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# Outer-sphere electron transfer in methylene chloride: concentration, salt, and temperature dependences of the oxidation of trans-ReX<sub>2</sub>(cis-1,2 bis(diphenylphosphino)ethylene)<sub>2</sub> (X = Cl, Br) by the clathrochelate [Co(1,2-cyclohexanedionedioximate)<sub>3</sub>(BButyl)<sub>2</sub>]BF<sub>4</sub><sup>-1</sup>

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## Abstract

The oxidation of  $\text{ReCl}_2(cis-1,2 \text{ bis}(\text{diphenylphosphino})\text{ethylene})_2$  and  $\text{ReBr}_2(cis-1,2 \text{ bis}(\text{diphenylphosphino})\text{ethylene})_2$  by the clathrochelate  $[\text{Co}(1,2\text{-cyclohexanedione dioximate})_3(\text{BButyl})_2]\text{BF}_4$  have been studied by the stopped-flow method as a function of temperature (-85 to -50°C), added Bu<sub>4</sub>NBF<sub>4</sub> (0-0.1 M), and reactant concentration in methylene chloride. The rate constants were fit to a mechanism involving separate paths for the free ion and the ion paired Co(III) oxidant. The result was the enthalpy and entropy of ion pairing for both Bu<sub>4</sub>NBF<sub>4</sub> and the oxidant, and the enthalpy and entropy of activation for both the free ion path and the ion paired path for each reaction. This study makes this one of the best characterized outer-sphere electron transfer reactions occurring in the low dielectric constant solvent methylene chloride. The results will allow comparison of the reactivity of these mononuclear complexes with that of metal-metal bonded dirhenium complexes. Using the temperature dependences of the reduction potentials of the Re and Co complexes as well as decamethylferrocene, and the kinetics of the reduction of the Co(III) complex by decamethylferrocene in methylene chloride, also as a function of added salt, estimates of the high electron self-exchange rate constants of the two Re complexes have been made. They are both very similar and are ca.  $10^8 \text{ M}^{-1} \text{ s}^{-1} \text{ at } 25^\circ\text{C}$ .

Keywords: Election transfer; Outer-sphere; Ion pair; Activation parameters; Rhenium complex; Bidentate phosphine complex

## 1. Introduction

This paper presents a study of the thermodynamics and kinetics of the oxidation of the *trans*-ReX<sub>2</sub>(dppee)<sub>2</sub> (X is Cl or Br, dppee is *cis*-1,2 bis(diphenylphosphino)ethylene) by a Co(III) clathrochelate with three chelating dioxime ligands capped by a butyl borate at each end,  $[Co(nox)_3(BButyl)_2]BF_4$  (nox is 1,2-cyclohexanedione dioximate), in methylene chloride. The current study is an extension of our previous investigations of non-aqueous outer-sphere electron transfer [1] and forms a reference point, involving mononuclear Re complexes, for a major study of the electron transfer reactivity of dirhenium and other metal-metal bonded systems. Both the mononuclear and dinuclear Re compounds typically have at least two

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oxidation states formed by reversible electron transfer. The compounds with Re–Re multiple bonds are particularly appealing because they form a large class of compounds that has been extensively studied in regard to molecular and electronic structures, spectroscopic properties, and electrochemical properties [2,3].

 $trans-\text{ReCl}_2(\text{dppee})_2 + \text{Co}(\text{nox})_3(\text{BButyl})_2^+ \rightleftharpoons$ 

 $trans-\text{ReCl}_2(\text{dppee})_2^+ + \text{Co}(\text{nox})_3(\text{BButyl})_2$  (1)

 $trans-\text{ReBr}_2(\text{dppee})_2 + \text{Co}(\text{nox})_3(\text{BButyl})_2^+ \Rightarrow$ 

 $trans-\text{ReBr}_2(\text{dppee})_2^+ + \text{Co}(\text{nox})_3(\text{BButyl})_2$  (2)

The use of methylene chloride as a solvent is dictated by the solubility of the neutral Re complexes and the need to work at low temperatures (-85 to  $-50^{\circ}$ C) in order to observe the reaction by the stopped-flow method. The cobalt

<sup>&</sup>lt;sup>1</sup> Dedicated to Harry Gray on the occasion of his 60th birthday.

clathrochelate is used because it is substitution inert in both oxidation states, has a similar electrochemical potential to the Re complexes, has adequate solubility in methylene chloride, gives a large absorbance change on reduction, has a rather low electron self-exchange reactivity thus leading to cross reactions that are slow enough to be observable, and has been extensively studied in our laboratory [4–8].

