Kinetics and Mechanisms of Some Electron Transfer Reactions of Ferrocenes[1a]

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Abstract: Kinetic studies have been carried out on two groups of electron transfer reactions: (1) the electron transfer between the oxidized and reduced forms of different ferrocene derivatives, and (2) the oxidation of the ferrocene derivatives by Fe^{3+}. The kinetic results in the first instance were correlated with the Marcus relation for outer-sphere electron transfer, permitting the computation of rate constants for the self-exchange reaction between each ferrocene compound and its respective oxidized form. The rates of the Fe^{3+} oxidations are considerably lower than the theoretical values. Studies were also carried out on $Fe(C_5H_5)(B_9C_2H_{11})^-$ and $Fe(B_9C_2H_{11})_2{}^{2-}$, although only the oxidation of the former compound by Fe^{3+} occurred at a measurable rate.

Relatively few quantitative studies have been carried out on the oxidation–reduction chemistry of ferrocene and ferricenium ion. Kinetics studies were reported on the oxidation of ferrocene by iodine[2] and on the reduction of ferricenium ions by Sn(II).[3] The limited data on ferrocene–ferricenium ion reactions may be due to the instability of $Fe(C_5H_5)_2{}^+$ in solution and to the rapidity of many of its reactions. With careful choice of conditions, a number of quantitative studies can be made.

Radiotracer experiments[4,5] have been carried out to measure the rate of the electron exchange process shown in eq 1. These measurements gave evidence of a very

$$Fe(C_5H_5)_2 + {}^*Fe(C_5H_5)_2{}^+ = Fe(C_5H_5)_2{}^+ + {}^*Fe(C_5H_5)_2 \quad (1)$$

rapid reaction, with a rate constant[4] which was barely within the scope of the method used (the mean half-time for exchange was 2 ± 0.5 msec, while the best mixing–quenching time was of the order of 3 msec); Stranks reports $k_{ex} \cong 1.7 \times 10^6\ M^{-1}\ sec^{-1}$ at $-70°$ in methanol. Nmr line broadening measurements[6] on the same electron exchange reaction were thwarted by the long transverse relaxation time of $Fe(C_5H_5)_2{}^+$. These experiments gave only a lower limit: $k_{ex} > 10^5\ M^{-1}\ sec^{-1}$ at 26° in acetone.[6] Ruff and coworkers[7] have utilized measurements of diffusion coefficients to evaluate the exchange rate. They find that the diffusion coefficient of $Fe(C_5H_5)_2{}^-$ is increased somewhat in the presence of $Fe(C_5H_5)_2$ and interpret the enhancement in terms of electron transfer. Their work indicates very rapid electron exchange in alcohols, with rate constants close to the diffusion controlled limit near room temperature.

We have found it possible to make rate measurements using the stopped-flow method on net electron transfer reactions between different substituted derivatives of ferrocene and ferricenium ions. For example, the following reaction was one on which kinetic studies were carried out

$$Fe(C_5H_4Ph)(C_5H_5)^+ + Fe(C_5H_4CH_3)_2 = Fe(C_5H_4Ph)(C_5H_5) + Fe(C_5H_4CH_3)_2{}^+ \quad (2)$$

These so-called cross reactions are of interest in their own right, because they relate to previously unstudied electron transfer processes between π complexes. Moreover, they are important because correlation of these results with the theoretical predictions of the Marcus relation[8] offers the possibility of evaluating the desired electron exchange rate constants as in reaction 1. A preliminary account of a part of this work has been published.[9]

Studies were also carried out on the oxidation of ferrocene and its substituted derivatives (including two caged borane compounds[10]) by $Fe(H_2O)_6{}^{3+}$, as in the equation

$$Fe(C_5H_4X)(C_5H_4Y) + Fe(H_2O)_6{}^{3+} = Fe(C_5H_4X)(C_5H_4Y)^+ + Fe(H_2O)_6{}^{2+} \quad (3)$$

The kinetic results on this group of reactions can also be considered in light of this theoretical model.

Issues of stereochemistry are also involved. The question of what relative geometry the oxidant and reductant must attain in the transition state may perhaps be approached by considering the bulk of substituent groups. Also, the pseudoferrocenes in the form of Hawthorne's carbollyl compounds can be studied in an attempt to see whether these compounds correlate with the ferrocene compounds.

Ferricenium ion is known to associate with chloride[11] and triiodide[12] ions in solution, and it appears that such association may stabilize ferricenium ion relative

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(1) (a) Based on the Ph.D. Thesis of J. R. Pladziewicz, Iowa State University, 1971; (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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Table I. Formal Electrode Potentials of Ferricenium Ions|Ferrocene Couples

No.	Compound	$E^{0\prime}$, V, *vs.* sce		
		25°[a]	0°[a]	25°[b]
	$Fe(H_2O)_6^{3+,2+}$	0.4960 ± 0.003	0.4613 ± 0.0006	0.5248 ± 0.0010
1	$Fe(C_5H_4CH_3)_2$	0.1899 ± 0.0005	0.1940 ± 0.0005	0.167
2	$Fe(C_5H_4\text{-}n\text{-}Bu)_2$	0.2354 ± 0.0004	0.2421 ± 0.0004	0.184 ± 0.003
3	$Fe(C_5H_5)(C_5H_4\text{-}n\text{-}Bu)$	0.2556 ± 0.0005	0.2614 ± 0.0003	0.219 ± 0.001
4	$Fe(C_5H_5)_2$	0.2719 ± 0.0005	0.2760 ± 0.0003	0.255 ± 0.002
5	$Fe(C_5H_4)(C_5H_4HgCl)$	0.2797 ± 0.0004		
6	$Fe(C_5H_5)(C_5H_4CH_2OH)$	0.2806 ± 0.0005	0.2861 ± 0.0003	0.270
7	$Fe(C_5H_5)(C_5H_4Ph)$	0.3267 ± 0.0010	0.3301 ± 0.0003	0.301 ± 0.001
8	$Fe(C_5H_5)(C_5H_4I)$	~0.427	~0.444	
9	$Fe(C_5H_5)(B_9C_2H_{11})^-$	−0.12[c]	*c*	*c*
10	$Fe(B_9C_2H_{11})^{2-}$	*d*	*d*	*d*

[a] In *n*-PrOH–H_2O (1:1 v/v), $\mu = 0.050$ *M*. [b] In THF–H_2O (1:1 v/v), $\mu = 1.00$ *M*. [c] A value of −0.08 V was determined in 1:1 acetone–H_2O, $\mu = 0.1$ *M*. [d] A value of −0.425 V was determined in 1:1 acetone–H_2O, $\mu = 0.1$ *M*.

to ferrocene.[13] The question whether anions will promote electron transfer was also considered.

