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Electron Transfer in a Series of Cobalt Clathrochelates in Nonaqueous Solution

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Electron transfer has been observed in a series of cobalt clathrochelates based on chelating dioximes and substituted borate caps. Cross-reactions have been studied for $Co(dpg)_3(BPh)_2^{0/+}$ with $[Co(nox)_3(BF)_2]BF_4$, $[Co(dmg)_3(BF)_2]BF_4$, $Co(nox)_3(BPh)_2$, and $Co(nox)_3(B\text{-}n\text{-}Bu)_2$ where the dioximes are respectively diphenylglyoxime, 1,2-cyclohexanedione, and dimethylglyoxime and the caps are phenyl-, fluoro-, or *n*-butyl-substituted borates. Effects of changes in reactant concentration, temperature, added electrolyte (tetra-*n*-butylammonium tetrafluoroborate), and the solvents acetonitrile, acetone, ethylene dichloride, and nitrobenzene have been measured. Second-order rate constants for all reactions in acetonitrile vary over a factor of 30 from 192 M^{-1} s^{-1} to 6000 M^{-1} s^{-1}. With the possible exception of the slowest reaction, these rates agree with Marcus theory and predictions based on previously studied reactions of the cobalt compounds with ferrocene. In acetonitrile, the values of ΔH^* vary from 20 to 34 kJ/mol, and the ΔS^* values are large and negative, from −59 to −130 J/(mol·K). ΔH^* and ΔS^* decrease by a factor of 2 in the other solvents. Increasing Bu_4NBF_4 concentration slows the reactions in all solvents. This is explained by a two-path reaction mechanism involving an ion-paired reactant. The activation parameters and solvent dependences vary substantially from Marcus theory predictions. It is concluded that subtle changes in solvation and in precursor structure and stability lead to these results.

Introduction

For decades, research into electron-transfer reactions has proceeded steadily due to its fundamental importance in chemistry and because of applications to energy transfer and transduction in nonliving as well as biochemical systems.[1,2] Only in recent years has attention turned to electron transfer in nonaqueous solutions.[3-10] Our laboratory continues experimental work with metal complexes in organic solvents as an opportunity to determine the limits of current theories in predicting nonaqueous reactions and also as an opportunity to investigate systems that are unstable in water.

The series of cobalt chlatrochelates originally developed by Rose and co-workers[11] presents an ideal system for investigation of the applicability of Marcus theory[12,13] to electron transfer in nonaqueous solutions. The cage structure ensures an outer-sphere mechanism, the complexes are soluble in a wide variety of solvents, and one reactant in each redox pair is neutral so all Coulombic work to bring reactants together and separate products is eliminated from calculations.

Earlier work in this laboratory measured the rate constant for the reaction of each cobalt complex versus ferrocene or one of its derivatives in acetonitrile.[14] By use of the self-exchange rate constant for ferrocene measured by Wahl,[15] calculation of an apparent self-exchange rate constant for each cobalt complex was then possible. The work reported here carries this study further by using Marcus theory and those calculated self-exchange rate constants for the cobalt complexes to calculate expected cross-reaction rate constants and activation parameters for reaction between two different cobalt clathrochelates. The calculated values are compared to experimental results. To learn more of the role of the medium in the chemistry of electron transfer, this work also looks at the dependence of the rate on temperature, added electrolyte and solvent.

Experimental Section

Synthesis and Characterization. Starting materials and solvents were purchased from Aldrich Chemical Co. and Baker Chemicals. Solvents were purified by the methods of Borchardt.[5] A distillation apparatus with all Teflon fittings was used and the solvents were stored under argon.

Diphenylglyoxime (dpg) and tetra-*n*-butylammonium tetrafluoroborate (Bu_4NBF_4) were prepared by literature methods.[16,17] All Co(II) compounds were prepared as previously described by Borchardt[14] for the phenylborate-capped clathrochelate, $Co(dpg)_3(BPh)_2$. The complex $[Co(dpg)_3(BPh)_2]BF_4$ was prepared by dissolving the Co(II) complex in methylene chloride and adding aliquots of nitrosonium tetrafluoroborate ($NOBF_4$). The disappearance of the intense peak at 494 nm was monitored, and a small excess of $NOBF_4$ was added to ensure complete oxidation of the cobalt. When no further spectroscopic change occurred, diethyl ether was added to form a solid quickly. The gold solid was washed thoroughly with methanol to remove excess $NOBF_4$ and vacuum dried. The infrared spectrum of the product showed no absorptions for $NOBF_4$.[18]

