CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA 47907

Kinetics of the Oxidation of 1,2-Diaminocyclohexanetetraacetatoferrate(II) Ion by Iodine

BY W. H. WOODRUFF, D. C. WEATHERBURN, AND D. W. MARGERUM*

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The oxidation of the complex $Fe^{II}CyDTA^{2-}$ (CyDTA is *trans*-1,2-diaminocyclohexane-N,N,N',N'-tetraacetate) by iodine is first order in $Fe^{II}CyDTA^{2-}$ concentration and first order in total iodine concentration. The observed second-order rate has contributions from oxidation rates due to I_2 (k_1) and I_3^- (k_2); $k_1 = 1.24 \times 10^5\ M^{-1}\ sec^{-1}$ and $k_2 = 5.0 \times 10^3\ M^{-1}\ sec^{-1}$ at 25.0°. The activation parameters for k_1 and k_2 are $\Delta H_1^{\ddagger} = 7.7$ kcal mol^{-1}, $\Delta S_1^{\ddagger} = -5$ cal deg^{-1} mol^{-1}, $\Delta H_2^{\ddagger} = 21$ kcal mol^{-1}, and $\Delta S_2^{\ddagger} = +28$ cal deg^{-1} mol^{-1}. The observed rate does not depend upon $[H^+]$ over the range studied (pH 3–4). Although the mixed complex $Fe^{III}(CyDTA)I^{2-}$ exists (the stability constant is 30 M^{-1}), its rate of dissociation is too rapid for it to be observed as an intermediate in the oxidation reaction.

The redox potential of the iron(III)–iron(II) couple is such that iodide ion is oxidized to iodine by $Fe^{3+}(aq)$.[1] Chelation of iron by CyDTA (as well as other aminocarboxylic acids), however, causes the potential of the iron(III)–iron(II) couple to shift in such a manner as to make the iron(II) complex a considerably stronger reducing agent than $Fe^{2+}(aq)$. Specifically, while the standard potential (IUPAC convention) of the $Fe^{3+}(aq)$–$Fe^{2+}(aq)$ couple is 0.771 V, that of the $Fe^{III}CyDTA^-$–$Fe^{II}CyDTA^{2-}$ couple is 0.088 V,[2,3] making the reduction of iodine by $Fe^{II}CyDTA^{2-}$ thermodynamically favorable.

In the present work, the kinetics of the reaction in eq 1 have been investigated by stopped-flow spectrophotometry. The observed kinetics are first order in

$$2Fe^{II}CyDTA^{2-} + \begin{bmatrix} I_2 + I^- \\ \uparrow\downarrow \\ I_3^- \end{bmatrix} \longrightarrow 2Fe^{III}CyDTA^- + 3I^- \qquad (1)$$

iron(II)–CyDTA complex and first order in total iodine. The oxidation rates depend on the molecular iodine and the triiodide ion concentrations, and rate constants have been resolved for each species. Compared to the corresponding rates which have been reported for reactions having the stoichiometry

$$2Fe^{2+}(aq) + X_2 \longrightarrow 2Fe^{3+}(aq) + 2X^-$$

(X = Cl,[4] Br[5]), the rates observed in this study are surprisingly fast. A mixed complex, $Fe^{III}(CyDTA)I^{2-}$, exists and has a stability constant of 30 M^{-1}. This species has not been observed as an intermediate in the reaction sequence.

Experimental Section

Reagents and Measurements.—Disodium 1,2-diaminocyclohexanetetraacetate was purified by two recrystallizations of reagent grade 1,2-diaminocyclohexanetetraacetic acid (Lamont Laboratories). CyDTA solutions were standardized against standard iron(III) by the mole ratio method. Sodium perchlorate solutions were prepared from the twice-recrystallized salt. All other chemicals were reagent grade, used without further purification.

Kinetic data were obtained using a Durrum–Gibson stopped-flow spectrophotometer with 2.0-cm cell path. Data were reduced using an on-line digital computer (Hewlett-Packard 2115A), interfaced to the stopped-flow instrument as described elsewhere.[6] Using this system, data can be taken at a rate of one point/msec. A least-squares analysis of the conformance of the data to a programmed rate law can be obtained within 1 min of the completion of the experiment. After on-line analysis, data from all stopped-flow experiments were recorded on punched paper tape, for possible later off-line calculations.

Visible and ultraviolet spectra were taken using a Cary 14 spectrophotometer. Difference spectra were obtained using split cells having a total path length of 2.0 cm, 1.0 cm for each compartment. For these measurements, the unmixed solutions were placed in the reference beam of the spectrophotometer.

Conditions.—The range of experimental conditions, under which the system under study can be conveniently observed, is fairly limited. The sources of the limitations and the experimental consequences of the limitations will now be discussed.

