Second, many pK's are estimated on the basis of the Hammett equation or on the basis of crude approximation of substituent effects, as explained in the footnotes to Table I. However, the effects observed are so large that uncertainties of even a power of ten in K_T appear insignificant. Thus, we can conclude that, at least occasionally, we may expect to see tautomeric equilibria shift completely from one side to the other upon electronic excitation. This fact may be of considerable importance in considerations of the mechanism of photochemical reactions, because the reacting species may be a tautomer not occurring in the ground state.

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(6) U. S. Public Health Service Fellow, 1963–1965.

(7) National Aeronautics and Space Administration Trainee, 1964–1966.

R. H. Ellerhorst,[6] H. H. Jaffé, Albert L. Miller[7]
Department of Chemistry, University of Cincinnati
Cincinnati, Ohio 45221

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Inner-Sphere Mechanisms for the Reduction of Cobalt(III) Complexes by Iron(II)[1]

Sir:

Since the discovery[2] of the bridged activated complex in the $Co(NH_3)_5Cl^{2+}$–Cr^{2+} reaction, many electron-transfer reactions have been studied in order to determine whether inner- or outer-sphere mechanisms obtain.[3] For reducing agents such as chromium(II)[4] and pentacyanocobaltate(II),[5] the product criterion of mechanism is applicable.[3] For other reducing agents (iron(II), vanadium(II), europium(II)),[6–9] however, the primary reaction products cannot, in general, be identified since the rates of substitution in the coordination spheres of the oxidation products are usually rapid compared to the rates of the oxidation–reduction reactions.[10,11]

In spite of the lability of iron(III) complexes, we have found that the reductions of $Co(C_2O_4)_3^{3-}$, $Co(H\cdot EDTA)Cl^-$, $Co(en)_2(OH_2)Cl^{2+}$, $Co(NH_3)_3(OH_2)_2Cl^{2+}$, $Co(NH_3)_3(OH_2)_2N_3^{2+}$, and $Co(NH_3)_3(OH_2)C_2O_4^+$ by iron(II) were sufficiently rapid so that the primary iron(III) products of these reactions could be identified.[12] The identification was performed by determining the spectrum of the iron(III) product and by observing its rate of formation and decay. These measurements were made with the rapid-flow apparatus described previously.[13]

