experimentally obtained for the reason mentioned above, but it is assumed to be at least as large as that of praseodymium and probably higher. If one imagines a smooth curve running through lanthanum, gadolinium, and lutetium, the actual values for all of the remaining complexes fall below the "normal" values and lie on a curve with two principal nodes. The effect is perhaps most apparent in the section from samarium to europium to gadolinium. The heat for the europium complex is actually smaller than that for gadolinium even though it is expected to be larger.

One must also consider a different possibility, i.e., a discontinuous change in the structure or ordering of the liquid melt. Admittedly, it is curious that of the 14 metal ions such a change should occur fortuitously at the complex with the half-filled f shell. Nevertheless, support for this explanation is given by trends in the changes of entropies of vaporization. The entropy changes were calculated and compared in two ways, in one case using an arbitrary constant temperature (225°) and in the other an arbitrary constant pressure (0.01 atm). When the entropy changes were plotted against atomic number, the plots had essentially the same shape as for the heats of vaporization, suggesting that a change in ordering in the liquid melt does occur. The question arises as to whether this is only an accidental function of packing or reflects a basic change in the molecular structure, for example, from octahedral to distorted octahedral or trigonal prismatic.

In an effort to see whether any fundamental changes in structure occur at the molecular level, the infrared spectra of all the complexes were examined. The spectra of all of the complexes in both halves of the series were remarkably similar both in band positions and intensities. Therefore if a change does occur, it is not detectable by infrared spectroscopy. The peak maxima (in cm⁻¹) assigned[38] to C∺O and C∺C, respectively, occur at: La, 1592, 1571; Pr, 1592, 1572; Nd, 1592, 1571; Sm, 1593, 1572; Eu, 1594, 1571; Gd, 1593, 1572; Tb, 1596, 1572; Dy, 1597, 1571; Ho, 1598, 1571; Er, 1597, 1571; Tm, 1598, 1571; Yb, 1598, 1571; and Lu, 1599, 1571. Clearly the changes are very small compared with variations in the spectra of other rare earth complexes known to exist in different forms.[39-41] It should be noted that the two explanations offered as possible causes of the discontinuity at gadolinium are not mutually exclusive and may indeed be interrelated.

(38) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 6, 433 (1967).
(39) A. I. Byrke, N. N. Magdesieva, L. I. Martynenko, and V. I. Spitsyn, *Russ. J. Inorg. Chem.*, 12, 348 (1967).
(40) M. F. Richardson, W. F. Wagner, and D. E. Sands, *J. Inorg. Nucl. Chem.*, 30, 1275 (1968).
(41) M. F. Richardson, W. F. Wagner, and D. E. Sands, *Inorg. Chem.*, 7, 2495 (1968).

Polarographic Kinetic Study of the Oxidation of Metal Complexes by Chlorite Ion. I. Oxidation of Ferrous Citrate, Tartrate, and Ethylenediaminetetraacetate and Cuprous Ammine Complexes

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Abstract: The kinetics of the oxidation of ferrous citrate, ferrous tartrate, ferrous EDTA, and cuprous ammine by chlorite ion, ClO_2^-, have been studied in 1 F NH₃–1 F NH₄Cl by the catalytic current technique of dc polarography. The reaction orders appear to be first order in both complex and chlorite. The oxidation rates of the citrate and tartrate complexes are not reproducible and are probably complicated by the presence of polymeric species in slow equilibrium with monomeric forms. The rate constants for the oxidation of the ferrous complexes are between 10³ and 10⁴ l./(mole sec). This value for FeEDTA²⁻ is 3.0 × 10⁴ ± 0.3 × 10⁴ l./(mole sec) as compared with 44 ± 3.7 l./(mole sec) for cuprous ammine. The difference in rate constants is attributed to the slowing effect of ligand rearrangement in the oxidation of Cu(NH₃)₂⁺ to Cu(NH₃)₄²⁺. Several types of mechanisms which are possible for the redox reactions considered are discussed.

U nder usual conditions, the limiting current through a polarographic cell is controlled by the diffusion of electroactive species and does not contain kinetic information; however, there are the so-called kinetic
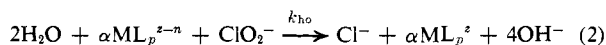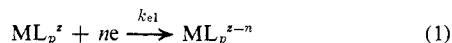
(1) To whom correspondence should be addressed.

and catalytic current cases where the limiting current is controlled by the rate of a chemical reaction. Recently Gierst, *et al.*,[2] found that chlorite ion, ClO_2^-, in 1 M

(2) L. Gierst, L. Vandenberghen, and E. Nicolas, *J. Electroanal. Chem.*, 12, 462 (1966).

