values of $K_1$ and $K_2$ in these systems (*cf.* Table I) are sufficiently close so that it is not possible to prepare a solution which contains almost exclusively $Co(H_2O)_4(A-B)^+$ and which also shows a temperature-jump effect. Therefore, precise values of $\Delta H^*$ and $\Delta S^*$ could not be obtained.

The consequence of the treatment discussed in this section is that if the potential energy curves for both normal and sterically controlled substitution, as exemplified by cobalt(II) with $\alpha$- and $\beta$-alanine, respectively, are superimposed on the same diagram, the result would be Figure 3. The maximum (a) for both ligands is essentially the same and represents the small activation for the diffusion-controlled formation of the ion pair. The peak labeled (b) represents the barrier for dissociation of a water molecule ($W_1$) from the inner coordination sphere. Thus, the curves would almost exactly coincide until the energy barrier at (c), which is higher for $\beta$-alanine than for $\alpha$-alanine by a small though detectable amount.

# Oxidation of Some Chelating Agents and Complexes with Alkaline Ferricyanide[1]

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**Abstract:** The rates of oxidation of a number of chelating agents by alkaline ferricyanide were determined in order to furnish a basis for determining the effect of chelation to a metal on such reaction rates. Examination of the rate of the oxidation of ethylenediaminetetraacetic acid ($H_4Y$) by ferricyanide in alkaline solution shows that the rate law is $-d[Fe(CN)_6^{3-}]/dt = k_2[Y^{4-}][Fe(CN)_6^{3-}]$. The reaction rate is not retarded by added ferrocyanide, cyanide, or fluoride but is strongly dependent on the cation in the "inert" electrolyte used to maintain constant ionic strength. Rate constants obtained for the magnesium and calcium complexes of ($Y^{4-}$) were 100-fold less than rate constants for the uncoordinated ligand. A linear relationship between the entropy of activation and heat of activation was found for the oxidation of a large number of chelating agents having charges from $-1$ to $-5$; no relation between the activation entropy and the charge was observed. Possible mechanisms for the oxidations are discussed.

Ferricyanide usually reacts with organic compounds by one-electron abstraction,[3] and, as might be anticipated, electron-rich compounds are reactive.[4] Kinetic studies show that radicals are produced from anions in the oxidation of mercaptans[5] and phenols,[6] though oxidation of aldehydes, ketones, and nitroparaffins with alkaline ferricyanide does not involve the production of radicals.[7]

Recent work from this laboratory[8] indicates that complexing with borate masks the ferricyanide oxidation of sugars. As part of a survey of the effect of coordination on ligand oxidation, the study of the ferricyanide oxidation of some chelating agents was undertaken. In particular, the oxidation of ethylenediaminetetraacetic acid (indicated as $H_4Y$ henceforth) and a few of its complexes was investigated in some detail. The goal of the present work was to establish some of the features of the rate behavior of ligand oxidations to facilitate work on their complexes.

## Experimental Section

**Materials.** Potassium ferricyanide, disodium ethylenedinitrilotetraacetate dihydrate ($Na_2H_2Y \cdot 2H_2O$), and the inorganic salts used were reagent grade. Chelating agents were the best commercially available grades. In each case the purity was checked by titration with standardized sodium hydroxide. Both the chromium(III)[9] and cobalt(III)[10] complexes, $[Cr(Y)]^-$ and $[Co(Y)]^-$, were prepared by standard methods. All solutions were prepared from deionized water.

**Determination of Stoichiometry.** The extinction coefficient for $K_3Fe(CN)_6$ in aqueous solution determined at 420 m$\mu$ with a Beckman Model B spectrophotometer was $0.972 \times 10^3$ (lit.[11] $1.00 \times 10^3$). A known excess of potassium ferricyanide was added to a known quantity of $Na_2H_2Y$ containing sodium hydroxide and potassium nitrate. The ratio of moles of ferricyanide consumed per mole of $Y^{4-}$ calculated from the absorbance at 420 m$\mu$ was 4.0 after six half-lives and increased slowly thereafter. From infinite time volumes of sodium hydroxide in kinetic studies using the Fischer titrimeter the moles of sodium hydroxide consumed per mole of $Y^{4-}$ were determined to be $4.0 \pm 0.3$. That potassium ferrocyanide is the inorganic reaction product was confirmed by comparison of the infrared spectrum of the product with that of an authentic specimen.