Other Co(III) compounds were prepared by the method developed by Jackel and Rose[19] for $[Co(dmg)_3(BF)_2]BF_4$, but 1,2-cyclohexanedione dioxime (nox) was substituted for dimethylglyoxime (dmg) and *n*-butaneboronic acid or benzeneboronic acid was substituted for boron trifluoride etherate as required. All cobalt compounds were characterized by infrared and visible spectroscopy. Anal. Calcd for $[Co(dpg)_3(BPh)_2]BF_4{\cdot}2CH_3OH$: C, 61.12; H, 4.40; N, 7.64. Found: C, 61.03; H, 4.45; N, 7.70. Evidence for the methanol solvate was also found in a crystallographic study.[20]

Kinetic Measurements. Experiments were performed with the concentration of one reactant in pseudo-first-order excess. All reactions were followed for a minimum of 5 half-lives. Each observed rate constant is the average of three reproducible trials. Error in the rate constants is taken as the higher of the standard deviation from the mean of the triplicates or 5% of the mean (10% for the $Co(nox)_3(BPh)_2$ series). All trials showed absorbance changes of 0.05–0.06, as expected.

A standard analytical balance was used for masses in excess of 0.0099 g. A Cahn gram electrobalance was used for smaller masses such as the individually made solutions discussed under Reactant Stability.

Stopped-flow kinetics were measured on a Dionex spectrophotometer (D-110). A dual-detector accessory (D-137) was used to follow the signal, log (I_{500}/I_{450}), which corresponds primarily to the intense $Co(dpg)_3(BPh)_2$ charge-transfer band at 494 nm. A circulating water bath controlled temperature to within 0.05 K. Rate constants for the stopped-flow trials were calculated from the 2048 points digitized and stored as previously described.[21] The data were fit to a pseudo-first-order rate law by using an iterative least-squares process that varied the infinity absorbance to minimize χ^2. A weighted least-squares program then gave second-order rate constants from the fit of k_{obs} to the concentration of the reactant in excess. Activation parameters were obtained from weighted least-squares fits of second-order rate constants to the Eyring equation. Error here was calculated by using a propagation of error analysis and the rate constant errors discussed above. Dependence of the

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Table I. Second-Order Rate Constants and Activation Parameters for Cross-Reactions with $Co(dpg)_3(BPh)_2^{0/+}$ in Acetonitrile[a]

complex	$10^{-3}k_{12}$,[b] M^{-1} s^{-1}	ΔH_{12}^{*},[c] kJ/mol	ΔS_{12}^{*},[c] J/(mol·K)
$[Co(nox)_3(BF)_2]^+$	6.0 ± 0.2	34 ± 1	−59 ± 5
$[Co(dmg)_3(BF)_2]^+$	1.54 ± 0.05	23 ± 2	−108 ± 7
$Co(nox)_3(BPh)_2$	0.192 ± 0.012	20 ± 1	−130 ± 5
$Co(nox)_3(B\text{-}n\text{-}Bu)_2$	2.43 ± 0.08	34 ± 1	−68 ± 4

[a] [Co(II)] ≈ 5 μM for all reactions. [Co(III)] = 50–500 μM for concentration dependences and typically 250 or 400 μM for temperature trials. Total $[BF_4^-]$ = 0.1 M. [b] Temperature = 298.2 K. [c] Temperature varied from ≈275.2 to 303.2 K. All experimental conditions and observed rate constants with their standard deviations are available in the supplementary material.

Table II. Rate Constants and Activation Parameters for the Cross-Reaction of $[Co(nox)_3(BF)_2]BF_4$ with $Co(dpg)_3(BPh)_2$ in Various Solvents[a]

solvent	$10^{-3}k_{12}$, M^{-1} s^{-1}	$10^{-3}k_{12}K_{eq}^{-1/2}$, M^{-1} s^{-1}	ΔH_{12}^{*}, kJ/mol	ΔS_{12}^{*}, J/(mol·K)
MeCN	6.0 ± 0.2	1.1	34 ± 1	−59 ± 5
Me_2CO[b]	3.9 ± 0.1	0.36	13 ± 1	−130 ± 5
$(CH_2Cl)_2$[c]	5.4 ± 0.3	1.0		
$PhNO_2$[d]	4.8 ± 0.2	0.51	17 ± 1	−117 ± 5

[a] All conditions as in Table I except as listed here. [b] Concentration dependence: [(CoII)] = 1.8 μM; [Co(III)] = 15–150 μM. Temperature dependence: [Co(II)] = 4.9 μM; [Co(III)] = 150 μM. [c] [Co(II)] = 1.6 μM; [Co(III)] = 15–150 μM. [d] [Co(II)] = 3.6 μM for all trials. [Co(III)] = 35–340 μM for concentration dependence and 50 μM for temperature dependence.

