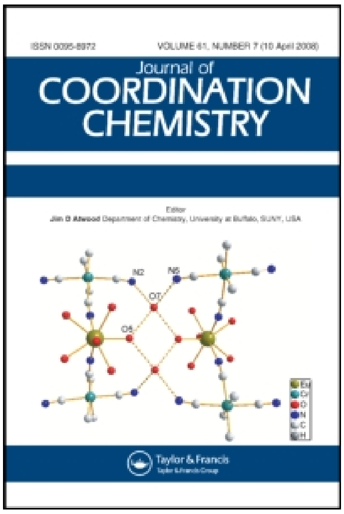

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE KINETICS OF ELECTRON TRANSFER FOR A SERIES OF IRON(II) CYCLIDENE COMPLEXES

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To cite this Article Kim, Soodan , Sauer-Masarwa, Alexandra , Warburton, P. Richard and Busch, Daryle H.(1996) 'THE KINETICS OF ELECTRON TRANSFER FOR A SERIES OF IRON(II) CYCLIDENE COMPLEXES', Journal of Coordination Chemistry, 37: 1, 237 — 255

To link to this Article: DOI: 10.1080/00958979608023556

URL: http://dx.doi.org/10.1080/00958979608023556

J. Coord. Chem., 1996, Vol 37, pp. 237–255
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THE KINETICS OF ELECTRON TRANSFER FOR A SERIES OF IRON(II) CYCLIDENE COMPLEXES

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(Received February 23, 1995; in final form January 24, 1995)

The kinetics of oxidation of a series of iron(II) cyclidene complexes by tris(1,10-phenanthroline)cobalt(III) in methanol have been measured by stopped flow spectrophotometry. The reactions obey a first order rate law when the cobalt(III) complex is present in large excess. The corresponding second order rate constants fall in the range 5.0–130 × 10^5 $M^{-1}s^{-1}$ (25°C). A linear correlation between the logarithm of the rate constant and the iron(III)/(II) redox potential indicates that the reactions behave as simple outer-sphere electron transfer processes. The self-exchange rate constants for the iron cyclidene complexes have been estimated from the Marcus equation and found to vary between 0.7 × 10^7 M^1s^1 and 9 × 10^7 M^1s^1. The dependence of the self-exchange rate constant on ligand structure is discussed.

KEYWORDS: electron transfer iron(II), cyclidene

INTRODUCTION

Electron transfer is of central importance to many branches of chemistry and biochemistry. Consequently there is much interest in understanding how the kinetics of electron transfer depend on molecular structure and experimental conditions. The key role of redox chemistry in the functions of the heme proteins in mitochondrial respiratory processes[1] has inspired many studies on redox and electron transfer processes, noteably those of cytochrome c[2] and simple iron macrocycle complexes.[3] The central importance of electron transfer in the chemistry of metal complexes further inspires study of the dependence of electron transfer on ligand enviroment including details of ligand structure. Outer-sphere electron transfer reactions constitute an important class of reactions amenable to theoretical study, as has been compellingly demonstrated by Marcus.[4] These considerations and indications that the autoxidation of hemoglobin, myoglobin, and their totally synthetic models, the iron(II) cyclidenes (Structure 1), involves outer sphere electron transfer[5] have led to the present investigations.

The iron(II) and cobalt(II) cyclidene complexes are totally synthetic macrocyclic complexes which have received much attention as functional mimics to the heme proteins. A desirable feature of the cyclidene complexes is the ease with which they

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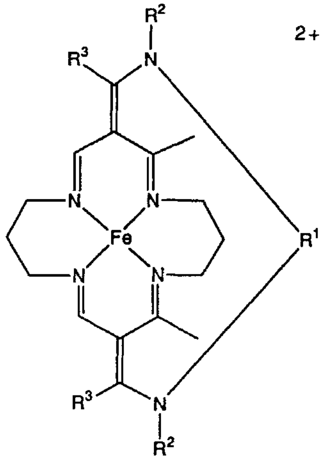

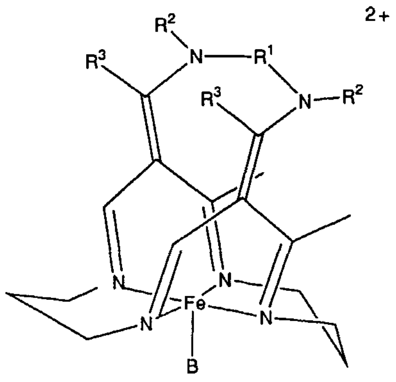

are derivatized, which facilitates systematic investigation of the effects of ligand substituents on physical and chemical properties. Planar and three dimensionals representations of a generalized metal cyclidene complex are shown in Structure 1. The ligand coordinates to the metal ion with its four co-planar nitrogen atoms; it has an intrinsic cavity, which provides a protected environment around one of the metal's remaining ligand binding sites, and the protected site is the location at which O_2 binds. The sixth binding site on the metal atom is usually occupied by a bulky nitrogen base such as pyridine or 1-methyl imidazole. For iron(II) complexes in methanol containing excess chloride, the iron is high spin and five-coordinate, with a chloride anion coordinated at the external axial site.

For simplicity, formulas based on the ligand substituents are used in this paper. The ligand is described by a sequence of substituent labels that are identified in Structure 1, followed by a number in brackets that indicates the ring size for the parent macrocycle, and then the abbreviation 'Cyc' for cyclidene. If there are substituents on the parent macrocycle, they are indicated inside the bracket, either before or after the number to distinguish between the side of the large opening into the lacuna (left of number) and the side of the small opening into the lacuna. Substituents on the parent macrocycle are limited to *gem*-dimethyl groups on the saturated chelate rings and they are denoted by DM, the three possibilities being [DM16], [16DM], and [DM16DM]. The metal is identified by its usual element symbol and its oxidation number appears as a superscripted Roman numeral. The general formula is $M^{\#}\{R^1R^2R^3[\#]Cyc\}^{n+}$, and a typical example is $Fe^{II}\{C6MeMe[16]Cyc\}MeIm(O_2)^{2+}$.

The iron(II) and cobalt(II) cyclidene complexes exhibit reversible dioxygen binding, making them models for hemoglobin and myoglobin,[6] and the iron(III) derivatives form peroxo complexes in analogy to the behavior of cytochromes P_{450} and catalase.[7] Particular interest focuses on the electron transfer properties of the lacunar iron(II) cyclidenes because observations indicate that these complexes autoxidize by an outer-sphere electron transfer mechanism,[5,6f,7] and because a close parallel is found in the autoxidation of hemoglobin and myoglobin.[5,8] Autoxidation processes of dioxygen carriers have been reviewed in more detail elsewhere.[9]

This contribution reports the kinetics of electron transfer of a series of iron(II) cyclidene complexes. Rate constants were determined for oxidation of the cyclidene complexes by tris(phenanthroline)cobalt(III) chloride. The results have been analyzed utilizing Marcus relationships to yield the iron(III)/(II) self-exchange rate constants for the cyclidene complexes.

EXPERIMENTAL

All chemicals were reagent grade or better, and solvents were purified and degassed by recommended procedures.[10] All inert atmosphere manipulations were performed in a nitrogen-filled Vacuum Atmospheres Corporation (VAC) glove box, equipped with a gas circulation and oxygen removal system (either a VAC MO40-1 or HE-493 dry train). Oxygen concentrations were maintained below 1 ppm.

The iron(II) cyclidene complexes were synthesized as described previously.[11] Tris(1,10-phenanthroline)cobalt(III) chloride was prepared by adding three equivalents of the ligand to an aqueous solution of cobalt(II) sulfate, which was acidified with 1M sulfuric acid and oxidized in the dark by addition of excess lead dioxide. After stirring for one hour, aqueous ammonium hexafluorophosphate was added and the beige precipitate which formed was collected by filtration and recrystallized from aqueous acetone. After dissolution in acetone, n-Bu_4NCl was added and the anhydrous chloride salt collected as a yellow precipitate. The identity was confirmed by ^1H NMR spectroscopy in nitromethane and by agreement with the published value for the UV-visible extinction coefficients ($\lambda_{max}(\varepsilon)$:330 nm (4660), 350 nm (3620), 450 nm (100)) of the perchlorate salt.[12]

Physical Measurements

UV-visible spectra were recorded using a Varian 2300 spectrometer or a Varian DM5-200 spectrometer. Cyclic voltammetric experiments were performed using a Princeton Applied Research Model 173 Potentiostat and model 175 programmer. The output was recorded directly to paper using a Houston Instruments Model 200 XY recorder. Potentials were measured *vs.* ferrocene which was used as an internal standard. The working electrode was a 3 mm diameter glassy carbon disk in Kel-F (Bioanalytical Systems Inc.), a silver wire was used as a *pseudo*-reference electrode and the secondary/auxiliary electrode was a platinum wire. ESR spectra were recorded with a Varian E-line Century Series spectrometer equipped with a liquid nitrogen insert dewar. The magnetic field was calibrated using DPPH ($g = 2.0036$) as an external standard. Samples were run as frozen glasses at 78 K in quartz tubes.