**Spectrophotometric Experiments.** Approximate quantities of chelating agent, sodium hydroxide, and "inert" electrolyte were placed in a 100-ml volumetric flask in a constant temperature bath. After 30 min, potassium ferricyanide solution at the bath tem-

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[2] To whom inquiries should be addressed.

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perature was pipetted into the flask; samples were then withdrawn at various time intervals for measurement of the absorbance at 420 m$\mu$, a wavelength which has been used in other kinetic studies.[5,8] Since the complexing agent was present in large excess, first-order rate constants were obtained by multiplying the slope of a plot of log ($D_t - D_\infty$) *vs.* time by 2.303. Second-order constants were found by dividing the first-order constant by the concentration of complexing agent. In some cases the absorbance was slightly higher during the initial stages than would be predicted from the first-order equation, but this behavior was ignored in computing the rate constants. Rate constants were reproducible to better than ±5%.

**Titrimetric Experiments.** A weighed excess of $Na_2H_2Y \cdot 2H_2O$ was added to a solution containing 0.45 *M* potassium nitrate and potassium ferricyanide which was purged with purified nitrogen. Standard sodium hydroxide in 0.45 *M* potassium nitrate was added with a Fischer titrimeter set at pH 11 or 11.5 while nitrogen was continuously passed through the solution; at various times the volume of base used was recorded. Because the initial reaction is followed by a slower reaction which also consumes base, the infinite time volume ($V_\infty$) was chosen so that a plot of log ($V_\infty - V_t$) *vs.* time was linear. The first-order rate constant is 2.303 times the slope of this plot multiplied by 4.0, the factor necessary from the stoichiometry. Dividing the first-order rate constant by the concentration of $Na_2H_2Y$ gives the second-order constant.

**Stoichiometry.** The reaction studied can be written

$$Y^{4-} + 4Fe(CN)_6{}^{3-} + 4OH^- = 4Fe(CN)_6{}^{4-} + \text{organic products} + H_2O \quad (1)$$

Recently the sequence of products formed when $H_4Y$ is oxidized by its N,N-dioxide and other oxidizing agents has been unraveled.[12] Initial products are iminodiacetic acid and glyoxal, in agreement with the oxidation products of simpler amines with several oxidizing agents.[13] Glyoxal was shown to react rapidly with ferricyanide in our reaction medium, and therefore it cannot be a final product. In basic solution glyoxal is converted to glycollic acid, which was shown to react only slowly with alkaline ferricyanide. The organic products are thus iminodiacetic acid and glycollic acid.

**Kinetic Data.** Good first-order plots were obtained over five half-lives for $Y^{4-}$ and two half-lives for the complexes in the reaction with ferricyanide. The data found by both the spectrophotometric and titrimetric methods are given in Table I, which shows the excellent agreement of the methods. Since the titrimetric data were obtained in a nitrogen atmosphere, oxygen has little effect on the rate of reaction.

Table I. Rate Constants[a] for Ferricyanide Oxidation of Ethylenediaminetetraacetic Acid ($H_4Y$) by Two Methods[b]

| Temp, °C | Spectrophotometric | Titrimetric[c] |
|---|---|---|
| 30.0 | 0.106 | 0.105 |
| 40.0 | 0.277 | 0.276 |
| 50.0 | 0.569 | 0.572 |

[a] Second-order constant, $M^{-1}$ sec$^{-1}$. [b] 1.00 × $10^{-2}$ *M* $Na_2H_2Y$, 4.89 × $10^{-2}$ *M* NaOH, 0.45 *M* $KNO_3$, 5 × $10^{-4}$ *M* $K_3Fe(CN)_6$. [c] Under nitrogen.