rate constants on the total BF_4^- concentration was analyzed as described previously[5] by using a nonlinear least-squares fit of second-order rate constants to a rate law including ion pairing (vide infra). Errors were evaluated by the method of support planes.[22]

Some slower $Co(dpg)_3(BPh)_2^+$ oxidations of $Co(nox)_3(BPh)_2$ were followed on a Cary 219 spectrophotometer. A circulating water bath and jacketed sample cell holder were used to establish and maintain thermal equilibrium at 298.2 ± 0.1 K. Two milliliters of the reagent in excess was placed in the sample cell in the light path. One milliliter of the limiting reagent was injected vigorously with a gastight syringe. Data collection was begun after turbulence subsided and the signal became stable. For each trial, 18–20 values were taken from absorbance versus time traces and fit to a pseudo-first-order equation by using the same process as for the stopped-flow kinetics.

Electrochemistry. Potentials of $Co(dpg)_3(BPh)_2$ and $[Co(nox)_3(BF)_2]BF_4$ in each solvent were measured in triplicate by cyclic voltammetry using a PAR 174A potentiostat and Model 303 cell with a platinum electrode. A thermostated jacket for the sample cell and a circulating water bath were used to hold solutions at 298.2 ± 0.1 K. Ferrocene was used as an external standard for each determination, and all values are reported versus this standard.

Reactant Stability. The visible spectra of $Co(dpg)_3(BPh)_2$ and $[Co(nox)_3(BF)_2]BF_4$, as representative compounds, were followed for over 1 day in each solvent. Spectra from MeCN showed no sign of change. In other solvents, the Co(III) species gave linear spectral changes of 2%–3% change/h in the first few hours.[20] To minimize this concentration change, samples for trials in all solvents except MeCN were made individually and used within 1 h of dissolution.

Results

Table I presents the second-order rate constant and activation parameters for each reaction with either $Co(dpg)_3(BPh)_2$ or $Co(dpg)_3(BPh)_2^+$, as required to give an equilibrium constant greater than one for the electron-transfer reaction, in acetonitrile. In all cases, the dependence of k_{obs} on the concentration of the reagent in excess was linear with an intercept near zero.

Table II gives the second-order rate constant and activation parameters for the reaction between $Co(nox)_3(BF)_2^+$ and $Co(dpg)_3(BPh)_2$ in acetone, ethylene dichloride, and nitrobenzene.

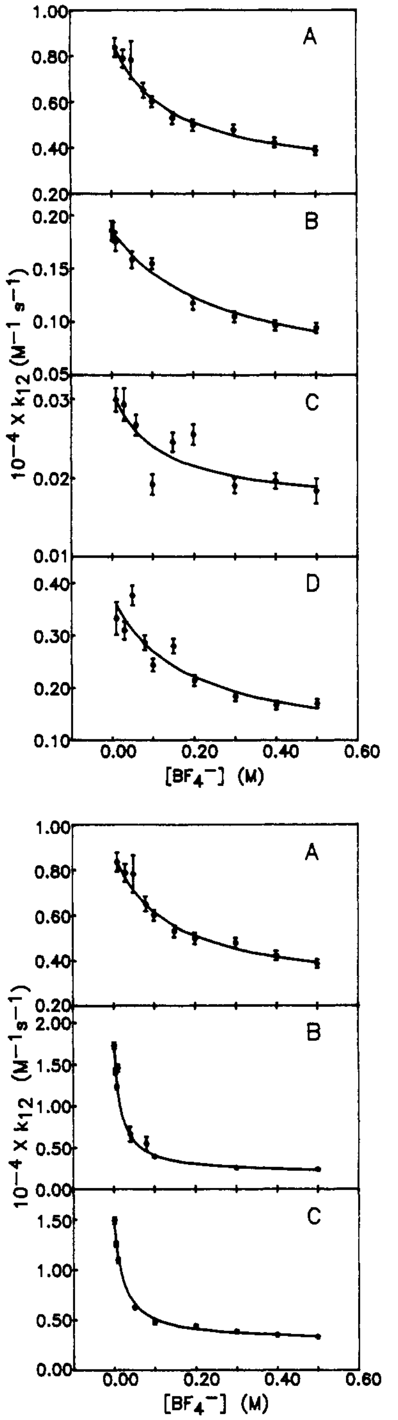

Figure 1. (a, Top) Dependence of the second-order rate constant on the BF_4^- concentration: (A) $[Co(nox)_3(BF)_2]BF_4$; (B) $[Co(dmg)_3(BF)_2]BF_4$; (C) $Co(nox)_3(BPh)_2$; (D) $Co(nox)_3(B\text{-}n\text{-}Bu)_2$. The solvent was acetonitrile and the temperature was 298.2 K for all trials. All experimental conditions and observed rate constants with their errors are available in the supplementary material. (b, Bottom) Dependence of the second-order rate constant on the BF_4^- concentration for the reaction of $[Co(nox)_3(BF)_2]BF_4$ with $Co(dpg)_3(BPh)_2$ at 298.2 K for the following solvents: (A) acetonitrile; (B) acetone; (C) nitrobenzene. All experimental conditions and observed rate constants with their errors are available in the supplementary material.

