A Kinetic Study of the Electron-Transfer Reaction between Europium(II) and Iron(III) in Solutions Containing Perchlorate and Chloride Ions[1]

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Abstract: The kinetics of the oxidation–reduction reaction of europium(II) and iron(III) ions in acidic solution has been studied by the stopped-flow technique. The rate equation in perchlorate solution is $-d[Eu^{2+}]/dt = (k_0 + k_{-1}/[H^+])[Eu^{2+}][Fe^{3+}]$ with $k_0 = 3.38 \times 10^3\ M^{-1}\ sec^{-1}$ and $k_{-1} = 2.24 \times 10^3\ sec^{-1}$ at 1.4° and unit ionic strength. Activation parameters are $\Delta H_0^{\ddagger} = 3.5$, $\Delta H_{-1}^{\ddagger} = 12.2$ kcal/mole and $\Delta S_0^{\ddagger} = -29.4$, $\Delta S_{-1}^{\ddagger} = 1.3$ eu. In chloride solution two reaction terms were resolved, since the rate of $FeCl^{2+}$ formation and aquation was slow relative to electron transfer. The rate terms were $k_{FeCl}[FeCl^{2+}][Eu^{2+}]$ and $k_{Cl}[Fe^{3+}][Eu^{2+}][Cl^-]$; with $k_{FeCl} = 2.0 \pm 0.4 \times 10^6\ M^{-1}\ sec^{-1}$ and $k_{Cl} = 7.0 \pm 1.6 \times 10^3\ M^{-2}\ sec^{-1}$. The mechanisms of these reactions are discussed. Comparisons are made to systems where the details of the reaction mechanism are known. On this basis it is inferred that inner-sphere activated complexes are involved.

No quantitative studies have been undertaken previously on the rate of the electron-transfer reaction between europium(II) and iron(III). In view of attempts by ourselves[2–6] and others[7–11] to understand the details of the mechanisms of electron-transfer reactions of metal complexes, additional data, especially on systems involving substances that have previously received scant attention, are especially useful.

Europium(II) reactions have not been widely studied although measurements have been made on the Eu(II)–Eu(III) exchange reaction,[12] on the reduction of several cobalt(III) complexes,[10] and on the reduction of V^{3+} and Cr^{3+}.[13] An earlier attempt to study the rate of the rather rapid oxidation of europium(II) by iron(III) perchlorate was not successful[14] although, as discussed later, this appears to be a consequence of the attempted techniques rather than of an excessively fast reaction, as Bennett and Sheppard[14] concluded.

The extent to which reactions of the strongly reducing ion Eu^{2+} should parallel those of the first-row transition metal ions is not clear, especially since the electron-transfer reactions involve f rather than d electrons. The results of Adin and Sykes[13] on the reaction

$$Eu^{2+} + V^{3+} = Eu^{3+} + V^{2+}$$

suggest that Eu^{2+} is more slowly reacting than Cr^{2+} in the comparable reaction. This observation holds despite the fact that Eu^{2+} and Cr^{2+} are reducing agents of equal strength. Similarly, the reactions of europium(II) with acidopentaamminecobalt(III) complexes of the type $(NH_3)_5CoX^{2+}$ are generally slower,[10] by factors of 10–10^4, than the analogous reactions of chromium(II).[15]

The results of a study of the rates of several reactions in the chromium(II)–iron(III) system, both in perchlorate and chloride solutions, have been published.[16] We have undertaken to make measurements of the kinetics of reactions of europium(II) and iron(III) over an extended range of conditions, including studies in the presence of complexes of iron(III). The reactions we have studied are as follows. In perchlorate solution, there is an electron-transfer reaction between the hydrated cations (eq 1). In the presence of chloride ion,

$$Eu_{aq}^{2+} + Fe(H_2O)_6^{3+} = Eu_{aq}^{3+} + Fe(H_2O)_6^{2+} \quad (1)$$

both an anion-catalyzed reaction (eq 2) and a specific

$$Eu_{aq}^{2+} + Fe(H_2O)_6^{3+} + Cl^- = Eu_{aq}^{3+} + Fe(H_2O)_6^{2+} + Cl^- \quad (2)$$

reaction of the inner-sphere complex $(H_2O)_5FeCl^{2+}$ (eq 3) are noted. The reaction kinetics of each process

$$Eu_{aq}^{2+} + (H_2O)_5FeCl^{2+} = Eu_{aq}^{3+} + Fe(H_2O)_6^{2+} + Cl^- \quad (3)$$

were studied under a variety of conditions by use of the stopped-flow technique, and the rate laws were obtained from these studies.

Some information is available on other iron(III) reductions, notably by $V(H_2O)_6^{2+}$, $Fe(H_2O)_6^{2+}$ (electron exchange), as well as by the previously mentioned $Cr(H_2O)_6^{2+}$. We hope to be able to compare reactivity patterns and thus obtain indications of the details of the reaction mechanisms.

Experimental Section

Materials. Solutions of europium(II) perchlorate were prepared by electrolytic reduction of europium(III) at a mercury cathode. The chloride concentrations in freshly prepared and in stored europium(II) stock solutions were below or at the limit of visual detection (*ca.* 6×10^{-5} *M*) in a test with silver ion. The effect of such levels of chloride contamination of the europium(II) solutions on rates measured in this study was too small to observe. Europium(II) solutions were stored and handled in an atmosphere of carefully purified nitrogen. The analysis of Eu(II) solutions was based on the reaction with a small excess of chloropentaamminecobalt(III).

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[1] (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2194. (b) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[2] J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

[3] J. H. Espenson, *ibid.*, **4**, 1025 (1965).

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[5] J. H. Espenson and J. P. Birk, *J. Am. Chem. Soc.*, **87**, 3280 (1965).

[6] J. H. Espenson, *ibid.*, **89**, 1276 (1967).

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[8] J. P. Candlin, J. Halpern, and S. Nakamura, *ibid.*, **85**, 2517 (1963).

[9] J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964).

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[13] A. Adin and A. G. Sykes, *J. Chem. Soc.*, *A*, 1230 (1966).

[14] L. E. Bennett and J. C. Sheppard, *J. Phys. Chem.*, **66**, 1275 (1962).