NaOH medium containing ferric species supports a catalytic polarographic current. The present investigation was undertaken to make a systematic kinetic study of first series transition metal complexes which are oxidized by ClO_2^- rapidly enough to give a limiting current which is controlled by the rate of this homogeneous oxidation reaction. Since ClO_2^- is a good oxidizing agent even in alkaline media,[3] it is not difficult to find a group of metal complexes which react completely with ClO_2^-. Thus the effect of structural changes in electronic and ligand configuration among the metal complexes selected should be discernible in the kinetic study if they influence the rate of reaction.

The generation of the so-called catalytic current comes about by the following process

$$ML_p^z + ne \xrightarrow{k_{el}} ML_p^{z-n} \quad (1)$$

$$2H_2O + \alpha ML_p^{z-n} + ClO_2^- \xrightarrow{k_{ho}} Cl^- + \alpha ML_p^z + 4OH^- \quad (2)$$

where z is the charge on the complex, p is the ligand number, α is $4/n$, n being the number of electrons involved in the electrochemical reduction (eq 1), and k_{el} and k_{ho} represent the rate constants for the electrochemical and homogeneous reactions. The complex is reduced by the electrode reaction and then regenerated by the homogeneous solution reaction. The couple ML_p^z-ML_p^{z-n} is in effect a catalyst for the reduction of ClO_2^-, and thus the current produced has been referred to as the catalytic current. A necessary condition for a simple theoretical treatment is that ClO_2^- itself is not reduced at the potential where reaction 1 is being followed. This condition is easily achieved since ClO_2^- has a high activation energy (over-potential) for reduction at a mercury electrode; i.e., $E_{1/2}$ is about -1.50 V vs. sce. The regeneration of the species ML_p^z causes an increase in the measured current which is then directly proportional to the rate of the oxidation process if this rate is fast, i.e., $k_{ho} = 10$ to 10^8 l./(mol sec). Thus reactions which in some instances could only be studied by relaxation techniques can be easily studied by this method.

Since ClO_2^- decomposes in acidic solution, a $1\ F$ NH_3–$1\ F$ NH_4Cl buffer electrolyte was used,[4] and the oxidation of Fe(II) complexes of citrate, tartrate, EDTA, and of the Cu(I) complex of NH_3 was studied. In a subsequent paper[5] the ammoniacal ClO_2^- oxidation kinetics of V(II), V(III), Cr(II), and Co(II) with various ligands are reported.[5]

Experimental Section

Current–potential and current–time measurements were made with the Heath controlled-potential polarographic instrument (Model EUW-401) in the three electrode configuration. The operational amplifiers were chopper stabilized. For controlled-potential electrolysis, the booster amplifier in the current measuring circuit

of the instrument was employed at the ouput of the potential control amplifier in order to give sufficient current (55-mA maximum). The readout of instantaneous current for the polarograms was obtained with a Varian F-50 x-y recorder which has a rise time of better than 1 sec for full-scale deflection and which was calibrated with a mercury battery and voltage divider. A Heath recorder was used for measuring the current-time curves; the coulombs passed through the electrolysis cell were calculated by integration (i.e., by weighing the curve). This method was sufficient for an accuracy of 1%. A direct reading Leeds & Northrup pH meter was used to measure pH.

A water-jacketed glass electrolysis cell with a machined Teflon top was used, and the temperature in the cell was controlled to $\pm 0.2°$ in the range 25-60° by a Tampson thermostated circulator (TZ3). The counter electrode was platinum wire; the dropping mercury electrode was made from commercial capillary tubing, and the reference electrode was a Coleman saturated calomel (3-512). The latter electrode's potential was typically about 10 mV off that of a large surface laboratory standard calomel reference; but this fact was not considered a source of significant error since the Coleman calomel was reproducible over long periods of time. For controlled-potential experiments, the counter electrode was placed inside a tube of porous Vycor which had been leached and soaked in supporting electrolyte, $1.0\ F$ NH_4Cl–$1.0\ F$ NH_3. The working electrode was a mercury pool, and stirring was achieved with a Teflon stirring bar and a magnetic stirrer.

A gas train was employed to deaerate the cell with prepurified nitrogen which was passed through a column of analytical reagent grade copper shot heated at 350-400° with heating tape, then through a liquid nitrogen trap and a presaturator gas bubbling tower containing the buffer, and finally through a gas needle valve on the Heath polarographic stand before entering the cell. The train was all glass except for heat-shrinkable Teflon tubing used to make flexible connections. Periodically hydrogen was used to clean up the black CuO formed on the copper.