Rapid kinetic studies were undertaken on a Durrum Dionex D110 stopped flow, interfaced with a Northstar Horizon computer. Software for data collection and processing were provided by On Line Instrument Systems Inc. The stopped flow uses a Kel-F flow system with a two cm path length and has glass drive syringes with Teflon-tipped plungers. Several minor modifications were made to the stopped flow system in order to enhance its anaerobicity. Nitrogen gas was fed into the hollow drive syringes (which emerged from four holes at 90° to each other drilled just behind the teflon tips) to reduce dioxygen leakage past the teflon tip; and the thermostated bath containing the drive syringes was covered with plastic and purged with nitrogen. Temperature control was maintained using a Neslab RTE-8 temperature bath connected to the stopped flow water bath by a heat exchange coil.

Prior to operation the drive syringe flow system was soaked with a dioxygen scavenging solution (sodium dithionite or iron(II) pyrophosphate) for at least thirty minutes.

Computation

A linear least squares fitting equation was applied to calculate the second order rate constants from the observed rate constants. The regression line was constrained to pass through the origin, and the points were weighted on the basis of the uncertainties of the observed rate constants. The weighing factors were squares of the inverses of the standard deviations from the means of the multiple determinations (from three to seven) performed from one or two fillings of the drive syringes.[13]

RESULTS AND DISCUSSION

The electrochemistry of the iron(II) cyclidene complexes has been previously examined over a range of experimental conditions.[5e,11b] In the presence of polar solvents containing a large excess of chloride, the iron(II) complex is coordinated to chloride ion at the external axial site.[5e,14] Cyclic voltammograms of the iron(II) cyclidene complexes were found to be reversible or *quasi*-reversible in methanol containing excess lithium chloride supporting electrolyte. Typically the iron(III)/(II) redox couples were found to be around −0.3 V *vs.* ferrocene. Values for the individual complexes are listed in Table 2 *vs.* tris(1,10-phenanthroline)cobalt(III)/(II) chloride (*vide infra*), the rational standard for present purposes. Reversibility of the iron(III)/(II) redox couple indicates that the coordination environment of the iron(III) complex is similar to that of the iron(II) cyclidene. Based on studies in acetonitrile[5e] the chloro(cyclidene)iron(II) complexes are high-spin (μ 5.0 B.M.) and the PF_6^- salts are uni-univalent electrolytes ($\lambda = 125-150\ \Omega^{-1}mol^{-1}cm^2$ at 1 mM), indicating that the chloride ligand is tenaciously bound in the fifth coordination site external to the cavity. It is known from ESR studies that the iron(III) complex is high spin, with a g-value of around 6.[6]

In order to examine the kinetics of electron transfer it was necessary to select a chemical oxidant with a redox potential more positive than that of the iron(III)/(II) couple, and which could be expected to undergo reduction by an outer-sphere process. For this work, tris(1,10-phenanthroline)cobalt(III) chloride was chosen as the oxidant. The Co(III)/(II) redox couple for this complex in methanol/0.1 M tetrabutylammonium tetrafluoroborate was found by cyclic voltammetry to be *quasi*-reversible with $E_{1/2} = 0.03$ V *vs.* ferrocene, $\Delta Ep = 95$ mV, at 100 mV/s.

Measurement of the Cross Reaction Rate Constants Between Iron Cyclidene Complexes and $[Co(phen)_3]^{3+}$

The kinetics of oxidation of a series of iron(II) cyclidene complexes by $Co(phen)_3{}^{3+}$ in methanol containing 0.05 M lithium chloride was examined by stopped flow spectrophotometry. The added chloride served both to maintain the ionic strength and to ensure that the axial ligand of iron(II) is chloride. The reactions were followed spectrophotometrically at 25 °C by monitoring the growth of an absorption band of the iron(III) cyclidene complexes between 610 and 650 nm. This absorbance increase can also be generated by the addition of Ce^{IV} to the iron(II) cyclidene solution. The spectra of the iron(II) and iron(III) cyclidenes and of $Co(phen)_3{}^{3+}$ are shown in Figure 1. The kinetic traces were satisfactorily fitted to first-order graphs for greater than three reaction half-lives for reactions conducted under *pseudo*-first order conditions with the concentration of $Co(phen)_3{}^{3+}$ in great excess over that of the iron(II) cyclidene complex. The original rate constants are reported for a variety of conditions in Table 1. The observed rate constants are linearly dependent on the concentration of $Co(phen)_3{}^{3+}$. A representative plot is shown in Figure 2. From the slopes of the lines, the second order rate constants k_{12} were calculated, and these results are summarized in Table 2. The rate constants for all of the iron complexes showed linear dependence on the concentration of the cobalt(III) complex over the entire accessible range of oxidant concentrations. The linear dependence on $[Co(phen)_3]^{3+}$ concentration, the absence of any indications of saturation, and the well-known substitution inertness of the oxidant, are consistent with the notion that electron transfer takes place by a simple outer-sphere mechanism.

The outer-sphere character of the electron transfer process is further indicated by the log-log graph of the second order rate constant for oxidation of the iron(II) cyclidene complexes *vs.* the equilibrium constant for the redox reactions. The Marcus theory[4,15] of adiabatic electron transfer reactions predicts that the rate constant of the cross reaction (k_{12}) will depend on the equilibrium constant for the reaction (K_{12}) in accord with equations [1] and [2]; where k_{11} and k_{22} are the self exchange rate constants for the

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

$$\ln f = (\ln K_{12})^2/(4\ln(k_{11}k_{22}/Z^2)) \tag{2}$$

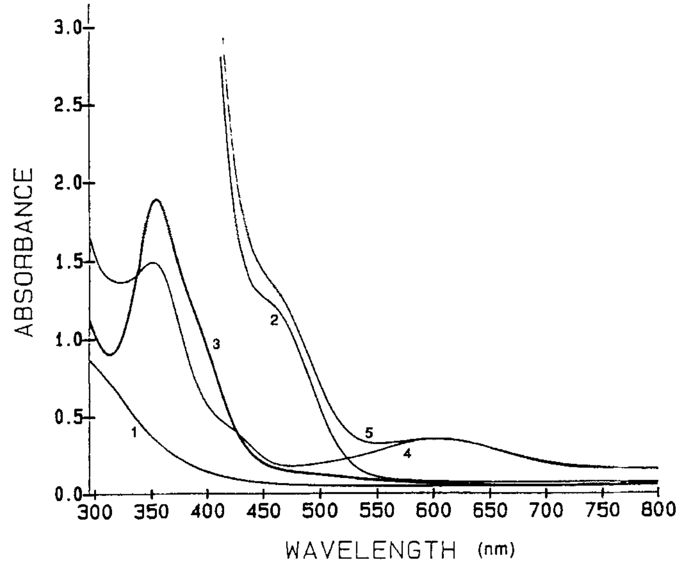

Figure 1 UV-Visible spectra for the oxidation of $[Fe^{II}(mXylMeMe[16]Cyc)Cl]^+$ by $[Co^{III}(phen)_3]^{3+}$ and Ce^{IV} in 0.05 M LiCl/MeOH. 1-Ce^{IV}, 2-Co^{III}, 3-Fe^{II}, 4-Fe^{II} + xs Ce^{IV}, 5-Fe^{II} + xs Co^{III}.

Table 1 The observed cross reaction rate constants for $[Fe\{R^1R^2R^3[16]Cyc\}Cl]^+$ at various concentrations of $[Co^{III}(phen)_3]^{3+}$ in 0.05M LiCl/MeOH at 25°C.