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 influence of ion pairing on the rate constants through 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<sub>4</sub>NBF<sub>4</sub> 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 (versus ferrocene) as a function of temperature allows the calculation of the equilibrium constant of the electron transfer reaction and its temperature dependence.

## 2. Experimental

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 P2O5 and stored under Ar prior to use. Ferrocene and decamethylferrocene were purified by sublimation. Bu<sub>4</sub>NBF<sub>4</sub> was prepared [9] from Bu<sub>4</sub>NBr and HBF<sub>4</sub>(aq), but was found to have unacceptable levels of Br-. Purification was performed by stirring the solid overnight in water, followed by thorough drying under vacuum, then two recrystallizations from ethyl acetate/pentane. It was then dissolved in ethyl acetate, an equal amount of water was added to from a two phase mixture, the mixture was rotary evaporated to 2/3 of its original volume, and the solid was collected by filtration and dried under vacuum. [Co(nox)<sub>3</sub>(BButyl)<sub>2</sub>]BF<sub>4</sub> [7,10], and trans-ReCl<sub>2</sub>(dppee)<sub>2</sub> and trans-ReBr<sub>2</sub>(dppee)<sub>2</sub> [11] were prepared by literature methods.

The reduction potentials were measured by Osteryoung square wave voltammetry and cyclic voltammetry using 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 versus the bath temperature with a copper-constantan thermocouple over the range of the experimental measurements. The  $E_{1/2}$  values for all of the complexes were measured in triplicate in methylene chloride with 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> as the supporting electrolyte, versus an internal standard of ferrocene. Potentials were measured over a temperature range of -30 to +25 °C with a Ag or a Ag 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  $(\varepsilon_{470} = 6399 \text{ M}^{-1} \text{ cm}^{-1})$ . 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 non-linear least squares techniques using programs written in QuickBasic based on the routines of Bevington [12]. The data for reaction (2) were fit to a pseudo-first order rate law and the data for reaction (1) were fit to a second order rate law with unequal concentrations [13]. Based on the high equilibrium constants of the reactions, they did not need to be treated as reversible. The dependence of the second order rate constants on reactant concentration, temperature, and the concentration of added Bu<sub>4</sub>NBF<sub>4</sub> were analyzed as described below using the Scientist mathematical modeling package.

Reactions (1) and (2) were both found to be quite rapid, thus low concentrations and low temperatures were required. Rate constants were measured over as large a range of temperature and reactant concentration as possible. 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 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 64 different conditions to give 191 second-order rate constants. In all cases the Co complex was in excess. The order with respect to each reactant was established by the ability of the second order (first order in each reactant) rate law to fit the absorbance versus time traces. The conditions included  $[Co(nox)_3(BButyl)_2]BF_4$  concentration from 0.0228 to 0.123 mM, *trans*-ReCl<sub>2</sub>(dppee)<sub>2</sub> concentration from 0.00868 to 0.0118 mM, Bu<sub>4</sub>NBF<sub>4</sub> concentration from 0 to 80 mM, and temperature from -86 to -55°C.

For reaction (2), data were collected for 43 different conditions to give 156 second-order rate constants. The conditions included  $[Co(nox)_3(BButyl)_2]BF_4$  concentration from 0.00997 to 0.620 mM, *trans*-ReBr<sub>2</sub>(dppee)<sub>2</sub> concentration from 0.00544 to 0.0987 mM, Bu<sub>4</sub>NBF<sub>4</sub> concentration from 0 to 87 mM, and temperature from -85 to -50°C. Most reactions were studied with the Co complex in excess, but some reactions had the Re complex in excess to establish the rate law.

