

Outer-Sphere Electron Transfer in Methylene Chloride: Concentration, Salt, and Temperature Dependences of the Oxidation of β -Re₂X₄(*cis*-1,2-bis(diphenylphosphino)ethylene)₂ (X = Cl, Br) by [Co(dimethylglyoximate)₃(BF)₂]₂BF₄ and the Oxidation of Re₂Br₄(PMe₂Ph)₄ by [Co(1,2-cyclohexanedione dioximate)₃(BBu)₂]₂BF₄

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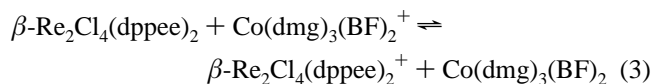
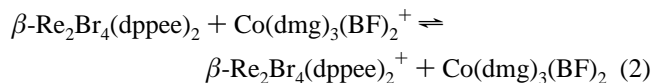
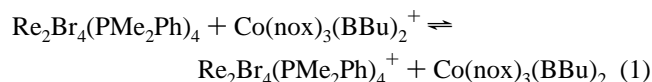
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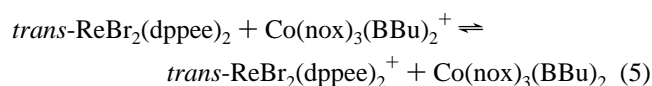
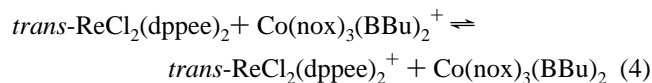
The kinetics of the oxidation of β -Re₂X₄(*cis*-1,2-bis(diphenylphosphino)ethylene)₂ (X = Cl, Br) by the cobalt clathrochelate [Co(dimethylglyoximate)₃(BF)₂]₂BF₄ and the oxidation of Re₂Br₄(PMe₂Ph)₄ by the cobalt clathrochelate [Co(1,2-cyclohexanedione dioximate)₃(BBu)₂]₂BF₄ have been studied by the stopped-flow method as a function of temperature (−85 to −19 °C), added Bu₄NBF₄ (0–0.100 M), and reactant concentration in the low dielectric solvent methylene chloride. For each reaction, ~100 different conditions were studied. The observed rate constants were well fit by a mechanism involving separate paths for free ion and the ion-paired Co(III) oxidant. The analysis yielded values for ΔH^\ddagger and ΔS^\ddagger for each path of each reaction and consistent ΔH° and ΔS° values for the ion-pairing of the cationic reactant and the electrolyte. In addition, temperature-dependent electrochemical measurements in 0.10 M Bu₄NBF₄ yielded ΔH° and ΔS° for the electron transfer process. This is the first measurement of the homogeneous electron transfer reactivity of the dirhenium complexes, and they showed the expected high reactivity. The most notable result is a very high inhibition (*ca.* 700-fold) by added salt of only the [Co(dmgl)₃(BF)₂]₂BF₄ reactions. We attribute this to a change of rate-controlling step, for the ion-paired path, to one involving anion migration. This appears only to occur when the magnitude of ion-pairing free energy is significantly greater than the magnitude of the free energy change for the electron transfer process.

Introduction

This paper presents the kinetics and thermodynamics of the oxidation of β -Re₂X₄(dppee)₂ (X = Cl, Br; dppee is *cis*-1,2-bis(diphenylphosphino)ethylene) by the cobalt clathrochelate [Co(dmgl)₃(BF)₂]₂BF₄ (dmgl is dimethylglyoximate) and the oxidation of Re₂Br₄(PMe₂Ph)₄ by the cobalt clathrochelate [Co(nox)₃(BBu)₂]₂BF₄ (nox is 1,2-cyclohexanedione dioximate) in the low dielectric constant solvent methylene chloride.



This study represents an extension of a previous study characterizing the oxidations of mononuclear rhenium complexes of the type ReX₂(dppee)₂ (X = Cl, Br) by [Co(nox)₃(BBu)₂]₂BF₄ (reactions 4 and 5),¹ and our previous investigations into nonaqueous outer-sphere electron transfer.²



Until now, very little attention has been given to the homogeneous electron transfer reactions of transition metal complexes with more than one metal center. Bimetallic complexes with direct metal–metal bonding are an appropriate choice for study because they generally have multiple stable oxidation states that are formed by reversible electron transfer, have flexibility in the number and type of ligands, and have been extensively investigated structurally, spectroscopically, and electrochemically.³ The dirhenium complexes studied here represent a class of complexes with an “electron-rich” triple bond. Oxidation of the complexes results in the removal of an electron from a δ^* orbital, resulting in an increase in the formal bond order to 3.5.