R^3	R^2	R^1	Conc. (× 10^4M)[a]	$k_{obs}(s^{-1})$	$\sigma_{n-1}(s^{-1})$[b]
Ph	Bz	m-xyl	2.1	94	2
			2.1	107	2
			3.2	163	6
			4.2	198	3
			4.2	201	3
			6.4	323	6
			8.0	476	6
Ph	Me	m-xyl	0.42	39	3
			0.85	89	8
			0.85	96	3
			1.3	160	10
			1.7	214	6
			1.7	270	10
			2.1	320	10
Ph	Me	$(CH_2)_4$	0.34	52	4
			0.42	66	4
			0.85	150	10
			0.85	180	10
			1.1	230	10
			1.3	290	40
			1.5	320	20
			1.7	370	20
			1.8	400	40
			2.0	440	10
Ph	Me	$(CH_2)_5$	0.42	69	3
			0.85	142	5
			1.1	221	9
			1.3	260	10
			1.7	360	20
Ph	Me	$(CH_2)_6$	1.0	230	20
			1.5	380	20
			0.8	450	10
			2.0	530	80
Me	Bz	m-xyl	0.42	200	6
			0.42	226	3
			0.64	270	10
			0.85	381	3
			1.1	620	60
			1.3	650	50
Me	Bz	$(CH_2)_5$	0.31	370	10
			0.40	430	10
			0.50	590	10
			0.63	740	20
Me	Me	m-xyl	0.34	370	50
			0.38	507	4
			0.42	420	10
			0.42	550	20
			0.50	600	40
			0.51	480	20
			0.65	700	200
			0.70	900	40
			0.72	820	50
			0.75	890	30

Table 1 *(Continued)*

R^3	R^2	R^1	Conc. (× 10^4M)[a]	$k_{obs}(s^{-1})$	$\sigma_{n-1}(s^{-1})$[b]
Me	Me	$(CH_2)_3$	0.40	590	70
			0.40	700	100
			0.40	890	80
[DM16]					
Ph	Bz	m-xyl	1.0	66	5
			2.0	123	4
			3.0	230	20
			3.5	260	10
			3.5	278	3
			4.5	318	7
			5.0	340	20
[16DM]					
Ph	Bz	m-xyl	1.0	68	2
			2.0	123	3
			3.0	211	3
			3.5	268	7
			3.5	270	10
			4.0	300	10
			5.0	343	6
[DM16DM]					
Ph	Bz	m-xyl	2.0	145	5
			2.5	176	6
			3.0	214	7
			3.5	245	6
Me	VD[c]		0.50	118	61
			0.75	170	10
			1.0	230	10
			1.0	289	3
			1.5	360	10
			2.0	521	3
			2.0	540	40
			2.5	650	20
Rates for 0.025 M LiCl/MeOH					
Ph	Bz	m-xyl	1.2	42	2
			2.4	78	2
			5.9	229	7
Ph	Me	m-xyl	0.85	83	3
Me	Bz	m-xyl	1.7	800	40
			0.85	330	10
Me	Me	m-xyl	0.21	280	20
			0.21	280	30
			0.32	180	40
			0.32	290	10
			0.42	360	30
			0.53	550	80
			0.64	490	50
			0.85	850	60

[a]concentration of $[Co^{III}(phen)_3]^{3+}$ ($[Fe^{II}] \cong 1.25 \times 10^{-5}$ M). [b]standard deviations of the observed rate constants at each $[Co^{III}(phen)_3]^{3+}$ concentration. [c]VD-vaulted durene, piperazine moieties occupy both the R_2 and R_1 positions as risers and are connected by a 3,6-bis(methylene)durene bridge.

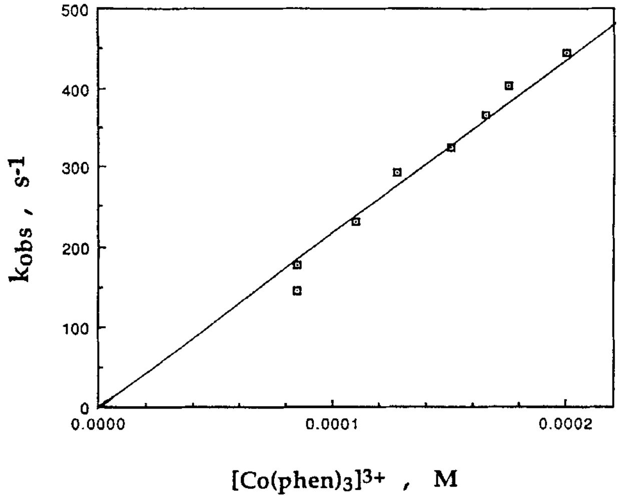

Figure 2 First order dependence of the rate constant for oxidation of $[Fe^{II}(C4PhMe[16]Cyc)Cl]^+$ on the concentration of $[Co^{III}(phen)_3]^{3+}$ in 0.05 M LiCl/MeOH.

two redox couples and Z is the collision frequency, usually taken to be $10^{11}M^{-1}s^{-1}$. Figure 3 depicts a plot of $\ln k_{12}$ *vs.* $\ln K_{12}^{corr}$. The plot for oxidation of the iron(II) cyclidene complexes by $[Co(phen)_3]^{3+}$ is linear with a slope of 0.44, in reasonable agreement with the predicted slope of 0.5 for outer-sphere electron transfer in the so-called normal region. This correlation accommodates the Marcus prediction that the reaction rate is mainly controlled by the free energy change. In addition, the electron transfer step is indeed the rate determining step, rather than precursor complex formation or successor complex dissociation.

Self Exchange Rate Constant for $Co(phen)_3^{3+/2+}$

The self exchange rate constant for $Co(phen)_3^{3+/2+}$ was measured for the conditions employed here by reaction with ferrocene. Since $Co(phen)_3^{3+}$ is known to undergo photo-racematization,[16] kinetic experiments were always undertaken with freshly prepared solutions of the complex. Operating with the concentration of $Co(phen)_3^{3+}$ in large excess over that of ferrocene in order to maintain *pseudo*-first order kinetics, the reaction was found to be first order. The reaction was monitored by measuring the increasing absorption at 617 nm due to increasing concentrations of ferrocinium ion. A linear dependence was observed for the rate constants for oxidation of ferrocene by $[Co(phen)_3]^{3+}$ in 0.05 M LiCl/MeOH (Figure 4). From the slope of the graph the second order cross reaction rate constant k_{12} was found to be $5.0(\pm 0.1) \times 10^{-3}$ $M^{-1}s^{-1}$.

Using the Marcus cross relationship (eqs. [1] and [2]), the self exchange rate constant k_{11} for $[Co^{II/III}(phen)_3]^{2+/3+}$ was calculated to be $1.45(\pm 0.30)$ $M^{-1}s^{-1}$, taking the self-exchange rate constant of $Fe(Cp)_2/Fe(Cp)_2^+$ to be $5.4(\pm 1.0) \times 10^6$ $M^{-1}s^{-1}$ in methanol at 25°C (based on nuclear magnetic resonance studies).[17] The value of the self-exchange rate constant for $[Co^{II/III}(phen)_3]^{2+/3+}$ is consistent with other reported values at 25°C: 45 $M^{-1}s^{-1}$ for water with 0.1 M KNO_3,[18] and 1.1