Table II contains data for the oxidation of ($Y^{4-}$) which confirm the fact that the reaction is second-order. A graph of the second-order rate constant as a function of hydroxide ion concentration is shown in Figure 1. From these data the rate law is seen to be

$$-d[Fe(CN)_6{}^{3-}]/dt = k_2[Y^{4-}][Fe(CN)_6{}^{3-}] \quad (2)$$

Although the equilibrium constants for protonation of $Y^{4-}$ are not known for these conditions, when the fraction of $Y^{4-}$ computed from constants[14] at 0.1 *M* $KNO_3$ and 42° (using measured pH values) is plotted *vs.* sodium hydroxide added, the curve is similar to Figure 1 showing that $Y^{4-}$ is the reactive species.

**Table II.** Rate Constant as a Function of $Y^{4-}$ Concentration for Oxidation of $Y^{4-}$ with Ferricyanide[a]

| ($Y^{4-}$) × $10^2$ *M* | $k_1 \times 10^3$, sec$^{1}$ | $k_2$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|
| 0.272 | 1.59 | 0.585 |
| 0.436 | 2.50 | 0.572 |
| 0.858 | 4.91 | 0.572 |
| 1.000 | 5.69 | 0.569 |
| 1.600 | 8.42 | 0.525 |

[a] 50°, 0.45 *M* $KNO_3$, 4.89 × $10^{-2}$ NaOH, 5 × $10^{-4}$ *M* $K_3Fe(CN)_6$.

Addition of cyanide, fluoride, or excess ferrocyanide in *10–1000*-fold excess of the ferricyanide concentration did not retard the rate, but rather resulted in a small rate acceleration (data in Table III).

**Table III.** Effect of Added Substances on the Rate of Ferricyanide Oxidation of $Y^{4-}$ [a]

| Compound | $k_2$, $M^{-1}$ sec$^{-1}$ |
|---|---|
| None added | 0.105 |
| 0.05 *M* KCN | 0.231 |
| 0.10 *M* KCN | 0.207 |
| 5 × $10^{-3}$ *M* $K_4Fe(CN)_6$ | 0.122 |
| 0.05 *M* KF | 0.125 |
| 0.10 *M* KF | 0.175 |

[a] 0.45 *M* $KNO_3$, 0.01 *M* $Na_2H_2Y$, 4.89 × $10^{-2}$ *M* NaOH, 5 × $10^{-4}$ *M* $K_3Fe(CN)_6$, at 30°.

Strikingly specific cation effects were observed in this reaction. Table IV shows that the second-order rate constant increases by over 100-fold on changing the cation from lithium to cesium at the same ionic strength. From Figure 2 it is seen that the rate does not increase linearly with cesium ion concentration in sodium chloride–cesium chloride mixtures of the same total ionic strength.

**Table IV.** Effect of Salts on the Oxidation of $Y^{4-}$ by Ferricyanide at 0.50 Ionic Strength[a]

| Salt | $k_2$, $M^{-1}$ sec$^{-1}$ |
|---|---|
| $LiNO_3$ | 0.00268 |
| $NaNO_3$ | 0.0206 |
| NaCl | 0.0342 |
| $KNO_3$ | 0.105 |
| RbCl | 0.268 |
| CsCl | 0.392 |
| $CsNO_3$ | 0.376 |

[a] 0.45 *M* salt, 5.0 × $10^{-2}$ NaOH, 1 × $10^{-2}$ *M* $Na_2H_2Y$, 5.0 × $10^{-4}$ *M* $K_3Fe(CN)_6$, at 30°.

In order to ascertain the effect of structure on reactivity, rate constants as a function of temperature were obtained for several compounds and these data are given in Table V. Examination of Table V shows that the rate constant depends largely on the nature of the amine group and varies in the order tertiary > secondary > primary, but some structural effects are evident. The rate is sensitive to the position of the amino group (compare no. 2 with no. 3 in Table V) and to the distance from the amino group to the carboxyl function (compare no. 10, 11, and 12 in Table V). Figure 3 shows the linear trend observed when the heat of activation is plotted *vs.* the entropy of activation for the data in Table V.