The sensitivity of $Fe^{II}CyDTA^{2-}$ to air oxidation has been noted previously.[7] This reaction is fast enough to make the handling of $Fe^{II}CyDTA^{2-}$ solutions difficult, particularly when stopped-flow techniques are employed. However, the oxygen reaction is not fast enough to interfere with the reaction between $Fe^{II}CyDTA^{2-}$ and iodine, under the experimental conditions used in this work. Species concentration calculations, performed using the Hewlett-Packard 2115A computer and a modified version of program COMICS,[8] show that in the presence of excess CyDTA, the $Fe^{II}CyDTA^{2-}$ complex is fully formed at pH ≥3. The species distribution of the iron(II)–CyDTA system as a function of pH is shown in Figure 1. In the presence of excess CyDTA, the complexation reaction is faster than the oxidation of the complex by iodine. Thus, to avoid the problems associated with the handling of reducing solutions, the reactants $Fe^{2+}(aq)$ and CyDTA were contained in separate solutions on the stopped-flow apparatus.

At pH >3, solutions containing both $Fe^{2+}(aq)$ and iodine were observed to decompose with precipitation of iron(III) hydroxides. Likewise at pH >4, $Fe^{2+}(aq)$ forms ferric hydroxide suspensions slowly, as a result of oxidation of air-saturated iron(II) solutions by oxygen. If, as is desired, the Fe(II)–$CyDTA^{2-}$ complex is to be formed *in situ* during an experiment and the pH is to be such that the complex is fully formed, then the iodine must be contained in the same solution as the CyDTA. It has been reported,[9] however, that solutions of aminocarboxylic acids will reduce iodine in the presence of light. This effect was observed during this study with CyDTA, and, if the oxidation of $Fe^{II}CyDTA^{2-}$ by iodine is to be carried out under stoichiometric conditions, the iodine–CyDTA solution must be protected from light.

With the above limitations in mind, solutions for stopped-flow experiments were prepared in the following manner. Iron(II) solutions were prepared from the desired weight of iron(II) ammonium sulfate hexahydrate. Acetate buffer and sodium iodide

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(1) A. J. Fudge and K. W. Sykes, *J. Chem. Soc.*, 119 (1952), and references therein.

(2) J. Bond and T. J. Jones, *Trans. Faraday Soc.*, **55**, 1310 (1959).

(3) M. M. T. Khan and A. E. Martell, *J. Amer. Chem. Soc.*, **90**, 3386 (1968).

(4) J. H. Crabtree and W. P. Schaeffer, *Inorg. Chem.*, **5**, 1348 (1966).

(5) P. R. Carter and N. Davidson, *J. Phys. Chem.*, **56**, 877 (1952).

(6) B. G. Willis, J. A. Bittikoffer, H. L. Pardue, and D. W. Margerum, *Anal. Chem.*, **42**, 1340 (1970).

(7) Y. Kurimura, R. Ochiai, and N. Matsuura, *Bull. Chem. Soc. Jap.*, **41**, 2234 (1968).

(8) D. D. Perrin and I. G. Sayce, *Talanta*, **14**, 833 (1967).

(9) J. Faure and J. Joussot-Dubian, *Bull. Soc. Chim. Fr.*, 3064 (1967).

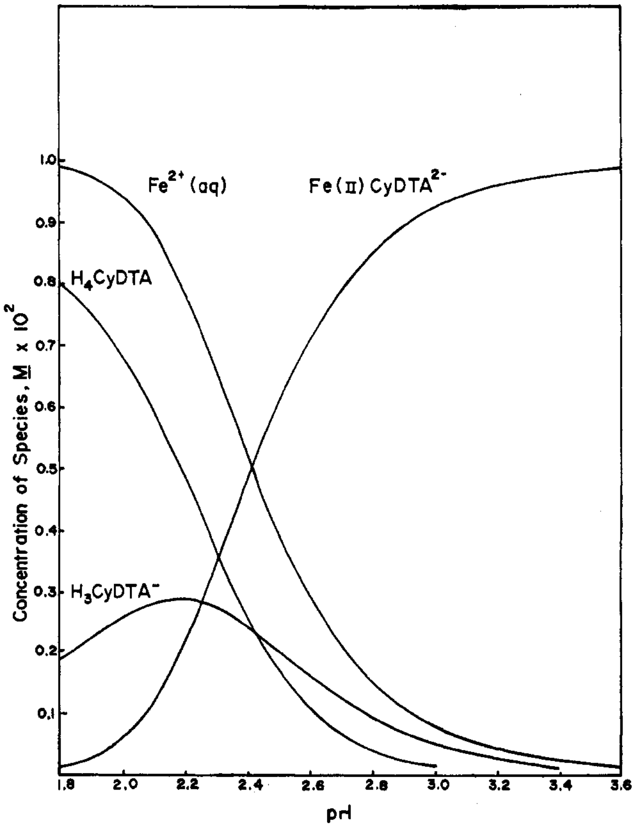

Figure 1.—Species distribution as a function of pH for a solution with 10^{-2} *M* total iron(II) and 10^{-2} *M* total CyDTA. The maximum concentration of H_2CyDTA^{2-} is 2×10^{-4} *M* at pH 2.5.