In addition to the two reactions central to this study, the cross reaction between  $[Co(nox)_3(BButyl)_2]BF_4$  and decamethylferrocene  $(Fe(cp^*)_2)$  was studied, under second-order conditions  $([Co(nox)_3(BButyl)_2]BF_4$  concentration 0.0379 mM,  $Fe(cp^*)_2$  concentration 0.107 mM), as a function of temperature at seven temperatures from -80 to  $-50^{\circ}$ C in methylene chloride with no added Bu<sub>4</sub>NBF<sub>4</sub>. In addition, a dependence on added salt at  $-50^{\circ}$ C was performed at nine salt concentrations over the range 0 to 108 mM Bu<sub>4</sub>NBF<sub>4</sub> ([Co(nox)<sub>3</sub>(BButyl)<sub>2</sub>]BF<sub>4</sub> concentration 0.0467 mM, Fe(cp<sup>\*</sup>)<sub>2</sub> concentration 1.21 mM). Electrochemical data were also obtained for Fe(cp<sup>\*</sup>)<sub>2</sub> in order to calculate the temperature dependent equilibrium parameters.

Supplementary tables (13 pages) listing all reaction conditions and the rate constants obtained, as well as the electrochemical results, were available to the reviewers and are available from the authors.

# 3. Results and calculations

The thermodynamic parameters  $\Delta H^0$  and  $\Delta S^0$  were calculated from plots of  $\Delta E_{1/2}$  versus T using Eq. (3) and the equilibrium constant at any temperature was calculated using Eq. (4), where R is the gas constant, T is the absolute temperature, F is the Faraday constant and n is 1.

$$\Delta E_{1/2} = E_{1/2}(\text{Co}) - E_{1/2}(\text{Re}) = -(\Delta H_{\text{rxn}}^0 + T\Delta S_{\text{rxn}}^0)/nF \quad (3)$$

$$K_{\rm rxn} = \exp(n\Delta E_{1/2}/RT) \tag{4}$$

The results are a  $\Delta H_{rxn}^0$  of -7.3 kcal mol<sup>-1</sup> and  $\Delta S_{rxn}^0$  of 3.5 cal (mol-K)<sup>-1</sup> for reaction (1),  $\Delta H_{rxn}^0$  of -5.9 kcal mol<sup>-1</sup> and  $\Delta S_{rxn}^0$  of 3.2 cal (mol-K)<sup>-1</sup> for reaction (2). The equilibrium constant at 298 K is  $1.2 \times 10^6$  M<sup>-1</sup> for reaction (1) and  $1.2 \times 10^5$  M<sup>-1</sup> for reaction (2). The values of  $E_{1/2}$  (298 K, 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>, methylene chloride, versus ferrocene) are -679, -620 and -320 mV (all ±2 mV) for *trans*-ReCl<sub>2</sub>(dppee)<sub>2</sub>, *trans*-ReBr<sub>2</sub>(dppee)<sub>2</sub>, and [Co(nox)<sub>3</sub>-(BButyl)<sub>2</sub>]BF<sub>4</sub>, respectively.

For both reactions, the second-order rate constants measured at a single temperature varied with the initial concentration of the  $[Co(nox)_3(BButyl)_2]BF_4$  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 [1], 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.

$$\operatorname{Bu}_4\mathrm{N}^+ + \operatorname{BF}_4^- \stackrel{K_{\mathrm{N}}}{\rightleftharpoons} \operatorname{Bu}_4\mathrm{NBF}_4$$

$$\operatorname{Co}(\operatorname{nox})_3(\operatorname{BButyl})_2^+ + \operatorname{BF}_4^- \rightleftharpoons [\operatorname{Co}(\operatorname{nox})_3(\operatorname{BButyl})_2]\operatorname{BF}_4$$

 $Co(nox)_3(BButyl)_2^+ + ReX_2(dppee)_2 \xrightarrow{k_0}$ 

 $Co(nox)_3(BButyl)_2 + ReX_2(dppee)_2^+$ 

$$[Co(nox)_{3}(BButyl)_{2}]BF_{4} + ReX_{2}(dppee)_{2} \xrightarrow{k_{1}} \\Co(nox)_{3}(BButyl)_{2} + ReX_{2}(dppee)_{2}BF_{4}$$