Table 2 Comparison of self-exchange rate constants for substituted iron(II) cyclidenes in MeOH/LiCl (0.05 M) from the cross reaction rates with $[Co^{III}(phen)_3]^{3+}$

ligand	r[Å]	$^{(1)}E_{1/2}$[V]	$^{(2)}K_{12}$	$^{(3)}K_{12}^{corr}$	$^{(4)}k_{12}$ [$M^{-1}s^{-1}$]	$^{(5)}k_{11}$[$M^{-1}s^{-1}$]	$^{(6)}k_{11}^{corr}$[$M^{-1}s^{-1}$]
m-XylPhBz[16]Cyc	6.9	0.24	$1.1_4 \times 10^4$	$8.3_5 \times 10^3$	$5.0_4 \times 10^5$	3.0×10^7	2.3×10^7
m-XylPhMe[16]Cyc	6.2	0.26	$2.5_0 \times 10^4$	$1.7_5 \times 10^4$	$1.2_5 \times 10^6$	9.6×10^7	9.2×10^7
C_4PhMe[16]Cyc	5.4	0.31	$1.7_5 \times 10^5$	$1.1_6 \times 10^5$	$2.0_7 \times 10^6$	5.2×10^7	6.3×10^7
C_5PhMe[16]Cyc	5.5	0.32	$2.5_8 \times 10^5$	$1.7_3 \times 10^5$	$1.8_3 \times 10^6$	2.9×10^7	3.4×10^7
C_6PhMe[16]Cyc	5.5	0.32	$2.5_8 \times 10^5$	$1.7_3 \times 10^5$	$2.5_2 \times 10^6$	5.6×10^7	6.6×10^7
m-XylMeBz[16]Cyc	6.8	0.36	$1.2_3 \times 10^6$	$8.8_9 \times 10^5$	$4.6_4 \times 10^6$	5.5×10^7	4.4×10^7
m-XylMeMe[16]Cyc	5.8	0.43	$1.8_7 \times 10^7$	$1.2_8 \times 10^7$	$1.2_8 \times 10^7$	5.2×10^7	5.9×10^7
m-XylPhBz[DM16]Cyc	7.2	$^{(7)}$0.24	$1.1_4 \times 10^4$	$8.4_7 \times 10^3$	$7.5_2 \times 10^5$	6.7×10^7	4.6×10^7
m-XylPhBz[16DM]Cyc	7.2	$^{(7)}$0.29	$8.0_3 \times 10^4$	$5.9_4 \times 10^4$	$6.8_9 \times 10^5$	1.0×10^7	7.2×10^6

(1) redox potential *vs.* $[Co^{III/II}(phen)_3]^{3+/2+}$ couple in 0.1 M TBAT/MeOH; $E_{1/2}$ of $[Co^{III/II}(phen)_3]^{3+/2+}$ *vs.* ferrocene = 0.030V. (2) $\ln K = nFE/RT$ (3) $\ln K = (nFE + w_{12} - w_{21})/RT$ (4) cross reaction rate constant with $[Co^{III}(phen)_3]^{3+}$ at 0.05 M LiCl/MeOH (5) self-exchange rate constants for iron complexes without workterm corrections (values 40% for error of 0.01V in E) (6) self-exchange rate constants for iron complexes with workterm corrections (values 40% for error of 0.01V in E) (7) values in MeCN/xs LiCl; potential values for iron cyclidenes are very similar in the two solvents.

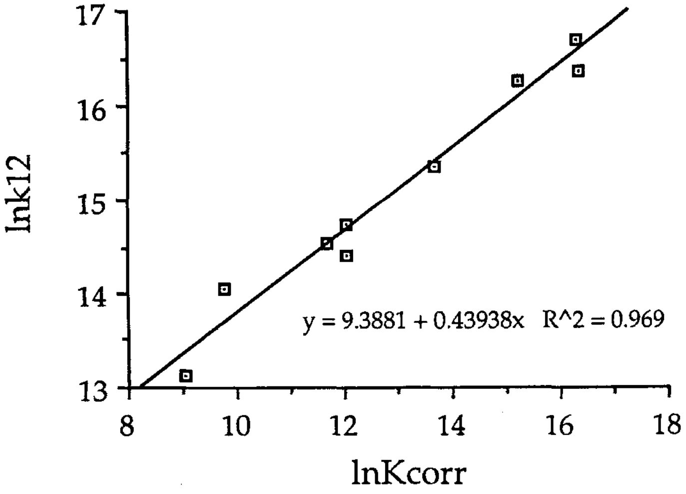

Figure 3 Log-log graph of the second order rate constant for oxidation of the iron(II) cyclidene complexes by $[Co^{III}(phen)_3]^{3+}$ in 0.05 M LiCl/MeOH *vs.* the corrected equilibrium constant for the redox reactions.

$M^{-1}s^{-1}$ in 1:1 water/propanol with 0.02 M KNO_3[19](both from the cross reaction with ferrocene). The differences can be accounted for by considering the greater electrostatic work required to form the precursor complex in media of lower dielectric constant and lower ionic strength.

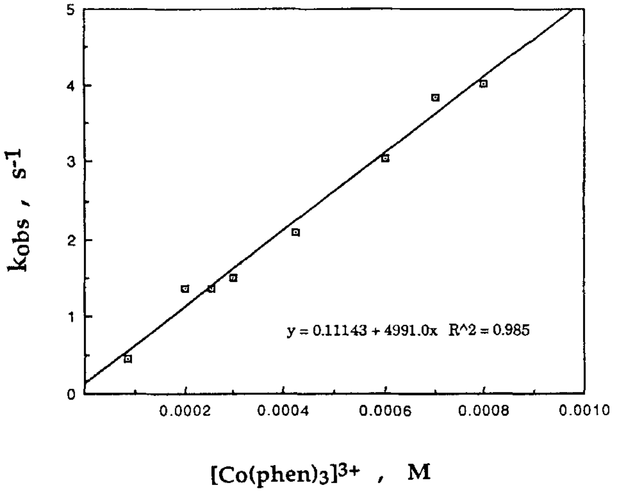

Figure 4 Linear dependence of the cross-reaction rate constants for oxidation of ferrocene by $[Co^{III}(phen)_3]^{3+}$ on the concentration of $[Co^{III}(phen)_3]^{3+}$ in 0.05 M LiCl/MeOH.

Calculations of the Self Exchange Rate Constants for the Iron Cyclidene Complexes

Utilizing the Marcus cross-relationship, the iron(III)/(II) self-exchange rate constants for the iron cyclidene complexes were calculated from the rate constants and equilibrium constants for oxidation of the iron(II) cyclidenes by $Co(phen)_3{}^{3+}$ and the homogeneous self exchange rate constant for the cobalt(III)/(II) redox couple. Consideration must be given to certain corrections and errors associated with various parameters. The precursor complex is considered to be short-lived, so that work term corrections are applied rather than introducing the formation constants for the precursor complexes. No correction has been made for the loss of solvating ions in going to the transition state. This procedure simplifies the calculations and does not decrease their accuracy, since the parameters are poorly defined.[1,20] Although the importance of correcting for differences in the work terms (electrostatic effects) is most readily seen for cross reactions involving ions of opposite charge, the work term differences are not necessarily negligible for reactions between ions of the same charge since these terms also include non-electrostatic contributions. For reactions of like-charged ions at high ionic strength and a collision diameter of greater than *ca.* 5 Å the work term correction W_{12} approaches unity. The biggest error in calculating the self-exchange rate constants is probably introduced by using reduction potentials for its calculatiion. A possible error of ±0.01 V in ΔE leads to error-limits of ±40% in the self-exchange rate constants.

The following relevant equations including the work term corrections were used to calculate $k_{11}{}^{corr}$ with the help of a computer program,[13] which uses, in part, Borland Turbo Pascal's numerical routines to solve the equation by the secant method (until a root is approximated with specified accuracy; 10^{-8} was the chosen tolerance):

$$k_{12} = (k_{11}k_{22}k_{12}f)^{1/2}W_{12} \tag{3}$$

$$\text{with } \ln f = \frac{\left[\ln K_{12} + \dfrac{[w_{12} - w_{21}]}{RT}\right]^2}{4\left[\ln\left(\dfrac{k_{11}\,k_{22}}{Z^2}\right) + \dfrac{(w_{12} + w_{22})}{RT}\right]} \tag{4}$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})|RT] \tag{5}$$

$$w_{ij} = \frac{Z_iZ_je^2}{2D_sr}\left(\frac{\exp(\beta\sigma_i\sqrt{\mu})}{1 + \beta\sigma_i\sqrt{\mu}} + \frac{\exp(\beta\sigma_j\sqrt{\mu})}{1 + \beta\sigma_j\sqrt{\mu}}\right)\exp(-\beta r\sqrt{\mu}) \tag{6}$$

where the terms labeled *w* represent the Coulombic work to bring the reactants together ($\beta = (8\pi Ne^2/1000D_skT)^{1/2}$), Z_i and Z_j are the charges on the two reactants, σ_i is equal to the radius of the reactant a_i plus the radius of the main ion of opposite charge in the reactants ions atmosphere (here it was assumed that $a_i = \sigma_i$ (similarly $a_j = \sigma_j$)), and the closest approach of the metal centers (collision diameter) is equal to the sum of the radii of the reactants, $r = a_i + a_j$. D_s is the static dielectric constant of the medium (32.63 for methanol). N (Avogadro's number) =

Table 3. Literature Values for Self-Exchange Rate Constants for Selected Iron Complexes.