and/or sodium perchlorate were added in varying amounts to control pH, ionic strength, and the iodine:triiodide ratio. In preparation of the iodine–CyDTA solutions, first the desired volumes of CyDTA, sodium iodide, acetate buffer, and sodium perchlorate (if used) solutions were mixed. Then, before the stopped-flow experiment, the desired volume of a standard potassium iodate solution was added, forming iodine *in situ.* Light was excluded from the solution until the experiment. Depending upon the degree of exclusion of light, the desired concentrations of iodine could be attained in this manner. The reaction between the two solutions described above was followed at 470 nm. At this wavelength the molar absorptivities of the significantly absorbing species are 740 M^{-1} cm^{-1} for I_2,[10] 630 M^{-1} cm^{-1} for I_3^-, and 17 M^{-1} cm^{-1} for $Fe^{III}CyDTA^-$. The molar absorptivity of total iodine, at 470 nm, was determined on the stopped-flow instrument by observing the final absorbance upon mixing a large excess of iodide ion and iodate ion, at pH 4. The rate constants observed for the iodate–iodide reaction, during these determinations, were in satisfactory agreement with those predicted using the rate expression reported by Barton and Wright.[11]

The study of the temperature dependence of the resolved rate constants was carried out using precautions to ensure accurate results, including special insulation of the stopped-flow apparatus and continuous monitoring of the temperature of the reactants. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined by a weighted, linear least-squares fit to the appropriate function.

At low concentrations of iodide ion, small uncertainties in $[I^-]$ lead to large variations in the observed second-order rate constant for the oxidation reaction. For this reason, $[I^-]$ was always made greater than 0.01 *M*. Stainless steel cuvette material, when used in the stopped-flow instrument, was found to cause experimental error (high k_0 values) in the system under study. The kinetic measurements reported were made using a Kel-F stopped-flow cuvette.

Results

The reaction between $Fe^{II}CyDTA^{2-}$ and iodine is first order in the $Fe^{II}CyDTA^{2-}$ concentration and first order in the total iodine concentration. In the pH range 3–4, the rate is independent of the CyDTA concentration and of pH. The observed second-order rate constant, k_o, is dependent upon the concentration of iodide ion and the temperature, as shown in Table I.

TABLE I

DEPENDENCE OF OBSERVED RATE CONSTANT, k_o, UPON IODIDE ION CONCENTRATION[a]

$[I^-]$, *M*	$10^4\Sigma[I_2]_o$, *M*	$10^4[Fe^{II}CyDTA^{2-}]_o$, *M*	$10^{-4}k_o$, M^{-1} sec^{-1}	No. of detns
		25.0°		
0.0125[b]	1.00	50.0	15.2 ± 1.3	6
0.030	0.815	3.00	5.3 ± 0.6	4
0.035	2.50	5.00	5.0 ± 0.5	8
0.040	1.03	3.00	4.5 ± 0.6	5
0.050	0.980	3.00	3.5 ± 0.3	7
0.070	1.89	5.00	3.0 ± 0.4	7
0.080	4.06	10.0	2.5 ± 0.2	5
0.090	2.50	5.00	2.26 ± 0.10	9
0.100	2.02	5.00	2.02 ± 0.07	4
0.150	2.50	5.00	1.50 ± 0.05	7
0.175	2.11	5.00	1.4 ± 0.2	5
		10.0°		
0.025	2.50	5.00	2.1 ± 0.2	4
0.050	2.50	5.00	1.07 ± 0.03	6
0.100	2.50	5.00	0.57 ± 0.02	8
0.150	2.50	5.00	0.38 ± 0.01	4
		40.2°		
0.025	2.50	5.00	24.4 ± 0.2	3
0.050	2.50	5.00	14 ± 2	6
0.100	2.50	5.00	7.1 ± 0.4	6
0.150	2.50	5.00	5.8 ± 0.2	6

[a] pH 3.8–4.2, acetate buffer, μ = 0.2. CyDTA in excess, $[CyDTA]_T = 10^{-3}$–10^{-2} *M*. [b] pH 3.2.