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The cobalt(II) produced was analyzed spectrophotometrically using thiocyanate (1.3 *M*) in 50% acetone. The absorbance of the solution was measured at 6230 Å, a wavelength of maximum absorption, where the molar absorptivity is 1842 M^{-1} cm^{-1}. Lithium chloride was twice recrystallized from the reagent grade salt. Reagent grade hydrochloric acid and perchloric acid were used without further purification. The preparation, purification, and analysis of iron(III) perchlorate and lithium perchlorate have been described.[17] Water used for most solutions was redistilled from an alkaline permanganate solution although laboratory distilled water was also used for some of the kinetic studies in perchlorate solution. This change in the source of water did not affect the rate.

Rate Measurements. All rate measurements on these very rapid reactions were accomplished by the stopped-flow technique. The stopped-flow apparatus used has been described.[17] All reactant solutions were bubbled continuously with deoxygenated nitrogen to prevent oxidation of Eu(II) by atmospheric oxygen. A fresh dilution of Eu(II) was necessary for successive kinetic experiments in order to vary the Eu(II) concentration. Since the concentration levels ranged as low as 5×10^{-5} *M* Eu^{2+}, it was not regarded as a satisfactory procedure to assume that concentrations of such solutions could be calculated from the dilution. Rather, each Eu(II) solution was sampled, generally in triplicate, directly in the stopped-flow reservoir at the conclusion of the rate measurements. In some experiments Eu(II) was analyzed at the start of the measurements as well, although the decrease in Eu(II) noted was generally so slight that this double analysis was eventually abandoned.

Reactions were initiated by mixing the solution containing iron(III) with the solution containing europium(II). All the reactions were observed by measuring the transmittance[18] of monochromatic light through the reacting solution. Reaction 1 was studied at wavelengths where absorption is due mainly to Eu^{2+} (4000–3200 Å) as well as at wavelengths where both reactants absorb (2700–2400 Å). Reaction 2 involving chloride was monitored at 3300 and 3200 Å. Reaction 3 was followed at 3500 Å, where both $FeCl^{2+}$ and Eu^{2+} absorb. Molar absorptivities of reactants (those of the products were negligible in these experiments) are as follows at the wavelengths of interest: Fe^{3+}, λ 2700–2400 Å (ϵ 1200–4200 M^{-1} cm^{-1}); $FeCl^{2+}$, λ 3350 Å (a maximum, ϵ 2400); Eu^{2+}, λ 4000–2400 Å (ϵ 75–1600), with maxima at 3200 Å (ϵ ~640) and about 2500 Å (ϵ ~1700).

The processes observed in this study obeyed second-order or pseudo-second-order kinetics. Because of the high specific rates and/or high molar absorptivities of the reactants, it was generally not desirable or practicable to make the processes pseudo-first order by adding large excesses of one reactant. Thus, most of the oscilloscope traces (deflection–time plots) were treated according to the standard integrated second-order rate law given in eq 4, in which A

$$\ln([B]/[A]) = \ln([B]_0/[A]_0) + ([B]_0 - [A]_0)kt \quad (4)$$

and B designate reactants and *k* is defined by the equation

$$-d[A]/dt = -d[B]/dt = k[A][B]$$

The concentration of limiting reagent (say A) was calculated as a function of time from the fractional change of deflection *D* (eq 5). Values of D_0 and D_∞ were read from the oscilloscope trace. The

$$[A] = [A]_0 \frac{(D - D_\infty)}{(D_0 - D_\infty)} \quad (5)$$

concentration of the ion in excess is then obtained from the stoichiometry, $[B] = [B]_0 - [A]_0 + [A]$. On this basis one readily obtains the quantities needed to evaluate *k* according to eq 4.

Since the point of observation was removed from the mixing chamber by a distance corresponding to a time lag between mixing and first observation of 3–4 msec, in the faster experiments appreciable A was used before the first observation. In these experiments it appeared preferable to estimate [A] at first observation, rather than extrapolate to a value of D_0. The value of [A] at first observation was computed from its initial concentration, an estimated rate constant, and the time delay. The latter quantity was calculated from fast pseudo-first-order reactions (involving iron(III) and hydrazoic acid[17]) in which *k* was independent of time delay; *D* at time of mixing was known by measuring separately the individual reactants. The time delay was typically 3.5 msec and was obtained as a function of instrument speeds to a precision of *ca.* ±0.2 msec.

Results

Rate Law in Perchlorate Solution. Iron(III) oxidizes europium(II) in perchlorate solution according to the stoichiometry given in eq 1; the rate shows a first-order dependence on each reagent. The rate law at constant hydrogen ion concentration is given by the equation

$$-d[(Eu^{2+})]/dt = k'[Fe^{3+}][Eu^{2+}]$$

where *k'* is the calculated second-order rate constant. In a series of 13 experiments at $(H^+) = 0.876$ *M* at 15.8° and 1.00 *M* ionic strength, reactant concentrations were varied over the ranges $2 \times 10^{-5} < [Fe^{3+}] < 1.5 \times 10^{-2}$ *M* and $8 \times 10^{-5} < [Eu^{2+}] < 3 \times 10^{-3}$ *M*. These studies included experiments both with excess Fe^{3+} and with excess Eu^{2+}. These results are summarized in Table I. For each experiment about four concentration–time plots were obtained from the given pair of solutions; the values in Table I are the averages of the four individual values. The adequacy of eq 4 is strongly supported by the absence of trends in *k'* over the wide ranges of $[Fe(III)]_0$ and $[Eu(II)]_0$. In addition, the presumed absence of unusual rate patterns or undisclosed concentration dependences was demonstrated by the lack of wavelength dependence, as shown in Table I. The mean value of *k'* under these conditions is 1.51×10^4 M^{-1} sec^{-1}, and it is independent of the concentrations of the products Eu^{3+} and Fe^{2+} (expt 4 and 8).