For each reaction in acetonitrile, the dependence of k_{12} on the total BF_4^- concentration is depicted in Figure 1a. Figure 1b illustrates the effect of varying the solvent on this same dependence for the reaction between $Co(dpg)_3(BPh)_2$ and $Co(nox)_3(BF)_2^+$.

The reduction potential of each complex in the various solvents used is reported in Table III.

Discussion

Marcus Theory Correlations. The second-order rate constants from Table I cover a 30-fold range over the series of cobalt complexes, while the enthalpies (ΔH^*) and entropies (ΔS^*) of activation vary by 14 kJ/mol and 71 J/(mol·K), respectively. The

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Table III. Reduction Potentials and Equilibrium Constants for all Reactants[a]

reactant	solvent	$E_{1/2}$, mV	K_{eq}
$Co(nox)_3(BF)_2^+$	MeCN	−13	28
$Co(dmg)_3(BF)_2^+$	MeCN	−28	16
$Co(nox)_3(BPh)_2$	MeCN	−200	51
$Co(nox)_3(B\text{-}n\text{-}Bu)_2$	MeCN	−282	1200
$Co(dpg)_3(BPh)_2$	MeCN	−108	
$Co(nox)_3(BF)_2^+/Co(dpg)_3(BPh)_2$	Me_2CO	−13, −135[b]	115
$Co(nox)_3(BF)_2^+/Codpg)_3(BPh)_2$	$(CH_2Cl)_2$	−36, −122[b]	28
$Co(nox)_3(BF)_2^+/Co(dpg)_3(BPh)_2$	$PhNO_2$	−34, −149[b]	88

[a] Values reported vs $FeCp_2$. Supporting electrolyte was 0.1 M Bu_4NBF_4; temperature was 298.2 K. Values in MeCN taken from ref 14. [b] The first reduction potential in each pair refers to $[Co(nox)_3(BF)_2]BF_4$ and the second to $Co(dpg)_3(BPh)_2$.

Table IV. Rate Constants and Activation Parameters for the Cobalt Cross-Reactions in Acetonitrile as Calculated from Marcus Theory

complex	$10^{-3}k_{12}$,[a] $M^{-1}\ s^{-1}$	$\Delta H_{12}^{\ddagger}$, kJ/mol	$\Delta S_{12}^{\ddagger}$, J/(mol·K)
$[Co(nox)_3(BF)_2]^+$	1.8	16	−120
$[Co(dmg)_3(BF)_2]^+$	0.9	23	−100
$Co(nox)_3(BPh)_2$	2.8	24	−100
$Co(nox)_3(B\text{-}n\text{-}Bu)_2$	8.7	32	−110

[a] Values of k_{22} used in this calculation for $FeCp_2$ are from ref 14. The second-order rate constants are calculated as 1300, 600, 1900, and 6000 $M^{-1}\ s^{-1}$, respectively, if an interpolated anion concentration value from ref 23 is used.

self-exchange rate constant and the activation parameters for each complex have been calculated previously on the basis of cross-reactions with ferrocene and ferrocene derivatives.[14] This allows comparison of the experimental k_{12} values and activation parameters obtained in this study with the values that can be calculated from the Marcus theory equations. Similar comparisons have been pursued for many systems, but seldom for non-aqueous reactions. The Marcus cross-reaction equation (eq 1) relates the

$$k_{12} = \sqrt{k_{11}k_{22}K_{eq}f} \tag{1a}$$

$$\ln f = \frac{(\ln K_{eq})^2}{4 \ln \left(\dfrac{k_{11}k_{22}}{A_{12}^2} \right)} \tag{1b}$$

$$A_{12} = \sqrt{A_{11}A_{22}} \tag{1c}$$

rate constant for the reaction between two different complexes, k_{12}, to that for the self-exchange reactions of the individual complexes and the equilibrium constant of the reaction. In these equations, each k_{ij} value is actually the product of a precursor complex formation constant and a unimolecular electron-transfer rate constant, $K_p k_{et}$. The separate term for the formation of a precursor complex is omitted since the complexes are of similar structure and the same charge type. In eq 1, k_{ii} is the self-exchange rate constant for a reactant, K_{eq} is the equilibrium constant for the reaction and A_{ii} is a frequency factor taken to be $10^{11}\ s^{-1}$. Furthermore, both $\Delta H_{12}^{\ddagger}$ and $\Delta S_{12}^{\ddagger}$ may be calculated from eq 3 and 4. In these equations, ΔG, ΔH, and ΔS are the Gibbs free