All reagents were analytical reagent grade. Matheson Coleman and Bell analytical reagent sodium chlorite was recrystallized by dissolving it in methanol, 0.75 M in NaOH. The resulting cloudy solution was filtered and benzene added rapidly to the clear filtrate. The precipitate was collected by suction, washed with mother liquor, and dried under vacuum. The yields were about 50%. The pure white precipitate was stored in a vacuum desiccator in the dark. Stock solutions of ferric complexes were made up determinately with $FeCl_3 \cdot 6H_2O$. This salt was added to supporting electrolyte buffer containing excess ammonium or sodium salts of the citrate, tartrate, and EDTA ligands. A ratio of 10:1 ligand to Fe(III) was found sufficient to completely solubilize the complex, although after many months, precipitation was observed to occur in solutions containing citrate. The copper–ammine complex was also made up determinately from $Cu(NO_3)_2 \cdot 3H_2O$ and the supporting electrolyte buffer. The purity of the buffer was established by running a polarogram and checking for a clean inversion of the current at the electrocapillary maximum of -0.56 V vs. sce.

Results and Discussion

The steady-state limiting current for the catalytic process depicted in eq 1 and 2 is shown to be of the following form by the reaction layer treatment[6]

$$i = nFA\mu\frac{d[ML_p^z]}{dt} = nFA\mu k_{ho}[ClO_2^-][ML_p^z]^\alpha \quad (3)$$

where n is the number of electrons exchanged, F the faraday constant, A the area of the electrode, which for a dropping mercury electrode, dme, depends on mass flow rate (m) and drop time (τ), μ the thickness of reaction layer which is a function of the ClO_2^- concentration and whose exact form is found by solution of the boundary value problem for the system, and α the reaction order with respect to complex which may not have the same value as the α in eq 2. Equation 3 shows that the current is directly proportional to the rate of reaction 2. It is convenient to consider the ratio, i/i_d, a

(3) The formal potential of the half-reaction $4e + ClO_2^- + 4H^+$ = $Cl^- + 2H_2O$ is $E = 1.60 + 0.0592 \log [H^+] + 0.0148 \log [ClO_2^-]/[Cl^-]$ according to W. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952, p 56. At pH 9.2, $[Cl^-] = 1\ M$, $[ClO_2^-]$ = 0.01 M, E is 1.0 V more oxidizing than the standard hydrogen potential.

(4) This is a convenient medium since iron impurities are present in small concentration even in reagent grade alkali hydroxides. In ammoniacal media iron(III) hydroxide precipitates, and thus the ferric species is not available to interfere in measurements where other metal ions are of interest. The high value of ionic strength was chosen to reduce the effect of the diffuse double layer field on the homogeneous reaction.

(5) R. Birke and W. Marzluff, Jr., J. Am. Chem. Soc., in press.

(6) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954, p 107.

dimensionless variable, where i_d is the diffusion current in the absence of ClO_2^- and is constant for a given $[ML_p^2]$ and capillary characteristics m and τ. This ratio is much greater than unity for a fast homogeneous reaction, *i.e.*, if k_{ho} is large.

In order to determine the reaction order and rate constants, the current was measured at various concentrations of complex at a fixed $[ClO_2^-]$ and *vice versa*. These data are given in Tables I, II, and III for

Table I. Limiting Current Data for Ferric Citrate[a]

$[Fe^{3+}]$	$[ClO_2^-]$	i	i_d	i/i_d
2.00×10^{-5}	1.00×10^{-2}	2.72	0.0184	148
2.00×10^{-5}	5.00×10^{-3}	1.94	0.0184	105
2.00×10^{-5}	2.00×10^{-3}	1.07	0.0184	58.2
5.00×10^{-5}	1.00×10^{-2}	6.32	0.0450	140
1.00×10^{-4}	1.00×10^{-2}	12.6	0.0920	137

[a] In this and other tables, concentrations are molar and currents are given in microamperes.

Table II. Limiting Current Data for Ferric Tartrate

$[Fe^{3+}]$	$[ClO_2^-]$	i	i_d	i/i_d
2.00×10^{-5}	1.00×10^{-2}	5.22	0.0362	144
2.00×10^{-5}	5.00×10^{-3}	3.43	0.0362	94.5
2.00×10^{-5}	2.00×10^{-3}	1.84	0.0362	50.8
5.00×10^{-5}	1.00×10^{-2}	12.6	0.0930	136
1.00×10^{-4}	1.00×10^{-2}	24.8	0.186	134

Table III. Limiting Current Data for Ferric EDTA

$[Fe^{3+}]$	$[ClO_2^-]$	i	i_d	i/i_d
2.00×10^{-5}	1.00×10^{-2}	5.20	0.0500	104
2.00×10^{-5}	5.00×10^{-3}	3.40	0.0500	68.0
2.00×10^{-5}	2.00×10^{-3}	2.25	0.0500	45.0
5.00×10^{-5}	1.00×10^{-2}	11.6	0.125	92.8
1.00×10^{-4}	1.00×10^{-2}	21.8	0.250	87.5

ferric citrate, ferric tartrate, and ferric EDTA, respectively. These data were taken at 27.0°, with $m = 1.07$ mg/sec, E *vs.* sce at -0.90 V, and $\tau = 6.09$ sec for ferric EDTA and 6.00 sec for the other two ferric complexes. It is apparent that the regeneration reaction is fast since i/i_d values are quite large.[7]