Complex	Medium	$k/M^{-1}s^{-1}$.	Spin	T/°C	Method	ref
Cytochrome c_{550}	pH 5.2	$0.7 - 5.3 \times 10^2$		40	b	f
Horse Heart Cytochrome C	aq.	$4 - 700 \times 10^4$	L	25	a	g
	D_2O	5×10^4		~25	b	h
$FeOEC(1-MeIm)_2$	aq. acetone	$2.8 \pm 1.1 \times 10^7$	L	-20	b	i
$FeOEP(1-MeIm)_2$	aq. acetone or CD_2Cl_2	$4.0 \pm 1.6 \times 10^7$	L	-20	b	i
$FeOEiBC(1-MeIm)_2$	aq. acetone	$17 \pm 9 \times 10^7$		-20	b	i
$Fe(CN)_6^{3-/4-}$	aq.?	5×10^3	L	25?		j
	aq.	$2 - 30 \times 10^3$		25		k
		1.5×10^4				g
	aq.	$1.6 - 8.4 \times 10^4$		25		l
	aq.	$9.2 \pm 1.3 \times 10^4$		32	b	m
	aq.	7.4×10^2		25		n
$Fe(CN)_5py^{2-}$	aq.?	3.4×10^5		25?	a	o
$Fe(CN)_5(His)^{-3/-2}$	aq.	3.3×10^5		25	a	g
$Fe(CN)_5(Im)^{-3/-2}$	aq.	3.1×10^5		25	a	g
$Fe(CN)_5(4-PyNH_2)^{-3/-2}$	aq.	2.8×10^6		25	a	g
$Fe(CN)_5(Gly^-)^{-4/-3}$	aq.	4.1×10^2		25	a	g
$Fe(CN)_5(Ala^-)^{-4/-3}$	aq.	5.5×10^2		25	a	g
$Fe(CN)_5(Glu^{2-})^{-5/-4}$	aq.	6.0		25	a	g
$FeTMPyP(H_2O)^{5+/4+}$	pH 2-4	1.2×10^6	H	25	a	p
$FeTMPyP(H_2O)(OH)^{4+/3+}$	pH 2-4	$>1 \times 10^9$	L	25	a	p
$FeTPPS(H_2O)^{3-/4-}$	pH 2 $HClO_4$	$>1 \times 10^3$	H	25	a	q
$Fe(Por)(CN)_2^{-/2-}$ c	aq.	$10^6 - 10^8$	L	25	a	r
$Fe(Por)(CN)_2-/2-^{d}$	DMSO	$10^7 - 10^8$	L	37	b	s
$Fe(R-TPP)(1-MeIm)_2$e	CD_2Cl_2	$5.3 - 16 \times 10^7$	L	-21	b	t
$[Fe_4S_4(SCH_2Ph)_4]^{2-/3-}$	MeCN	$2.4 \pm 0.2 \times 10^6$		27	b	u
$[Fe_4S_4(S-p-C_6H_4Me)_4]^{2-/3-}$	MeCN	$2.8 \pm 0.3 x 10^6$		28	b	u
$[Fe_4Se_4(S-p-C_6H_4Me)_4]^{2-/3-}$	MeCN	$9.7 \pm 0.9 \times 10^6$		31	b	u
Spinach $Fd^{ox/red}$	aq.	$1.7 \times 10^{-3} - 1.5 \times 10^6$		25	a	v
C. pasteurianum $Rd_{ox,red}$	aq.	10^8-10^9		25	a	w
$Fe(phen)_3^{3+/2+}$	CD_3CN	1.3×10^7	L	25	b	x
	D_2O	1.5×10^7		25	b	
	aq.	3.3×10^8		25	transfer diffusion	y
	CD_3CN/ClO4	1.4×10^7		25	b	z
$Fe(5,6-Me_2phen)_3^{3+/2+}$	CD_3CN/PF6	1.0×10^7		25	b	z
$Fe(5-Clphen)_3^{3+/2+}$	CD_3CN/PF6	0.7×10^7		25	b	z
$Fe(4,7-Me_2phen)_3^{3+/2+}$	CD_3CN/ClO4	3.0×10^7		25	b	z
$Fe(4,7-Ph_2phen)_3^{3+/2+}$	CD_3CN/ClO4	1.5×10^7		25	b	z
$Fe(bpy)_3^{3+/2+}$	aq.	$3-5 \times 10^8$		25	estimate	j
	CD_3CN/PF6	3.7×10^6		25	b	z
$Fe(4,4'-Me_2bpy)_3^{3+/2+}$	CD_3CN/ClO4	1.6×10^7		25	b	z
$Fe(EDTA)^{-/2-}$	aq.	4.5×10^3		25	a	aa
	aq.	3×10^4		25	a	bb,n
$Fe([9]aneS_3)_2^{3+/2+}$	CD_3CN	5.3×10^4	L	0	b	cc
$Fe([9]aneS_3)_2^{3+/2+}$	D_2O	3.2×10^6	L	0	b	cc
$Fe([9]aneN_3)_2^{3+/2+}$	D_2O	4.6×10^3	L	25	a	dd
$Fe(\eta-C_5H_5)_2^{0/+}$	CD_3CN	3.5×10^6	L	0	b	ee
		9.3×10^6	L	25	b	ee
$Fe(H_2O)_6^{3+/2+}$	pH 2.0	0.25	H	25	a	ff
		6.2×10^{-3}			a	gg
	$HClO_4$/ $NaClO_4$	$1.1 - 4.0$		25	^{55}Fe tracer	hh
					^{59}Fe tracer	ii
					^{59}Fe tracer	jj

Table 3 (*Continued*)

Complex	Medium	k/M^{-1}s^{-1}.	Spin	T/°C	Method	ref
Fe(SO$_4$)	pH 2.0	8.7		25	a	ff
Fe(Cl)$_2$	pH 2.0	19000		25	a	ff
Fe(Br)$_2$	pH 2.0	45		25	a	ff
Fe(sar)$^{3+/2+}$	aq.	6.0×10^3	L	25	a	gg

Abbreviations: OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; OEC = trans-2,3-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinato dianion (octaethylchlorin); OEiBC = mixture of tct- and ttt-2,3,7,8-tetrahydro-2,3,7,8,12,13,17,18-octaethylporphyrinato dianion (octaethylisobacteriochlorin) TMPyP = tetrakis[4-N-methylpyridyl)]porphine; TPPS = porphinetetrakis(4-benzenesulfonate); Fd = Ferredoxin; sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane);