We report here on the following: (a) a potentiometric evaluation of the electrode potentials for eight ferrocene–ferricenium ion couples in propanol–water, (b) kinetic measurements on 22 cross reactions between ferrocenes and ferricenium ions for different pairwise combinations as suggested by reaction 2, and (c) kinetic measurements on the oxidation of each ferrocene compound by $Fe(H_2O)_6^{3+}$ as in reaction 3.

Experimental Section

Materials. Most of the ferrocene derivations were commercially available. Ferrocene (Alfa Inorganics) was purified by vacuum sublimation; 1,1′-dimethylferrocene (Alfa Inorganics) was recrystallized twice from 1:1 water–ethanol; chloromercuriferrocene, $Fe(C_5H_5)(C_5H_4HgCl)$ (Research Organic Chemicals), was recrystallized from acetone; and hydroxymethylferrocene, $Fe(C_5H_5)(C_5H_4CH_2OH)$ (Research Organic Chemicals), was recrystallized twice from Skelly B. Phenylferrocene, $Fe(C_5H_5)(C_5H_4C_6H_5)$, and iodoferrocene, $Fe(C_5H_5)(C_5H_4I)$, were prepared as described in the literature.[14,15] The *n*-butyl and 1,1′-di-*n*-butyl derivatives were purchased from Alfa Inorganics and used without further purification. The identity and purity of the ferrocene compounds were established by melting point (solids) or refractive index (liquids) and by visible–uv spectrophotometric methods in comparison with known values. In four cases elemental analyses were also obtained. The agreement with literature values was close in every case and the complete data are given in the thesis cited.[1a]

Mono- and bis-π-(3)-1,2-dicarbollyl derivatives of both iron(III) and iron(II) were prepared[16] as their tetramethylammonium salts: $Fe(C_2B_9H_{11})(C_5H_5)$, $[(CH_3)_4N]Fe(C_2B_9H_{11})(C_5H_5)$, $[(CH_3)_4N]Fe(C_2B_9H_{11})_2$, and $[(CH_3)_4N]_2Fe(C_2B_9H_{11})_2$ and characterized by their uv–visible spectra according to Hawthorne and coworkers.[17]

Ferricenium ions were prepared in solution, and used as such without the isolation of solid compounds which tend to be unstable. The oxidation with Fe^{3+} in dilute perchloric acid according to reaction 3 (which proved to be quantitative except for iodoferrocene) provided a convenient source of ferricenium solutions, as did the oxidations with Cr(VI) and Ce(IV). In all cases the ferricenium ion spectra were identical, and solutions prepared using any of these oxidizing agents gave identical kinetic results.

Stock solutions of the ferrocene derivatives in aqueous 1-propanol, acetone, and ethanol were stable indefinitely. Ferricenium solutions generally proved less stable, but the derivatives studied here had solutions which decomposed no more than 5% in 30 min, which was sufficient for our purposes. Many ferricenium ion solutions are, in fact, stable over much longer periods; the least stable derivatives are those having the higher electrode potentials, such as $Fe(C_5H_5)(C_5H_4I)^+$.

Hydrated iron(III) perchlorate was prepared by fuming iron(III) chloride in perchloric acid. The chloride-free salt was recrystallized twice from perchloric acid solution. Solutions of iron(II) perchlorate were prepared by oxidation of iron by dilute perchloric acid under nitrogen.

Triply distilled water was used throughout. Baker analyzed THF, freshly distilled after refluxing over sodium for 6–12 hr, was stored under nitrogen and used within 6 hr of distillation. Reagent grade 1-propanol was used without further purification.

Reaction Media. The electrode potentials for the ferrocene–ferricenium couples were evaluated in 1:1 v/v *n*-PrOH–H_2O in solutions having 0.050 *M* ionic strength maintained by barium perchlorate. The rate measurements on reaction 2 were performed in the same medium. The kinetic studies on reaction 3 were carried out in 1:1 v/v H_2O–THF (mol fraction THF = 0.180), with 1.00 *M* ionic strength maintained by lithium perchlorate–perchloric acid; $[H^+]$ was ≥ 0.1 *M* to avoid hydrolysis of Fe(III). In addition, a few kinetic measurements in each case were performed with different solvents, different solvent compositions, or different ionic strengths to explore the effect of these variables.

Electrode Potentials. Evaluation of the formal potentials ($E^{0\prime}$) corresponding to the half-reactions given in eq 4 was accomplished

$$Fe(C_5H_4X)(C_5H_4Y)^+ + e^- = Fe(C_5H_4X)(C_5H_4Y) \qquad (4)$$

by the direct measurement of emf using a Leeds and Northrup potentiometer and galvanometer. The titrations were done as follows. The ferrocene solution, typically 6×10^{-4} *M*, was placed in the titration cell and equilibrated at the desired temperature. The solution was first purged with nitrogen and then titrated with nitrogen-purged $Fe(H_2O)_6^{3+}$ according to reaction 3, the system being maintained at 25° under nitrogen. After each addition of Fe^{3+}, the emf was measured. Plots of *E vs.* ln $[FeCp_2^+]/[FeCp_2]$ according to the relation

$$E = E^{0\prime} + RT/F \ln [FeCp_2^+]/[FeCp_2] \qquad (5)$$

proved to be linear and in each case had the expected slope. $E^{0\prime}$ was taken as the value of *E* at the half-equivalence point on the graph of *E vs.* ln $[FeCp_2^+]/[FeCp_2]$.

This method was successful for all the ferrocene compounds except iodoferrocene, where the potential is close enough to that of Fe^{3+}–Fe^{2+} that reaction 3 does not proceed to completion. In this case a solution of $Fe(C_5H_5)(C_5H_4I)^+$ was prepared by oxidizing iodoferrocene with an exactly equivalent quantity of cerium(IV) perchlorate. This solution was added incrementally to the iodoferrocene solution, and the data treated according to eq 5. The formal electrode potentials determined in this manner are summarized in Table I.

Spectrophotometric and Stoichiometric Measurements. Uv-visible spectra were measured using a Cary Model 14 recording spectrophotometer. All of the ferrocene derivatives except iodoferrocene are quantitatively oxidized by Fe^{3+} in *n*-PrOH–H_2O according to reaction 3. The wavelength region 600–700 nm proved particularly convenient for following the course of the oxidations by Fe^{3+} because only the ferricenium ions have significant molar absorptivity values. In every case the spectrophotometric titrations with Fe^{3+} agreed to within 1% of the concentration based on the weighed amount of ferrocene compound.

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[14] V. Weinmayr, *J. Amer. Chem. Soc.*, 77, 3012 (1955).

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[16] We are grateful to Professor M. F. Hawthorne and Mr. Donald F. Dustin for the gift of 1,2-$B_{10}C_2H_{12}$ used in this study.

[17] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and B. A. Wegner, *J. Amer. Chem. Soc.*, 90, 879 (1968).