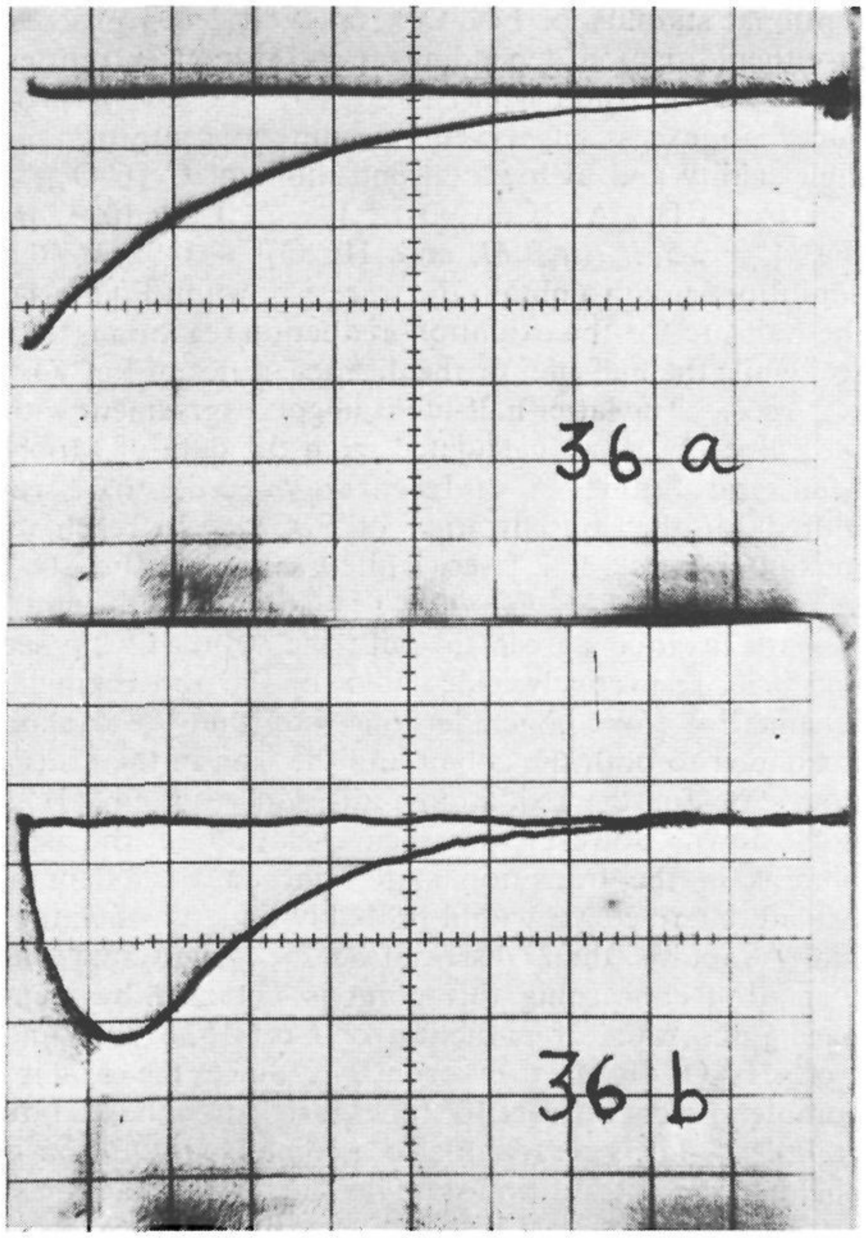

Figure 1. Transmittance *vs.* time curves for the $Co(C_2O_4)_3^{3-}$–Fe^{2+} reaction at 25°. $[Co(C_2O_4)_3^{3-}] = 1.0 \times 10^{-3}$ *M*, $[Fe^{2+}] = 2.5 \times 10^{-2}$ *M*, $[HClO_4] = 0.92$ *M*, ionic strength = 1.0 *M*. Upper curve (36a) shows the disappearance of $Co(C_2O_4)_3^{3-}$: wavelength, 600 mμ; abscissa scale, 500 msec per major division. Lower curve (36b) shows the formation and disappearance of the intermediate $FeC_2O_4^+$: wavelength, 310 mμ; abscissa scale, 2 sec per major division.

The $Co(C_2O_4)_3^{3-}$–Fe^{2+} Reaction. This reaction proceeds in two stages.

$$Co(C_2O_4)_3^{3-} + Fe^{2+} \longrightarrow FeC_2O_4^+ + Co^{2+} + 2C_2O_4^{2-} \quad (1)$$

$$FeC_2O_4^+ + 2H^+ \rightleftharpoons Fe^{3+} + H_2C_2O_4 \quad (2)$$

By using different wavelengths, both the disappearance of $Co(C_2O_4)_3^{3-}$ and the formation and subsequent decay of $FeC_2O_4^+$ were observed. The disappearance of the cobalt(III) complex was followed at 600 mμ, an absorption maximum of $Co(C_2O_4)_3^{3-}$ and a region where none of the other reactants or products absorb significantly. The rate constant for the oxidation–reduction reaction is $(3.3 \pm 0.1) \times 10^1$ M^{-1} sec^{-1} at 25.0° and ionic strength 1.0 *M*.[14] The formation and disappearance of $FeC_2O_4^+$ was followed at 310 mμ. As shown in the lower curve of Figure 1, a rapid decrease in transmittance associated with the oxidation–reduction step is followed by an increase in transmittance corresponding to the disappearance of the $FeC_2O_4^+$ formed in the first step. Because of the ex-

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. Taube, H. Myers, and R. L. Rich, *J. Am. Chem. Soc.*, **75,** 4118 (1953).

(3) For a recent review of this subject, see N. Sutin, *Ann. Rev. Phys. Chem.*, **17,** 119 (1966).

(4) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1,** 1 (1959).

(5) J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85,** 2517 (1963).

(6) A. M. Zwickel and H. Taube, *ibid.*, **83,** 793 (1961).

(7) J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86,** 1019 (1964).

(8) J. H. Espenson, *Inorg. Chem.*, **4,** 121 (1965).

(9) H. Diebler and H. Taube, *ibid.*, **4,** 1029 (1965).

(10) It must be noted, however, that $FeCl^{2+}$ has been identified as the primary product of the $CoCl^{2+}$–Fe^{2+} reaction.[11]

(11) T. J. Conocchioli, G. H. Nancollas, and N. Sutin, *J. Am. Chem. Soc.*, **86,** 1453 (1964).

(12) This criterion appears to be applicable to the $Co(NH_3)_5C_2O_4H^{2+}$–Fe^{2+} reaction. Calculations indicate that at low acid concentration the rate of this reaction[8] becomes comparable to the rate of dissociation of $FeC_2O_4^+$.[15] We are planning to study this reaction in detail.