The kinetics are consistent with the reactions

$$I_2 + I^- \underset{}{\overset{\text{rapid}}{\rightleftarrows}} I_3^- \tag{2}$$

$$Fe^{2+}(aq) + (CyDTA)_T \xrightarrow[\text{complete}]{\text{rapid}} Fe^{II}CyDTA^{2-} \tag{3}$$

$$Fe^{II}CyDTA^{2-} + I_2 \xrightarrow{k_1} Fe^{III}CyDTA^- + I\cdot + I^- \tag{4}$$

$$Fe^{II}CyDTA + I_3^- \xrightarrow{k_2} Fe^{III}CyDTA^- + I\cdot + 2I^- \tag{5}$$

$$Fe^{II}CyDTA^{2-} + I\cdot \xrightarrow{\text{rapid}} Fe^{III}CyDTA^- + I^- \tag{6}$$

The reaction given in eq 2 is known to be very fast,[12] the rate constant for the formation of I_3^- being 2×10^9 M^{-1} sec^{-1} and the stability constant of I_3^- being 768 M^{-1} at 25.0°.[13] It was desired to work at a pH such that $Fe^{II}CyDTA^{2-}$ is fully formed[2,14,15] (see Figure 1), and, under conditions of excess CyDTA, the reaction in eq 3 is complete before the reactions in eq 4 and 5 can proceed substantially. Below pH 3 the observed kinetics are complex due to contributions from reaction 3.

Given the above reaction scheme and boundary conditions, the expected rate expression for the oxidation of

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[10] J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **8**, 1407 (1969).

[11] A. F. M. Barton and G. A. Wright, *J. Chem. Soc. A*, 2096 (1968).

[12] G. von Bünau and M. Eigen, *Z. Phys. Chem.* (*Frankfurt am Main*), **32**, 27 (1962).

[13] M. Davies and E. Gwynne, *J. Amer. Chem. Soc.*, **74**, 2748 (1952).

[14] L. G. Sillén and A. E. Martell, Ed., "Stability Constants," The Chemical Society, London, 1964.

[15] J. D. Carr and D. G. Swartzfager, *Anal. Chem.*, **42**, 1238 (1970).

$Fe^{II}CyDTA^{2-}$ by iodine is given in the equation

$$\frac{-d[(I_2)_T]}{dt} = k_1[I_2][Fe^{II}CyDTA^{2-}] + k_2[I_3^-][Fe^{II}CyDTA^{2-}] \qquad (7)$$

The concentration of molecular iodine is related to the concentration of triiodide ion by

$$[I_2] = \frac{[I_3^-]}{K_{I_3}[I^-]} \qquad (8)$$

where K_{I_3} is the stability constant of triiodide ion. Thus, with iodide ion in sufficient excess to keep the ratio of iodine to triiodide ion constant during the oxidation reaction, eq 7 becomes eq 9. Since the observed

$$\frac{-d[(I_2)_T]}{dt} = \left(\frac{k_1[I_3^-]}{K_{I_3}[I^-]} + k_2[I_3^-]\right)[Fe^{II}CyDTA^{2-}] \qquad (9)$$

kinetics follow the rate law given in eq 10, the expected

$$\frac{-d[(I_2)_T]}{dt} = k_o([I_2] + [I_3^-])[Fe^{II}CyDTA^{2-}] \qquad (10)$$

relationship among k_o, k_1, and k_2 is given in eq 11.

$$k_o(1 + K_{I_3}[I^-]) = k_1 + k_2K_{I_3}[I^-] \qquad (11)$$

The rate constants k_1 and k_2 are resolved by plotting $k_o(1 + K_{I_3}[I^-])$ against $K_{I_3}[I^-]$ as shown in Figure 2, for each temperature studied. The resolved rate constants, temperatures, and activation parameters are presented in Table II.

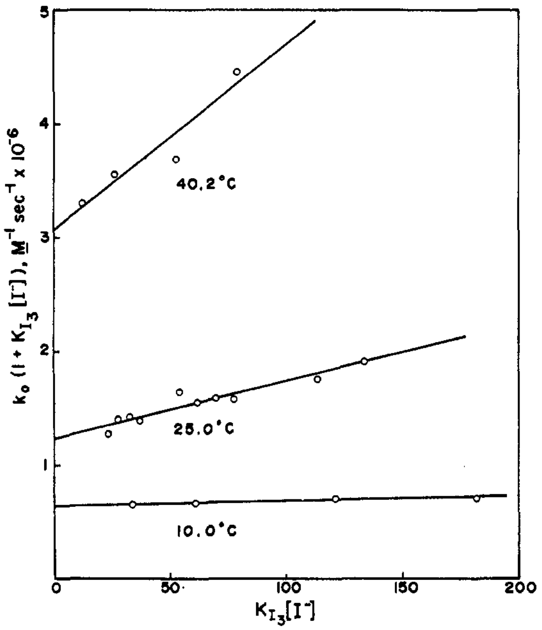

Figure 2.—Plot of data used to resolve k_1 and k_2 at the three temperatures studied. The function plotted is taken from eq 11. The straight lines are the least-squares lines. The slopes (k_2) and the intercepts (k_1) for the three temperatures and their standard deviations are given in Table II.