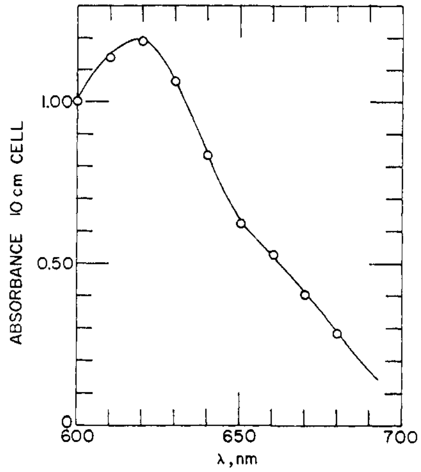

Figure 1. Observed spectrum (solid line) for a mixture of $Fe(C_5H_5)_2$ (1.43×10^{-4} *M*), $Fe(C_5H_5)_2^+$ (1.30×10^{-4} *M*), $Fe(C_5H_5)(C_5H_4Bu)$ (1.03×10^{-4} *M*), and $Fe(C_5H_5)(C_5H_4Bu)^+$ (1.79×10^{-4} *M*) in *n*-PrOH–H_2O at 25°, $\mu = 0.05$ *M*. The points give the anticipated spectrum for the indicated mixture based on the independently determined molar absorptivities and equilibrium constant.

As expected from the electrode potentials cited in Table I, the reactions between ferrocene and ferricenium ions proceeded to measureable equilibria in most instances. In principle the final absorption spectrum of such a solution should be sufficient to permit the determination of K_{eq} since the molar absorptivity of each of the four species present in a particular solution is known. In practice sufficient accuracy cannot be attained to evaluate K_{eq} by this method with adequate precision because of the presence of four absorbing species having comparable molar absorptivities. Some spectral measurements of this sort were made, however, and the observed spectrum compared with that calculated on the basis of K_{eq} derived from E^0 values and the known molar absorptivities. One such example is shown in Figure 1, which illustrates the good agreement between the theoretical and experimental spectra.

Kinetic Measurements. A Durrum stopped-flow spectrophotometer equipped with a Kel-F mixing block having a 2-cm optical path was employed for these measurements. The ferrocene–ferricenium ion reactions (eq 1) were studied at wavelengths between 240 and 300 nm where the ferricenium species have large molar absorptivities. Generally, wavelengths slightly off the ferricenium ion maxima[16] were chosen to maximize the difference between the two $FeCp_2^+$ compounds and achieve a larger absorbance change with a smaller background absorbance. The rate constants proved independent of the wavelength used to follow the reaction; at each wavelength studied the magnitude and direction of the absorbance change was consistent with the cross reaction occurring based on the values of K_{eq} and the independently determined molar absorptivities.

The reactions between iron(III) and the ferrocene derivatives were studied primarily at λ 600–700 nm where only the various ferricenium ions absorb. Experiments with lower reactant concentrations were followed in the region λ 300–340 nm, where the molar absorptivities of the ferricenium species are much larger. In all cases the reaction rate proved independent of wavelength. The THF–water solutions of the ferrocenes and of iron(III) were prepared and transferred under nitrogen, using glass syringes with Teflon needles. Since the peroxide formed in the THF in the presence of oxygen was shown to react with ferrocene in acidic solution, oxygen was excluded from the solution at all stages and only freshly distilled solvent was used.

Kinetic Data. The concentration conditions for the $FeCp_2$–Fe^{3+} reactions were chosen to ensure pseudo-first-order kinetics. The excess reagent was generally present to at least a tenfold stoichiometric ratio. The kinetic data in terms of absorbance (*D*) were treated in accord with the equation

$$\ln (D_\infty - D_t) = \ln (D_\infty - D_0) - k_2[X]_{av}t \qquad (6)$$

where k_2 is the second-order rate constant corresponding to the kinetic expression applicable to reaction 3

$$-d[FeCp_2]/dt = k_2[Fe^{3+}][FeCp_2] \qquad (7)$$

and $[X]_{av}$ is the average concentration of the reactant in excess, either Fe(III) or the ferrocene compound, in that particular kinetic run. Plots of log $(D_\infty - D_t)$ *vs.* time were linear, and from their slopes values of k_2 were computed for each run.

The only exception to this is iodoferrocene, where the reaction with Fe^{3+} did not proceed to completion. In this case the experiments were designed so that both Fe^{3+} and Fe^{2+} were added in relatively high concentration. Under these conditions the slope of a plot of ln $(D_\infty - D_t)$ *vs.* time defines a pseudo-first-order rate constant for the rate of approach to equilibrium

$$k_{obsd} = k_2[Fe^{3+}]_{av} + k_{-2}[Fe^{2+}]_{av} \qquad (8)$$

and to evalute the rate constants a plot was made of $k_{obsd}/[Fe^{3+}]$ *vs.* $[Fe^{2+}]_{av}/[Fe^{3+}]_{av}$.

The reactions between ferrocenes and ferricenium ions proceed as in the following kinetic pattern

$$A + B^+ \underset{k'}{\overset{k}{\rightleftarrows}} A^+ + B \quad K_{eq} = k/k' \qquad (9)$$

$$-d[A]/dt = k[A][B^+] - k'[A^+][B] \qquad (10)$$

The integrated rate law for eq 10 has been given by Frost and Pearson;[18] the form depends upon the concentration conditions. With $[B^+]_0 \neq [A]_0$, and A^+ and B initially absent, the following expression applies

$$[Q(1 - K_{eq}^{-1})]^{-1} \ln \left\{\frac{X_e([A] - [A]_e + Q)}{([A] - [A]_e)(X_e + Q)}\right\} = kt \qquad (11)$$

in which the subscript e refers to equilibrium, $[A] = [A]_0 - X$, $X_e = [A]_0 - [A]_e$, $X = X_e(D_0 - D_t)/(D_0 - D_e)$, and $Q = [1/(K_{eq} - 1)]\{K_{eq}^2([B^+]_0 - [A]_0)^2 + 4[A]_0[B^+]_0K_{eq}\}^{1/2}$. In the case with equal starting rate concentrations, again with A^+ and B initially absent, the integrated expression simplifies to the form

$$(K_{eq}^{1/2}/2[A]_0) \ln \left\{\frac{X([A]_0 - 2X_e) + [A]_0X_e}{[A_0](X_e - X)}\right\} = kt \qquad (12)$$

The conditions chosen for these experiments were such that either eq 11 or 12 was applicable. The kinetic data from each run were fit to the appropriate expression using the value of K_{eq} derived from the potentiometric data in Table I. For many of the combinations of reactants in eq 2, experiments starting with mixtures of A^+ and B, rather than A and B^+, were also performed. Expressions entirely analogous to eq 11 and 12 were applicable, and the reverse rate constant thus evaluated, *k′* of reaction 9, was used to compute the forward rate constant *k* by the relation $k = k'K_{eq}$.