The low solubility of the neutral Re complexes in most solvents and the need to work at low temperatures (*ca.* −85 to −20 °C) in order to observe the reactions by the stopped-flow method required the use of methylene chloride as the solvent. The Co complexes were suitable choices for redox partners, since they have good solubility in methylene chloride at low temperatures, are substitution inert in both oxidation states, show a large absorbance change upon reduction, have low self-exchange reactivity, and have been studied extensively in our laboratory.^{4–8} A slightly different partner had to be used in the case of the dirhenium complexes of dppee in order to observe the reactions on the time scale of the stopped-flow technique.

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The low dielectric constant of methylene chloride induces ion-pairing, even in the absence of added electrolyte. A proper characterization of the electron transfer reaction thus requires us to investigate the dependence of the electron transfer rate constants on the concentration of added tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as well as temperature and reactant concentration. The result of this analysis gives apparent equilibrium constants for ion-pairing by Bu_4NBF_4 and the cobalt clathrochelate, the rate constants for the free ion and ion-paired cobalt oxidant reacting with the neutral Re complexes, and the temperature dependences of these parameters. Measurement of the reduction potentials of the Co and Re complexes (*vs* ferrocene) as a function of temperature allows the calculation of the equilibrium constant of the electron transfer reaction and its temperature dependence.

Experimental Section

Starting materials were purchased from Aldrich Chemical Co. or Strem Chemical Co. and were used as received except as noted. Methylene chloride was distilled from P_2O_5 and stored under Ar prior to use. Ferrocene and decamethylferrocene were purified by sublimation. Bu_4NBF_4 was prepared as previously described.¹⁹ $[\text{Co}(\text{nox})_3(\text{BBu})_2]\text{BF}_4$ was prepared by the method for the synthesis of $[\text{Co}(\text{dpg})_3(\text{BC}_6\text{H}_5)_2]\text{BF}_4$ with the reaction time reduced to 3 h while the reaction mixture was stirred at room temperature. $[\text{Co}(\text{dmg})_3(\text{BF})_2]\text{BF}_4$,¹⁰ $\text{Re}_2\text{Br}_4(\text{PMe}_2\text{Ph})_4$,¹¹ and $\text{Re}_2\text{X}_4(\text{dppee})_2$ ($\text{X} = \text{Cl}$, or Br) were prepared by literature methods. The purity of all the complexes was verified by their electronic spectra and electrochemical properties. The purity of single samples of each of the Re complexes was analyzed by determination of Re and P using inductively coupled plasma emission analysis after digestion in hot nitric acid. The resulting molar ratios of P/Re were 1.96 for $\beta\text{-Re}_2\text{Br}_4(\text{dppee})_2$, 1.94 for $\text{Re}_2\text{Br}_4(\text{PMe}_2\text{Ph})_4$, and 2.02 for $\beta\text{-Re}_2\text{Cl}_4(\text{dppee})_2$. The reduction potentials were measured by Osteryoung square-wave voltammetry and cyclic voltammetry employing a BAS 100A electrochemical analyzer with a jacketed cell for temperature control using a Neslab Endocal Model LT-50dd circulating low-temperature bath. The cell temperature was calibrated *vs* the bath temperature over the range of the experimental measurements with a copper–constantan thermocouple. The $E_{1/2}$ values for all of the complexes were measured in triplicate in methylene chloride with 0.1 M Bu_4NBF_4 as the supporting electrolyte *vs* an internal standard of ferrocene or decamethylferrocene. Potentials were measured every 5 deg over the temperature range -30 to $+25$ °C with a Ag wire or a Ag wire coated with silver chloride reference electrode, a Pt wire counter electrode, and a 1.6 mm Pt disk working electrode.

Low-temperature stopped-flow kinetics were performed with a Hi-Tech SF-40 instrument. The optical signal followed was due to the change in absorbance caused by the appearance of the Co(II) complex ($\epsilon_{470} = 6399 \text{ M}^{-1} \text{ cm}^{-1}$ for $[\text{Co}(\text{nox})_3(\text{BBu})_2]\text{BF}_4$, $\epsilon_{460} = 5450 \text{ M}^{-1} \text{ cm}^{-1}$ for $[\text{Co}(\text{dmg})_3(\text{BF})_2]\text{BF}_4$).⁶ The data were collected for a minimum of 3–4 half-lives, and the observed rate constants were calculated from the 2048 digitized points by nonlinear least-squares techniques, using equal weights, with programs written in QuickBasic based on the routines of Bevington.¹³ The reactions had large equilibrium constants and were treated as irreversible. The dependence of the observed second-order rate constants on reactant concentration, temperature, and the concentration of added Bu_4NBF_4 were analyzed as described below using the Scientist mathematical modeling package. All fits were weighted by $1/k^2$ where k is the observed rate constant, and errors were taken as the standard deviation given by the Scientist program.

All three reactions were found to be quite rapid; therefore, low concentrations and low temperatures were required. Rate constants

were measured over as large a range of temperature and reactant concentration as possible. The effect of added Bu_4NBF_4 was studied only up to *ca.* 100 mM since the major influence of the added salt has been observed by this concentration and higher concentrations may lead to other small effects that have been attributed to associations of ion-paired complexes or ion multiples.