a) calculated from cross reactions using Marcus theory
b) determined by NMR line broadening methods
c) 2,4-disubstituted deuterohemins. d) para substituted tetraphenylporphyrins + 2,4-disubstituted deuterohemindimethylesters. e) R = H-, 3-Me-, 4-Me-, 4-OMe-, 2,4,6-Me$_3^-$.
f) Lommen, A.; Ratsma, A.; Bijlsma, N,; Canters, G.W.; Van Wielink, J.E.; Frank, J.; Van Beeumen, J.; Eur. J. Biochem. (1990), *192*, 653
g) Toma, H.E.; Batista, A.A.; J. Inorg. Biochem. (1984), *20*, 53
h) Kowalski, A.; Biochem. (1965), *4*, 2382
i) Dixon, D.W.; Woehler, S.; Hong, X.; Stolzenberg, A.M.; Inorg. Chem. (1988), *27*, 3682
j) Stanbury, D.M.; Wilmarth, W.K.; Khalaf, S.; Po, H.N.; Byrd, J.E.; Inorg. Chem. (1980), *19*, 2715
k) Wherland, S.; Gray, H.B.; in Biological Aspects of Inorganic Chemistry; Addison, A.W.; Cullen, W.R.; Dolphin, D.; James, B.R.; (Eds.), Wiley, New York, (1977), 323
l) Kurland, R.J.; Winkler, M.E.; J. Biochem. Biophys. Methods (1981), *4*, 215
m) Shporer, M.; Ron, G.; Loewenstein, A.; Navon, G.; Inorg. Chem. (1965), *4*, 215
n) Pennington, D.; in 'Coordination Chemistry, Vol. 2'; ACS Monograph 174, Martell, Ed.; Am. Chem. Soc., Washington, D.C. (1978), 476
o) Johnson, M.D.; Wilkins. R.G., unpublished data, cited in Balahura, R.J.; Johnson, M.D.; Inorg. Chem. (1987), *26*, 3860
p) Pasternak, R.F.; Spiro, E.G.; J. Am. Chem. Soc. (1978), *100*, 968
q) Taniguchi, V.T.; Ph.D. Thesis, Univ. California, Irvine, (1978); cited by R.D.; Fleisher, E.B.; J. Am. Chem. Soc. (1982), *104*, 1575
r) Langley, R.; Hambright, P.; unpublished results, cited in Langley, R.; P.; Williams, R.F.X.; Inorg. Chim. Acta. (1985), *104*, L25; Worthington, P.; Hambright, P.; J. Inorg. Nucl. Chem. (1980), *42*, 1651
s) Dixon, D.; Barbush, M.; Shiraz, A.; Inorg. Chem. (1985), *24*, 1081
t)Shirazi, A.; Barbush, M.;Ghosh, S.; Dixon, D.W.; Inorg. Chem. (1985), *24*, 2495
u) Reynolds, J.G.; Coyle, C.L.; Holm, R.H.; J. Am. Chem. Soc. (1980), *102*, 4350
v) Rawlings, J.; Wherland, S.; Gray, H.B.; J. Am. Chem. Soc. (1977), *99*, 1968
w) Jacks, C.A.; Bennett, L.E.; Raymond, W.N.; Lovenberg, W; Proc. Natl. Acad. Sci. USA. (1974), *71*, 118
x) Doine, H.; Swaddle, T.W.;.Can.J. Chem. (1988), *66*, 2763
y) Ruff, I.; Zimonyi, M.; Electrochim. Acta (1973), *18*, 515
z) Chan, M-S.; Wahl, A.C.; J. Phys. Chem. (1978), *82*, 2542
aa) Dimmock, P.W.; McGinnis, J.M.; Ooi, B-L.; Sykes, A.G.; Inorg. Chem. (1990), *29*, 1085
bb) Mehrotra, R.N.; Wilkins, R.G.; Inorg. Chem. (1980), *19*, 2177
cc) Doine, H.; Swaddle, T.W.; Can. J. Chem. (1990), *68*, 2228
dd) Küppers, H-J.; Wieghardt, K.; Steenken , S.; Nuber, B.; Weiss, J.; Z. Anorg. Chem. (1989), *573*, 43
ee) Kirchner, K.; Dang, S-Q.; Stebler, M.; Dodgen, H.W.; H.W.; Wherland, S.; Hunt, J.P.; Inorg. Chem. (1989), *28*, 3604
ff) Blake, R.C. II.; White, K.J.; Shute, E.A.; Biochem. (1991), *30*, 9443
gg) Bernhard, P.; Sargeson, A.M.; Inorg. Chem. (1987), *26*, 4122
hh) Silverman, J.W.; Dodson, R.W.; J. Phys. Chem. (1952), *56* 846
ii) Fukushima, S.; Reynolds, W.L.; Talanta 1964, *11*, 283
jj) Brunschwig, B.S.; Creutz, C.; Macartney, D.H.; Sham, T.K; Sutin, N.; Discuss. Faraday Soc. (1982), *74*, 113

6.022045×10^{23} mol^{-1}, e (electronic charge) = 4.803242×10^{-10} statcoul, k (Boltzmann constant) = 1.380662×10^{-16} ergK^{-1}, R (gas constant) = 8.31441 $\text{JK}^{-1}\text{mol}^{-1}$, (Faraday constant) = 96484.56 Cmol^{-1}, Z (collision frequency) = 1×10^{11} $\text{M}^{-1}\text{s}^{-1}$, μ (ionic strength) = 0.0500, T (temperature) = 298.15 K. The parameters r, $\sigma_{i,j}$ are in units of cm. Values of 7.0 and 7.1 Å, respectively,[21] were used as the radii of $[\text{Co(phen)}_3]^{3+/2+}$.

An average radius for the cyclidene complexes ca be calculated from space-filling models or crystallographic data where available[5e,22] (see Table 2). The average radius represents the average distance from the redox center to the periphery of the molecule. It is often determined by equating the volume of the molecule to the volume of a sphere calculated from the appropriate geometric formula. The dimensions of the cyclidenes were determined from a hypothetical 3-dimensional box such that it extends to the external van der Waals radius of the last atom of the cyclidenes at each side. Then the average radius of the molecules is the radius of the equivalent sphere, such that $<rr> = 1/2(d_x d_y d_z)^{1/3}$ for ellipsoidal molecules.[23] These methods for calculating <rr> have a flaw because they do not account for voids in the molecular structure, but nevertheless, the error exists even in so-called spherical molecules, such as tris(phenantroline) complexes, since there are gaps between the ligands that could be penetrated by solvent molecules or small reactants.[21b]

For work term corrections, the charge on iron(II) cyclidene complexes is considered to be one electronic unit because of chloride coordination. Based on studies in acetonitrile[5e] the chloro(cyclidene)iron(II) complexes are high-spin (μ 5.0 B.M.) and the PF_6^- salts are uni-univalent electrolytes ($\lambda = 125\text{–}150\ \Omega^{-1}\text{mol}^{-1}\text{cm}^2$ at 1 mM), indicating that the chloride ligand is tenaciously bound in the fifth coordination site opposite the cavity.

The oxidized iron(III) cyclidene complexes produced by $[\text{Co(phen)}_3]^{3+}$ were characterized by ESR spectroscopy (frozen solution) to be in a high spin state (g *ca.* 7)[6]. In spite of the structural differences in the macrocycle between lacunar cyclidenes and porphyrins, a variety of similar observations have been made due to extensive electron delocalization in the six-membered chelate rings which leads to similar average Fe-N-distances.[5e,24] The effective radius of the high spin Fe^{2+} ion is considerably larger than that of high-spin Fe^{3+} ion. For octahedral coordination, the difference is approximately 0.12 Å.[25]

The corrected self-exchange rate constants k_{11}^{corr} for the iron cyclidenes are listed in Table 2, which also summarizes the values without workterm corrections. The rate constants are in the range of 7×10^6 = 9×10^7 $\text{M}^{-1}\text{s}^{-1}$ and fall well into the range of values reported for low and high-spin iron complexes (see Table 3). The much larger range for rate constants of the cross reaction, a factor of about 35, emphasizes the typical outer sphere dependence of the exchange rate on the driving force for the reaction. Remarkably, no obvious trends depending on the substituents of the cyclidene ligands are noticeable (calculated k_{11}^{corr} could be a monitor of the accessibility of the redox site). For the examples where reliable electrode potential data are available for the same solvent system, the set of self-exchange rate constants give an average of $5.44(\pm 1.79) \times 10^7$ $\text{M}^{-1}\text{s}^{-1}$. Two compounds exhibit k_{11}^{corr} values differing from the average by 2σ and one more compound, by 2.6σ. On this basis, we can conclude that the self-exchange rate is insensitive to a variety of structural changes, including length of bridging polymethylene chain, and the nature of the bridging group and other substituents. Admittedly, only a limited range of species has been investigated.

The relatively small differences in self-exchange rate constants for the various substituted complexes suggests a similar transition state throughout the series with little sensitivity to substituents. Two probable regions of the structure which might be associated with the electron transfer event are (1) the polar area around and including the axial chloride ligand, and (2) the hydrophobic delocalized π-system providing the upper walls of the lacuna and the periphery of the open site of the pocket (Figure 5). Various possible axial and peripheral electron transfer paths through porphyrins have been discussed by Castro[26] and Sutin,[27] but conclusions are not definitive in microscopic detail. Little is known concerning the effect of intervening material on the distance dependence in the cross reactions. Differences in the σ *vs.* π-systems[28] or hydrophobic effects[4c,29] will surely be present.[20b,30] Electron transfer to metalloporphyrins can occur through axial ligands or through the porphyrin ring system with the preferred pathway likely dependent on the nature of the axial ligands as well as on the metalloporphyrin, its environment, and the oxidizing agent. It has been suggested that for electron transfer processes proceeding *via* the prophyrin π-system, the self-exchange rate constants for iron porphyrins will be similar to the value obtained for the $Fe(phen)_3{}^{2+/3+}$ (10^7 $M^{-1}s^{-1}$), provided that the spin state of the metal is the same in both complexes.[31] The cyclidene complexes are distinctly different from phenanthroline or porphyrin systems. Both iron(II) and iron(III) states are high spin and the iron is positioned in a shielded region close to the center of the nonplanar saddle-shaped ligand structure. The cyclidene ligand contains two chelate rings that have delocalized π-systems and two that are saturated.