Results

Kinetic Data on Fe^{3+} Reactions. The second-order rate expression given by eq 7 was shown to be applicable to the reactions in eq 3 by the constancy of the rate constant values with concentration variations. The values of k_2 proved to be independent of which reagent, Fe^{3+} or ferrocene, was in excess. Values of k_2 were also independent of hydrogen ion concentration in the range $0.10 \leq [H^+] \leq 1.00$ *M*. The results of these experiments are summarized in Table II.[19]

The reaction of Fe^{3+} with iodoferrocene, unlike the other ferrocene compounds, did not proceed to completion under the conditions studied. As discussed in a preceding section, both Fe^{3+} and Fe^{2+} were added to simplify the treatment of the data under the reversible reaction conditions. A plot of $k_{obsd}/[Fe^{3+}]_{av}$ *vs.* $[Fe^{2+}]_{av}/[Fe^{3+}]_{av}$, as suggested by eq 8, is shown in Figure 2, is linear and leads to the rate constants $k_2 = 5.5 \times 10^2$ M^{-1} sec^{-1} and $k_{-2} = 19$ M^{-1} sec^{-1}. From

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(18) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," Wiley, New York, N. Y., 1961, pp 187–188.

(19) The data for the original kinetic runs are given in the thesis cited.[11]

Table II. Kinetic Data for Iron(III)–Ferrocene Reactions[a]

Ferrocene compound[b]	Concn range × 10^3, *M* [Fe^{3+}]	[$FeCp_2$]	$10^{-4}k_2$,[c] M^{-1} sec^{-1}
1	0.030–3.00	0.003–0.50	3.2 ± 0.15 (3)
2	0.030–3.00	0.010–1.00	1.43 ± 0.10 (4)
3	0.030–3.00	0.030–1.00	1.50 ± 0.05 (4)
4	0.010–1.00	0.010–1.00	1.05 ± 0.04 (4)
4 (10.0°)	0.10–5.00	0.10–2.00	0.42 ± 0.01 (2)
4 (40.0°)	0.020–0.30	0.020–0.20	2.56 ± 0.13 (2)
6	0.050–3.00	0.010–1.00	1.79 ± 0.07 (4)
7	0.050–2.00	0.010–1.00	0.50 ± 0.02 (5)
8	0.050–10.00	0.05–0.50	0.055 (8)[d]

[a] Rate constants measured at 25° in 1:1 v/v H_2O–THF with perchloric acid (0.1–1 *M*) and lithium perchlorate added to maintain 1.00 *M* ionic strength. [b] The numbering of the ferrocene compounds is given in Table I. Compound **5** decomposes too rapidly in these acidic solutions. [c] The uncertainty shown represents the average deviation of the individual rate constants from the mean; the number of individual rate experiments under different conditions is given in parentheses. [d] The results for this compound were obtained by a modified method (as discussed in the text) because this oxidation does not proceed to completion; the value cited here corresponds to the calculated second-order rate constant for the reaction of Fe^{3+} and $Fe(C_5H_5)(C_5H_4I)$ as in reaction 3.

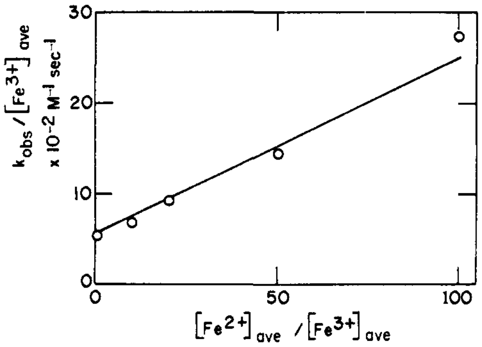

Figure 2. A plot of the kinetic data for the reaction between Fe^{3+} and $Fe(C_5H_5)(C_5H_5I)$.

Table III. Summary of Second-Order Rate Constants k_{ij} for the Electron Transfer Reactions of Ferrocenes and Ferricenium Ions[a]

Reaction	$10^{-6}k_{ij}$, M^{-1} sec^{-1}	Reaction	$10^{-6}k_{ij}$, M^{-1} sec^{-1}	Reaction	$10^{-6}k_{ij}$, M^{-1} sec^{-1}
13	33 ± 4	25	14 ± 1	47	28 ± 4
14	23 ± 3	26	11.8 ± 0.8	48	145 ± 30
15	26 ± 1	27	67 ± 5	56	4.2 ± 0.3
16	38 ± 2	34	7.3 ± 0.5	57	29 ± 2
17	107 ± 10	35	8.3 ± 0.5	67	20 ± 2
18	≥150	37	39 ± 3	68	95 ± 10
23	8.9 ± 1	45	8.2 ± 0.8	78	109 ± 15
24	12.8 ± 1.4	46	6.0 ± 0.7		

[a] At 25.0°, in 1:1 v/v *n*-PrOH–H_2O at μ = 0.050 *M*; reactions are listed according to the convention stated in ref 20.

the quotient k_2/k_{-2}, a value of 29 is computed for K_{eq}. The value based on the formal electrode potential (in PrOH–H_2O, however, not THF–H_2O) is 9.

Kinetic Data on $FeCp_2$–$FeCp_2^+$ Reactions. These reactions all occurred too rapidly to be followed under the pseudo-first-order approximation. The kinetic measurements on these reactions were carried out on solutions with comparable amounts of each reactant. In the cases where the initial concentrations were chosen to be equal (within the experimental error of preparing the reactant solutions) the data were evaluated as suggested by eq 12; whereas eq 11 was used for runs having unequal starting concentrations. (In the latter category runs having only small differences in reactant concentration were avoided.)

Considering the eight ferrocene derivatives, 28 distinct reactions are possible. Of these, 22 were studied in the course of this work.[20] Typical results from two individual studies are presented in Table IV, and a summary of the kinetic data on all 22 reactions is given in Table III.

Table IV. Rate Constants for Individual Experiments in Ferrocene–Ferricenium Ion Reactions[a]

Initial concn × 10^6, *M* [A]	[B^+]	[A^+]	[B]	$10^{-6}k_{ij}$,[b] M^{-1} sec^{-1}
Part A: $Fe(C_5H_4\text{-}n\text{-}Bu)_2 + Fe(C_5H_5)_2^+$ (reaction 24)				
6.0	6.0			15.0 ± 1.0
1.0	1.0			16.0 ± 2.0
8.0	8.0			15.0 ± 2.0
3.0	3.0			11.3 ± 2.0
4.0	8.0			13.8 ± 1.0
6.0	4.0			11.8 ± 1.3
		6.0	6.0	13.0 ± 1.2
		9.0	9.0	11.5 ± 1.0
			Av	12.8 ± 1.4
Part B: $Fe(C_5H_5)_2 + Fe(C_5H_5)(C_5H_4CH_2OH)^+$ (reaction 46)				
6.0	6.0			5.8 ± 0.3
12.0	12.0			6.2 ± 0.3
6.0	6.0			5.6 ± 0.5
		6.0	6.0	4.6 ± 0.4
		12.0	12.0	6.7 ± 0.3
		9.0	9.0	7.3 ± 0.6
			Av	6.0 ± 0.7

[a] At 25.0° in 1:1 v/v *n*-PrOH–H_2O at μ = 0.050 *M*. [b] The uncertainty indicated for the individual rate constants represents the average deviation from the mean of three or four determinations using the same set of solutions. The uncertainty cited for the average rate constant represents the average deviation from the unweighted mean of the individial determinations.