(13) G. Dulz and N. Sutin, *Inorg. Chem.*, **2,** 917 (1963).

(14) The rate constant for reaction 1 is 1.15×10^3 M^{-1} sec^{-1} at 20° and zero ionic strength: J. Barrett and J. H. Baxendale, *Trans. Faraday Soc.*, **52,** 210 (1956). The lower rate constant determined in the present work is consistent with the effect of ionic strength on the reaction rate.

ceptional stability of $FeC_2O_4^+$, reaction 2 can proceed in either direction depending upon the concentrations of $Co(C_2O_4)_3^{3-}$ and iron(III).[15] The $FeC_2O_4^+$ is produced in excess of its equilibrium concentration at high acidity and at low concentrations of $Co(C_2O_4)_3^{3-}$ and iron(III). At $[Co(C_2O_4)_3^{3-}] = 1.0 \times 10^{-3}$ *M*, $[Fe^{2+}] = 2.5 \times 10^{-2}$ *M*, and $[HClO_4] = 0.92$ *M* (the conditions used to obtain the traces shown in Figure 1), the half-life for the oxidation–reduction reaction is 0.85 sec, while the half-life for the disappearance of $FeC_2O_4^+$ is 2.4 sec. The latter half-life is in good agreement with the value of 2.1 sec calculated from the data of Moorhead and Sutin.[15,16] Moreover, t_{max}, the time required for the concentration of $FeC_2O_4^+$ to reach its maximum value, is 2.1 sec, while the yield of $FeC_2O_4^+$ at t_{max}, $[FeC_2O_4^+]_{max}/[Co(III)]_0$, is 0.51. These quantities are in good agreement with the values of 2.0 sec and 0.56, respectively, calculated for the above kinetic scheme.[17,18] We conclude, therefore, that the oxalate is bonded to both the cobalt and the iron in the transition state for the oxidation–reduction reaction. It is not known, however, whether chelation of the iron obtains in the transition state, since a monodentate oxalate intermediate would probably undergo chelation more rapidly than dissociation.[15] Additional information concerning this point is obtained by comparing the rates of reduction of $Co(NH_3)_5C_2O_4^+$ and $Co(NH_3)_5OCOCH_3^{2+}$ by iron(II). Since the oxalato complex reacts at least 10^4 times faster than the acetato complex,[8,19] it is reasonable to assume that the iron is chelated in the transition state for the former reaction.[20]

The $Co(H \cdot EDTA)Cl^-$–Fe^{2+} Reaction. This reaction also proceeds in two stages.

$$Co(H \cdot EDTA)Cl^- + Fe^{2+} + 3H^+ \longrightarrow FeCl^{2+} + Co^{2+} + H_4EDTA \quad (3)$$

$$FeCl^{2+} \longrightarrow Fe^{3+} + Cl^- \quad (4)$$

The rate constant for reaction 3, obtained by following the disappearance of the cobalt(III) complex at 580 mμ (an absorption maximum of $Co(H \cdot EDTA)Cl^-$), is 1.9 ± 0.2 M^{-1} sec^{-1} at 25°, $[HClO_4] = 2.2$–2.8 *M*, and ionic strength 3.0 *M*.[21] The formation of $FeCl^{2+}$ and its subsequent disappearance were followed at 336 mμ, an absorption maximum of $FeCl^{2+}$. In order to interpret the kinetics of the disappearance of $FeCl^{2+}$, it is necessary to compare the rate constant for reaction 3 with the rate constant for the dissociation of $FeCl^{2+}$.[22] In the range of iron(II) and hydrogen ion concentrations used in the present study ($[Fe^{2+}] = 0.05$–0.26 *M* and $[HClO_4] = 2.85$–2.25 *M*), the rate constant for the latter reaction varies from 2.9 to 5.9 sec^{-1}.[23] Thus, even at the highest iron(II) concentration used, the system eventually reaches a state of transient equilibrium in which the half-life for the disappearance of $FeCl^{2+}$ becomes equal to the half-life for the disappearance of the cobalt(III) complex.[18] For example, at $[Co(H \cdot EDTA)Cl^-] = 5.0 \times 10^{-4}$ *M*, $[Fe^{2+}] = 6.7 \times 10^{-2}$ *M*, $[HClO_4] = 2.8$ *M*, and ionic strength = 3.0 *M*, the half-lives for the disappearance of $FeCl^{2+}$ and of $Co(H \cdot EDTA)Cl^-$ are 5.2 and 5.1 sec, respectively. The values $t_{max} = 1.15$ sec and $[FeCl^{2+}]_{max}/[Co(III)]_0 = 0.046$ determined in this experiment are in satisfactory agreement with the calculated values of 1.05 sec and 0.038, respectively.[17] We conclude, therefore, that the reaction of $Co(H \cdot EDTA)Cl^-$ with iron(II) proceeds *via* a chloride-bridged transition state, a conclusion consistent with previous suggestions based on less direct evidence.[21]