From a plot of log i *vs.* log [ferrous complex] for the three systems at $[ClO_2^-] = 1.00 \times 10^{-2} M$, slopes are found with values of 0.96, 0.98, and 0.88 for the citrate, tartrate, and EDTA complexes, respectively. Note that under conditions of a limiting current a good assumption here is that the concentration of the reduced species, *i.e.*, ferrous complex, in the reaction layer is equal to the initial concentration of ferric complex if their diffusion coefficients are equal. As can be seen from the slopes, the reaction is close to first order with respect to the complex. A log–log plot of the i/i_d current ratio *vs.* $[ClO_2^-]$ has slopes of 0.55, 0.64, and 0.45 for the citrate, tartrate, and EDTA complexes, respectively. This value should be one-half for a reaction mechanism which is first order in chlorite since the theory gives μ as proportional to $[ClO_2^-]^{-1/2}$ for a

(7) Values of i_d were found by measuring the diffusion current at 1.00 $\times$ 10^{-3} F for the $[ML_p^s]$ and scaling this number for the appropriate concentration, since by definition i_d is directly proportional to $[ML_p^s]$. Residual current was appropriately subtracted out of all currents measured.
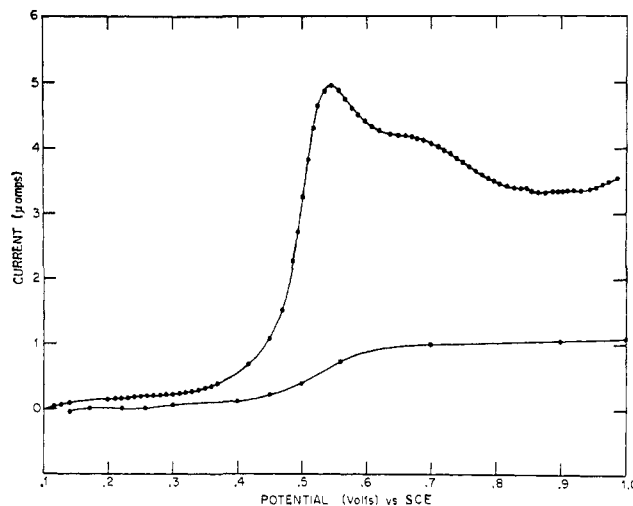

Figure 1. Current–potential curve for ferric citrate with and without chlorite. Lower curve is for 1.00 $\times$ 10^{-3} F ferric citrate in 1 F NH_3–1 F NH_4Cl buffer with 0.005% gelatin in the absence of ClO_2^-. Upper curve is for 2.00 $\times$ 10^{-5} F ferric citrate, 1.00 $\times$ 10^{-2} M chlorite, and 0.005% gelatin in the same buffer. The current is the maximum current in the drop life and the drop oscillations have not been reproduced.

pseudo-first-order treatment.[8] Although there is some scatter to the few points that were used to make the plots, especially for the citrate complexes, a first-order reaction with respect to ClO_2^- is indicated by all the slopes. Thus these plots indicate that the reaction is first order in both the complex and ClO_2^- which is reasonable from a mechanistic point of view.

The morphology of the current–potential curves, however, adds an element of complication to this somewhat simple mechanistic picture. Figure 1 shows the $i–E$ curve of the ferric citrate complex with and without chlorite. The current exhibited a maximum around $E = -0.56$ V *vs.* sce when chlorite was added. At various potentials all along the curve, the current was found to be independent of the mercury column height as is expected when the current is controlled by a catalytic process.[9] Furthermore, this maximum did not have the properties that are commonly found for other maximums which are caused by hydrodynamic effects. Ferric tartrate exhibited this same maximum; however, ferric EDTA did not. This maximum could not be reproduced when fresh solutions of the complexes and chlorite were made up several months later. The polarograms of the complexes without chlorite always showed the same $i–E$ morphology. The values of diffusion current, however, although constant for one stock solution changed from one batch to the next for ferric citrate and tartrate. This change was thought to reflect a change in the values of the diffusion coefficient.

Calculating the diffusion coefficient by means of the Ilkovic equation, the ferric citrate solution which showed the maximum effect had $D = 9 \times 10^{-7}$ cm²/sec. Ferric EDTA and ferric tartrate had diffusion coefficients of 6×10^{-6} and 3×10^{-6} cm²/sec, respectively. These solutions were made up with a citrate to Fe(III) ratio of 10:1 in the 1 F buffer. In a solution with a 1:1 ratio, $D = 5 \times 10^{-7}$ cm²/sec was found for

(8) J. Heyrovsky and J. Kuta, "Principles of Polarography," Academic Press, New York, N. Y., 1966, p 382.