To determine whether the oxidation of $Fe^{II}CyDTA^{2-}$ by oxygen was affecting the k_o values, a series of experiments was run under anaerobic (nitrogen atmosphere) conditions. The kinetics observed in these experiments were identical with those observed using air-saturated solutions.

In experiments performed at lower iodide ion concentrations (larger k_o values), small induction periods were evident which were assigned to the complexation reaction (eq 3). From these induction periods an approximate rate constant of 1×10^5 M^{-1} sec^{-1} was calculated, for the formation of $Fe^{II}CyDTA^{2-}$ from Fe^{2+}(aq) and CyDTA at pH 4. This value is in agreement with the fact that, when CyDTA is not present in large excess, complex kinetics are observed. Due to experimental complications discussed earlier, no attempt at direct measurement of the rate of formation of $Fe^{II}CyDTA^{2-}$ was made.

Table II

Resolved Rate Constants and Activation Parameters

Temp, °C	K_{I_3}, M^{-1}	k_1, M^{-1} sec^{-1}	k_2, M^{-1} sec^{-1}
10.0	1215[a]	$(6.45 \pm 0.11) \times 10^5$	$(3.3 \pm 1.0) \times 10^2$
25.0	768[b]	$(1.24 \pm 0.04) \times 10^6$	$(5.0 \pm 0.6) \times 10^3$
40.2	503[a]	$(3.1 \pm 0.2) \times 10^6$	$(1.6 \pm 0.4) \times 10^4$

$\Delta H_1^{\ddagger} = 7.7 \pm 0.3$ kcal mol^{-1} $\Delta S_1^{\ddagger} = -5 \pm 1$ cal deg^{-1} mol^{-1}
$\Delta H_2^{\ddagger} = 21 \pm 3$ kcal mol^{-1} $\Delta S_2^{\ddagger} = +28 \pm 9$ cal deg^{-1} mol^{-1}

[a] Calculated from the data of A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, **73,** 1842 (1951), and of G. Daniele, *Gazz. Chim. Ital.*, **90**, 1068 (1960). [b] Reference 13.

Haim and Sutin[16] have observed the formation and decay of iron(III) intermediates which demonstrate inner-sphere mechanisms, in certain reductions by iron(II). The existence of a mixed complex between $Fe^{III}CyDTA^-$ and iodide ion is indicated by differences between the visible absorption spectra of $Fe^{III}CyDTA^-$, in perchlorate and iodide solutions. The mixed complex $Fe^{III}(CyDTA)I^{2-}$ absorbs light more strongly than $Fe^{III}CyDTA^-$ at wavelengths shorter than 450 nm, with a maximum difference in absorbance at 360 nm, Δ(molar absorptivity) = 160 M^{-1} cm^{-1}. Measurements of the stability constant of the mixed complex were made, using divided cells, at wavelengths of 385, 380, 375, and 370 nm. Total concentration of $Fe^{III}CyDTA^-$ was 1.02×10^3 M, and $[I^-] + [ClO_4^-]$ was 1.0 M. Iodide ion concentrations were 0.0100, 0.100, 0.50, and 0.75 M. The mixed complex was essentially fully formed at 0.75 M I^-. Absorbance measurements at $[I^-] = 0.100$ and 0.0100 M using four wavelengths yield a value for the stability constant of the mixed complex of 30 ± 7 M^{-1}. The dissociation of this mixed complex is too fast to be detectable by stopped-flow techniques, indicating a maximum half-life, for the dissociation, of 2 msec. In the oxidation of $Fe^{II}CyDTA^{2-}$ by iodine, the presence of an intermediate $Fe^{III}(CyDTA)I^{2-}$ species would strongly suggest that coordination of iodine to $Fe^{II}CyDTA^{2-}$ must occur prior to electron transfer. The speed of the dissociation of the mixed complex, however, renders its detection, as an intermediate in the oxidation reaction, virtually impossible.

Discussion

Aside from the reaction scheme which is proposed in the preceding section, another possibility which fits the kinetic facts equally well is a two-electron oxidation as the rate-determining step (rds) (eq 12 and 13). This

$$Fe^{II}CyDTA^{2-} + I_2 \xrightarrow{\text{rds}} Fe^{IV}CyDTA + 2I^- \qquad (12)$$

$$Fe^{IV}CyDTA + Fe^{II}CyDTA^{2-} \xrightarrow{\text{rapid}} 2Fe^{III}CyDTA^- \qquad (13)$$

type of mechanism has been proposed previously,[17] in

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(16) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 5343 (1966).