The constancy of the k_{ij} values over the range of initial concentrations in every case was taken as confirming evidence for the assumed rate expression as given in eq 10. Two of the ferrocene–ferricenium ion reactions were also examined over a range of temperatures. The temperature studies on $E^{0\prime}$ afforded the values of K_{eq} at different temperatures needed to evaluate these kinetic data according to the integrated rate expressions of eq 11 and 12. The rate constants and activation parameters are summarized in Table V.

Carbollyl Derivatives. The oxidation of $Fe(C_5H_5)$-

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[20] Using the designations listed in Table I the second-order rate constant for the reaction of ferrocene (i) with ferricenium ion (j) is designated k_{ij}. In a number of cases the reverse reaction (rate constant k_{ji}) was also evaluated. As the kinetic data are being presented each reaction will be referred to by the ij designation in which K_{eq} exceeds unity.

Table V. Temperature Effects and Activation Parameters

	Reaction 14	Reaction 47
$10^{-6}k$, M^{-1} sec^{-1} (10°)	14.5 ± 2.5	19.2 ± 1.0
$10^{-6}k$, M^{-1} sec^{-1} (25°)	23.0 ± 3.0	28.0 ± 4.0
$10^{-6}k$, M^{-1} sec^{-1} (40°)	27.0 ± 1.5	35.3 ± 2.0
$\Delta H^{\ddagger}$, kcal mol^{-1}	3.0 ± 1.0	3.0 ± 0.6
$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	−15.0 ± 3.0	−14.4 ± 2.1

Table VI. Kinetic Studies on Carbollyl Derivatives[a,b]

Reactions	Initial concn × 10⁵, *M* $[A]_0$	$[B^+]_0$	k, M^{-1} sec^{-1}
$Fe(C_5H_5)(C_2B_9H_{11})^- + Fe^{3+}$	0.25	2.5	$(4.8 \pm 0.3) \times 10^6$
$Fe(C_5H_5)(C_2B_9H_{11})^- + Fe^{3+}$	2.5	0.25	$(4.6 \pm 0.3) \times 10^6$
$Fe(C_5H_5)(C_2B_9H_{11})^- + Fe^{3+}$	1.0	0.15	$(5.3 \pm 0.3) \times 10^6$
			Av $(4.9 \pm 0.3) \times 10^6$
$Fe(C_2B_9H_{11})_2^{2-} + Fe^{3+}$	0.3	0.3	$\geq 10^8$
$Fe(C_5H_5)(C_2B_9H_{11})^- + Fe(C_5H_5)_2^+$	0.65	0.60	$\geq 10^8$
$Fe(C_2B_9H_{11})_2^{2-} + Fe(C_5H_5)_2^+$	0.30	0.30	$\geq 2 \times 10^8$
$Fe(C_2B_9H_{11})_2^{2-} + Fe(C_5H_5)(C_2B_9H_{11})$	0.20	0.20	$\geq 2 \times 10^8$

[a] At 25°. [b] Fe^{3+} reactions in H_2O–THF at $\mu = 1$ *M* and $FeCp_2$ reactions in H_2O–PrOH at $\mu = 0.05$ *M*.

$(C_2B_9H_{11})^-$ by Fe^{3+} was found to have an average rate constant $(4.9 \pm 0.3) \times 10^6$ M^{-1} sec^{-1} as shown by the experiments in Table VI. The analogous oxidation of $Fe(C_2B_9H_{11})_2^{2-}$ was too rapid for the methods used, and only a lower limit, $k \geq 10^8$ M^{-1} sec^{-1}, could be set.

Several attempts were also made to study ferrocene–ferricenium ion reactions for the carbollyl derivatives. In these cases also the rates were too high for our method (see Table VI), including the following reaction between the two carbollyl derivatives

$$Fe(C_5B_9H_{11})_2^{2-} + Fe(C_5H_5)(C_2B_9H_{11}) \rightleftarrows Fe(C_2B_9H_{11})^- + Fe(C_5H_5)(C_2B_9H_{11})^- \quad (13)$$

Electron Exchange Rates. The kinetic data for the 22 "cross reactions" of the type given by eq 2, summarized in Table III, can be considered in light of the theoretical model of outer-sphere electron transfer developed by Marcus.[7,8] The relation can be expressed as

$$k_{ij} = (k_{ii}k_{jj}K_{ij}f_{ij})^{1/2} \quad (14)$$

where k_{ii} and k_{jj} are the self-exchange rate constants for each ferrocene and its oxidized ferricenium ion corresponding to the process shown in eq 1, K_{ij} is the equilibrium constant for the cross reaction as in eq 2, and where f_{ij} is given by the expression

$$\log f_{ij} = (\log K_{ij})^2/4 \log (k_{ii}k_{jj}/Z^2) \quad (15)$$

Z being the collision frequency of neutral molecules, 10^{11} M^{-1} sec^{-1}.

One approach, clearly only an approximate one, would be the assumption that all of the exchange rate constants have identical values. Were that the case, eq 14 would reduce to the form $k_{ij} = k_{ex}K_{ij}^{1/2}f_{ij}^{1/2}$, and (since the f_{ij} values would then all be quite close to unity for this series) a linear plot of log k_{ij} *vs.* log K_{ij} having a slope of 0.5 would be expected. As shown in Figure 1 of ref 9, the indicated plot is reasonably linear having a slope of 0.55; the exchange rate so calculated is 6×10^6 M^{-1} sec^{-1}.

A more realistic quantitative approach recognizes that the different ferrocene derivatives may each undergo the exchange reaction at a characteristic rate. The 22 values of k_{ij} represent an over-determination of the 8 exchange rate constants. To utilize all the kinetic and equilibrium data obtained in the course of this work to arrive at the "best" values for the exchange rates, eq 14 was recast in the form

$$\ln k_{ii} + \ln k_{jj} = A_{ij} \quad (16)$$

where A_{ij} is a function only of the collision frequency Z, and the experimental k_{ij} and K_{ij} values according to the expression

$$A_{ij} = (\ln k_{ij} - {}^1/_2 \ln K_{ij} + \ln Z) - [(\ln Z - \ln k_{ij})^2 + \ln K_{ij}(\ln Z - \ln k_{ij})]^{1/2} \quad (17)$$

The 22 simultaneous equations of the form of eq 16 which result from the experimental rate determinations were solved for the 8 values of the unknown k_{ii} and k_{jj} parameters. The results of this computation, given as compound $10^{-6}k_{ii}$ (M^{-1} sec^{-1}), are the following: **1**, 6.6; **2**, 6.7; **3**, 6.5; **4**, 5.7; **5**, 5.3; **6**, 4.2; **7**, 18.0; and **8**, 13.7.