(9) J. Heyrovsky and J. Kuta, ref 8, p 340.

ferric citrate, but no current maximum was observed with chlorite. These low values of diffusion coefficient for ferric citrate, especially when below 10^{-6} cm²/sec, indicate a very bulky species and are good evidence of colloidal phenomena. Recently Spiro, et al.,[10] have given evidence that equal molar concentrations of Fe(III) and citrate in basic solution yield a polymeric species. It seems reasonable to interpret the non-reproducible values of diffusion currents in terms of a slow equilibrium between polymeric and monomeric forms of the complex as suggested by these authors. Increase of citrate ion was shown to have a depolymerization effect. Although such equilibria must certainly exist for both ferric citrate and ferric tartrate in basic media, it is difficult to give a clear explanation of the maximum phenomena described here in terms of such solution reactions.

The pH dependency of the limiting current was measured in a pH range of 8.3–10.2 for 2×10^{-5} F ferric citrate in the presence of 5×10^{-3} M chlorite. Between pH 9.2 and 10.2 the current increases as a 1.5 power of the hydrogen ion concentration. Ferric tartrate and ferric EDTA showed only a slight uneven decrease over the pH range 8.3–10.2. In these cases it was concluded that hydrogen ion did not enter as a primary effect in the rate law.

The irreproducibility of the current maximum in the presence of chlorite for ferric citrate and ferric tartrate and the irreproducibility of diffusion currents for a given concentration of these complexes is evidence of a complicated solution chemistry for these complexes in basic media. However, this complication does not affect the basic conclusion that the Fe(II) species in citrate and tartrate media, as well as in EDTA medium where no irreproducibility was found, is rapidly oxidized by chlorite ion in a reaction which is first order with respect to both the complex and chlorite.

The catalytic limiting current mechanism is nicely illustrated for the case of copper ammine. In the absence of chlorite the i-E curve shows two waves for Cu(II) to Cu(I) reduction ($E_{1/2} = -0.19$ V vs. sce) and for Cu(I) to Cu(0) reduction ($E_{1/2} = -0.46$ V vs. sce), the waves being of equal height. Addition of ClO_2^- causes an increase of the first wave without affecting the second wave. This is to be expected since the Cu(0) formed upon reduction at the second wave diffuses in the Hg drop and cannot be reoxidized. Data for the reaction order calculations are given in Table IV. These data

Table IV. Limiting Current Data for Cupric Ammine

$[Cu^{2+}]$	$[ClO_2^-]$	i	i_d	i/i_d
1.00×10^{-4}	1.00×10^{-2}	1.50	0.372	4.05
1.00×10^{-4}	5.00×10^{-3}	1.00	0.372	2.70
1.00×10^{-4}	2.00×10^{-3}	0.66	0.372	1.77
2.00×10^{-4}	1.00×10^{-2}	2.65	0.744	3.56
5.00×10^{-4}	1.00×10^{-2}	6.64	1.86	3.57

were taken at 27.0°, with $m = 1.07$ mg/sec, E vs. sce at -0.35 V, and $\tau = 6.35$ sec. From log–log plots reaction orders of 0.93 with respect to cuprous ammine and of 0.46 with respect to chlorite were obtained,

(10) T. G. Spiro, L. Pape, and P. Saltman, J. Am. Chem. Soc., 89, 5555 (1967); T. G. Spiro, G. Bates, and P. Saltman, ibid., 89, 5559 (1967).

again indicating a first-order reaction with respect to both the complex and ClO_2^-.

An experiment was also performed to determine the stoichiometry of the reaction, i.e., the value of α in reaction 2. A polarogram of a known volume of solution 1.0×10^{-3} M in copper ammine was taken, and the solution reduced to the Cu(I) state at -0.26 V vs. sce by the controlled-potential technique. With nitrogen bubbling through the solution, a known amount of chlorite was rapidly pipetted into solution and the polarogram rerun. The ratio of the number of moles of Cu(II) produced to the number of moles of chlorite added was calculated to be 3.9. It was concluded that within the accuracy of the experiment that 4 moles of Cu(I) reacts with 1 mole of ClO_2^-, indicating that ClO_2^- is completely reduced to Cl^- in the reaction.

The rate constants for the homogeneous oxidation reactions were calculated on the basis of a reaction which is first order in both ClO_2 and complex. The calculations were made using the instantaneous current expression for a second-order reaction, first rigorously derived by Koutecky[11] and expressed in a closed form by Birke and Marzluff[12] in the following expression

$$\frac{i}{i_d} = 1.160\sqrt{[ClO_2^-]k_{ho}\tau\alpha}\left(\frac{1}{2} + \frac{1}{2}\sqrt{1 - 1.5\frac{i}{i_d'}}\right) \quad (4)$$