For reaction 1, data were collected for 95 different conditions to give 297 second-order or pseudo-first-order rate constants. The concentration of the Co complex was varied from 0.0284 to 0.191 mM, and the concentration of the Re complex ranged from 0.0181 to 0.0791 mM. Separate reaction conditions were chosen under which each reactant was in excess. The Bu_4NBF_4 concentration was varied from 0 to 101 mM. The temperature was varied from -85.0 to -50.0 °C. For conditions in which one reactant was less than *ca.* 10-fold in excess, the data were fit to a second-order rate law with unequal concentrations. The remainder of the data were fit to a pseudo-first-order rate law. The order of the reaction was established by the satisfactory fit of the absorbance *vs* time data to the appropriate rate law. Data for reaction 2 were collected for 98 different conditions to give 299 pseudo-first-order rate constants. The concentration of the Re complex was varied from 0.182 to 2.27 mM, and the concentration of the Co complex was varied from 0.0200 to 0.0460 mM. The Bu_4NBF_4 concentration was varied from 0 to 92.6 mM, and the temperature was varied from -80.0 to -19.0 °C. Data for reaction 3 were collected for 118 different conditions to give 337 pseudo-first-order rate constants. The concentration of the Re complex was varied from 0.240 to 2.37 mM, and the concentration of the Co complex was varied from 0.0237 to 0.0321 mM. The concentration of Bu_4NBF_4 was varied from 0 to 101 mM, and the temperature was varied from -80.0 to -30.0 °C. For reactions 2 and 3, all data were collected with the Re complex in at least a 9-fold excess and were analyzed as pseudo-first-order. In each of these cases, the order was verified by a linear dependence of the pseudo-first-order rate constant on the concentration of the Re complex.

Results and Calculations

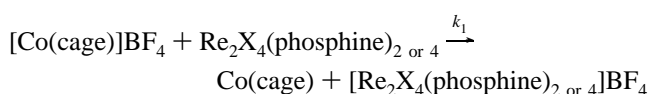
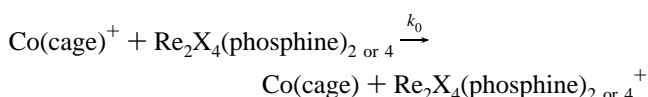
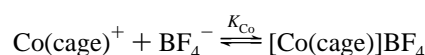
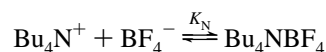
The thermodynamic parameters ΔH° and ΔS° were calculated from plots of $\Delta E_{1/2}$ *vs* T using eq 6, and the equilibrium constant at any temperature was calculated using eq 7, where R is the

$$\Delta E_{1/2} = E_{1/2}(\text{Co}) - E_{1/2}(\text{Re}) = -(\Delta H_{\text{rxn}}^\circ + T\Delta S_{\text{rxn}}^\circ)/nF \quad (6)$$

$$K_{\text{rxn}} = \exp(nF\Delta E_{1/2}/RT) \quad (7)$$

gas constant, T is the absolute temperature, F is the Faraday constant, and n is 1. The electrochemical results for all reactions are listed in Table 1.

For all reactions, the second-order rate constants measured at a single temperature varied with the initial concentration of the Co complex as well as with added salt. It is expected that ion-pairing will influence the rate constant for the cross reaction, but unlike studies in more polar solvents,² no condition can be chosen under which only ion-free or ion-paired reactants are involved. A further complication is that the added salt must be undergoing ion association as well as the cationic Co reactant and the cationic Re product.



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Table 1. Equilibrium Parameters^a

	$\Delta H_{\text{rxn}}^\circ, ^b$ kcal/mol	$\Delta S_{\text{rxn}}^\circ, ^b$ cal/(mol K)	$K_{\text{rxn}}, \text{M}^{-1}$ (298 K)	$\Delta H_{\text{Co}^\circ}, \text{kcal/mol}$	$\Delta S_{\text{Co}^\circ}, \text{cal/(mol K)}$	$K_{\text{Co}}, \text{M}^{-1}$ (298 K)
reaction 1	-3.4	7.6	1.4×10^3	7.5 ± 0.9	47.2 ± 4.3	6.5×10^4
reaction 2	2.8	17.4	58	9.9 ± 0.3	69.6 ± 1.3	8.9×10^7
reaction 3	1.4	17.9	7.1×10^2	9.1 ± 0.3	66.7 ± 1.2	8.0×10^7
reaction 4 ^{c,d}	-7.3	3.5	1.2×10^6	7.4 ± 1.8	53.7 ± 8.6	2.1×10^6
reaction 5 ^{c,d}	-5.9	3.2	1.2×10^5	7.4 ± 1.8	53.7 ± 8.6	2.1×10^6

^a For all reactions, $\Delta H_{\text{N}}^\circ = 11.7 \pm 3.3$ kcal/mol, $\Delta S_{\text{N}}^\circ = 76.9 \pm 15.7$ cal/(mol K), and $K_{\text{N}}(298 \text{ K}) = 1.7 \times 10^8 \text{ M}^{-1}$. ^b Errors in $\Delta H_{\text{rxn}}^\circ$ are ± 0.3 kcal/mol and errors in $\Delta S_{\text{rxn}}^\circ$ are ± 1.3 cal/(mol K) and are both calculated from an error in $\Delta E_{1/2}$ of ± 3 mV. ^c Ion-pairing parameters for reactions 4 and 5 were obtained from a simultaneous fit to both reactions. ^d Taken from ref 1.