The experimental k_{ij} rate constants and the values recalculated according to eq 14 using the exchange rates given in Table VII amounted to a mean deviation of 13%. Figure 3 depicts the extent of this agreement, and it is evident that the eight exchange rate constants

Table VII. Medium Effects

Rate constant (25°), M^{-1} sec^{-1}	Conditions[a]
Part A: $Fe(C_5H_4CH_3)_2 + Fe(C_5H_5)_2^+$, k_{14}	
$(2.2 \pm 0.1) \times 10^7$	$[Cl^-] = 0.010$, $\mu = 0.05$ *M*
$(1.6 \pm 0.2) \times 10^7$	$[Cl^-] = 0.50$, $\mu = 0.50$ *M*
$(1.2 \pm 0.1) \times 10^8$	Neat MeOH, 10^{-3} *M* $HClO_4$, $\mu \cong 0.001$ *M*
Part B: $Fe(C_5H_4Bu)_2 + Fe(C_5H_5)_2^+$, k_{34}	
$(7.4 \pm 0.5) \times 10^6$	$\mu \cong 0.0007$
$(2.1 \pm 0.1) \times 10^7$	$\mu = 0.50$ *M* ($LiClO_4$)
$(3.9 \pm 0.2) \times 10^6$	1:1 v/v THF–H_2O, $\mu = 0.05$ *M*
$(1.0 \pm 0.1) \times 10^7$	1:1 v/v THF–H_2O, $[Cl^-] = 0.50$, $\mu = 1.00$ *M*
$(2.4 \pm 0.2) \times 10^7$	1:1 v/v THF–H_2O, $[H^+] = 0.50$, $\mu = 1.00$ *M*
Part C: $Fe(C_5H_5)_2 + Fe^{3+}$, k_4	
$(4.0 \pm 0.3) \times 10^4$	1:1 acetone–H_2O, $\mu = 1.00$ *M*[b]
2.6×10^4	3:2 acetone–H_2O, $\mu = 1.00$ *M*[b]
1.15×10^4	1:1 acetone–H_2O, $\mu = 0.14$ *M*[c]

[a] The medium is 1:1 v/v *n*-PrOH–H_2O except as noted. [b] Reference 22. [c] Reference 23.

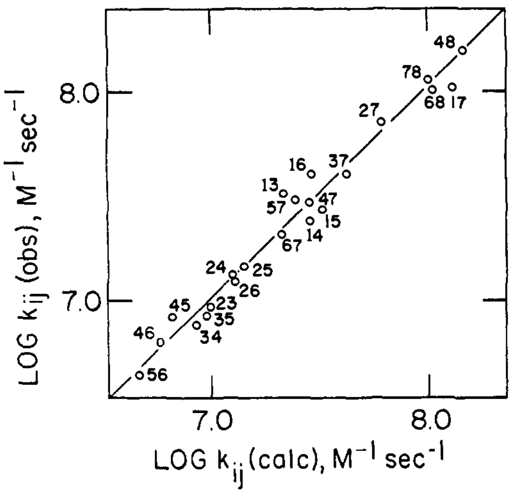

Figure 3. A plot of the observed value of log k_{ij} *vs.* the calculated value, the latter based upon the Marcus relation using the rate constants computed from eq 14–17.

together with the known equilibrium constants constitute a reliable basis for accounting for all the experimental kinetic data when considered in light of the Marcus theory as expressed by eq 14.

Correlation of the Ferrocene–Fe^{3+} Kinetic Data. The rates of oxidation of the ferrocene derivatives, and of one carbollyl compound, as given in Tables II and V, proved to be a function of the respective equilibrium constants. Figure 4 depicts a plot of log k *vs.* log K, which is the relation suggested by the Marcus equation (eq 14). The plot is reasonably linear with a slope of *ca.* 0.44. Again, this treatment must be regarded as only an approximate one since the ferrocene exchange rate is not constant throughout the series, and in particular since the f value appropriate to eq 14 and 15 changes substantially as a result of the large range of K values for this series of reactions.

Estimates of the exchange rates of the ferrocene–ferricenium ions are available from the calculations described in the preceding section (which have been shown to increase by a factor of only *ca.* 2 in going to the THF-H_2O medium), and the Fe(II)–Fe(III) isotopic exchange rate has been measured in various solvents.[21] Based on these data a computation can be made[22] to check the predictive value of eq 14 as applied to the Fe^{3+} reactions. The results are summarized in Figure 5, from which it is seen that the agreement is rather poor: the observed rate constants are *ca.* 10^2-fold smaller than calculated; a possible reason will be cited in the Discussion.

Medium Effects. A few experiments were carried out to learn the effect of electrolytes on the reaction rates, particularly in view of Stranks' observation[4] that salts in general and chloride ions in particular increase the rate of electron transfer. As shown by the data in Table VII, the effect of electrolytes is small, as expected for a reaction between a cation and a neutral molecule. Moreover, no marked rate enhancement by chloride ions was noted; comparing the last two experiments, the change from 0.5 M $HClO_4$ and 0.5 M $LiClO_4$ to 0.5 M HCl and 0.5 M $LiClO_4$ actually decreases the rate by a factor of 2.4.

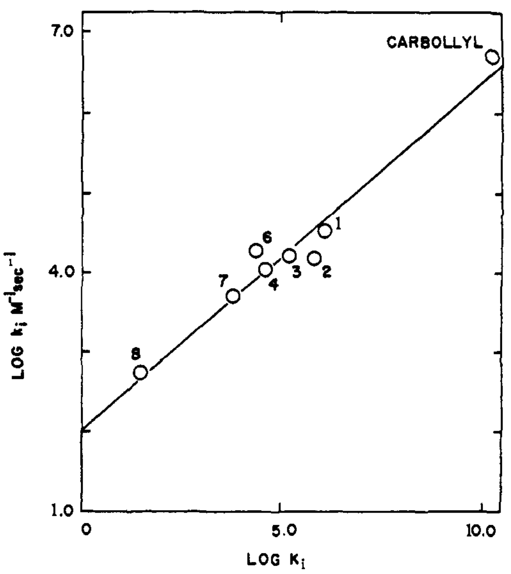

Figure 4. A plot of log k_i for the oxidation of the ferrocene derivatives by Fe^{3+} *vs.* log K_i.