(17) T. J. Conocchioli, E. J. Hamilton, Jr., and N. Sutin, *ibid.*, **87**, 926 (1965).

the fast oxidations of iron(II) by ozone and hypochlorous acid. The I_2 reaction under study here is unusually fast, but speed is not a criterion which may be used to differentiate between one- and two-electron mechanisms in the oxidation of iron(II). Table III presents a series of second-order oxidation reactions of bivalent metal centers, together with the standard potentials and the rate constants of the reactions and the activation parameters in the cases for which they are known. It is seen that the reaction between Fe^{2+}(aq) and the radical ion Br_2^- is among the fastest reactions tabulated, and it almost certainly proceeds *via* a one-electron mechanism. Moreover, the overall free energy change (as reflected by $E°$, Table III) of the $Fe^{II}CyDTA^{2-}$ reaction is intermediate between the free energy changes for the oxidation of Fe^{2+}(aq) by chlorine and bromine. The former reaction is postulated[4,18] to proceed by one-electron steps, and the latter reaction can be inferred,[5] by its inverse $[Br^-]$ dependence, to proceed in this manner. It is suggested, therefore, that the reaction sequence proposed in eq 2-5 is the correct one in this case.

TABLE III

STANDARD POTENTIALS[a] AND RATE CONSTANTS[b] FOR SELECTED SECOND-ORDER REDOX REACTIONS

Reaction	$E°$, V	k, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
$Fe^{2+}(aq) + Br_2$	+0.294	0.76[c]	...	...
$Cr^{2+}(aq) + N_3^-$	...	4.0[d]	...	...
$Cr^{2+}(aq) + HN_3$	+1.10	25[d]	...	...
$Fe^{2+}(aq) + Br_3^-$	+0.294	34[e]	7.8	−25.6
$Fe^{2+}(aq) + Cl_2$	+0.589	80[e]	...	...
$Fe^{2+}(aq) + Cl_2$	+0.589	163 (30°)[f]	...	...
$Fe^{2+}(aq) + Cl_3^-$	+0.589	910 (40°)[f]	...	...
$V^{2+}(aq) + I_3^-$	+0.791	970[g]	9.1	−14
$Co^{II}EDTA^{2-} + H_2O_2$	+1.39[h]	1.4×10^{3}[h]	...	...
$Fe^{2+}(aq) + HOCl$	+0.86	3.2×10^{3}[e]	...	...
$Fe^{II}CyDTA^{2-} + I_3^-$	+0.448[i]	5.0×10^{3}[j]	21	+28
$V^{2+}(aq) + I_2$	+0.791	7.5×10^{3}[g]	5.9	−21
$Cr^{2+}(aq) + S_2O_8^{2-}$	+2.42	2.5×10^{4}[k]	...	...
$V^{2+}(aq) + Br_2$	+1.32	3.0×10^{4}[q]	3.5	−26
$Fe^{II}EDTA^{2-} + ClO_2^-$	...	3×10^{4}[l]	12.4	+2.5
$Fe^{II}(CN)_6^{4-} + S_2O_8^{2-}$	+1.65	$\sim 10^{5}$[m]	...	...
$Fe^{2+}(aq) + O_3$	+1.30	1.7×10^{5}[e]	...	...
$Fe^{2+}(aq) + H_2O_2$	+1.00	7.0×10^{5}[n]	6.7	−9.5
$Fe^{II}CyDTA^{2-} + I_2$	+0.448[i]	1.24×10^{6}[j]	7.7	−5
$Fe^{2+}(aq) + Br_2^-$	...	8.2×10^{6}[o]	...	...
$Fe^{II}(DMP)_3^{2+} + IrCl_6^{2-}$[p]	−0.152[q]	2.2×10^{8}[q]	...	...

[a] In acid solution, from W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952, unless otherwise noted. Potentials given are for reaction to final products. [b] At 25°, unless otherwise noted. [c] Reference 5. [d] C. F. Wells and M. A. Salam, *J. Chem. Soc. A*, 1568 (1968). [e] Calculated from data in ref 17. [f] Reference 3. [g] Reference 10. [h] R. G. Yalman, *J. Phys. Chem.*, **65,** 556 (1961). [i] Reference 2. [j] Present work. [k] D. E. Pennington and A. Haim, *J. Amer. Chem. Soc.*, **90,** 3700 (1968). [l] Reference 18. [m] M. K. Basu and M. N. Das, *J. Chem. Soc. A*, 2182 (1968). [n] Calculated from data by C. F. Wells and M. A. Salam, *ibid.*, *A*, 24 (1968). [o] A. T. Thornton and A. S. Laurence, *Chem Commun.*, 443 (1970). [p] DMP = 4,6-dimethyl-1,10-phenanthroline. [q] P. Hurwitz and K. Kustin, *Inorg. Chem.*, **3,** 823 (1964).