$$k_{12} = A_{12}e^{-\Delta G_{12}^{*}/RT} = \frac{k_bT}{h}e^{-\Delta G_{12}^{\ddagger}/RT} \tag{2a}$$

$$\Delta G_{12}^{\ddagger} = \Delta G_{12}^{*} + RT \ln \left(\frac{hA_{12}}{k_bT} \right) \tag{2b}$$

$$\Delta H_{12}^{\ddagger} = \Delta H_{12}^{*} - RT/2 \tag{3a}$$

$$\Delta H_{12}^{*} = \left(\frac{\Delta H_{11}^{*} + \Delta H_{22}^{*}}{2} \right)[1 - 4(\alpha^{*})^2] + \left(\frac{\Delta H^{\circ}}{2} \right)(1 + 2\alpha^{*}) \tag{3b}$$

$$\alpha = \frac{\Delta G^{\circ}}{\Delta G_{11}^{*} + \Delta G_{22}^{*}} \tag{3c}$$

$$\Delta S_{12}^{\ddagger} = \Delta S_{12}^{*} + R \ln \left(\frac{hA_{12}}{k_bT} \right) - \frac{R}{2} \tag{4a}$$

$$\Delta S_{12}^{*} = \left(\frac{\Delta S_{11}^{*} + \Delta S_{22}^{*}}{2} \right)[1 - 4(\alpha^{*})^2] + \frac{\Delta S^{\circ}}{2}(1 + 2\alpha^{*}) \tag{4b}$$

energy, the enthalpy, and the entropy, respectively; R is the gas constant, T is absolute temperature, k_b is Boltzmann's constant, h is Planck's constant, and the superscripts "$*$", "$\ddagger$", and "$\circ$" indicate respectively the Marcus theory activation parameters, the transition-state theory activation parameters, and the standard-state parameters taken as those at reaction conditions. Table I gives the calculated values for the cobalt clathrochelate cross-reactions in acetonitrile.

For all cases in acetonitrile except the oxidation of $Co(nox)_3(BPh)_2$, the calculated rate constants are within a factor of 4 of the observed values. This is reasonable agreement with Marcus predictions considering the simplicity of the theory and the number of experimental parameters that are required to make the calculation. Further, the self-exchange values used[15] for ferrocene and decamethylferrocene have recently come into question.[23,24] The new values were not used here because activation parameters were not determined for some and all were obtained at different ionic strengths than those used in these clathrochelate reactions. However, the caption for Table IV lists rate constants calculated for the present cobalt cross-reactions by using the most reasonable interpolated values currently available for the ferrocene self-exchange rate constant, and these values have no substantive effect on the following discussion. It is noted that the $Co(nox)_3(BPh)_2$ reaction is 14 times slower than expected. The lower observed reactivity might arise from nonadiabaticity, a difference in precursor complex stability, or a change in mechanism. All the cobalt cross-reactions have similar, low driving forces, and with loss of a ligand ruled out by the cage structure, only a difference in precursor stability seems likely as a cause for differences in the observed and calculated rate constants. The only structural distinction of this reactant pair is the phenyl ring on the Co(II) cap. A review of the reduction potentials of the clathrochelates supports the possible importance of the cap in the electron-transfer event since the ease of reduction varies with the identity of the cap as well as with that of the dioxime component of the ligand. A possibility for the low reactivity, then, is that a particularly unstable precursor is formed because of interaction between the phenyl rings of the two complexes or that the electron-transfer reactivity of this precursor is low. A complementary possibility is that a precursor complex formed between ferrocene and $Co(nox)_3(BPh)_2^+$ is particularly stable or more reactive than with the other clathrochelates.

Comparison of the predicted and observed activation parameters for the four reactions in acetonitrile (Tables I and IV) presents a much less clear picture. Again, since there are many experimental values that go into making these predictions and because the activation parameters themselves are less precisely defined than the rate constants, the predicted activation parameters are rather imprecise. Even if generous uncertainties are allowed, the $Co(nox)_3(BF)_2^+$ system shows a major disagreement between the calculated and observed activation parameters. Since the predicted values of $\Delta H_{12}^{\ddagger}$ and $\Delta S_{12}^{\ddagger}$ are both much lower than observed, they compensate and the value of k_{12} is similar to the measured one.