Table VI shows a comparison of the effect of coordination on the reactivity of $H_4Y$ with three oxidizing agents: chromate, permanganate, and ferricyanide. Contrary to a published report,[15] the disappearance of permanganate was first order for freshly prepared solutions. After the $KMnO_4$ solution was aged in the dark for 3 months, the reported behavior could be reproduced, suggesting that $MnO_2$ catalyzes the reaction. Table VI confirms the finding[14]

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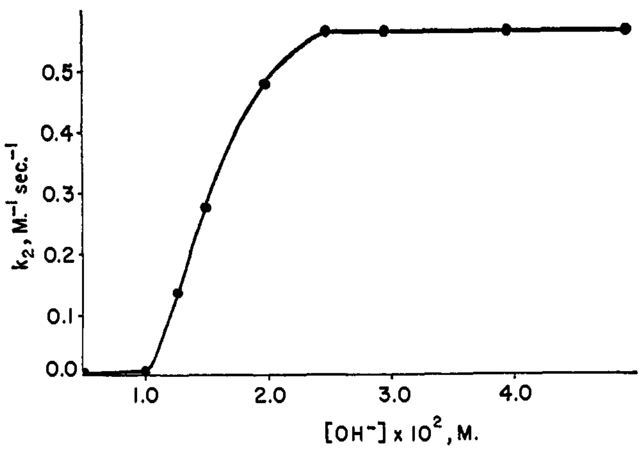

Figure 1. Variation of the rate of oxidation of $Na_2H_2Y$ with concentration of sodium hydroxide. Initial conditions: 0.01 *M* $Na_2H_2Y$, 5 × $10^{-4}$ *M* $K_3Fe(CN)_6$, 0.45 *M* $KNO_3$, 50°.

that coordination drastically reduces the rate of oxidation of $H_4Y$ by permanganate.

Rate constants reported in Table VI are calculated assuming a second-order rate law. Further study of the oxidation of the $[Co(Y)]^-$ complex by ferricyanide revealed that the reaction is more complicated, probably due to concurrent base hydrolysis of the complex.[16] A second-order rate law was definitely established for the $Ca^{2+}$ and $Mg^{2+}$ complexes. At the sodium hydroxide concentrations used, the rate of oxidation of the complexes was independent of the hydroxide ion concentration, which shows that $[Mg(Y)(OH)]^{3-}$ is not the reactive species.[17]

Direct comparison of the reactivity of coordinated ethylenediaminetetraacetate with the uncoordinated ligand is complicated by the fact that only a small percentage of the uncoordinated ligand is present as ($Y^{4-}$) at the sodium hydroxide concentrations which could be used to measure rates of oxidation of the complexes. Comparison of the hydroxide-ion independent rate constants shows that coordination of ($Y^{4-}$) reduces the rate of its reaction with ferricyanide, but protonation has an equally obvious effect.

## Discussion

**Reactivity of Complexes.** One parameter which is changed in the complexes compared with the uncoordinated ligand is the charge. Since entropy effects are important in the complexation of $(Y^{4-})$[18] part of the activation entropy difference between ($Y^{4-}$) and its complexes for the oxidation reaction should be due to the change in charge brought about by complexation. Examination of the activation entropies of the other chelating agents reveals no obvious correlation of the activation entropy with charge; such a lack of correlation has been noticed in other systems.[19] How much of the difference in activation entropy between the coordinated and uncoordinated ligand is because of the change in charge, therefore, is uncertain.