The smaller value found for k_2 compared to k_1 might be expected as a result of electrostatic repulsion in the approach of the I_3^- and $Fe^{II}CyDTA^{2-}$ ions. However, the activation parameters do not support such an explanation because this would require $\Delta S^{\ddagger}_{\text{electrostatic}}$ to be negative for the reaction with I_3^-, and $\Delta S_2^{\ddagger}$ would be expected to be more negative than $\Delta S_1^{\ddagger}$. In fact, the opposite is true and $\Delta S_2^{\ddagger}$ is +28 cal deg^{-1} mol^{-1} compared to a value of −5 cal deg^{-1} mol^{-1} for $\Delta S_1^{\ddagger}$. The large positive value for $\Delta S_2^{\ddagger}$ indicates that the rate-determining step is not the formation of an inner-sphere complex but rather is a later stage in the reaction. The positive value of $\Delta S_2^{\ddagger}$ may be contrasted to the negative entropies of activation which are observed in the majority of redox reactions involving metal ions.[19] Abnormally high entropies of activation have been observed in gas-phase reactions of the type ABC → A + B + C.[20] There may be similarities in the activation step of these gas-phase reactions and the triiodide oxidation. Study of this point is continuing. The lower reactivity of I_3^- compared to I_2 is a result of the much larger value of $\Delta H_2^{\ddagger}$ (21 kcal mol^{-1}) compared to $\Delta H_1^{\ddagger}$ (7.7 kcal mol^{-1}). In the reactions with V^{2+} ion (see Table III) the $\Delta H^{\ddagger}$ for I_3^- also is greater than that for I_2 but the two values differ by only 3.2 kcal mol^{-1}.

The value for $\Delta H_1^{\ddagger}$ is similar to the $\Delta H^{\ddagger}$ values for a number of other redox reactions given in Table III. The value of $\Delta S_1^{\ddagger}$ agrees in general with the entropies of activation observed for a number of substitution reactions of octahedral complexes with neutral ligands.[19] This fact is, however, at most only mild support for a substitution-controlled rate step in the oxidation of $Fe^{II}CyDTA^{2-}$ by iodine.

The kinetic data do not distinguish whether the iodine-containing product of the initial oxidation steps (eq 4 and 5) is the iodine atom or the species I_2^-. The equilibrium between iodine atoms and I_2^- is probably very rapid, by analogy to the iodine–triiodide equilibrium and to the reaction between bromine atoms and bromide ions, the relaxation time of which is about 0.5 μsec in 10^{-3} M Br^-.[21] This being the case, the reaction in eq 6 is the most likely final step in the oxidation sequence, considering the large electrostatic effect evident in the relative sizes of k_1 and k_2. There is kinetic evidence, from the oxidation of iodide ion by Fe^{3+}(aq)[1,22] and from the reverse rate of the oxidation of Fe^{2+}(aq) by bromine, that the species I_2^- exists. The oxidant in the rapid reaction in eq 6, therefore, may be either atomic iodine as shown or I_2^-.

The question of whether the oxidation of $Fe^{II}CyDTA^{2-}$ by iodine proceeds *via* an inner- or outer-sphere mechanism is likewise not conclusively resolved. Direct evidence on this point is very difficult to obtain, since the dissociation reaction in eq 14 has a rate constant of at least 350 sec^{-1}. There is direct evidence for an inner-sphere mechanism in the oxidation of $Co^{II}EDTA$ by bromine,[23,24] by isolation of the $Co^{III}(EDTA)Br^{2-}$ product. In the reactions of $Cr^{II}EDTA^{2-}$ with chlorine and bromine,[25] the sole product detected, within 3 min of the oxidation, is $Cr^{III}(EDTA)H_2O^-$. Other evidence in the same report indicates, however, that the dissociation rate of $Cr^{III}(EDTA)X^{2-}$

$$Fe^{III}(CyDTA)I_2^- \longrightarrow Fe^{III}CyDTA^- + I^- \tag{14}$$

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complexes is remarkably fast, and any mixed complexes which are produced by the oxidation reactions may be entirely dissociated in less than 3 min. Although the reaction studied in the present work is surprisingly fast for the oxidation of a metal center by a molecular oxidizing agent (see Table III), it is not fast enough to be classified as an outer-sphere reaction on the basis of speed.[26] The rate constant for the loss of coordinated water by $Fe^{2+}(aq)$ is 3×10^6 sec^{-1} [27] and the outer-sphere association constant expected for an ion and a neutral molecule is approximately 0.1 M^{-1}. This leads to a maximum predicted substitution-limited rate for the reaction of $Fe^{2+}(aq)$ with I_2 of 3×10^5 M^{-1} sec^{-1}, which is slower than the observed rate for the iodine oxidation reported here. What effect, however, coordination with CyDTA might have upon the water-exchange rate is not known. The nature of the reactants does not preclude an inner-sphere mechanism.[23,24,28] The values of the entropies of activation indicate that displacement of a coordinated group by the oxidant probably occurs.