Table I. Rate Measurements for the Reaction of Fe^{3+} and Eu^{2+} at 15.8°, 0.876 *M* H^+, and 1.0 *M* Ionic Strength in Perchlorate Solution

Expt no.	$[Fe^{3+}]_0$, $M \times 10^4$	$[Eu^{2+}]$, $M \times 10^4$	λ, Å	$10^{-4}k'$,[a] M^{-1} sec^{-1}
1	0.200	0.774	2400	1.54 ± 0.04
2	2.50	10.3	3300	1.34 ± 0.29
3[b]	3.43	3.355	3300	1.64 ± 0.14
4[c]	5.00	10.6	3500	1.57 ± 0.09
5	6.00	10.3	3500	1.52 ± 0.05
6	9.00	32.3	4000	1.48 ± 0.03
7 (1)	11.0	5.89	3300	1.60 ± 0.07
7 (2)	11.0	5.89	3800	1.51 ± 0.14
8[d]	12.25	8.75	3400	1.62 ± 0.06
9	50.0	4.42	3400	1.41 ± 0.05
10	50.0	4.8	3400	1.53 ± 0.02
11	50.0	5.30	3400	1.36 ± 0.07
12	75.0	4.80	3400	1.47 ± 0.04
13	150.0	4.80	3300	1.62 ± 0.12

[a] The indicated uncertainty is the average deviation from the mean of successive measurements of the same reaction. [b] Equation 4 does not apply in this run since initial concentrations of each reactant are quite close. A suitable integrated equation using an average concentration was applied here. [c] Added Eu^{3+}, 1×10^{-3} *M*. [d] Added Fe^{2+} and Eu^{3+}, each 8.8×10^{-4} *M*.

Hydrogen Ion and Temperature Variations. Experiments at 15.8° demonstrated that *k'* is a function of $[H^+]$. At the lower limits of iron(III) concentration, its acid dissociation must be taken into account. The data of Milburn[19] were used for this correction, which took the form that the fraction of iron(III) in the form of

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[17] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).

[18] Deflection of the oscilloscope trace was proportional to transmittance, and, under the conditions of these experiments, transmittance was proportional to absorbance and to concentration. These points have been previously discussed in some detail.[17]

[19] R. M. Milburn, *J. Am. Chem. Soc.*, **79**, 537 (1957).

Table II. Observed and Calculated Rate Constants for the Reaction of Eu^{2+} and Fe^{3+}, as a Function of Temperature and $[H^+]$ in Perchlorate Solution

$[H^+]$, M	$10^{-4}k'$ at 1.4°, M^{-1} sec^{-1} Obsd	Calcd[a]	$[H^+]$, M	$10^{-4}k'$ at 15.8°, M^{-1} sec^{-1} Obsd	Calcd[a]	$[H^+]$, M	$10^{-4}k'$ at 25.0°, M^{-1} sec^{-1} Obsd	Calcd[a]
0.015	18.0[b]	15.2	0.0150	53.2	45.5	0.0286	54.9	47.7
0.020	14.4[b]	11.5	0.0167	46.7	41.2	0.0300	51.7	45.6
0.0310	8.14	7.49	0.020	36.1	34.7	0.0400	38.9	34.8
0.0360	5.95[b]	6.51	0.0310	22.9	23.0	0.0500	28.8	28.2
0.040	6.92	5.99	0.0360	17.9	19.9	0.0571	27.7	24.9
0.0500	4.92	4.79	0.0500	13.4	14.6	0.0667	24.6	21.5
0.100	2.70	2.58	0.0700	8.54	10.6	0.0800	18.1	18.1
0.200	1.33	1.46	0.100	6.86	7.60	0.100	13.6	14.6
0.500	0.729	0.788	0.130	5.91	5.97	0.111	13.3	13.2
0.879	0.616	0.595	0.200	3.30	4.07	0.133	13.0	11.2
0.939	0.613	0.579	0.876	1.51	1.31	0.167	9.14	9.08
			1.00	1.25	1.21	0.200	7.63	7.68
						0.400	4.08	4.16
						0.953	2.11	2.11

[a] Calculated values of k' are those obtained from the activation parameters in Table III. [b] $T = 1.6°$.

Fe^{3+} was $[H^+]/([H^+] + K_a)$. At all the temperatures studied, with values of $[H^+]$ ranging from 0.015 to 1.0 M, the hydrogen ion dependence shown in eq 6 was observed. The results of these experiments are given in Table II and Figure 1. All data at each acidity and each temperature were fitted simultaneously to this hydrogen ion dependence assuming the Eyring equation describes the temperature dependence of each of the rate constants k_0 and k_{-1}. Table III lists the parameters that best fit the observed data, according to a nonlinear least-squares computer program.[20]

$$k' = \left(k_0 + \frac{k_{-1}}{[H^+]}\right)\left(\frac{[H^+]}{[H^+] + K_a}\right) \tag{6}$$

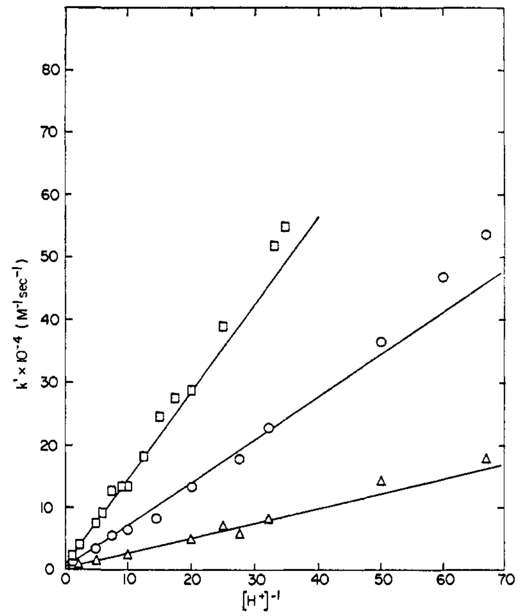

Figure 1. Temperature and hydrogen ion dependence of k'. The temperatures 1.4, 15.8, and 25.0° are denoted by the symbols △, ○, and □, respectively.

Table III. Activation Parameters for the Reaction of Fe^{3+} and Eu^{2+} in Perchlorate Solution

Rate term	$\Delta H^{\ddagger}$, kcal mole^{-1} [a]	$\Delta S^{\ddagger}$, eu[a]
$k_0[Fe^{3+}][Eu^{2+}]$	3.5 ± 2.6	-29.4 ± 9.2
$k_{-1}[Fe^{3+}][Eu^{2+}]/[H^+]$	12.2 ± 0.5	1.3 ± 1.8
$k_{FeOH}[FeOH^{2+}][Eu^{2+}]$[b]	2.0 ± 0.8	-20.3 ± 2.8

[a] Uncertainties represent standard deviations. [b] Calculated from the values associated with k_{-1} and Q_a as described in the text.