**Mechanism of Reaction.** The kinetics are consistent with interaction of $Y^{4-}$ with ferricyanide in the rate-determining step of the reaction. Because ferrocyanide does not retard the rate, this step is essentially irreversible, as in the ferricyanide oxidation of hydrazine.[20]

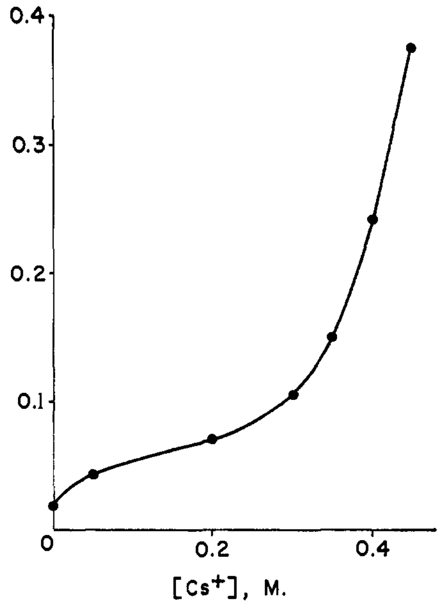

Figure 2. Rate of oxidation of $Y^{4-}$ by ferricyanide in cesium chloride–sodium chloride mixtures at 0.5 *M* ionic strength. Initial condition: 0.01 *M* $Na_2H_2Y$, 5 × $10^{-4}$ *M* $K_3Fe(CN)_6$, 0.05 *M* NaOH, 30°.

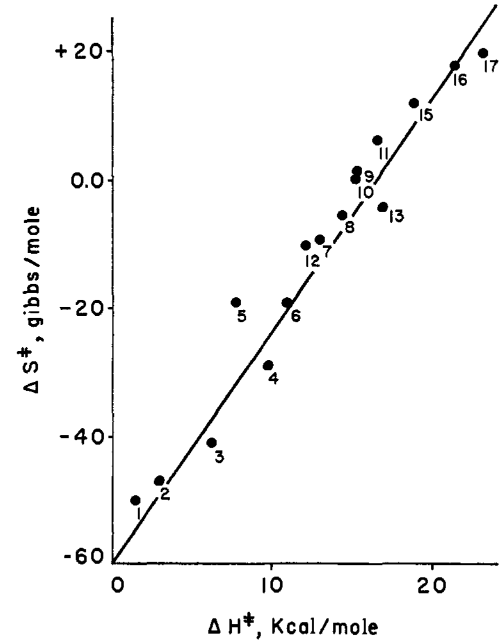

Figure 3. Entropy of activation *vs.* the heat of activation for the oxidation of chelating agents by basic ferricyanide. Numbers on the graph refer to numbers in Table V.

An outer-sphere mechanism of electron transfer[21] as opposed to a mechanism involving dissociation of cyanide[5] is indicated by the fact that neither cyanide nor fluoride ion retards the rate of reaction.

The salt effects observed in the present system parallel those seen in the ferricyanide–ferrocyanide exchange,[22] the manganate–permanganate exchange,[23] and other

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Table V. Rate Constants and Activation Parameters for Oxidation of Some Chelating Agents with Ferricyanide[a]

| No. | Compound | $k_2 \times 10^3$, $M^{-1}$ sec$^{-1}$ 50° | 40° | 30° | $\Delta H^*$, kcal | $\Delta S^*$, gibbs |
|---|---|---|---|---|---|---|
| 1 | Iminodiacetic acid | 0.452 | 0.337 | 0.293 | 1.5 | −50 |
| 2 | β-Alanine | 0.215 | 0.178 | 0.145 | 3.0 | −47 |
| 3 | α-Alanine | 0.0288 | 0.0195 | 0.0139 | 6.3 | −41 |
| 4 | Glycine | 0.162 | 0.104 | 0.0507 | 9.8 | −29 |
| 5 | Ethylenediaminepentaacetic acid | 730 | 457 | 304 | 7.9 | −19 |
| 6 | Imidazole | 3.45 | 1.97 | 1.13 | 10.9 | −19 |
| 7 | $(Mg(Y))^{2-}$ [b] | 8.10 | 4.29 | 1.98 | 13.0 | −9.2 |
| 8 | Histidine | 14.0 | 6.90 | 3.02 | 14.4 | −5.3 |
| 9 | Nitrilotriacetic acid | 65.8 | 27.5 | 12.8 | 15.3 | 1.5 |
| 10 | Ethylenebis(oxyethylenenitrilo)-tetraacetic acid | 310 | 134 | 61.8 | 15.1 | 0.50 |
| 11 | Ethylenediamine-tetraacetic acid | 569 | 276 | 105 | 16.6 | 6.8 |
| 12 | Ethylenediaminetetrapropionic acid | 7.84 | 3.49 | 1.92 | 12.8 | −10 |
| 13 | $(Ca(Y))^{2-}$ [b] | 0.271 | 0.115 | 0.0445 | 16.9 | −3.9 |
| 14 | Proline | 3.11 | 1.29 | 0.425 | 18.9 | 7.2 |
| 15 | Glutamic acid | 2.85 | 0.911 | 0.240 | 22.4 | 17.7 |
| 16 | Methionine | 1.85 | 0.493 | 0.155 | 23.3 | 19.6 |
| 17 | Acetic acid | . . . | . . . | 0.007 | . . . | . . . |