The following equations for the rate constant of the cross reaction were obtained from the mechanism, where k is the observed second-order rate constant, $[\text{Bu}_4\text{NBF}_4]_{\text{tot}}$ is the total amount of added salt, $[\text{Co}(\text{cage})\text{BF}_4]_{\text{tot}}$ is the total amount of the respective Co complex added, $[\text{BF}_4^-]_{\text{free}}$ is the concentration of free tetrafluoroborate ion in solution, k_{B} is the Boltzmann constant, and h is Planck's constant. Enthalpy and entropy of ion-pairing (degree sign) and activation (superscript ‡) are represented by ΔH and ΔS with subscripts which match the mechanism above.

$$k = (k_0 + k_1 K_{\text{Co}} [\text{BF}_4^-]_{\text{free}}) / (1 + K_{\text{Co}} [\text{BF}_4^-]_{\text{free}})$$

$$K_{\text{N}} = \exp(-(\Delta H_{\text{N}}^\circ - T\Delta S_{\text{N}}^\circ)/RT)$$

$$K_{\text{Co}} = \exp(-(\Delta H_{\text{Co}^\circ} - T\Delta S_{\text{Co}^\circ})/RT)$$

$$k_0 = (k_{\text{B}}T/h) \exp(-(\Delta H_0^\ddagger - T\Delta S_0^\ddagger)/RT)$$

$$k_1 = (k_{\text{B}}T/h) \exp(-(\Delta H_1^\ddagger - T\Delta S_1^\ddagger)/RT)$$

$$\begin{aligned} [\text{BF}_4^-]_{\text{tot}} &= [\text{Bu}_4\text{NBF}_4]_{\text{tot}} + [\text{Co}(\text{cage})\text{BF}_4]_{\text{tot}} \\ &= [\text{BF}_4^-]_{\text{free}} \{ 1 + ([\text{Co}(\text{cage})\text{BF}_4]_{\text{tot}} K_{\text{Co}} / (1 + K_{\text{Co}} [\text{BF}_4^-]_{\text{free}})) + ([\text{Bu}_4\text{NBF}_4]_{\text{tot}} K_{\text{N}} / (1 + K_{\text{N}} [\text{BF}_4^-]_{\text{free}})) \} \end{aligned}$$

In the data analysis for reaction 1, initial estimates of $\Delta H_{\text{Co}^\circ}$, $\Delta S_{\text{Co}^\circ}$, $\Delta H_{\text{N}}^\circ$, and $\Delta S_{\text{N}}^\circ$ were taken from ref 1. The entire data set was then fit with these parameters held fixed, in order to arrive at estimates for the values of ΔH_0^\ddagger , ΔS_0^\ddagger , ΔH_1^\ddagger , and ΔS_1^\ddagger . The entire data set was then fit simultaneously while all eight parameters were allowed to vary. In the final fit, the best fit values of $\Delta H_{\text{N}}^\circ$ and $\Delta S_{\text{N}}^\circ$ did not change significantly from those reported previously¹ and were fixed in the final fit of the data to the other six parameters. Figure S1 (Supporting Information) is a plot of calculated *vs* observed rate constants which includes all data points. The data for reactions 2 and 3 were analyzed similarly, except that initial estimates of $\Delta H_{\text{Co}^\circ}$ and $\Delta S_{\text{Co}^\circ}$ were developed as follows. For reaction 3 the data were analyzed by fitting individual salt dependences at a series of temperatures and temperature dependences at a series of added salt concentrations to obtain reasonable estimates for $\Delta H_{\text{Co}^\circ}$, $\Delta S_{\text{Co}^\circ}$, ΔH_0^\ddagger , ΔS_0^\ddagger , ΔH_1^\ddagger , and ΔS_1^\ddagger . Estimates for the entropy and enthalpy of the ion-pairing of the Bu_4NBF_4 were made as in the analysis of reaction 1. The entire data set was then fit simultaneously with all parameters allowed to vary. $\Delta H_{\text{N}}^\circ$ and $\Delta S_{\text{N}}^\circ$ remained unchanged and so were fixed in the final fit. Figures 1 and 2 show plots of calculated *vs* observed rate constants for reaction 3. Figure 3 shows the dependence of the observed rate constant on added Bu_4NBF_4 at three different temperatures, and Figure 4 shows Eyring plots for three different concentrations of Bu_4NBF_4 . The best fit lines in Figures 3 and 4 are based on the parameters resulting from the fit to all the points. Reaction 2 was modeled in the same manner