As has been noted in many reactions, a failure of the "constant ionic strength principle" can introduce rate terms that do not correspond to reaction pathways.[21–25] In the present instance the rate term $k_{-1}[Fe^{3+}][Eu^{2+}]\cdot[H^+]^{-1}$ carries the bulk of the reaction, although at $[H^+] = 1.00$ M and 1.4° the term $k_0[Fe^{3+}][Eu^{2+}]$ constitutes 40% of the observed rate. Could the relatively minor k_0 term represent an activity effect, the consequence of replacing H^+ by Li^+ (despite the constancy of ionic strength), rather than a true reaction pathway? Assume that the activity effect can be represented by a Harned-type correction factor[26] and that the k_{-1} term provides the sole path. The observed rate constant k' can then be represented as the product of an intrinsic rate constant $k_{-1}{}^0$ and a correction term

$$k' = k_{-1}{}^0[H^+]^{-1}\exp(\beta[H^+])$$

For small values of $\beta[H^+]$ this relation becomes

$$k' = k_1{}^0[H^+]^{-1}(1 + \beta[H^+] + \cdots) \cong k_{-1}{}^0[H^+]^{-1} + k_{-1}{}^0\beta$$

According to this model the rate term k_0 is solely a medium effect. The data given in Table II were fitted to this functional relationship, assuming $k_{-1}{}^0$ obeyed the Eyring relation and that $\beta = \beta^0(1 + at)$, where a is a temperature coefficient and t the temperature (°C). Values of the constants which best reproduce the data

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(20) This program is based on a report from Los Alamos Scientific Laboratory, LA 2367 + Addenda. We are grateful to Drs. T. W. Newton and R. H. Moore for supplying us with the computer programs and to Mr. J. P. Birk for adapting them to the IBM 360 computing facilities.

(21) (a) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963); (b) *Inorg. Chem.*, **4**, 1166 (1965).

(22) D. H. Huchital and H. Taube, *J. Am. Chem. Soc.*, **87**, 5371 (1965).

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(24) J. H. Espenson and D. E. Binau, *Inorg. Chem.*, **5**, 1365 (1966).

(25) Similar considerations apply to medium effects on equilibrium constants and electrode potentials: A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, **66**, 1065 (1962).

(26) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co., Ltd., London, 1955, Chapter 15.

are $k_{-1}^0 = (RT/Nh)\exp[(0.7 \pm 1.4)/R - (12{,}000 \pm 400)/RT]$ and $\beta = (0.96 \pm 0.10)[1 - (0.027 \pm 0.005)t]$. The data in Table II were reproduced with a mean deviation of 8.0%, compared to 8.6% based on the two-term model of eq 6.

Are the two alternatives equally acceptable? Each fits the data about equally well and predicts the same functional dependence of rate upon $[H^+]$. The value of the Harned factor β is, however, abnormally large[21,24] (a reasonable value of β would be 0.1, not 1[21a]). On this basis we conclude that medium effects are not the sole contributors to the rate effect, and that the k_0 term almost certainly represents a genuine pathway. The k_0 term may include, of course, substantial medium effects. The preceding discussion has shown that these cannot be resolved at present.

Bennett and Sheppard[14] reported a value of $k' > 10^5$ $M^{-1}\,sec^{-1}$ at 0°, 1.0 M $HClO_4$, obtained from a quenched-flow experiment in which $[Eu^{2+}]_0 = [Fe^{3+}]_0 = 10^{-4}$ M. Our results, extrapolated to 0°, 1.0 M acid, give 5.5×10^3 $M^{-1}\,sec^{-1}$ for k'. Were Bennett and Sheppard able to quench their reaction after 0.06 sec, only about 3% reaction should have occurred. The difficulty appears to be that the Bennett and Sheppard bipyridine–acetate ion quench solution had the opposite effect. The quench had been proved effective on a reaction of $Fe^{2+} + Co^{3+}$, where presumably it acts by formation of $Fe(bipy)_3{}^{2+}$. The effect on $Eu^{2+} + Fe^{3+}$ would probably be an acceleration, however, due to strong complexing of the Fe^{2+} product and a simultaneous lowering of $[H^+]$ thereby sharply increasing the rate.

Kinetic Studies in the Presence of Chloride Ion. The effect of chloride ion was studied in two distinct types of kinetics experiments. The difference in the two experiments takes advantage of the slowness of the chloroiron(III) complexation equilibrium (eq 7), relative to the rates of the various electron-transfer reactions. As a consequence of this slowness, we were able to add Cl^- to Eu^{2+} before mixing with Fe^{3+} and to measure the rate of the resulting processes without appreciable formation of $FeCl^{2+}$. On the other hand, when Cl^- was added to Fe^{3+} before mixing with Eu^{2+}, we were able to observe the reduction of the species $(H_2O)_5FeCl^{2+}$ in times short relative to its aquation.

$$(H_2O)_6Fe^{3+} + Cl^- \underset{k_{aq}}{\overset{k_f}{\rightleftharpoons}} (H_2O)_5FeCl^{2+} + H_2O \qquad (7)$$

Consider first the studies in which Cl^- was added to Eu^{2+}. The rate of oxidation of Eu^{2+} followed a simple second-order rate equation, just as in solutions containing only perchlorate anions. However, the observed second-order rate constants were appreciably higher than in perchlorate solution and increased linearly with chloride ion concentration. These observations suggest the following two-term rate law (eq 8 and 9), in which k' retains the significance of the definition in eq 6. These relations can be shown to be only approximate, however, since, in their derivation, we ignored a reaction sequence consisting of the formation of $FeCl^{2+}$ in reaction 7 and its subsequent very rapid oxidation of Eu^{2+} (at a specific rate k_{FeCl}) in eq 3. Were such a sequence considered in eq 8, there would be an added term, $+k_f[Fe^{3+}][Cl^-]$. This effect can be shown to be a minor one, based on the known values of k_f and k_{FeCl} under all the conditions employed in these experiments designed to evaluate k_{Cl}. The correction applied to k_{obsd} in eq 9 would be an addition of the term $k_f[Cl^-]/[Eu^{2+}]$ since k_{FeCl} is sufficiently large (see below) that virtually every $FeCl^{2+}$ formed from $Fe^{3+} + Cl^-$ reacts very quickly with Eu^{2+}.