In contrast to the speed of the reaction between $Fe^{II}CyDTA^{2-}$ and iodine, preliminary results show that the oxidations of $Co^{II}CyDTA^{2-}$ by iodine and bromine are slow. The observed rate constant for the oxidation by total bromine species is 3.6×10^{-2} M^{-1} sec^{-1} at pH 7.0 and $[Br_2]_T = 0.05$ M. The iodine oxidation of $Co^{II}CyDTA^{2-}$ is slower than that of bromine, by about two orders of magnitude. Although it is expected that electron-transfer reactions of cobalt will be slower than analogous reactions of iron, the magnitude of the difference in rate in this instance is perhaps surprising. A study of similar reactions with analogous complexes of iron and other transition elements is in progress.

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Contribution from the Department of Chemistry,
The Catholic University of America, Washington, D. C. 20017

Kinetics of the Acid Cleavage of the Di-μ-hydroxo-tetrakis(ethylenediamine)dicobalt(III) Ion in the Presence of Various Anions

By M. M. deMaine and J. B. Hunt*

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The acid cleavage of the binuclear ion $(en)_2Co(OH)_2Co(en)_2{}^{4+}$ has been followed by spectrophotometry at 525 mμ and by uptake of hydrogen ion in $HClO_4$, HNO_3, HCl, and H_2SO_4 solutions. In $HClO_4$ and HNO_3 solutions the sole reaction product is *cis*-$Co(en)_2(H_2O)_2{}^{3+}$, but *cis*-$Co(en)_2SO_4{}^{2+}$ is also a product in H_2SO_4 solutions and *cis*-$Co(en)_2(H_2O)Cl^{2+}$ and *cis*- and *trans*-$Co(en)_2Cl_2{}^{+}$ are also products in HCl solutions. In $HClO_4$ and HNO_3 solutions the cleavage follows the rate law $-\mathrm{d}\ln[\text{dimer}]/\mathrm{d}t = k_0 + a[H^+]/(1 + b[H^+])$, where $k_0 = (5.0 \pm 0.2) \times 10^{-5}$ sec^{-1} for both $HClO_4$ and HNO_3, $a = (3.8 \pm 0.3) \times 10^{-2}$ M^{-1} sec^{-1} and $b = 1.9 \pm 0.2$ M^{-1} in HNO_3, and $a = (8.4 \pm 0.3) \times 10^{-3}$ M^{-1} sec^{-1} and $b = 0.77 \pm 0.08$ M^{-1} in $HClO_4$, all at 35° and $\mu = 1.0$. In HCl–$HClO_4$ solutions an additional rate term of the form $k_{Cl}[H^+][Cl^-]$ is observed, where $k_{Cl} = (2.8 \pm 0.1) \times 10^{-2}$ M^{-2} sec^{-1} at 25° and $\mu = 1.0$. In 1 M $HClO_4$ or 1 M HCl the absorbance at 635 mμ first increases and then decreases at the beginning of the reaction, which is interpreted as evidence for the involvement of single-bridged intermediates.

Introduction

Rasmussen and Bjerrum[1] reported that the double-bridged binuclear complex ion $(en)_2Co(OH)_2Co(en)_2{}^{4+}$, where en = ethylenediamine, cleaves in nitric acid solution to form the monomeric diaquo species *cis*-$(en)_2Co(OH_2)_2{}^{3+}$. These authors also measured the kinetics of the cleavage of the dimer by nitric acid, and a rate law of the form $-\mathrm{d}[\text{dimer}]/\mathrm{d}t = (k_1 + k_2[H^-])[\text{dimer}]$ describes their data. A reinvestigation of this reaction was prompted by the observation that the cleavage of the analogous chromium(III) complex, $(en)_2Cr(OH)_2Cr(en)_2{}^{4+}$, obeys entirely different rate laws in nitric and perchloric acids.[2] The form of the rate law given above for the cobalt(III) complex is identical with that found for the chromium(III) complex in nitric acid at constant nitrate ion concentration. In the present study the kinetics of the cleavage of the cobalt(III) dimer by perchloric acid have been measured to determine whether the complex behaves differently in the presence of perchlorate and nitrate ions, as does the chromium(III) complex.

Since the completion of most of the work reported here, Hoffman and Taube[3] have reported that the cleavage of the analogous ammonia complex, $(NH_3)_4Co(OH)_2Co(NH_3)_4{}^{4+}$, obeys the rate law $-\mathrm{d}\ln[\text{dimer}]/\mathrm{d}t = a[H^+]/(1 + b[H^+])$ in $HClO_4$–$NaClO_4$ solutions. Taube and Hoffman noted that the very different rate laws reported for the very similar ammonia and ethylenediamine complexes both reduce to an approximately first-order dependence on hydrogen ion concentration at the low acidities used by Rasmussen and Bjerrum. It will be seen that our kinetic data over a wider range of acidities than used by Rasmussen and Bjerrum show the behavior of the ethylenediamine complex to be qualitatively similar to

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