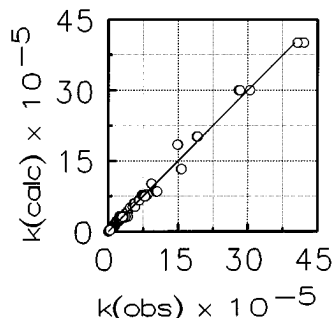


Figure 1. Calculated *vs* observed rate constants for 337 observations of reaction 3 under 118 different conditions. The line is based on the parameters in Table 2.

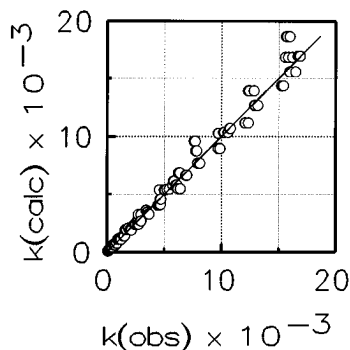


Figure 2. The lowest 189 of 337 total calculated *vs* observed rate constants for reaction 3.

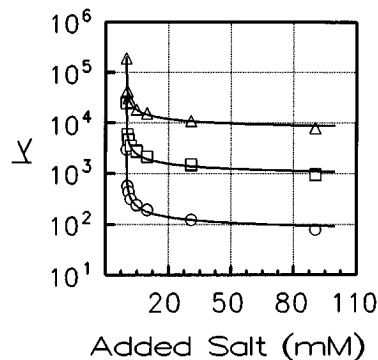


Figure 3. Dependence of the rate constant of reaction 3 on added Bu_4NBF_4 at -80 °C (○), -60 °C (□), and -40 °C (△). $[\text{Co}(\text{dmg})_3(\text{BF}_2)_2\text{BF}_4]$ concentration was 0.0237 mM and $\beta\text{-Re}_2\text{Cl}_4(\text{dppee})_2$ concentration was 0.252 mM for all points shown. The lines are based on the parameters in Table 2.

using the values of $\Delta H_{\text{Co}^\circ}$ and $\Delta S_{\text{Co}^\circ}$ from reaction 3 as initial estimates and then proceeding with the fit with all parameters allowed to vary. As in the case of reactions 3 and 1, $\Delta H_{\text{N}}^\circ$ and $\Delta S_{\text{N}}^\circ$ did not change when allowed to vary and were fixed in the final fit. Figures S2 and S3 (Supporting Information) are plots of the calculated *vs* observed rate constants. The equilibrium parameters resulting from the fits to each reaction are listed in Table 1, and the activation parameters for all the

Table 2. Fit Parameters from the Kinetic Data

	ΔH_0^\ddagger , kcal/mol	ΔS_0^\ddagger , cal/(mol K)	k_0 , $M^{-1} s^{-1}$ (298 K)	ΔH_1^\ddagger , kcal/mol	ΔS_1^\ddagger , cal/(mol K)	k_1 , $M^{-1} s^{-1}$ (298 K)	k_0/k_1
reaction 1	6.2 ± 0.1	-0.6 ± 0.6	1×10^8	6.2 ± 0.2	-2.4 ± 1.1	5×10^7	2
reaction 2	13.1 ± 0.2	24.2 ± 1.0	3×10^8	10.0 ± 0.2	0.8 ± 0.7	4×10^5	750
reaction 3	12.4 ± 0.2	22.8 ± 0.9	5×10^8	10.1 ± 0.2	2.4 ± 0.8	8×10^5	625
reaction 4 ^a	5.0 ± 0.2	-3.7 ± 1.1	2×10^8	4.9 ± 0.3	-6.4 ± 1.4	6×10^7	3
reaction 5 ^a	5.6 ± 0.2	-2.6 ± 1.1	1×10^8	5.5 ± 0.7	-5.8 ± 3.2	3×10^7	3

^a Taken from ref 1.

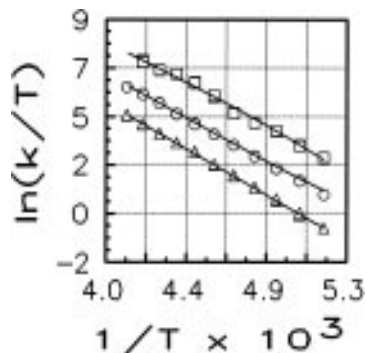


Figure 4. Eyring plots for reaction 3 at no added Bu_4NBF_4 (\square), 0.49 mM added Bu_4NBF_4 (\circ), and 31.0 mM added Bu_4NBF_4 (\triangle). The reactant concentrations are the same as in Figure 4. The lines are based on the parameters in Table 2.

reactions are listed in Table 2. The equations used do not employ activity coefficients. One reason is that they are particularly difficult to estimate in such low dielectric solvents. A further reason is that the ionic strength of the solutions does not vary as much as does the added salt concentration. On the basis of the fit parameters, the highest ionic strength was obtained at the lowest temperatures. In the presence of 0.10 M Bu_4NBF_4 , the ionic strengths were *ca.* 6 mM at $-75^\circ C$ and 30 μM at $25^\circ C$.