[a] $4.89 \times 10^{-2}$ $M$ NaOH, 0.45 $M$ $KNO_3$. [b] $4.89 \times 10^{-3}$ $M$ NaOH, 0.45 $M$ $KNO_3$.

Table VI. Reaction of Some Complexes of Ethylenediaminetetraacetic Acid with Three Oxidizing Agents at 50°[a]

| Compound | Oxidizing agent: Ferricyanide | Chromate[b] | Permanganate[c] |
|---|---|---|---|
| $H_4Y$ | 569[d] | 36.1 | 97.6 |
| $[Co(Y)]^-$ | 5[e] | No change in 90 hr | No change in 24 hr |
| $[Cr(Y)]^-$ | 5[e] | No change | No change |
| $[Ca(Y)]^{2-}$ | 0.271[e] | . . . | . . . |
| $[Mg(Y)]^{2-}$ | 8.07[e] | . . . | . . . |

[a] $k_2 \times 10^3$, sec$^{-1}$. [b] Acetic acid–acetate buffer 0.01 $M$, pH 4.50, 1.0 $M$ $KNO_3$. [c] 0.05 $M$ $HClO_4$, 1.0 $M$ $KNO_3$. [d] For oxidations of $Y^{4-}$. [e] $4.89 \times 10^{-3}$ $M$ NaOH, 0.45 $M$ $KNO_3$.

reactions between large negative ions.[24] In contrast to the linear variation of the rate with cesium ion found in the manganate–permanganate exchange,[25] the deviation of the rate with cesium ion concentration from linearity in the present system is far greater than would be anticipated from changes in the cesium ion activity.[26] Since ferricyanide forms complexes with alkali metal ions[27] the composition of the transition state relative to that of reactants remains unknown.

The order of reactivity observed for the chelating agents, tertiary > secondary > primary amine, is the same as the order in demethylation of amines with ferricyanide.[28] Just the opposite order of reactivity is found in amine oxidations with permanganate,[29] for which a hydrogen-atom transfer mechanism involving the hydrogen atoms *alpha* to the amine function has been proposed.[30] Although the hydride transfer mechanism cannot be definitely excluded, the observed reactivity order suggests that ferricyanide oxidation occurs at the amine function itself. A linear trend between the heat of activation and entropy of activation for a series of compounds indicates that a single effect predominates throughout the series.[31] Perhaps the observed isokinetic relationship is indicative of attack at the nitrogen atom, but caution is necessary in such an interpretation.[32]

Although the present data do not permit a clear distinction among possible intermediates,[33] if attack at the nitrogen atom occurs, a singly charged imine[34,35] could be the reactive intermediate, since such species hydrolyze rapidly in alkaline solution, yielding aldehydes and secondary amines.[36] If such attack occurs, the masking of reactivity of ethylenediaminetetraacetic acid upon coordination would indicate that the amine function is less susceptible to attack in the coordinated state.

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