where i_d' is a hypothetical diffusion current given by the Ilkovic equation when the concentration is that of the $[ClO_2^-]$ used, $D_{ClO_2^-} = 3.5 \times 10^{-3}$ cm²/sec, and the capillary characteristics are those found at the potential where i is measured; all other symbols have been defined previously. In calculating k_{ho} by using eq 4, α is taken to be 4 in all cases. The rate constants obtained are: Fe(II) tartrate, $6.2 \times 10^4 \pm 0.2 \times 10^4$; Fe(II) citrate, $6.3 \times 10^4 \pm 0.5 \times 10^4$; Fe(II) EDTA, $3.0 \times 10^4 \pm 0.3 \times 10^4$; and Cu(I) ammine, 44 ± 3.7. This value is the average of the five measurements given in Tables I–IV. The error estimation is the standard deviation. It is seen that the precision is much lower for the smaller rate constant found for copper(I) ammine. The values of k_{ho} for the tartrate and citrate complexes are those found when the i-E curve had a maximum. When the maximum did not occur in the latter measurements, the rates were a factor of 10 smaller. Thus in all cases the oxidation of ferrous complexes was rapid, and the values of the rate constants were within about an order of magnitude of each other.

Since the exact nature of the reacting species is in doubt for the citrate and tartrate complexes, it is worthwhile to focus attention on the oxidation of the ferrous EDTA and cuprous ammine complex where the species participating in the redox chemistry are well known. Activation energy E_a and entropy $\Delta S^{\ddagger}$ were found for these cases. The activation energies were calculated with the Arrhenius plot shown in Figures 2 and 3.[13] E_a is 13 kcal/mole for both reactions; however, the apparent entropy of activation, $\Delta S^{\ddagger}$, calculated using the approximate transition state theory equation

$$k = 10^{13} \exp(\Delta S^{\ddagger}/R) \exp\{-[(E_a - RT)/RT]\} \quad (5)$$

(11) J. Koutecky, Collection Czech. Chem. Commun., 22, 160 (1957).
(12) R. Birke and W. Marzluff, Jr., J. Electroanal. Chem., 17, 1 (1968).
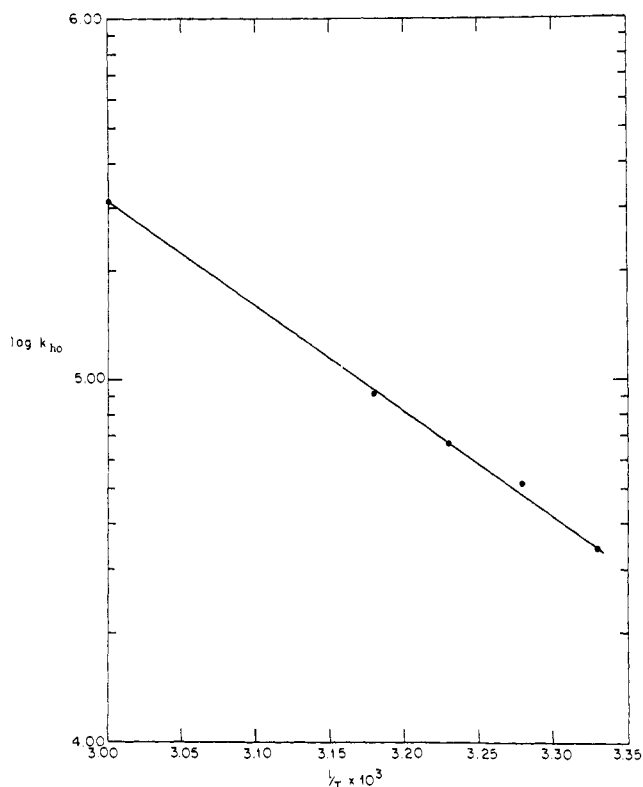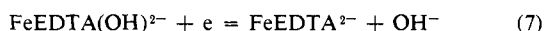(13) In making this calculation, i_d and i_d' as well as i were obtained as a function of temperature.

Figure 2. Arrhenius activation energy plot for the oxidation of ferrous EDTA by chlorite.

Figure 3. Arrhenius activation energy plot for the oxidation of cuprous ammine by chlorite.

is $+2.5 \pm 0.2$ eu for the ferrous EDTA oxidation and -11.2 ± 0.2 eu for the cuprous oxidation. The large negative entropy is indicative of a rearrangement process in going from reactants to activated state. Since the ions in this reaction are of opposite sign, one would have expected a positive entropy contribution from coulombic interaction, not a negative one. On the other hand, a negative value of $\Delta S^{\ddagger}$ would be expected for the ferrous EDTA oxidation, since both ions are of the same sign. A possible explanation for the positive $\Delta S^{\ddagger}$ for the ferrous EDTA oxidation is that a positive ion is participating in the transition state complex lowering coulombic interaction.