In the previous study of the oxidation of the mononuclear rhenium complexes (see reactions 4 and 5), an attempt was made to calculate the approximate inherent electron transfer reactivity of the Re complexes using the Marcus theory. This gave a result of *ca.* $10^8 M^{-1} s^{-1}$ for the electron self-exchange rate constant. This was highly approximate since only the apparent self-exchange value of the cobalt complex was known and this was calculated using the cross reaction with ferrocene. The ferrocene self-exchange was directly measured but only under conditions for which ion-paired reactants probably predominate.¹⁴ These difficulties are compounded in this study by the fact that changing the structure of the cobalt complex slightly has a dramatic effect on the k_0/k_1 value. These uncertainties force us to refrain from calculation of apparent self-exchange values.

Discussion

This study has provided the first detailed investigation of the homogeneous electron transfer reactivity of metal–metal-bonded complexes. The reactivity observed is high, and comparable to the reactivity of the mononuclear rhenium complexes studied previously,¹ but only when the ion-free path is resolved. The high reactivity is expected because of the low inner-sphere reorganization energy which accompanies electron transfer to or from a δ^* orbital.³ The most surprising result of this work is the observation that some cases show a very large and unprecedented effect of added salt on bimolecular electron transfer reactivity. Through extensive temperature and salt dependence studies this effect has been carefully characterized

and modeled as the result of differential reactivity between a cationic reactant and an ion-paired cationic reactant.

Before any attempt to discuss the origin of the effect is made, it is important to establish that the model used adequately represents the data. The ion-pairing model is a simple one but still results in eight parameters when the temperature dependence of the rate constant and ion-pairing equilibrium parameters are considered. The basic observation that the data fit the model well over the full range of experimental conditions establishes the rate law for each case. The ion-pairing parameters of the cations involved were established separately for each reaction, and the values displayed in Table 1 demonstrate excellent agreement for the same cation, within the precision of the experiments. The ion-pairing equilibrium parameters for the added salt, Bu_4NBF_4 , were established from the study of reactions 4 and 5,¹ and found to be consistent with the data taken for reactions 1–3. The activation parameters for the rate constants in each case are necessarily independent and are well-defined, as shown in Table 2.

The ion-pairing parameters of the three cations show a distinct trend with size. All enthalpies of ion-pairing are positive, but the smallest cation, Bu_4N^+ , has the greatest ΔH° at 12 kcal/mol, while the next largest, $Co(dmg)_3(BF)_2^+$, has 9.5 kcal/mol and the largest, $Co(noX)_3(BBu)_2^+$, has 7.5 kcal/mol. The ΔS° values are all large, positive values, consistent with charge neutralization, and decrease in the same order that the enthalpies decrease, from 77, to 69, to 50 cal/(mol K). These values are consistent with a decreasing charge density with increasing size. Using 298 K as a conventional temperature for comparison, the free energy changes to form the ion pairs is -11.2 kcal/mol for Bu_4NBF_4 , -10.8 kcal/mol for $[Co(dmg)_3(BF)_2]BF_4$, and -7.6 kcal/mol (average from reaction 1 and reactions 4 and 5) for $[Co(noX)_3(BBu)_2]BF_4$. The parameters result in large ion-pairing association constants that decrease with increasing cation size and decreasing temperature.

The most significant difference among the five reactions is found by considering the k_0/k_1 ratio shown in Table 2. Reactions 1, 4, and 5 show inhibition by ion-pairing by only a factor of 2–3, and this ratio is temperature independent. Reactions 2 and 3 show an inhibition of *ca.* 700-fold at 298 K, which is the largest effect we have ever observed. This cannot be attributed to activity effects since these are primarily determined by the concentration of the added Bu_4NBF_4 and thus consistent in all cases. In reactions 2 and 3, there is a 2–3 kcal/mol decrease in the ΔH^\ddagger on going from the free-ion to the ion-paired path, but this is offset by 20–23 cal/(mol K) decrease in the activation entropy. For these two reactions the k_0/k_1 ratio is temperature dependent, decreasing to *ca.* 70 at $-75^\circ C$. When all of the activation parameters in Table 2 are considered, reactions 2 and 3 stand out by their higher ΔH^\ddagger for both paths and the compensating high ΔS^\ddagger for the ion-free path only. Thus the activation parameters and not just the rate constants show that reactions 2 and 3 are significantly different from reactions 1, 4, and 5.

