origin of this behavior is not known but it may involve properties of the electrolyte and solvent system. A similar behavior is observed for the cytochrome *c* potential in aqueous NaCl solution above 30 °C.[25]

Conclusion

This study has characterized the electron-transfer reactivity of the cobalt clathrochelate $Co(dmg)_3(BF)_2BF_4$ in CH_3CN through the kinetics and thermodynamics of its reaction with ferrocene. The complex has proven to have a reactivity similar to that of $Co(phen)_3^{3+/2+}$. Because the Co(II) form of the clathrochelate is uncharged, as is ferrocene, there is no electrostatic work involved in the precursor complex formation or successor complex dissociation. This property simplifies the Marcus theory analysis of the reaction and makes possible a study in the absence of added electrolyte. The decrease in rate constant with increasing $n\text{-}Bu_4NBF_4$ is attributed to ion pairing or an activity coefficient effect. The highly unfavorable entropy of activation that is calculated for the self-exchange rate constant must be a characteristic of the precursor complex formation or electron transfer, independent of electrostatic interaction.

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This study is the basis for further work that will probe the effect of solvent on the reaction and the effect of changing the electron-transfer distance through study of derivatives of the cobalt complex and ferrocene.

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Registry No. $Fe(cp)_2$, 102-54-5; $Co(dmg)_3(BF)_2BF_4$, 34248-48-1; n-Bu_4NBF_4, 429-42-5.

Supplementary Material Available: Tables of kinetic and thermodynamic data (5 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Tris(2,2′-bipyridine)ruthenium(III) in Zeolite Y: Characterization and Reduction on Exposure to Water

WILLIAM H. QUAYLE and JACK H. LUNSFORD*

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A $[Ru^{III}(bpy)_3]$–Y zeolite containing 2.1 wt % Ru was reduced by water at 70 °C to $[Ru^{II}(bpy)_3]$–Y; however, dioxygen was not a product of the reaction. The immobility of the Ru(III) complex in the zeolite, as well as an unfavorable local chemical environment, probably inhibits the secondary electron-transfer processes necessary for O_2 formation. The $[Ru^{III}(bpy)_3]$–Y zeolite was prepared by exposure of $[Ru^{II}(bpy)_3]$–Y to chlorine gas. The low-spin d^5 complex was characterized by EPR ($g_\perp = -2.67$, $g_\parallel = 1.24$) and visible diffuse-reflectance (λ_{max} = 685 and 420 nm) spectroscopies. XRD and XPS studies confirm that the complex in the original $[Ru^{II}(bpy)_3]$–Y material was intrazeolitic.

Introduction

We have shown recently that tris(2,2′-bipyridine)ruthenium(II) complex cations are formed within the cavities of Y type zeolites when 2,2′-bipyridine (bpy) is mixed and heated with Ru^{III}–Y zeolites.[1] The spectroscopic properties of these $[Ru^{II}(bpy)_3]$–Y zeolites were similar to those exhibited by $[Ru^{II}(bpy)_3]^{2+}$ complexes in aqueous solution. The zeolite complexes, however, displayed anomalous variability in their photophysical behavior, which was dependent upon the extent of hydration and the degree of complex loading within the zeolite. These preliminary studies indicated the importance of detailed consideration of the effects of ligand and chemical environments on the photophysics and therefore their effects on the photoreactivities of transition-metal complexes. This study also indicated that zeolites might be attractive supports within which the environments of transition-metal complexes could be selectively altered to enhance desired photoreactions and photocatalytic processes. An interest in the redox and photochemical properties of transition-metal complexes in zeolites prompted us to examine the oxidation of degassed $[Ru^{II}(bpy)_3]$–Y to $[Ru^{III}(bpy)_3]$–Y by chlorine gas and the subsequent reduction of $[Ru^{III}(bpy)_3]$–Y by H_2O.

The oxidation of water by $[Ru^{III}(bpy)_3]^{3+}$ salts has been known for some time. Dwyer and Gyarfas[2] detected ozone and H_2O_2 formation on dissolution of tris(bipyridine) salts of Fe(III), Ru(III), and Os(III) in water. Creutz and Sutin[3] investigated the kinetics of the reaction of hydroxide ion with the Ru(III) complex (eq 1) and discussed the potential use

$$[Ru^{III}(bpy)_3]^{3+} + OH^- \rightarrow [Ru^{II}(bpy)_3]^{2+} + {}^1/_4O_2 + {}^1/_2H_2O \quad (1)$$

of this reaction for the photocatalytic splitting of water (eq 2). The successful coupling of eq 1, or analogous reactions, with either photoassisted water-reduction processes[4-13] or other $[Ru^{III}(bpy)_3]^{3+}$ initiated water-oxidation reactions,[14-17] has resulted in potentially attractive solar energy storage systems.

$$H_2O \xrightarrow[\text{cat}]{h\nu} H_2 + {}^1/_2O_2 \quad (2)$$

Results and Discussion

$[Ru^{II}(bpy)_3]$–Y. The visible-region diffuse-reflectance spectrum of the degassed (>95% of the intrazeolitic H_2O removed[1]) synthesized $[Ru^{II}(bpy)_3]$–Y sample containing 2.1 wt % Ru is shown in Figure 1, curve a. It exhibits the λ_{max} = 450 nm absorption band characteristic of orange $[Ru^{II}(bpy)_3]^{2+}$ complexes.[18] In our preliminary studies,[1] synthesized $[Ru^{II}(bpy)_3]$–Y zeolites were prepared by mixing bpy with a $[Ru^{III}(NH_3)_6]$–Y zeolite in a 4:1 bpy:Ru mole ratio. Our initial employment of the 4:1 ratio was based on the stoichiometry of Burstall's[19] original preparation of $[Ru^{II}(bpy)_3]Cl_2$ (eq 3). We have since found that 3:1 or preferably

$$2Ru^{3+} + 8bpy \xrightarrow{200\ °C} 2[Ru^{II}(bpy)_3]^{2+} + C_{20}H_{14}N_4 + 2H^+ \quad (3)$$

3.5:1 mole ratios of bpy:Ru also form $[Ru^{II}(bpy)_3]$–Y. Intrazeolitic ammonia was probably the ruthenium-reducing

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