$$-d[Eu^{2+}]/dt = k_{obsd}[Fe^{3+}][Eu^{2+}] \qquad (8)$$

$$k_{obsd} \cong k' + k_{Cl}[Cl^-] \qquad (9)$$

The equilibrium quotient for $FeCl^{2+}$ formation at 1.6° and $\mu = 1.00$ M is $Q_{FeCl} = 1.56$ M^{-1}, extrapolated to this temperature from the values of Woods, Gallagher, and King.[27] From the values of Connick and Coppel[28] for the aquation kinetics, we estimate at 1.6°, $\mu = 1.0$ M, $k_f = 0.85 + 0.42/[H^+]$ $M^{-1}\,sec^{-1}$ and $k_{aq} = 0.54 + 0.27/[H^+]$ sec^{-1}. The extrapolated rates are undoubtedly quite uncertain but suffice to show that the corrections are small, within the range 2–8%. The most useful kinetic quantity contains a correction for this term, and the values we shall cite are those for k_{cor} (eq 10).

$$k_{cor} = k_{obsd} - k_f[Cl^-]/[Eu^{2+}] = k' + k_{Cl}[Cl^-] \qquad (10)$$

Aside from the computed effect of the relative unimportance of the k_f pathway, there is the experimental point that the rate equation in the presence of chloride ion is consistent with a dependence on $[Eu^{2+}]$ that is first order throughout; such would not be the case were the alternate sequence carrying substantial reaction.

Experiments to evaluate k_{Cl} were carried out with the following concentration variation: $2 \times 10^{-4} < [Fe^{3+}]_0 < 4 \times 10^{-4}$ M, $1.8 \times 10^{-3} < [Eu^{2+}]_0 < 2.9 \times 10^{-3}$ M, $0.24 < [Cl^-] < 0.90$ M, and $0.10 < [H^+] < 1.0$ M. These experiments are summarized in Table IV. The scatter of the experiments is relatively magnified by subtracting the large k' value and prevents our confirming a complete lack of variation of k_{Cl} with $[H^+]$. The data are sufficiently precise, however, to show clearly that the predominant rate term is independent of $[H^+]$, within experimental error, over the range 0.1–1.0 M, as formulated above. The value of k_{Cl} is $(7.0 \pm 1.6) \times 10^3$ $M^{-2}\,sec^{-1}$.

Table IV. Kinetic Data on the Reaction of Eu^{2+} with $Fe(H_2O)_6{}^{3+}$ in the Presence of Chloride Ion at 1.6° and $\mu = 1.00$

$[Cl^-]$, M	$[H^+]$, M	10^4 $[Fe^{3+}]_0$, M	10^4 $[Eu^{2+}]_0$, M	10^3k_{cor},[a] M^{-1} sec^{-1}	10^3k_{Cl},[b] M^{-2} sec^{-1}
0.24	0.953	4.00	20.5	7.19	5.2
0.474	0.953	4.00	18.0	10.3	9.3
0.474	0.953	4.00	23.4	7.89	4.2
0.60	0.100	2.20	14.4	28.4	9.4
0.70	0.953	4.00	19.4	9.79	5.6
0.80	0.400	2.20	28.9	15.2	8.1
0.90	0.953	4.00	20.5	11.2	7.3
					Av = 7.0 ± 1.6

[a] k_{cor} is defined by eq 10. [b] Calculated from the relation $k_{Cl} = (k_{cor} - k')/[Cl^-]$.

When Eu^{2+} was mixed with iron(III) solutions in which equilibrium 7 had been established, the depletion of absorbing species ($FeCl^{2+}$ and Eu^{2+}) was at first very rapid. During this rapid period, the rate again obeyed

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(27) Sr. M. J. M. Woods, P. K. Gallagher, and E. L. King, *Inorg. Chem.*, **1**, 55 (1962).

(28) R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959).

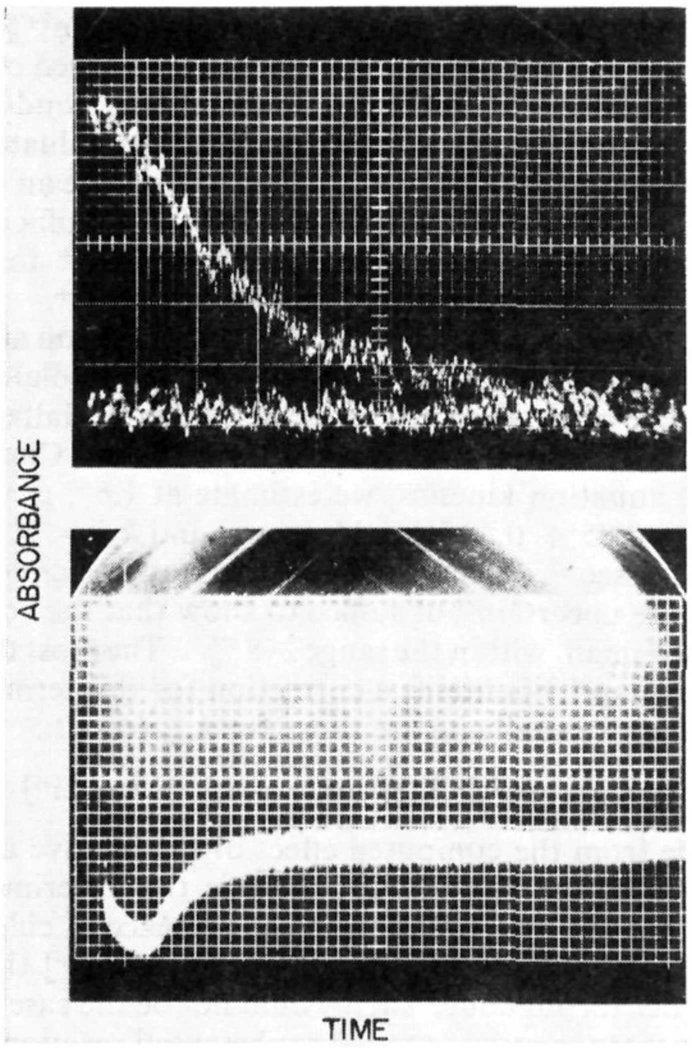

Figure 2. Oscilloscope deflection–time plots obtained in experiment 5, Table V. The upper plot spans the first 50 msec after mixing. The lower plot spans the first 20 sec after mixing.

a simple second-order equation. The rapid period had initial half-times in our experiments ranging from 5 to 11 msec at 1.6°, which is near our limit of measurement. The data are consistent with a rapid reaction of $(H_2O)_5FeCl^{2+}$ and Eu^{2+} (eq 3) and the slower reaction of $Fe(H_2O)_6^{3+}$ and Eu^{2+}. The latter process is a combination of two independent reactions: one independent of $[Cl^-]$ (k', eq 1) and one catalyzed by Cl^- (k_{Cl}, eq 2). The total rates of these processes are given by eq 11 and 12, in which terms for the still slower chloroiron(III) substitution reaction are also included.