Possible docking models for the collision complex between $[Fe^{II}(m\text{-}XylMeMe[16]Cyc)]^{2+}$ and $Co(phen)_3{}^{3+}$ have been studied using the computer programs SYBYL, CAChe, and MM2/MMP2. The internal coordinates within the two species were fixed using an energy-minimized model for $[Fe^{II}(m\text{-}XylMeMe[16]Cyc)]^{2+}$ [32] and the X-ray crystal structure of $Co(phen)_3.{}^{3+}$ [33] Each

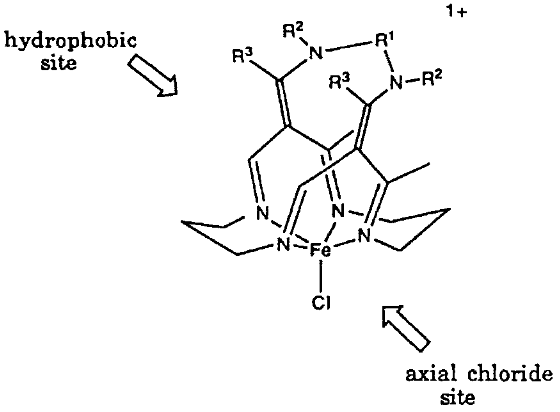

Figure 5 Approaches of an oxidizing agent may be from the polar axial chloride side or from the hydrophobic superstructure side of the iron(II) cyclidene complex.

structure in the colliding pair of molecules was allowed to move to obtain a geometry with minimum intermolecular interaction. Shorter distances between the two metal centers, Fe^{II}-Co^{III}, were obtained with the cobalt complex approaching the iron complex from the side containing the chloride iron (7.0 Å), (Figure 6) as opposed to the hydrophoblic superstructured portion of the iron complex (9.1 Å). This might suggest that the chloride provides the more favorable orientation for electron transfer in this particular cross reaction. The π-systems of phenanthroline and the cyclidene appear to exhibit a π-stacking interaction for one such orientation (separation between atoms of the respective π-systems being approximately 4 Å). This possibility is made more compelling by the fact that the opposite superstructured side varies substantially in size as the substituents R^1, R^2 and R^3 are varied, whereas the self-exchange constants change relatively little. The sustituents should have little or no effect on the dimensions of a collision complex in which the chloride region of the cyclidene complex makes contact with the second reacting molecule.

As indicated in the introduction, strong evidence for an outer-sphere mechanism for the autoxidation of the iron(II) cyclidenes[5,6f,7] motivated the present studies. The autoxidation studies found that the rate depends greatly on details of the superstructure;[5] a result contrasting with those reported here. The obvious conclusion is that dioxygen selects the hydophobic portions of the cyclidene complex as it

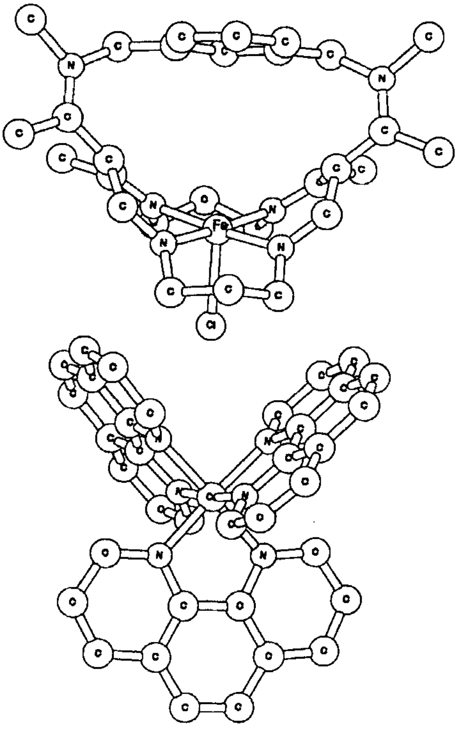

Figure 6 Docking model showing the approach of $[Co^{III}(phen)_3]^{3+}$ from the axial chloride side of $[Fe^{II}(mXylPhBz[16]Cyc)Cl]^+$; the ligand π systems are in close proximity.

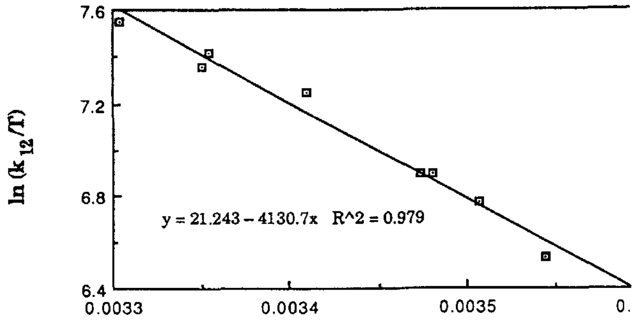

Figure 7 Temperature dependence of the electron transfer reaction rate constant for the oxidation of $[Fe^{II}(mXylPhBz[16]Cyc)Cl]^+$ by $[Co^{III}(phen)_3]^{3+}$ (Eyring's equation).

positions itself for electron transfer with the central iron(II) atom. That result is fully consistent with the general hydrophobic selectivity of O_2; *e.g.*, greater solubilities in organic solvents than water.

Measurement of Activation Parameters

The kinetic activation parameters, ΔH^* and ΔS^*, were obtained from the temperature dependence of the rate constants. Commonly, in a Marcus process, ΔS^* is more directly connected with the molecularity, structure, and charge of the activated complex, thereby providing greater insight into the reaction mechanism. Highly negative ΔS^* values have been observed for inner-sphere electron transfer and for nonadiabatic outer-sphere electron transfer processes.[30b,34] Calculations of the activation parameters are made on the basis of the Eyring Activated Complex theory.

$$k = \frac{k_B T}{h} \exp - \frac{\Delta G^*}{RT} = \frac{k_B T}{h} \exp\left(- \frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R} \right)$$

From the linear dependence of ln(k/T) on 1/T (Figure 7), for $[Fe^{II}(mXylPhBz[16]Cyc)Cl]^+$, $\Delta H^* = 34.3$ kJ/mol, $\Delta S^* = -20.9$ $Jmol^{-1}K^{-1}$ and for $[Fe^{II}(mXylMeBz[16]Cyc)Cl]^+$, $\Delta H^* = 37.5$ kJ/mol, $\Delta S^* = 9.2$ $Jmol^{-1}K^{-1}$, respectively. The fact that both activation parameters are small supports the view that the mechanism is an adiabatic outer-sphere process.

Acknowledgement

The support of the National Science Foundation is gratefully acknowledged.

References

1. a) M. Wilström, M. Saraste, *New Comprehensive Biochemistry, Volume 9, Bioenergetics*; Ernster (Ed.), Elsevier, Amsterdam, 1984; b) H.A. Harbury, R.H.L. Marks, *Inorganic Biochemistry, Vol 2*;

G.L. Eichhorn, (Ed.) Elsevier, Amsterdam, 1973; c) *Oxidases and Related Redox Systems, Vol. 2*; King, T.E.; Mason, H.S.; Morrison, M.; (Eds.), John Wiley & Sons, New York, 1964; d) S. Wherland, H.B. Gray, *Biological Aspects of Inorganic Chemistry*; A.W. Addision, et al; Eds.; Wiley-Interscience, 1977, pp. 289–365.