An entirely analogous situation obtains in the *trans*-$Co(en)_2(OH_2)Cl^{2+}$–Fe^{2+} reaction. In one experiment at $[Fe^{2+}] = 0.26$ *M*, [*trans*-$Co(en)_2(OH_2)Cl^{2+}] = 5.0 \times 10^{-3}$ *M*, $[HClO_4] = 2.25$ *M*, and ionic strength = 3.0 *M*, the yield of $FeCl^{2+}$ reached a maximum value of 0.014 after 1.0 sec. The calculated values are 0.017 and 0.96 sec, respectively.[24,25] Again, the formation of $FeCl^{2+}$ in the oxidation–reduction reaction provides conclusive evidence for a chloride-bridged transition state and confirms previous speculations[25] concerning the mechanism of reduction of chloroamminecobalt(III) complexes by iron(II).

In order to explore the generality of the inner-sphere mechanism for cobalt(III)–iron(II) reactions, preliminary experiments were performed with $Co(NH_3)_3(OH_2)_2Cl^{2+}$, $Co(NH_3)_3(OH_2)_2N_3^{2+}$, and $Co(NH_3)_3(OH_2)C_2O_4^+$. In all these cases we observed the formation and subsequent disappearance of the iron(III) complex expected for a bridged transition state.[26] An inner-sphere mechanism has also been demonstrated for the $Co(OH_2)_5Cl^{2+}$–Fe^{2+} reaction.[11] This type of mechanism thus obtains in all the cobalt(III)–iron(II) reactions studied so far in which the primary products could be identified. On the basis of this evidence we conclude, therefore, that iron(II), like chromium(II), generally reacts with cobalt(III) complexes containing suitable ligands by an inner-sphere mechanism.

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(15) E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **5**, 1866 (1966).

(16) In this calculation, allowance is made for the contribution of the reverse of reaction 2.

(17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 166.

(18) G. Friedlander, J. W. Kennedy, and J. M. Miller, "Nuclear and Radiochemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 71.

(19) Espenson[8] reported a rate law of the form $-d \ln [Co(NH_3)_5C_2O_4H^{2+}]/dt = k[Fe^{2+}]/[H^+]$, where $k = 3.8 \times 10^{-3}$ sec^{-1} at 25° and ionic strength 1.0 *M*. Using the value 8.8×10^{-3} for the dissociation constant of $Co(NH_3)_5C_2O_4H^{2+}$ (C. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1087 (1966)), we calculate a rate constant of 0.43 M^{-1} sec^{-1} for the $Co(NH_3)_5C_2O_4^+$–Fe^{2+} reaction.

(20) H. Taube, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 107.

(21) Previously reported values are 2.2 M^{-1} sec^{-1} at 30°, $[HClO_4] = 2.0$ *M*, and ionic strength 3.0 *M* (A. Pidcock and W. C. E. Higginson, *J. Chem. Soc.*, 2798 (1963)) and 1.33 M^{-1} sec^{-1} at 20°, $[HClO_4] = 0.20$ *M*, and ionic strength 0.90 *M* (J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 1086 (1965)).

(22) The rate of disappearance of $FeCl^{2+}$ in the system is, of course, equal to the difference between the rates of its formation and decay.

(23) E. G. Moorhead and N. Sutin, submitted for publication.

(24) The rate constant for the *trans*-$Co(en)_2(OH_2)Cl^{2+}$–Fe^{2+} reaction at 3.0 *M* ionic strength was estimated from the value reported[25] at $[ClO_4^-] = 1.0$ *M*.

(25) P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965).

(26) The quantitative interpretation of the observations is complicated because the cobalt(III) complexes are mixtures of geometrical isomers which are reduced at different rates.

(27) (a) Fellow of the Alfred P. Sloan Foundation. (b) Visiting Chemist from the Department of Chemistry, State University of New York, Stony Brook, N. Y. 11790.

Albert Haim,[27] Norman Sutin
Department of Chemistry, Brookhaven National Laboratory
Upton, New York 11973

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A Solid-State Edman Degradation

Sir:

The Edman degradation,[1] in which amino acids are removed sequentially from the N terminus of