Possible origins of the observed differences in reactivity can now be considered. Reactions 2 and 3 differ from reactions 1, 4, and 5 in several respects. The primary difference is that in

(14) Yang, E. S.; Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1980**, *84*, 3094–9.

reactions 2 and 3 the oxidant is $\text{Co}(\text{dmg})_3(\text{BF})_2^+$ while in the other reactions the oxidant is $\text{Co}(\text{nox})_3(\text{BBu})_2^+$. They also differ in the driving force for the reaction. Whereas reactions 2 and 3 are thermodynamically favored by 95 and 163 mV (0.10 M Bu_4NBF_4 , 298 K), reactions 1, 4, and 5 have driving forces of 244, 354, and 300 mV. From Table 1 we can see that reactions 2 and 3 have small, positive enthalpies of reaction, and large positive entropies of reaction whereas reactions 1, 4, and 5 have larger, negative enthalpies of reaction and smaller, positive entropies of reaction. Unfortunately, these parameters cannot be evaluated without added electrolyte.

The inhibition of electron transfer rate constants by added salt has previously been attributed to interference, by the counterion, with the formation of the transition state. To the extent that it is thermodynamically unfavorable to form a product in which the anion is greatly separated from the newly formed cation, a transition state in which both reactants and the counterion are mutually tangential, or can rapidly become so after precursor complex formation, is envisioned. This blocking of part of the surface of the ionic reactant limits the number of possible transition states and limits the freedom of the two reactants to reorganize. This should lead to inhibition, but certainly not the factor of several hundred observed in reactions 2 and 3. We have interpreted our extensive previous results on cobalt clathrochelates reacting with ferrocenes and with each other, primarily in solvents of moderate dielectric constant, such as acetonitrile, using this triangular transition state model.² In those reactions the ion pair reacts *ca.* 5-fold more slowly. The largest effects previously observed were factors of 19 in nitrobenzene and 9 in 1,2-dichloroethane. The origin of the much larger effect observed here must be sought elsewhere.

One possibility is that the ion-pairing greatly affects the driving force of the reaction. We have established the reduction potentials of the reactants only in the presence of 0.10 M Bu_4NBF_4 , and our electrochemical techniques do not allow us to work at concentrations of added salt below 10 mM, where the complexes will not be fully ion-paired. However, the driving force for the reaction in the absence of ion-pairing can be evaluated from the data when the cations are ion-paired and the ion-pairing constants. The driving force will change with ion-pairing, only if the ion-pairing constant for the cationic rhenium product is much different from that of the cationic cobalt clathrochelate. Assuming the large rhenium complexes all have similar ion-pairing constants and that these are smaller than the ion-pairing constants of the smaller clathrochelates, there would be less driving force for the electron transfer process, the higher the ion-pairing association constant with the cobalt oxidant. To the extent that the reaction is inhibited more for the smaller $\text{Co}(\text{dmg})_3(\text{BF})_2^+$, this prediction is the observed direction. However, according to Marcus' theory, a difference in K_{eq} of a factor of 700² is required to reduce the rate constant for the cross reaction by a factor of 700. This is a difference of *ca.* 8 kcal/mol in the difference in the free energy of ion-pairing between the Co and Re complexes, and thus beyond any effect we can expect. Thus, this factor may contribute but is not the entire explanation.

A more interesting interpretation can be found in the work of Piotrowiak on intramolecular electron transfer accompanied by cation transfer in some systems involving electron transfer between organic radical anions and neutral organic acceptors linked by a bridge.^{15,16} The authors concluded that the electron transfer process proceeds by a rate-controlling step involving motion of the cation, the counterion in their case, rather than