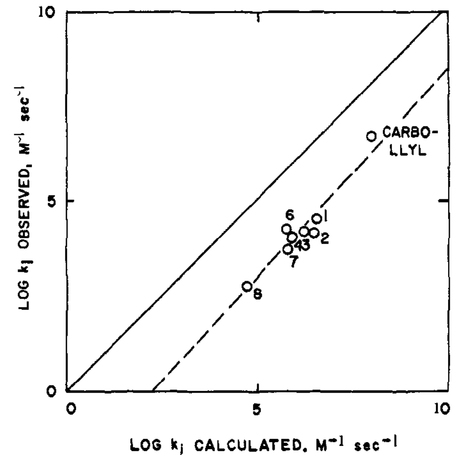

Figure 5. The attempted correlation of k_i for the Fe^{3+} reactions according to the Marcus relation using 4 M^{-1} sec^{-1} for the Fe^{3+}–Fe^{2+} exchange rate constant.

While the reaction rate did increase with increasing salt concentration, the effect was smaller than that observed by Stranks, whose reactions became immeasurably rapid at salt concentrations exceeding 1 × 10^{-3} M.[4]

The net rate effect on changing from n-PrOH–H_2O (1:1 v/v) at μ = 0.05 M, this being the medium in which the ferrocene–ferricenium ion reactions were studied, to THF–H_2O (1:1 v/v) at μ = 1.00 M, the medium in which the iron(III)–ferrocene reactions were studied, is to increase the electron transfer rate by a factor of about 2. This result was used to estimate the medium effect on the exchange rate constants for

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(21) (a) R. A. Horne, "Exchange Reactions," International Atomic Energy Agency, Vienna, 1965, p 67. (b) J. Menashi, W. L. Reynolds, and G. VanAnken, *Inorg. Chem.*, 4, 299 (1965).

(22) The rate of Fe(II)–Fe(III) exchange has been measured by Horne[21a] in n-PrOH–H_2O and by Reynolds and coworkers[21b] in DMSO–H_2O. At a mole fraction of n-PrOH of 0.18 (which corresponds to the mole fraction of THF in the 1:1 v/v THF–H_2O experiments), the rate constant is about twofold smaller than in pure water (data at 20.5°, $[H^+]$ = 0.55 M). An estimate of 4 M^{-1} sec^{-1} was made for the Fe(II)–Fe(III) exchange rate in THF–water for the purposes of this comparison, which is not intended to be an attempt at a precise calculation.

the Marcus-relation calculations concerning the Fe(III) reactions.

The solvent sensitivity of the rate of oxidation of $Fe(C_5H_5)_2$ by Fe^{3+} has been considered briefly.[23] At unit ionic strength, the change from acetone–water to THF–water, both 1:1 by volume, produced a rate change of only a factor of 4, as summarized in Tables II and VII.

Discussion

Obviously the direct measurement of some of the calculated electron exchange rates using isotopic labeling or some other method would be useful in confirming the validity of the present correlations. The value[4] reported by Stranks for the ferrocene–ferricenium ion exchange rate constant k_{44} was $(1.7 \pm 0.4) \times 10^6\ M^{-1}\ sec^{-1}$ in methanol at $-70°$. The narrow temperature range makes extrapolation to 25° unreliable, and the value so computed, *ca.* $3 \times 10^8\ M^{-1}\ sec^{-1}$ (MeOH, 25°), must be taken with reservation. One experiment in the present series was carried out in pure methanol.[24] The reaction of $Fe(C_5H_4CH_3)_2$ with $Fe(C_5H_5)_2^+$ had a rate constant $k_{14} = 1.2 \times 10^8\ M^{-1}\ sec^{-1}$ (MeOH, 25°), which was approximately five times faster than the rate under the usual conditions $k_{14} = 0.23 \times 10^8\ M^{-1}\ sec^{-1}$ (n-PrOH–H_2O, 25°). Assuming the same factor applies to the exchange rates, the calculated value of k_{44} in MeOH would be *ca.* $3 \times 10^7\ M^{-1}\ sec^{-1}$ (MeOH, 25°). The difference amounts to a factor of 10. This difference may not be meaningful considering the long temperature extrapolation (from -75 to $+25°$) for Stranks' data and the experimental uncertainties in the present measurements.

On the other hand the disagreement between the rate constant for the isotopic exchange reaction of $Fe(C_5H_5)_2$ and $Fe(C_5H_5)_2^+$ calculated in the present work and that measured using the diffusion method by Ruff and coworkers[7] is very large. They find rate constants in alcohol–water solvents which approach the diffusion-controlled limit, and are of the order of 10^3 times faster than the values reported here. While the experimental conditions are not really the same, they are close enough that a large discrepancy is evident. We do not claim to know the cause for the disagreement but offer the following comments. First, in the present work the exchange rates are not directly measured, but are inferred from direct determinations of the rate constants for cross reactions. We consider it unlikely that the model provided by the Marcus expression should be incorrect, however: in particular, that the cross reactions could have rate constants two to three orders of magnitude smaller than the exchange reactions of the corresponding components. Second, we note that Ruff's very inventive experimental method depends upon the measurement of small enhancements of the diffusion coefficient. As such, the method is highly sensitive to any factor which would increase its value. In particular, small amounts of decomposition of the $Fe(C_5H_5)_2^+$ solutions during the extended times required for the diffusion measurements could lead to an apparent increase in diffusion coefficient. At the low $[H^+]$ and $[H_2O]$ in those experiments,[7] some decomposition of $Fe(C_5H_5)_2^+$ solutions might have occurred, as observed by Yang and Wahl under similar conditions.[25] Further work to clarify the problem is clearly needed.

Reaction Mechanisms. A rather good fit was obtained for the measured cross-reaction rate constants for the ferrocene–ferricenium ion rate constants based on the Marcus relation, using an internally consistent set of exchange rate constants for the $FeCp_2$–$FeCp_2^+$ reactions. Far less success was obtained in attempting a similar quantitative correlation in the Fe^{3+} reactions. The present situation is not unique in this respect, however. Sutin and coworkers[26] have observed that the reaction rates between substituted $Fe(phen)_3^{3+}$ complexes and Fe^{2+}, and between $Fe(phen)_3^{2+}$ and Ce(IV), Mn(III), and Co(III) are all lower than the calculated rates. They suggested that the discrepancies may arise for reactants of very diverse structural types from the noncancellation of a part of the work terms responsible for bringing the reactants together.