2. a) M.A. Cusanovich, T.E. Meyer, G. Tollin, *Advances in Inorganic Chemistry, Vol. 7 Heme Proteins;* G.L. Eichhorn, L.G. Marzilli (Eds.) Elsevier, New York, 1987; b) F.A. Armstrong, H.A.O. Hill, N.J. Walton, *Acc. Chem. Res.* **21**, 407 (1988); c) G. McLendon, R. Hake, *Chem. Rev.* **92**, 481 (1992); d) B.E. Bowler, A.L. Raphael, H.B. Gray, *Prog. Inorg. Chem.* **38**, 259 (1990); e) M.J. Therein, J. Chang, A.L. Raphael, B.E. Bowler, H.B. Gray, *Struct. Bond.* **75**, 109 (1991); f) B.G. Malmstrom, *Chem. Rev.* **90** 1247 (1990).
3. a) R.S. Wade, M.L. Chu, C.E. Castro, *Oxidases and Related Redox Systems*; T.E. King, H.S. Mason, M. Morrison, (Eds.), Pergamon Press, Oxford, 1982; b) K.M. Kadish, *Prog. Inorg. Chem.* **34**, 435 (1986); c) D.H. Busch, D.G. Pillsbury, F.V. Lovecchio, A.M. Tait, Y. Hung, S. Jackels, M.C. Rakowski, W.P. Schammel, L. Y. Martin, *Electrochemical Studies of Biological Systems*; ACS Symposium Series No. 38; D.T. Sawyer, (Ed.), American Chemical Society, Washington, 1977; d) M.Y. Chavan, T.J. Meade, D.H. Busch, T. Kuwana, *Inorg. Chem.* **25**, 314 (1986).
4. a) R.A. Marcus, *J. Chem. Phys.* **43**, 679 (1965); b) R.A. Marcus, *Ann. Rev. Phys. Chem.* **15**, 155 (1964); c) R.A. Marcus, *J. Phys. Chem.* **67**, 853 (1963); d) R.A., Marcus, N. Sutin, *Inorg. Chem.* **14**, 213 (1975); e) R.A. Marcus, *Science* **256**, 1523 (1992).
5. a) L.D. Dickerson, A. Sauer-Masarwa, N. Herron, C.M. Fendrick, D.H. Busch *J. Am. Chem. Soc.* **115**, 3623 (1993); b) N. Herron, M.Y. Chavan, D.H. Busch, *J. Chem. Soc., Dalton Trans.* 1491 (1984).
6. a) W.P. Schammel, K.S.B. Mertes, G.G. Christoph. D.H. Busch. *J. Am. Chem. Soc.* **101**, 1622 (1979); b) N. Herron, D.H. Busch, *J. Am. Chem. Soc.* **25**, 1236 (1981); c) N. Herron, D.H. Busch, *J. Am. Chem. Soc.* **102**, 3285 (1980); d) N. Herron, J. H. Cameron, G.L. Neer, D.H. Busch, *J. Am. Chem. Soc.***105**, 298 (1983); e) N. Herron, L.L. Zimmer, J.J. Grzybowski, D.J. Olszanski, S.C. Jackels, R.W. Callahan, J.H. Cameron, G.G. Christoph, D.H. Busch, *J. Am. Chem. Soc.* **105**, 6585 (1983); f) N. Herron, L. Dickerson, D.H. Busch, *J. Chem. Soc., Chem. Commun.* 884, (1983); g) D.H. Busch, *La Transfusione del Sangue* **33**, 57 (1988); h) D.H. Busch, *Oxygen Complexes and Oxygen Activation by Transition Metals*; A.E. Martell, D.T. Sawyer, (Eds.), Plenum Publ. Corp., 1988, 359–380.
7. a) A. Sauer-Masarwa, N. Herron, C.M. Fendrick, D.H. Busch, *Inorg. Chem.* **32**, 1086 (1993); b) A. Sauer-Masarwa, L.D. Dickerson, N. Herron, D.H. Busch, *Coord. Chem. Rev.* **128**, 117 (1993).
8. a) J.A. Watkins, S. Kawanishi, W.S. Caughey, *Biochem. Biophys. Res. Commun.* **132**, 742 (1985); b) P. George, C. Stratmann,J. *Biochem. J.* **51**, 418 (1952).
9. P.R. Warburton, D.H. Busch, *Perspectives in Bioinorganic Chemistry Vol. 2*; R.W. Hay, (Ed.) 1993, 1–79.
10. R. Battino, T.R. Rettich, T. Tominaga, *J. Phys. Chem. Ref. Data* **12**, 163 (1983).
11. a) C.J. Cairns, D.H. Busch, *Inorg. Synth.* **27**, 261 (1990); b) P.A. Padolik, A.J. Jircitano, N.W. Alcock, D.H. Busch, *Inorg. Chem.* **30**, 2713 (1991).
12. M.G. Segal, A.G. Sykes, *J. Am. Chem. Soc.* **100**, 4585 (1978).
13. Soodan Kim, Ph. D. Thesis; The Ohio State University, 1989.
14. K.A. Goldsby, B.D. Beato, D.H. Busch, *Inorg. Chem.* **25**, 2342 (1986).
15. a) R.A. Marcus, *Discuss Faraday Soc.*, **29**, 21 (1960); b) R.A. Marcus, *Can. J. Chem.* **37**, 155 (1959).
16. R.J. Mureinik, *Inorg. Nucl. Chem. Lett.* **12**, 319 (1976).
17. E.S. Yang, M. Chan, A.C. Wahl, *J. Phys. Chem.* **79**, 2049 (1975).
18. a) R. Farina, R.G. Wilins, *Inorg. Chem.* **7**, 514 (1968); b) B.R. Baker, F. Basolo, H.M. Neumann, *J. Phys. Chem.* **63**, 371 (1959).
19. E. Pelizzetti, *Inorg. Chem.* **18**, 1386 (1979).
20. N. Sutin, *Prog. Inorg. Chem.* **30**, 441 (1983).
21. a) H.E. Toma, A.C. Silva, C. *Can. J. Chem.* **64**, 1280 (1986); b) C.A. Koval, M. E. Ketterer, C.M. Reidsema, *J. Phys. Chem.* **90**, 4201 (1986); c) R.M.L. Warren, A.G. Lappin, B.D. Mehta, H.M. Neumann, *Inorg. Chem.* **29**, 4185, 1990.
22. a) W.-K. Lin, Ph. D. Thesis, The Ohio State University, 1988; b) D.H. Busch, L. L. Zimmer, J.J. Grzybowski, D.J. Olszanski, S.C. Jackels, R.W. Callahan, G.G. Christoph, *Proc. Natl. Acad. Sci. USA* **78**, 5919, 1981.
23. G.M. Brown, N. Sutin, *J. Am. Chem. Soc.* **101**, 883, 1979.

24. J.A. Streeky, D.G. Pillsbury, D.H. Busch, *Inorg. Chem.* **11**, 3148 (1980); b) N.W. Alcock, W. Lin, A. Jircitano, J.D. Mokren, P.W.R. Corfield, G. Johnson, G. Novotnak, C. Cairns, D.H. Busch, *Inorg. Chem.* **26**, 440 (1987).
25. L. Pauling, *The Nature of the Chemical Bond*; 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, pp. 256–264.
26. C.E. Castro, *The Porphyrins, V. 5*; D. Dolphin, Ed.; 1978, pp. 1–27.
27. J.V. McArdle, H.B. Gray, C. Creutz, N. Sutin, *J. Am. Chem. Soc.* **96**, 5737, 1974.
28. a) S. Larsson, *J. Chem. Soc. Faraday Trans. 2* **79**, 1375 (1983); b) S. Larsson, *J. Am. Chem. Soc.* **103**, 4031 (1981); c) D.N. Beratan, J. J. Hopfield, *J. Chem. Soc.* **106**, 1584 (1984); d) P. Siders, R.J. Cave, R.A. Marcus, *J. Chem. Phys.* **81**, 5613 (1984).
29. a) M. Chou, C. Creutz, N. Sutin, *J. Am. Chem. Soc.* **99**, 5615 (1977); b) R.J. Campion, N. Purdie, N. Sutin *Inorg. Chem.* **3**, 1091 (1964); c) C.-T. Lin, W. Bottcher, M. Chou, C. Creutz, N. Sutin, *J. Am. Chem. Soc.* **98**, 6536 (1976).
30. a) E. Koenig, K.J. Watson, *Chem. Phys. Lett.* **6**, 457 (1970); b) H. Taube, *Adv. Chem. Ser.* **162**, (1977); c) S. Wherland, H.B. Gray, *Proc. Natl. Acad. Sci., USA* **73**, 2950, 1976.
31. a) N. Sutin, *Chem. Brit.* **8**, 148, 1972; b) R.F. Pasternack, E.G. Spiro, *J. Am. Chem. Soc.* **100**, 968, 1978.
32. Calculations used the program MM2/MMP2, as modified by Wang and Ye of this research group.
33. E.C. Niederhoffer, A.E. Martell, P. Rudolf, A. Clearfield, *Cryst. Struct. Comm.* **11**, 1951 (1982).
34. H. Taube, *Electron Transfer Reactions of Complex Ions in Solution*; Academic Press, New York, 1970.