The very negative entropies of activation observed cannot arise from concentration of charge in the activated complex since one reactant is always neutral. Inner-sphere reorganization re-

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Table V. Fit Parameters for the Cross-Reaction Dependence on Concentration of BF_4^- in Acetonitrile[a]

complex	$10^{-3}k_0$, M^{-1} s^{-1}	$10^{-3}k_{ip}$, M^{-1} s^{-1}	K_{ip}, M^{-1}	K_{ip},[b] M^{-1}
$[Co(nox)_3(BF)_2]^+$	9.0 (+0.4, −0.3)	2.9 (+0.1, −0.2)	9 (+2)	5 (+0.5, −0.4)
$[Co(dmg)_3(BF)_2]^+$	1.86 (+0.04, −0.03)	0.4 (+0.2)	4 (+1)	9 (+1.2, −1.5)
$Co(nox)_3(BPh)_2$	0.30 (+0.02)	0.12 (+0.04, −0.01)	4 (+3, −2)	
$Co(nox)_3(B\text{-}n\text{-}Bu)_2$	3.7 (+0.5, −0.4)	0.8 (+0.4, −0.8)	6 (+6, −3)	

[a] [Co(II)] and [Co(III)] as in Table II for temperature trials. $[BF_4]$ was varied from 0.001 to 0.5 M. Temperature = 298.2 K. All experimental conditions and observed rate constants with their standard deviations are available in the supplementary material. [b] Taken from ref 14, which reports ion pairing for the same species reacted with ferrocene.

Table VI. Dependence on the Concentration of BF_4^- for the Reaction of $[Co(nox)_3(BF)_2]BF_4$ with $Co(dpg)_3(BPh)_2$ in Various Solvents[a]

solvent	$10^{-3}k_0$, M^{-1} s^{-1}	$10^{-3}k_{ip}$, M^{-1} s^{-1}	k_0/k_{ip}	k_0/k_{ip}[b]	K_{ip}, M^{-1}	K_{ip},[b] M^{-1}
MeCN	9.0 (+0.4, −0.3)	2.9 (+0.1, −0.2)	3.1	5.3	9 (±2)	17
Me_2CO[b]	18 (±1)	1.8 (+0.2, −0.1)	10	5.6	62 (+20, −10)	200
$PhNO_2$[c]	15.0 (+0.9, −1)	2.9 (+0.1, −0.2)	5.1	19.3	44 (+9, −10)	53

[a] All conditions as in Table I except the concentrations listed here. [b] Taken from ref 5, which reports ion pairing of the $Co(dmg)_3(BF)_2^+$ species with ferrocene. [c] Concentration dependence: [Co(II)] = 5 μM; [Co(III)] = 370 μM. [d] [Co(II)] = 3.6 μM; [Co(III)] = 53 μM.

quirements are expected to be similar and reflected more by the enthalpies of activation than by ΔS^*. Likely contributors to the activation entropy are orientation requirements of the reactants, solvent orientation from nonelectrostatic interaction, and low electron-transfer probability. To the extent that certain highly preferred precursors for electron transfer do exist, large negative entropies of activation are expected. The values observed here are compatible with such a requirement, generally, and the particularly negative value of the $Co(nox)_3(BPh)_2$ reaction may reflect such a contribution.

In solvents other than acetonitrile, no comparison of observed to predicted rate constants is possible because the self-exchange rate constants have not been calculated previously. Comparison to previous work is possible, however. The second column of Table II shows the observed rate constant adjusted for the driving force of the reaction through division by $K^{1/2}$, as suggested by Marcus theory. If the inherent reactivity of the reactant pair, $(k_{11}k_{22})^{1/2}$, is unchanged by solvent, then the values in this column should be constant. The data show that the reactivity is similar in acetonitrile and ethylene dichloride and somewhat lower in acetone and nitrobenzene. These results can be compared to a previous study[5] of the ferrocene reduction of $Co(dmg)_3(BF)_2^+$ in 0.1 M Bu_4NBF_4. In that study a similar data treatment also shows a lower reactivity in acetone than in acetonitrile, but a higher reactivity in ethylene dichloride and nitrobenzene. The Marcus theory prediction of a solvent effect is given in eq 5. Here, the

$$k_{12} = K_p k_{et} = K_p A \exp(-\Delta G_{12}^*/RT) \quad (5a)$$

$$\Delta G_{12}^* = \Delta G_{out} + \Delta G_{in} \quad (5b)$$

$$\Delta G_{out} = \left(\frac{e^2}{4}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \quad (5c)$$