It has been known for a long time[14] that there is a change in the number of ammine ligands on going from cuprous to cupric ammine. This change in ligand structure is no doubt the reason for the slow rate as evidenced by the negative value of $\Delta S^{\ddagger}$. The polarographic reduction process[15] was found to be

$$Cu(NH_3)_4{}^{2+} + e = Cu(NH_3)_2{}^+ + 2NH_3 \qquad (6)$$

illustrating a change in ligand number from four to two. Kolthoff and Auerbach[16] found at pH >8 that polarographic reduction process for the ferric EDTA was

$$FeEDTA(OH)^{2-} + e = FeEDTA^{2-} + OH^- \qquad (7)$$

A very recent electrochemical study[17] confirmed that in fact there is a distribution of dimeric and monomeric

(14) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Haase and Son, Copenhagen, 1941, p 13.
(15) S. L. Gupte and M. K. Challergee, *Indian J. Chem.*, 4, 22 (1966); M. von Stackelberg and H. von Freyhold, *Z. Electrochem.*, 46, 120 (1940).
(16) I. M. Kolthoff and C. Auerbach, *J. Am. Chem. Soc.*, 74, 1452 (1952).
(17) H. J. Schugar, A. T. Hubbard, F. C. Anson, and H. B. Gray, *ibid.*, 91, 71 (1969).
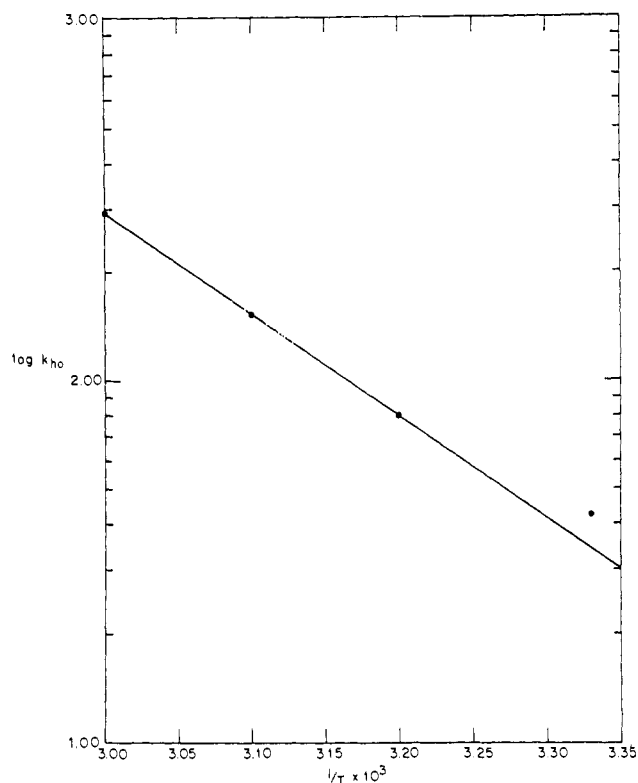
forms of Fe(III) EDTA species in solution at pH 9 as reported by Gustafson and Martell.[18] Kolthoff and Auerbach[16] could not see these dimer species in their polarographic experiment which was executed at a slow sweep rate, since there is rapid equilibrium between monomer and dimer. Schugar, *et al.*,[17] found that with a fast voltage sweep, the i-E curve shows two cathodic waves and only one anodic wave. Thus, upon reduction of dimeric and monomeric forms, only the monomer, $Fe^{II}EDTA^{2-}$, is formed. The latter authors suggest that the major form of the dimer species is the oxo-bridged Fe–O–Fe with two pentadentate EDTA groups and a free acetate group on each EDTA. A proposed mechanism for the break-up of the oxo-bridged dimer is through the unstable hydroxo-bridged species formed as an intermediate on attack of a H_2O at the oxo bridge. We infer that the reduction product in the electrochemical experiment is $FeEDTA(OH_2)^{2-}$ where on acetate group of the ligand is free and replaced by H_2O. Thus, eq 7 could be represented as

$$FeEDTA(OH)^{2-} + e + H^+ = FeEDTA(OH_2)^{2-} \qquad (7a)$$
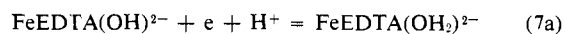
and the only structural change in oxidation, either electrochemically or by ClO_2^-, would be a fast dissociation of a hydrogen ion.
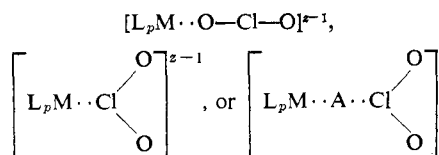
The oxidation of $Cu(NH_3)_2{}^+$ by ClO_2^- involves the half-reaction 6 preceeding from right to left in which there is considerable ligand rearrangement which most certainly has a slowing effect on the rate. On the other hand, it has been inferred that half-reaction (7a) is involved in the oxidation of ferrous EDTA by ClO_2^-, and in this case there would be very little ligand rearrangement going on which could slow down the

(18) R. L. Gustafson and A. B. Martell, *J. Phys. Chem.*, 67, 576 (1963).

reaction rate. The fact that a pH effect was not observed in the rate measurements means that if eq 7a is the correct half-reaction, the hydrolytic reaction must occur after the rate-determining step. From the kinetic data, activation parameters, and the coordination chemistry of the complexes, it is concluded that the change in ligand structure upon oxidation is a major factor affecting the rate of oxidation.