$$-d[FeCl^{2+}]/dt = k_{FeCl}[FeCl^{2+}][Eu^{2+}] + k_{aq}[FeCl^{2+}] - k_f[Fe^{3+}][Cl^-] \quad (11)$$

$$-d[Eu^{2+}]/dt = k_{FeCl}[FeCl^{2+}][Eu^{2+}] + k'[Fe^{3+}][Eu^{2+}] + k_{Cl}[Fe^{3+}][Eu^{2+}][Cl^-] \quad (12)$$

The qualitative observations on the details of the absorbance changes are consistent with this scheme. In experiments where $[Eu^{2+}] > [FeCl^{2+}]$ and where $[Eu^{2+}] > [Fe(III)]_{total}$, the initial absorbance decrease (at 3350 Å, where $FeCl^{2+}$ and Eu^{2+} absorb) was followed by a much slower decrease. We explain this pattern as follows. The first change arose from the reduction of $FeCl^{2+}$ by Eu^{2+} (eq 3), and the slower decrease was the disappearance of excess Eu^{2+} by reactions 1 and 2. (An additional contribution to the reduction of Eu^{2+} is the formation of $FeCl^{2+}$ (eq 7) and its subsequent reduction (eq 3), but this is a minor pathway.)

In experiments where $[Eu^{2+}]_0 > [FeCl^{2+}]_0$, but where iron(III) was in excess over Eu^{2+} ($[Fe(III)]_{total} > [Eu^{2+}]$), the absorbance at 3350 Å passed through a minimum (Figure 2). The initial drop was again the reaction of $FeCl^{2+}$ and Eu^{2+} in eq 3. After Eu^{2+} had been completely oxidized, $FeCl^{2+}$ was slowly formed from Fe^{3+} and Cl^- in eq 7 at its equilibrium concentration and was not subject to further reduction. The rate constant for approach to equilibrium in eq 7 is known, and the value obtained for this composite in these experiments is 0.72 sec^{-1}, in fair agreement with the value 0.91 sec^{-1} for the independently observed $(k_f[Cl^-] + k_{aq})$ at 1.0 M H^+ and 1.6° (in an experiment starting with iron(III) and chloride ion under comparable conditions).

The data from these experiments were treated according to eq 11 and 12 as though only the k_{FeCl} terms were important during the initial rapid portion. The results of this treatment are shown in Table V. For all the experiments described in Table V, the temperature was 1.6°, and $[Cl^-]$ was 0.5 M. The mean value of k_{FeCl} is $(2.0 \pm 0.4) \times 10^6$ M^{-1} sec^{-1} at 1.6°. The value proves that this path is indeed dominant at short times; even after 90% of the $FeCl^{2+}$ has been depleted, it continues to dominate (11) and (12) by factors of 10 and 30, respectively, in experiment 1, the least favorable case. Thus, neglect of all paths other than k_{FeCl} in the data treatment is justifiable. This approximation, the use of an extrapolated value for Q_{FeCl}, and the extreme rapidity (near the limit of our apparatus) of reaction 3 limited the precision we could obtain. The concentrations of $FeCl^{2+}$ and Eu^{2+} were varied by factors of about 4.4 and 2.6. Absence of a rate trend with these variations constitutes good evidence for the form given in eq 11 and 12. It was assumed that k_{FeCl} is independent of $[H^+]$, and a single experiment, no. 6, was carried out at $[H^+] = 0.10$ M to verify this point.

Table V. Kinetics of the Reaction of $FeCl^{2+}$ and Eu^{2+} at 1.6°, 0.5 M Cl^-, and 1.0 M H^+

Expt	10^5 $[Fe(III)]_0$,[a] M	10^5 $[FeCl^{2+}]_0$,[a] M	10^5 $[Eu^{2+}]_0$,[a] M	$10^{-6}k_{FeCl}$, M^{-1} sec^{-1}
1	2.69	1.66	3.63	2.4 ± 0.2[b] (4)[c]
2	2.69	1.66	5.20	1.4 ± 0.2 (4)
3	2.69	1.66	7.80	1.5 ± 0.1 (7)
4	5.42	3.30	7.45	1.7 ± 0.0 (4)
5	12.0	7.30	9.55	2.1 ± 0.2 (4)
6[d]	2.69	1.66	2.46	1.9 ± 0.2 (4)
				Av k = 2.0 ± 0.4

[a] All concentrations reported are those after mixing. [b] The indicated uncertainty is the average deviation from the mean. [c] The figure in parentheses is the number of individual rate measurements. [d] $[H^+] = 0.10$ M.

Interpretation and Discussion

Reaction Mechanism in Perchlorate Solution. The rate equation found for the reaction of Fe^{3+} and Eu^{2+} in acidic solution consists of two terms, suggesting a mechanism involving two parallel reaction paths. Net activation processes consistent with the kinetics are

$$Fe(H_2O)_6^{3+} + Eu_{aq}^{2+} = [FeEu(H_2O)_m^{5+}]^{\ddagger} \quad (13)$$

$$Fe(H_2O)_6^{3+} + Eu_{aq}^{2+} + H_2O = [FeEu(H_2O)_nOH^{4+}]^{\ddagger} + H^+ \quad (14)$$

There are several possible sequences of elementary reactions that account for the second of these reactions. The one we consider the most plausible involves formation of hydroxoiron(III) ion in a labile equilibrium (eq 15) and its subsequent reduction by Eu^{2+} (eq 16). The

$$Fe(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_5OH^{2+} + H^+ \text{ (rapid, } Q_a) \quad (15)$$

$$Fe(H_2O)_5OH^{2+} + Eu_{aq}^{2+} \longrightarrow \text{(rate determining, } k_{FeOH}) \quad (16)$$

rate constant k_{-1} was defined in terms of concentrations of species in the forms predominant under the conditions of the experiments, as is most appropriate. In terms of the sequence eq 15 and 16, k_{FeOH} is calculated from the known acid dissociation quotient by the relation $k_{\mathrm{FeOH}} = k_{-1}/Q_a$. Milburn[19] gives values for Q_a as a function of temperature at $\mu = 1.0\ M$. Values of $10^{-6} \cdot k_{\mathrm{FeOH}}$ (M^{-1} sec^{-1}) so computed are 5.2 at 1.4°, 7.0 at 15.8°, and 8.4 at 25.0°. The activation parameters for k_{FeOH} are given in Table III and were calculated on this basis.