symbols A, ΔG_{out}, ΔG_{in}, e, a_1, a_2, r, D_{op}, and D_s are the Marcus preexponential factor, the solvent or outer-sphere component of the activation energy, the inner-sphere activation energy, the charge on an electron, the radii of the two reactants, the distance between reactant centers at the transition state, the optical frequency dielectric constant, which is equal to the square of the refractive index, and the static dielectric constant. All other symbols were previously defined. For the solvents under consideration, rate constants should depend on solvent primarily through the ΔG_{out} term and follow the order MeCN < $(CH_3)_2CO$ ≪ $C_6H_5NO_2 \approx (CH_2Cl)_2$. The results for the ferrocene reduction of $Co(dmg)_3(BF)_2^+$ do roughly follow this prediction,[5] as do the $Ru(hexafluoroacetylacetonate)_3^{0/-}$ electron self-exchange[3] and the ferrocene/ferrocenium electron self-exchange.[23] The lack of correlation observed here is notable and is taken to indicate that some other factor or factors overcome the variation in the outer-sphere reorganization energy. A likely candidate for such a factor is the precursor complex stability constant, K_p. The earlier assumption that K_p could be dropped from Marcus equations due to charge and structure similarity of the reactants, although common, may not be appropriate here. Another possibility is that the precursor complex has the same stability in all of the solvents, as was assumed in the analysis presented in eq 5, but that the actual structure of the precursor complex changes and the structure in the lower dielectric solvents has a lower electron transfer reactivity, k_{et}.

For further comparison with previous work, activation parameters were also studied as a function of solvent and are given in Table II. They fall into two classes. In acetone and nitrobenzene, ΔH^* is smaller and ΔS^* is more negative than the respective results in acetonitrile. These can also be compared to the results for different complexes in acetonitrile in Table I, which also show the same two categories. The oxidation of $Co(nox)_3(B\text{-}n\text{-}Bu)_2$ has activation parameters similar to those for the reduction of $Co(nox)_3(BF)_2^+$, while the reactions of $Co(dmg)_3(BF)_2^+$ and $Co(nox)_3(BPh)_2$ in acetonitrile are more like the reaction of $Co(nox)_3(BF)_2^+$ in acetone or nitrobenzene. Enthalpy–entropy compensation, especially with regard to solvent variation, has been noted previously.[14] It has been suggested that such variation is related to changes in precursor complex structure and stability and leads to poor correlation with solvent dielectric continuum theory. To the extent that solvation changes are involved, ΔV^* should vary. Experiments to test this supposition are in progress.

Salt Dependence. The cobalt clathrochelates are inert to substitution, ensuring an outer-sphere electron-transfer mechanism. Since one of the two reactants is neutral in each reaction, there is no Coulombic work required to bring the complexes together or to separate the successor complexes. Given these considerations, the salt dependence exhibited by each reaction is expected to arise principally from ion pairing by the Co(III) complexes and different electron-transfer reactivities of the free and ion-paired species. This is supported by previous findings for reactions of the Co(III) clathrochelates with ferrocene and its derivatives.[14] Assuming the ion-pair equilibrium in eq 6, the rate law is given by eq 7, where

$$Co_1^+ + BF_4^- \overset{K_{ip}}{\rightleftharpoons} Co_1\text{–}BF_4 \quad (6a)$$

$$Co_1^+ + Co_2 \xrightarrow{k_0} Co_1 + Co_2^+ \quad (6b)$$

$$Co_1\text{–}BF_4 + Co_2 \xrightarrow{k_{ip}} Co_1 + Co_2\text{–}BF_4 \quad (6c)$$

$$\frac{d[Co_1]_T}{dt} = \frac{k_0 + k_{ip}K_{ip}[BF_4]}{1 + K_{ip}[BF_4^-]}[Co_1]_T[Co_2] \quad (7)$$

the subscripts "1" and "2" on Co indicate two different cage ligands, $[Co_1]_T$ represents the total Co(III) concentration and K_{ip} is the ion-pair association constant.

The results of fitting kinetic data to eq 7 are given in Table V for all reactions in acetonitrile and in Table VI for reactions between $Co(nox)_3(BF)_2^+$ and $Co(dpg)_3(BPh)_2$ in all solvents. As Figure 1 indicates, the free ion (k_0 path) is more reactive than the ion pair (k_{ip} path) in all cases. No salt study was performed in ethylene dichloride since dilution of solutions was impractical due to the instability of the Co(III) complexes in this solvent.

The ion-pair association constants (K_{ip}) from fits of kinetic data to concentration of BF_4^- are below 10 for all the reactions in acetonitrile. Such slight association is expected in species of low charge-to-size ratio. The ion pairing of $[Co(nox)_3(BF)_2]^+$ and $[Co(dmg)_3(BF)_2]^+$ calculated here can be compared with that of the same complexes in their reaction with ferrocene from an earlier study.[14] The extent of association in both studies should be the same, within the precision of the measurements, since the rate variation is being attributed to the same ion-pairing process. Table V shows that similar values are obtained, but in this study the nox complex showed more association, while in the previous study the dimethylglyoxime complex gave a larger K_{ip}. The differences are not considered large enough to justify an interpretation. Also shown in Table V is the agreement in K_{ip} observed in the two reactions where $[Co(dpg)_3(BPh)]BF_4$ reacts in acetonitrile.