It is interesting to compare the chlorite oxidation of cuprous ammine and ferrous EDTA with their electron-transfer reactions. Adamson and Vorres[19] found the rate of electron transfer between ferrous and ferric EDTA complexes in acid solution to be too fast to measure by conventional techniques. McConnell and Weaver[20] found by an nmr technique that the second-order rate constant for electron transfer between Cu(I) and Cu(II) in 12 F HCl is 5×10^7 l./(mole sec). At such a high chloride concentration, it is likely that both Cu(I) and Cu(II) are in an environment of four chlorides leading to a low Franck–Condon barrier and thus a fast reaction. It would be worthwhile to find a system of Cu(I) and Cu(II) complexes which had similar geometry in both states and existed in basic solution in order to compare its rate of oxidation by chlorite with the slow rate of oxidation of the ammine complexes.

Finally, we speculate on the reaction mechanism and the nature of the activated complex. The reactions considered here are examples of a more general type of reaction where an oxyhalogen anion oxidizes a metal ion or metal complex and is itself reduced to its lowest oxidation state. Thus the over-all process involves rupture of all the oxygen bonds of the oxyanion. The rate-determining step could be electron transfer from the central metal ion to an orbital on the halogen. On the other hand, it is possible that atom transfer takes place either with an oxygen atom in a two-equivalent change or with an O^- ion in a one-equivalent change. These mechanisms, which would cover the reactions considered here, have been suggested by Sykes[21] for the oxidation of Ti(III) by perchlorate, ClO_4^-, in acid medium. Possibilities which could be postulated for the geometry of the activated complex based on a bimolecular mechanism would be

$$[L_pM \cdot \cdot O\text{—}Cl\text{—}O]^{z-1},$$

$$\left[L_pM \cdot \cdot Cl \begin{matrix} O \\ \diagup \\ \diagdown \\ O \end{matrix} \right]^{z-1}, \text{ or } \left[L_pM \cdot \cdot A \cdot \cdot Cl \begin{matrix} O \\ \diagup \\ \diagdown \\ O \end{matrix} \right]$$

(19) A. W. Adamson and K. S. Vorres, *J. Inorg. Nucl. Chem.*, 3, 206 (1956).

(20) H. M. McConnell and A. E. Weaver, *J. Chem. Phys.*, 25, 30 (1956).

(21) A. G. Sykes, "Kinetics of Inorganic Reactions," Pergamon Press, Oxford, 1966, p 208.

where A is a uncharged cation which might be ion paired to chlorite. Presumably if these former two complexes were of the inner-sphere type, the fully coordinated metal complex would have to lose an L ligand before or during formation of the complex. The oxygen-bridged complex could participate in a redox mechanism with or without atom transfer. It is evident that a variety of geometries is possible for the activated complex of these redox processes just as in electron-transfer reactions. Once the rate-determining step takes place, any oxyanion intermediate formed is considered to be extremely short-lived.

A very important consideration is the influence of chlorite on the polarographic reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$. This wave is well defined in the 1 F NH_3–1 F NH_4Cl medium with an $E_{1/2}$ of about -0.10 V $vs.$ sce. The wave height is not affected by chlorite, indicating that the $Fe(CN)_6^{4-}$ oxidation is slow, *i.e.*, $k_{ho} < 1$ l./(mole sec). Since there are many examples of fast outer-sphere electron-transfer reactions involving the $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$ couple, it is concluded that the distinguishing aspect of the reaction under consideration is the inertness to substitution of the $Fe(CN)_6^{4-}$. In the $Fe^{II}EDTA(OH_2)^{2-}$ species the substitution rate for H_2O is fast and the ammine groups of cuprous ammine are also labile, so there is no hindrance to a ClO_2^- substitution before or during the transition state in the oxidation of these complexes. This indirect evidence indicates that these reactions involve an inner-sphere mechanism.

A detailed mechanism involving the nature of elementary steps and the geometry of the activated complex has not been established, but the results reported here and those to be published[5] strongly suggest that the rate of oxidation of the metal complexes is governed by the structural properties of the complex. The effects of change in ionic strength and the nature of the medium have not been investigated, but such study would give further information as to the nature of the mechanism. Especially interesting would be the study of these reactions in NH_4NO_3–NH_3 media which would allow investigation of the effect of chloride ion on the rate. It should be possible with carefully selected experiments to answer some of the more detailed questions concerning the mechanism of the oxidation of metal complexes by ClO_2^-.