The mechanism consists of parallel pathways, differing in the number of protons involved, similar to that found for a large number of electron-transfer reactions involving aquometal ions. It is useful to compare values of the molar entropies of the transition states involved here to values obtained for related reactions. Newton and coworkers have found a significant correlation between the molar entropy of transition states for reactions of actinide elements and their net ionic charges.[21,29,30] This concept has been extended with some success to other electron-transfer reactions as well.[3]

The $\Delta S^{\ddagger}$ values have been used to estimate the formal ionic entropy of the activated complexes.[31] For [FeEu^{5+}]‡ the molar ionic entropy $S^{\ddagger}$ is -117 eu and that for [FeEuOH^{4+}]‡ is -70 eu. Both lie very close to representative values for transition states of similar charge.[21,29] Some typical values for $\bar{S}^{\ddagger}$ in related reactions between ions of charge 3+ and 2+ are shown in Table VI.

Table VI. Formal Ionic Entropies of Transition States

Reaction $M^{2+} + N^{3+}$	$\bar{S}^{\ddagger}$, eu $(MN^{5+})^{\ddagger}$	 $(MNOH^{4+})^{\ddagger}$	Ref
$Eu^{2+} + Fe^{3+}$	-117	-70	This work
$Eu^{2+} + V^{3+}$	-113	-81	13
$Cr^{2+} + V^{3+}$	-128	-71[a]	3
$Fe^{2+} + Fe^{3+}$	-120	-70	*b*
$Co^{2+} + Co^{3+}$	-112	-84	*c*
$Cr^{2+} + (NH_3)Cr^{3+}$	-120	-77	4

[a] The value in ref 3 for $\bar{S}^{\ddagger}$ was -88 eu; this value was calculated incorrectly. [b] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952). [c] H. S. Habib and J. P. Hunt, *J. Am. Chem. Soc.*, **88**, 1668 (1966).

It should be noted that the major reaction path was inversely dependent upon [H$^+$], suggesting that FeOH^{2+} was a particularly effective reactant. The reactions of Cr^{2+} with aquo complexes generally exhibit a similar rate pattern, such as the reduction of $Co(NH_3)_5H_2O^{3+}$,[32] Fe^{3+},[16] Cr^{3+},[33] and Cu^{2+}.[34] In contrast to this, rates of similar reductions by V^{2+} do not depend on [H$^+$].[34-36] The Cr(II) reductions are known or suspected to involve inner-sphere mechanisms, whereas the V(II) reactions are thought to be outer sphere. Related reactions of iron(II) also have fairly large OH$^-$ components, and the current view is that they are inner sphere. The reactions of $[Ta_6Cl_{12}]^{2+}$ with $Co(NH_3)_4Cl(OH_2)^{2+}$ and $Co(NH_3)_5H_2O^{3+}$ are independent of [H$^+$],[37] but the tantalum cluster ion is sufficiently different from divalent transition metal ions that considerable caution is called for in drawing a parallel between these cases. The high reactivity of FeOH^{2+} toward Eu^{2+} suggests that an inner-sphere mechanism operates in this case.

Reactions in the Presence of Chloride Ion. The kinetic equations obtained for the reaction of europium(II) and iron (III) in the presence of chloride ion are consistent with the scheme previously summarized by the reactions in eq 2 and 3. The two chloride-containing transition states have the same composition, (FeEuCl^{4+})‡, disregarding the indeterminate number of solvent molecules. They are clearly not identical, however, and may be regarded as isomeric, again disregarding the role of water.

The reaction of $(H_2O)_5FeCl^{2+}$ with Eu^{2+} may proceed by an inner-sphere mechanism (H$_2$O or Cl$^-$ bridging), or by an outer-sphere reaction. The third-order reaction involving chloride ion catalysis very likely occurs by either of the following mechanisms: (1) reaction of a labile and unstable Eu(II) complex, EuCl$^+$, with $Fe(H_2O)_6^{3+}$, (2) reaction of the labile and unstable ion pair $Fe(H_2O)_6^{3+} \cdot Cl^-$ with Eu^{2+}. The first possibility may proceed by a transition state that is outer sphere, or inner sphere with H$_2$O bridging. Chloride bridging is not possible since $Fe(H_2O)_6^{3+}$ cannot be substituted rapidly enough. The same alternatives are open to the latter reactants.

The interesting question should be considered of whether electron transfer in some or all of the Eu(II) and Fe(III) reaction pathways proceeds by inner-sphere transition states. The solvent exchange rate of Eu_{aq}^{2+} is undoubtedly so high that such substitution in the primary coordination sphere does not appear to be a barrier even in this instance of quite rapid reaction, unlike the situation in very rapid reductions of $V(H_2O)_6^{2+}$. The europium(III) products are also very labile relative to electron transfer so that a direct answer to the question of inner- or outer-sphere mechanism is not available.

An indirect approach to this important question can be made by examining the reactivity pattern of different reducing agents toward these same oxidizing agents. Data are available for these reducing agents: Cr^{2+} (inner sphere), V^{2+} (outer sphere), Fe^{2+} (probably inner sphere),[38] and Eu^{2+}. The results are summarized in Table VII, in which k for $Fe(H_2O)_6^{3+}$ is taken as the reference standard. The parallel in reactivity pattern for Cr^{2+} and Eu^{2+}, in sharp contrast to the outline of V^{2+} behavior, leads us to suggest that all the reactions we have studied in the Eu^{2+}–Fe^{3+} system are proceeding by mechanisms similar to the Cr^{2+} reductions. The Cr^{2+}–FeCl^{2+} reaction[16] is known to be inner sphere (CrCl^{2+} is formed). Moreover, the reaction of Cr^{2+}

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(29) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

(30) T. W. Newton and F. B. Baker, Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1967, p 268.

(31) The equation for this computation is $\bar{S}^{\ddagger} = \Delta S^{\ddagger} - \Sigma\bar{S}°$(other products) + $\Sigma\bar{S}°$(reactants). In these computations the values used were $\bar{S}°(Fe^{3+}) = -70$ eu, and $\bar{S}°(Eu^{2+})$, $= -18$ eu. The latter value was obtained from R. L. Montgomery, U. S. Bureau of Mines, Report of Investigations, No. 5468, Pittsburgh, Pa., 1959.