We suggest, also, that it may be important to note the systematic nature of the deviations. In the present studies and in the other cases cited above, the experimental results were always smaller than the theoretical values. The model being used is that the reactions, including both electron exchange processes, proceed by electron transfer mechanisms (as opposed to an "atom transfer" or inner-sphere mechanisms). That is not necessarily true in the case of the Fe^{3+}–Fe^{2+} exchange reaction;[27] electron transfer constitutes only a part, possibly only a small part, of the exchange rate. That being the case, the failure of the Marcus relation to predict the correct cross-reaction rates is expected. The calculated rates are, in fact, too high as would be the case were an artificially high value of the Fe^{3+}–Fe^{2+} electron exchange rate constant used for this computation.

The electron exchange reaction between ferricenium ions and both of the carbollyl complexes are too rapid for measurement (Table V). This would be expected, however, considering the kinetic correlations based on eq 14. The K_{12} values are so large in this case that k_{12} would be $>10^9\ M^{-1}\ sec^{-1}$ if the electron exchange rate constant between oxidized and reduced forms of the carbollyl complex is as large as the other values found.

Only in the case of Fe^{3+} was the rate of oxidation measured, and there only in the case of $Fe(B_9C_2H_{11})(C_5H_5)^-$, the reaction of $Fe(B_9C_2H_{11})_2^{2-}$ occurring too rapidly (Table V). The one rate constant measured does agree with the value predicted on the basis of the Marcus relation, as does the lower limit for the second compound. This agreement suggests a similarity of mechanism.

The similarities between the carbollyl complexes and the ferrocene derivatives may include their reaction

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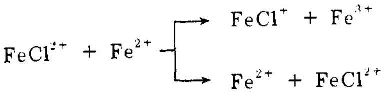
[23] (a) H. Higginbotham and J. H. Espenson, unpublished observations. (b) B. D. Peczon, Ph.D. Thesis, Purdue University, 1970.

[24] The ferricenium ion for these experiments was prepared by Cl_2 oxidation of ferrocene in dilute acid rather than using iron(III).

[25] E. S. Yang and A. C. Wahl, private communication from A. C. Wahl.

[26] R. J. Campion, N. J. Purdie, and N. Sutin, *Inorg. Chem.*, 3, 1091 (1964).

[27] The distinction can better be appreciated by considering the following pair of reactions [R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Amer. Chem. Soc.*, 87, 4591 (1965)], the first of which is electron transfer; the second, atom transfer. A similar analogy applies



$$FeCl^{2+} + Fe^{2+} \rightarrow FeCl^{+} + Fe^{3+}$$
$$FeCl^{2+} + Fe^{2+} \rightarrow Fe^{2+} + FeCl^{2+}$$

to the Fe^{3+}–Fe^{2+} exchange reaction, although in that case the relative importance of the two pathways has not been determined.

mechanisms. We infer that this similarity suggests a "side-by-side" positioning of the ferrocene derivatives in the transition state rather than a "sitting on top" arrangement. The rapid reactions of the carbollyl derivatives support this proposal, for a "side-by-side" configuration would not require electron transfer over such great distances or through the B–H framework of the carbollyl compound.

Acknowledgment. We are grateful to Professor Harlan H. Higginbotham III of Northeast Missouri State College for making the initial rate measurements on $Fe^{3+} + Fe(C_5H_5)_2$, and to Mr. D. F. Dustin and Professor M. F. Hawthorne for the gift of the carborane used to prepare some of the compounds studied. We are pleased to acknowledge interesting and helpful discussions with Professor A. C. Wahl.

Proton Magnetic Resonance Investigation of Antiferromagnetic Oxo-Bridged Ferric Dimers and Related High-Spin Monomeric Ferric Complexes

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Received June 1, 1972

Abstract: The pmr spectra of several types of antiferromagnetic Fe(III) dimeric complexes containing the nonlinear unit Fe–O–Fe have been investigated. The systems studied are of the $[Fe(salen)]_2O$ and $[Fe(P)]_2O$ types (P = tetraphenylporphine (TPP), tetra-*p*-tolylporphine (TTP), tetra-*n*-propylporphine, and octaethylporphyrin) and also include the structurally related high-spin monomers Fe(salen)OAc and Fe(P)Cl. An expression (eq 6) has been obtained for the temperature dependence of the contact shifts of a magnetically isotropic spin-coupled ($^5/_2$, $^5/_2$) dimer which admits different hyperfine coupling constants A_i for the different spin levels S'_i of the dimer (i = 0, 1, 2, . . .) and is valid provided the Curie law holds for each spin level. Isotropic shifts of salen monomers exhibit a Curie dependence and their signs and relative magnitudes are consistent with π-spin delocalization, indicating that the shifts are contact in origin and zero-field splittings (ZFS) are small. Shifts of salen dimers, whose patterns are similar to the monomer shifts, are treated as contact shifts. The temperature-dependent magnetic susceptibilities of $[Fe(salen)]_2O$ and $[Fe(salen)]_2O \cdot CH_2Cl_2$ (solid state) and $[Fe(5t\text{Bu-salen})]_2O$ (dichloromethane) do not superimpose with the contact shifts of the latter in dichloromethane solution when normalized at *ca.* 300°K. The direction of the deviation is shown to be consistent with $A_1 < A_2$. Isotropic shifts of the porphyrin monomer Fe(TTP)Cl are non-Curie and deviations from Curie behavior have been analyzed in terms of a dipolar (T^{-2}) contribution. The ZFS parameter D has been estimated from the pmr data and its value ($+11\ cm^{-1}$) is comparable to those directly determined for other porphyrin monomers by far-infrared methods. Using this value of D, dipolar shifts have been calculated for Fe(TPP)Cl and Fe(TTP)Cl and are found to be significant fractions of the total isotropic shifts. The probable existence of ZFS effects of comparable magnitude in porphyrin dimers indicates that their shifts cannot be treated in terms of eq 6 with or without all A_i equal. The results obtained in this work show that accurate values of the antiferromagnetic spin–spin coupling constant J for μ-oxo-salicylaldiminate and porphyrin iron(III) dimers cannot be obtained from a simple two-parameter fit of the temperature dependence of the isotropic shifts, as has been done previously.

It is now well established that antiferromagnetic spin coupling between metal centers is operative in a variety of important biological macromolecules.[4-6] The reported cases invariably involve iron, usually in the ferric state, coupled to another iron[4,5] or, in one case, to copper.[6] The most prominent class of metalloproteins exhibiting this behavior is the iron–sulfur proteins, for which pmr isotropic shifts,[4a] Mössbauer data,[4b] and magnetic susceptibility studies[4c] all indicate significant antiferromagnetic coupling. For two-iron systems this coupling occurs in both the reduced [Fe(II)–Fe(III)] and oxidized [Fe(III)–Fe(III)] forms of the proteins.

Proton magnetic resonance spectra[7] in such antiferromagnetic systems may be expected to lead to useful information on the electronic states of the coupled metal centers, inasmuch as monitoring the

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(1) University of California; Alfred P. Sloan Foundation Fellow, 1972–1974.

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