If the cationic Re product had a much different ion pairing equilibrium constant than the cationic Co reactant, the extent of ion pairing of the reactant would vary during the reaction and this would have to be considered in the fitting of the absorbance versus time data. There was no evidence that this was necessary. The following equations for the rate constant of the cross reaction were obtained from the mechanism, where k is the observed secondorder rate constant, [Bu<sub>4</sub>NBF<sub>4</sub>]<sub>tot</sub> and [Co(nox)<sub>3</sub>-(BButyl)<sub>2</sub>BF<sub>4</sub>]<sub>tot</sub> are the total amount of the respective electrolytes introduced into the solution, [BF4-]free is the concentration of free fluoroborate ion in solution,  $k_{\rm B}$  is the Boltzmann constant, and h is Planck's constant. Enthalpy and entropy of ion pairing (superscript 0) and activation (superscript  $\ddagger$ ) are represented by  $\Delta H$  and  $\Delta S$  with subscripts which match the mechanism above.

$$k = (k_0 + k_1 K_{Co} [BF_4^{-}])/(1 + K_{Co} [BF_4^{-}])$$

$$K_N = \exp(-(\Delta H_N^0 - T\Delta S_N^0)/RT)$$

$$K_{Co} = \exp(-(\Delta H_{Co}^0 - T\Delta S_{Co}^0)/RT)$$

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

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

$$[BF_4^{-}]_{tot} = [Bu_4 NBF_4]_{tot} + [Co(nox)_3 (BButyl)_2 BF_4]_{tot}$$

$$= [BF_4^{-}]_{free} \{1 + ([Co(nox)_3 (BButyl)_2 BF_4]_{tot} K_{Co}/RT)$$

$$= [BF_4]_{free} \{ I + ([Co(nox)_3(BButy])_2 BF_4]_{tot} K_{Co} / (1 + K_{Co}[BF_4^-]_{free})) + ([Bu_4 NBF_4]_{tot} K_N / (1 + K_N[BF_4^-]_{free})) \}$$

In the analysis of the data for reaction (1), estimates of the equilibrium and rate constants were obtained by fitting subsets of the data, particularly added salt dependences at a series of temperatures. The dependences on temperature of the rate and equilibrium constants obtained in this manner were then analyzed to give enthalpy and entropy of reaction, for the ion pairing, and activation, for the rate constants. These values were used as initial estimates in the final fitting of all of the data simultaneously to 8 parameters,  $\Delta H_{Co}^{0}$ ,  $\Delta S_{Co}^{0}$ ,  $\Delta H_{N}^{0}$ ,  $\Delta S_{N}^{0}$ ,  $\Delta H_0^{\ddagger}$ ,  $\Delta S_0^{\ddagger}$ ,  $\Delta H_1^{\ddagger}$ , and  $\Delta S_1^{\ddagger}$ . The results of this analysis are given in Table 1. Errors quoted are the standard deviations of the parameters as given by the Scientist program from the simultaneous 8 parameter fit. The rather high correlation between the parameters leads to high values of these error estimates. Much lower values are typically obtained when some of the parameters, such as the ion pairing constants, are held constant. Fig. 1 shows a plot of calculated versus observed rate constants as an indication of the scatter in the fit data. The standard deviation of the observed points about the fit line is  $1 \times 10^5$  $M^{-1}$  s<sup>-1</sup>. Fig. 2 shows the dependence on added Bu<sub>4</sub>NBF<sub>4</sub>



Fig. 1. Calculated versus observed rate constants for 191 observations of reaction (1) under 64 different conditions. The calculated rate constants are based on the parameters in Table 1.

at three different temperatures. Fig. 3 shows Eyring plots for data at three different concentrations of  $Bu_4NBF_4$ . The lines represent the fit to all of the points.

Reaction (2) was studied in a similar manner. Initial estimates of the ion pairing parameters were taken from the analysis of reaction (1), and initial estimates of the rate constants were taken from temperature dependences with no added salt and with the highest concentration of added salt. The data were then fit simultaneously holding the ion pairing parameters constant, then allowing them to vary. No significant change in the ion pairing parameters occurred, so the ion pairing constants are listed only once in Table 1 along with the rate constant parameters for each reaction. Fig. 4 shows a plot of the calculated versus the observed rate constants. The standard deviation of the data of the observed points about the fit line is  $7 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup>.