(32) R. K. Murmann, H. Taube, and F. A. Posey, *J. Am. Chem. Soc.*, 79, 262 (1957); W. Kruse and H. Taube, *ibid.*, **82**, 526 (1960).

(33) M. Anderson and N. A. Bonner, *ibid.*, **76**, 3826 (1954).

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(35) P. Dodel and H. Taube, *Z. Physik. Chem.* (Frankfurt), **44**, 92 (1965).

(36) B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967).

(37) J. H. Espenson and J. D. Boone, unpublished experiments.

(38) (a) N. Sutin, J. K. Rowley, and R. W. Dodson, *J. Phys. Chem.*, **65**, 1248 (1961); (b) R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 4591 (1964); (c) E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **6**, 428 (1967).

and $Fe(H_2O)_6{}^{3+}$ in Cl^- solution also produces exclusively $CrCl^{2+}$,[16] which could arise from either of the mechanisms outlined above for Eu^{2+}. Previous studies on Eu^{2+} reactions[10] have suggested inner-sphere reaction mechanisms, and we think the present work provides a strong indication that inner-sphere mechanisms are involved.

The theory of Marcus[39] on electron-transfer reactions has been applied quite successfully, especially by Sutin and co-workers[11,40] to reactions between metal ions such as those considered here. Although the theory was developed from a model of an outer-sphere reaction, attempts have recently also been made to extend its applicability to other situations. The predicted rate constant can be calculated, as shown by Sutin,[40] from exchange rates and standard potentials. Unfortunately only a lower limit has been determined for the $Eu^{2+,3+}$ exchange rate in perchlorate solution.[12] The prediction on this basis is $k_0 < 2.6 \times 10^6\ M^{-1}\ sec^{-1}$; this is not inconsistent with our experimental result $k_0 = 6.77 \times 10^3\ M^{-1}\ sec^{-1}$ at 25°. The comparison in this particular instance is not a fruitful one in view of the unknown exchange rate constant.

Table VII. Relative Reactivities[a] of Various Dipositive Metal Ion Reducing Agents toward Iron(III) Complexes

	$k_{Fe(III)}/k_{Fe(H_2O)_6{}^{3+}}$			
	Reducing agent			
	Cr^{2+}	V^{2+}	Fe^{2+}	Eu^{2+}
	Mechanism			
	Inner	Outer	Inner	
$Fe(H_2O)_6{}^{3+}$	1.0	1.0	1.0	1.0
$(H_2O)_5FeOH^{2+}$	1.4×10^3	≤ 22	8.2×10^2	1.35×10^3
$Fe^{3+} + Cl^-$	10	≤ 4	...[b]	1.8
$(H_2O)_5FeCl^{2+}$	1×10^3	26	≤ 3.8[c]	0.51×10^3
Ref	16	36	38	This work

[a] Relative rates at $\mu = 1.00\ M$ and 25°, except Eu^{2+}, 1.6°, and Fe^{2+}, 20°. [b] For the purposes of this table, the chloride catalysis has arbitrarily been assumed to occur by the path involving the inner-sphere $FeCl^{2+}$ complex. [c] The ratio of rates is 7.6, but the inner-sphere path contributes 50% at most to the chloride catalysis (*i.e.*, there is a "direct" exchange path that does not find a parallel in the systems where net reaction occurs).[38]

Acknowledgment. We are grateful to Drs. N. Sutin and T. W. Newton for their helpful comments and suggestions.

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Ethylenebis(diphenylphosphine) Complexes of Iron and Cobalt. Hydrogen Transfer between the Ligand and Iron Atom

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Abstract: Reduction of iron(III) acetylacetonate and cobalt(III) acetylacetonate with ethoxydiethylaluminum in the presence of ethylenebis(diphenylphosphine) (EDP) gives $Fe(EDP)_2 \cdot C_2H_4$ and $HCo(EDP)_2$, respectively. Ultraviolet irradiation of $Fe(EDP)_2 \cdot C_2H_4$ results in the formation of $HFe(C_6H_4PPh \cdot CH_2CH_2 \cdot PPh_2)(EDP)$, in which hydrogen transfer from a phenyl group of the ligand to the iron atom takes place. The hydrogen atom of the Fe–H bond of the iron hydride is labile and returns to the original ligand with ease. The iron hydride is converted into $Fe(EDP)_2 \cdot C_2H_4$ under ethylene pressure. Reaction of the iron hydride with deuterium chloride affords $DFeCl(EDP)_2$ and $HFeCl(C_6H_4DPPh \cdot CH_2CH_2 \cdot PPh_2)(EDP)$ in a ratio of 80:20. The iron complexes $Fe(EDP)_2 \cdot C_2H_4$ and $HFe(C_6H_4PPh \cdot CH_2CH_2 \cdot PPh_2)(EDP)$ react with hydrogen at atmospheric pressure to give $H_2Fe(EDP)_2$.

There have been several reports on the synthesis of 1,4-dienes by the reaction of 1,3-dienes with ethylene in the presence of catalysts consisting of some transition metal compounds and organoaluminum compounds.[1,2] Recently, it has been found that catalysts consisting of iron or cobalt compounds, ditertiary phosphines, and organoaluminum compounds show an excellent activity for this reaction.[3,4] Organoaluminum compounds in these catalyst systems are assumed to act as a reducing agent and as a Lewis acid. With the object of acquiring knowledge about the reducing property of the organoaluminum compounds and clarifying the active species of the catalysts, we have investigated the reaction of iron(III) acetylacetonate and cobalt(III) acetylacetonate with ethoxydiethylaluminum in the presence of ethylenebis(diphenylphosphine). The present paper describes the preparation and characterization of ethylenebis(diphenylphosphine) complexes of low-valent iron and cobalt. In the course of the study of the reactivities of the iron complex, we have found a reversible hydrogen transfer between the ligand and the iron atom.

Results and Discussion

Complexes of Iron. Reaction of iron(III) acetylacetonate with ethoxydiethylaluminum in the presence of ethylenebis(diphenylphosphine) (hereafter EDP) in ethyl ether at 0° gave a red complex **1a** in 85% yield. Repeated recrystallization of this complex from benzene–

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(2) T. J. Kealy, French Patent 1,388,305 (1964).
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