Data from the salt dependences in various solvents also agree with ion-pairing of the charged reactant. The fifth column in Table VI shows that, as expected, the association of $Co(nox)_3(BF)_2^+$ with BF_4^- increased as the dielectric constant of the solvent decreased. Again, a comparison of ion-pairing constants is possible. The K_{ip} values calculated here can be compared with those of $[Co(dmg)_3(BF)_2]^+$ in the same solvents[5] as shown in the last column of the same table. The $[Co(nox)_3(BF)_2]^+$ studied here gives somewhat lower K_{ip} values than the previous work with $Co(dmg)_3(BF)_2$,$^+$ but the trend in K_{ip} with the changing dielectric of the solvents is the same in both studies. The effect of added salt observed here corroborates previous findings[5,14,21] that ion pairing decreases the rate constant for electron transfer between a neutral reactant and a charged reactant.

The ratio of the free-ion rate to the ion-paired rate, (k_0/k_{ip}), is typically 4 but it increases to 10 for acetone, the lowest dielectric solvent studied. This agrees generally with predictions from Marcus theory as discussed above for the second-order rate constants. The ratio of the rate constants for the $[Co(nox)_3(BF)_2]BF_4$ reactions in various solvents can also be compared with previous results[5] for the ferocene reduction of $[Co(dmg)_3(BF)_2]BF_4$ as shown in Table VI. Comparable values are obtained with the possible exception of the reaction in nitrobenzene, the only solvent with an aromatic ring. A review of the k_0 and k_{ip} values for the two reactions in all solvents indicates that the k_0 value for the present study in nitrobenzene is uncharacteristically low. As discussed above, the rate constants for each path are predicted by Marcus theory to increase in the order MeCN < $(CH_3)_2CO \ll C_6H_5NO_2$ after correction for the driving force of the reaction. In the present work, the rate constant for neither path fulfills this expectation. This supports the conclusion, based on the rate constants at 0.1 M Bu_4NBF_4 shown in Table II, that precursor complex stability changes are influencing the reactivity pattern.

Conclusion

In conclusion, a series of reactions between cobalt clathrochelates has been studied as a function of the structure of the complexes, concentration, temperature, added electrolyte, and solvent. In general, the rate constants agree with Marcus theory predictions, decrease in the presence of added salt, and are consistent with previous measurements on the same complexes reacting with ferrocene. The possible exception is the oxidation of $Co(nox)_3(BPh)_2$ by $[Co(dpg)_3(BPh)_2]BF_4$, which occurs more slowly than predicted. The activation parameters and solvent dependence indicate that subtle changes in solvation or precursor complex structure or stability are occurring which do not lead to large changes in rate constants.

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Supplementary Material Available: Tables of all kinetic data, their standard deviations, and their conditions (6 pages). Ordering information is given on any current masthead page.

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Lamellar Inorganic Ion Exchangers. Alkali Metal Ion Exchange on α- and γ-Titanium Phosphate

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Alkali metal ion exchange on α- and γ-titanium phosphate is reported. In α-titanium phosphate, Li^+ and Na^+ exchange in acidic solution but K^+ and Cs^+ do not. Phases of half and full exchange are formed. In the γ-titanium phosphate, Li^+, Na^+, K^+, and Cs^+ exchange in acidic solution. Phases of 25, 50, and 100% substitution are formed. The selectivity sequences are obtained from the study of binary systems, and their validity for polyionic systems is discussed. Free energy, enthalpy, and entropy of the exchange reactions are also presented. A mechanism of exchange is proposed.

Introduction

The existence of molecular sieves with a pore size between 6 and 40 Å obtained from clays by intercalation of organic compounds has been known for a long time. These compounds can only be used at low temperatures, since temperatures higher than 300 °C result in their decomposition and a drastic decrease of the interlayer spacing.[1] In recent years, special attention has been paid to the properties of a new type of synthetic inorganic material, mainly in the catalysis field. These are the clays with pillars. Under this name are known the clays that, after the intercalation of inorganic polymeric species into their interlayer spacing, present a basal spacing close to 18 Å. These intercalation compounds show a microporous system and a thermal stability similar to those of the zeolites.[2,3]

In the last 20 years, noticeable efforts in the synthesis and characterization of a group of lamellar phosphates of tetravalent metals have been made.[4–6] These compounds behave as cationic exchangers. The viability of intercalating polar organic molecules

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