Apparent electron self-exchange rate constants for the Re complexes can be calculated from these data if a selfexchange value is known for the Co clathrochelate. However, only an apparent self-exchange value is known for



Fig. 2. Dependence of the rate constant for reaction (1) on added Bu<sub>4</sub>NBF<sub>4</sub> at -85°C ( $\diamondsuit$ ), -75°C ( $\triangle$ ), and -65°C ( $\square$ ). For all points shown the initial concentration of [Co(nox)<sub>3</sub>(BButyl)<sub>2</sub>]BF<sub>4</sub> was 2.51 × 10<sup>-5</sup> M and that of *trans*-ReCl<sub>2</sub>(dppce) was 1.15 × 10<sup>-5</sup> M. The lines are based on the parameters from Table 1.



Fig. 3. Dependence of the rate constant for reaction (1) on temperature at three concentrations of  $Bu_4NBF_4$ , no added salt ( $\Box$ ), 0.0099 M ( $\triangle$ ), and 0.075 M ( $\diamond$ ). The reactant concentrations are the same as in Fig. 2. The lines are based on the parameters in Table 1.

the cobalt complex, based on the cross reaction between  $[Co(nox)_3(BButyl)_2]BF_4$  and  $Fe(cp^*)_2$ . Furthermore, the self-exchange value for decamethylferrocene, although directly measured in methylene chloride, has not been resolved into free ion and ion paired contributions. The authors estimated that under their conditions, the Fe(cp)<sub>2</sub>+ ion was ca. 90% ion paired so  $Fe(cp^*)_2^+$  would also be extensively ion paired [14]. However, it is still worthwhile to make the approximate calculation as an indication of the inherent electron transfer reactivity of the Re complexes. The cross reaction between  $[Co(nox)_3 (BButyl)_2]BF_4$  and  $Fe(cp^*)_2$  with no added salt gave  $\Delta H^{\ddagger}$ of 4.77 kcal mol<sup>-1</sup> and  $\Delta S^{\ddagger}$  of -9.8 cal (mol-K)<sup>-1</sup>, which give a rate constant at 25°C of  $1.45 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>. The salt dependence of the cross reaction rate constant at -50°C was analyzed by the same ion pairing mechanism described above and using the value of  $K_N$  derived from  $\Delta H_N^0$  and  $\Delta S_N^0$ . The value of  $K_{C_0}$  was allowed to be fit by the data, and a value of  $1.2 \times 10^4 \text{ M}^{-1}$  was obtained, compared to a value of  $3.1 \times 10^4$  M<sup>-1</sup> at -50°C calculated from  $\Delta H_{\rm Co}^0$  and  $\Delta S_{\rm Co}^0$ . The relative values of  $k_0$  $(9.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})$  and  $k_1 (3.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})$ , at -50°C, reflect inhibition due to ion pairing by a factor of 3.2. Taking the apparent electron self-exchange of [Co(nox)<sub>3</sub>- $(BButyl)_2]BF_4$  as  $1.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 25°C (determined from the cross reaction rate constant with no added salt cited above, a self-exchange rate for  $Fe(cp^*)_2$  measured directly as  $4.4 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup> [14], and an equilibrium constant for the cross reaction of  $5.4 \times 10^3$  calculated from electrochemical data as described for the other cross reactions), and using the rate constants for the free ion path,  $k_0$ , and the equilibrium constant for the overall reaction, the approximate apparent electron self-exchange rate constant calculated from the Marcus cross reaction equation [15] for trans-ReCl<sub>2</sub>(dppee)<sub>2</sub> is  $1 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> and for trans-ReBr<sub>2</sub>(dppee)<sub>2</sub> is  $2 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>. Within the precision of these calculations, the two Re complexes have equal and quite high reactivity.