the more common case of inner-sphere reorganization and outer-sphere (solvent) reorganization. In the proposed situation, the precursor complex is not the triangular form but has the counterion in contact with only the ionic center. Electron transfer is effectively prevented because it would lead to a high-energy product in which charge separation, between the counterion and the anionic center of the product separated by the length of the bridge, has been caused. Electron transfer takes place instead when the counterion moves to a position between the ionic center of the reactant and the nascent ionic site of the product. For reactions in which electron transfer is rapid in the absence of the counterion, and this motion is slow, the counterion motion becomes rate controlling. This leads to observed inhibition by ion-pairing by as much as a factor of 2000 in the systems studied by Piotrowiak *et al.*^{15,16} As a diagnostic criterion, they observed that it was the relative free energies of the electron transfer process and the ion association process, not just the absolute free energy of the ion association process, that determined whether counterion motion was rate controlling. Although our systems are bimolecular, in a different solvent, involve reactants and counterions of opposite charge types, and differ structurally, our result is qualitatively in accord with the Piotrowiak study in that the large effect of ion-pairing is observed for the reactions with the strongest ion pair and the lowest driving force. Reactions with $\text{Co}(\text{nox})_3(\text{BBu})_2^+$ involve ion-pairing free energies ($\Delta G_{\text{Co}^\circ}$) at 298 K of *ca.* -7.6 kcal/mol while for $\text{Co}(\text{dmg})_3(\text{BF})_2^+$ it is -10.8 kcal/mol. At the same temperature the free energies of reaction ($\Delta G_{\text{rxn}^\circ}$) are -5.7 to -8.3 kcal/mol for the $\text{Co}(\text{nox})_3(\text{BBu})_2^+$ and -2.4 to -3.9 kcal/mol for $\text{Co}(\text{dmg})_3(\text{BF})_2^+$. Thus the difference between reaction free energy and the ion-pairing free energy ($\Delta G_{\text{rxn}^\circ} - \Delta G_{\text{Co}^\circ}$) is 0.3–1.8 kcal/mol for the reactions of $\text{Co}(\text{nox})_3(\text{BBu})_2^+$ but 6.9–8.5 kcal/mol for the $\text{Co}(\text{dmg})_3(\text{BF})_2^+$ reactions. Furthermore, as temperature decreases, the difference between the ion-pairing energy and the free energy of reaction changes for all systems, reaching +2.0 to -2.6 kcal/mol at -75 °C for reactions 2 and 3 and -3.1 to -4.8 kcal/mol for the other reactions. The k_0/k_1 ratio is invariant for reactions 1, 4, and 5 but decreases markedly with temperature for reactions 2 and 3. This directly parallels the change of the difference in free energies cited above. Furthermore, results of a less exhaustive study from our laboratory on the salt dependence of cross reactions between the cobalt clathrochelates and ferrocene or decamethylferrocene in methylene chloride also appear to follow these trends.

A major question remains concerning the minimum requirements for the switch over to rate-controlling counterion motion. Clearly there must be low inner-sphere reorganization energy and low solvent reorganization energy; otherwise, the electron transfer process will always be slower than the counterion dynamics. The interaction with the counterion must be strong, and this must be accompanied by relatively slow movement of the counterion in the precursor complex. This follows from a potential energy surface with deep Coulombic wells, brought on by the low dielectric solvent. Most critical to observation of this effect in bimolecular chemistry, however, may be the preferential formation of a precursor complex in which electron transfer, without counterion motion, is endoergic or otherwise forced to be slower than the alternative. This is designed into the organic intramolecular electron transfer systems in which the donor and acceptor are held apart by a long bridge. For a bimolecular system, the strong ionic interactions brought on by the low dielectric solvent will favor certain precursor geometries. It is unlikely that the optimal position for the anion associated with the cationic reactant, the optimal position for the anion

(15) Piotrowiak, P. *Inorg. Chim. Acta* **1994**, 225, 269–74.

(16) Piotrowiak, P.; Miller, J. R. *J. Phys. Chem.* **1993**, 97, 13052–60.

associated with the cationic product, and the relative distance and orientation of the two metal centers required to produce adequate orbital overlap for the electron transfer all can be accommodated in a single configuration. If the preferred structure is significantly different from the triangular arrangement proposed previously to explain slight inhibition, then some motion of the counterion must be coupled with the electron transfer and can be rate controlling.

Conclusion

In conclusion, we have investigated the bimolecular, outer-sphere oxidation of three neutral dirhenium complexes of halides and phosphines by cobalt clathrochelates with a +1 charge in methylene chloride. The dirhenium complexes show consistent, high intrinsic reactivity, comparable to the reactivity of related mononuclear complexes. The most surprising result is a large difference in the effect of added salt on the reactions. This led us to a detailed investigation of the temperature dependence of the added salt dependence for all three reactions. The results could be well modeled by simple ion-pairing of the cationic reactants and the added electrolyte and different reactivities of the ion-paired and free ions. The reactions studied here and previously involving $\text{Co}(\text{nox})_3(\text{BBu})_2^+$ showed only slight inhibition by ion-pair formation, whereas the reactions of $\text{Co}(\text{dmg})_3(\text{BF})_2^+$ showed the most pronounced effect we have ever

observed, *ca.* 700-fold at 298 K. We have concluded that the effect is due to a change in the rate-controlling step from one of typical inner-sphere and outer-sphere reorganization to one of anion migration and is only observed when the magnitude of ion-pairing free energy is significantly greater than the magnitude of the free energy change for the electron transfer process. Such a process has precedent in the intramolecular electron transfer studies of Piotrowiak and co-workers,^{15,16} but not in other bimolecular or organometallic systems. Further studies must establish whether this is a more general phenomenon through the study of reactions involving other reactants, different counterions, and other solvents. Self-exchange studies would be especially valuable. Development of methods to measure the electrochemical parameters in the absence of added electrolyte are being sought in order to evaluate the driving force for the electron transfer process in the absence of ion-pairing.

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Supporting Information Available: Tables listing all reaction conditions, rate constants, and electrochemical results as well as figures showing plots of calculated *vs* observed rate constants for reactions 1 and 2 (29 pages). Ordering information is given on any current masthead page.

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