Table 1Fit parameters from the kinetic data

Rate constants <sup>a</sup>	$\Delta H_0^{\ddagger}$ (kcal mol <sup>-1</sup> )	$\Delta S_0^{\ddagger}$ (cal (mol-K) <sup>-1</sup> )	k <sub>0</sub> (M <sup>-1</sup> s <sup>-1</sup> ) (298 K)	$\Delta H_1^{\ddagger}$ (kcal mol <sup>-1</sup> )	$\frac{\Delta S_1^{\ddagger}}{(\text{cal (mol-K)}^{-1})}$	k <sub>1</sub> (M <sup>-1</sup> s <sup>-1</sup> ) (298 K)
Reaction (1) Reaction (2)	5.0 ± 0.2 5.6 ± 0.2	$-3.7 \pm 1.1$ -2.6 ± 1.1	$2 \times 10^8$ $1 \times 10^8$	4.9 ± 0.3 5.5 ± 0.7	$-6.4 \pm 1.4$ -5.8 ± 3.2	$6 \times 10^7$ $3 \times 10^7$
Equilibria <sup>b</sup>	ΔH <sub>N</sub> <sup>0</sup> (kcal mol <sup>-1</sup> )	ΔS <sub>N</sub> <sup>0</sup> (cal (mol-K) <sup>-1</sup> )	К <sub>N</sub> (М <sup>-1</sup> ) (298 К)	$\Delta H_{\rm Co}^{0}$ (kcal mol <sup>-1</sup> )	$\Delta S_{Co}^{0}$ (cal (mol-K) <sup>-1</sup> )	<i>К</i> <sub>Со</sub> (М <sup>-1</sup> ) (298 К)
Both Rxns	11.7 ± 3.3	76.9 ± 15.7	$1.7 \times 10^{8}$	7.4 ± 1.8	53.7 ± 8.6	$2.1 \times 10^{6}$

<sup>a</sup>Errors are standard deviations obtained from the 8 parameter fit to each reaction.

<sup>b</sup>Errors are standard deviations obtained from the 8 parameter fit to reaction (1).

### 4. Discussion

The principal result of this study is the extensive characterization of the electron transfer kinetics of the two reactions in the low dielectric constant solvent methylene chloride. Within the kinetic model used the data are well described by two ion pairing constants, one for the added salt Bu<sub>4</sub>NBF<sub>4</sub> and the other for the cationic reactant  $Co(nox)_3(BButyl)_2^+$  as well as rate constants for each of the Re complexes with the ion free and ion paired forms of the Co clathrochelate. The thermodynamic parameters obtained for the ion pair formation show high and positive enthalpies for the formation of the ion pair and high and positive entropies, indicating a large contribution from desolvation of the ions on forming the neutral ion pair. The Co clathrochelate shows lower enthalpy and entropy than the  $Bu_4N^+$  ion, as would be expected for a larger ion. The ion pairing inhibits the reaction in both of these cases, and for the reduction by  $Fe(cp^*)_2$  by a factor of ca. 3. Origins of this effect have been discussed [1] and include steric interference or steric limitations on precursor complex formation, and the contribution to the overall thermodynamics of the transfer of the counter ion from the cationic reactant to the cationic product. The ion pairing parameters for the salt and the Co complex should



Fig. 4. Calculated versus observed rate constants for 156 observations of reaction (2) under 43 different conditions. The calculated rate constants are based on the parameters in Table 1.

be transferable to other reactions of similar complexes reacting in methylene chloride. Care must be taken, however, in predicting the ratio of  $k_0/k_1$ . We have observed ratios greater than 10 with Co clathrochelates of somewhat different structure.

These studies form the basis for establishing the reactivity of mononuclear complexes of Re containing phosphines and halides. Even without converting the observed rate constants to self-exchange rate constants, it is clear that the two Re complexes are highly reactive in electron transfer and that they have quite similar activation parameters for both of the kinetic paths resolved through the added salt and  $[Co(nox)_3(BButyl)_2BF_4]_{tot}$  dependences. Reaction (1) has rate constants approximately double those of reaction (2), but reaction (1) also has an equilibrium constant about 10 times that of reaction (2), leading through the Marcus cross reaction correlation to an expectation that the cross reaction would be threefold faster even if the self-exchange parameters of the two Re complexes were identical. The approximate calculation of an apparent electron self-exchange rate constant leads to a prediction that the two complexes have virtually identical reactivity. There are no crystal structures available for complexes of the type [ReX<sub>2</sub>(dppee)<sub>2</sub>]BF<sub>4</sub> to allow comparison of the structures of the oxidized and reduced species, but we can expect that the structures will be quite similar, thus leading to the small inner-sphere reorganization energies that are necessary for such high electron transfer reactivity. In later publications we will compare these results to similar studies of multiply bonded dirhenium complexes with halide and phosphine ligands, in which the electron being transferred comes from an orbital involved in metal-metal bonding.

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