Contribution from the Department of Chemistry,
Ahmadu Bello University, Zaria, Nigeria

Kinetics and Mechanism of the Oxidation of $Ti(H_2O)_6^{3+}$ and $TiEDTA^-$ by Aqueous Solutions of Iodine

ADE ADEGITE* and J. FEMI IYUN

Received February 5, 1979

The rate equation for the oxidation of $Ti(H_2O)_6^{3+}$ by iodine was found to be $-d[I_2]/dt = (k_2K_a/([H^+] + K_a))[Ti(III)][I_2] + (k_2K_a/([H^+] + K_a))[Ti(III)][I_3^-]$. For the conditions $[H^+] = 0.0036–0.20$ M, $I = 1.0$ M (LiCl), and $t = 25$ °C, $k_1 = 5.3 \times 10^2\ M^{-1}\ s^{-1}$, $k_2 = 6.9\ M^{-1}\ s^{-1}$ and $K_a = 3.2 \times 10^{-3}$ M. For the reaction of $TiEDTA^-$ with I_2, the rate law in the range pH 0.5–8.0, and $[I^-] = 0.004$ M, is $-d[I_2]_{total}/dt = ((k_1^{EDTA} + k^{EDTA}{}_{OH}K_a^{EDTA}[H^+]^{-1})/(1 + k_a^{EDTA}[H^+]^{-1}))\cdot[Ti^{III}EDTA^-][I_2]_{total}$, with $k_1^{EDTA} = 2.5 \times 10^3\ M^{-1}\ s^{-1}$, $k^{EDTA}{}_{OH} = 1.3 \times 10^5\ M^{-1}\ s^{-1}$, and $k_a^{EDTA} = 1.1 \times 10^{-7}$ M at $I = 1.0$ M and $t = 25$ °C. In the region pH <2.5 where rate is insensitive to pH changes, $k_1^{EDTA}(I_2)$ and $k_1^{EDTA}(I_3^-)$ were obtained as $8.5 \times 10^3\ M^{-1}\ s^{-1}$ and $2.6 \times 10^2\ M^{-1}\ s^{-1}$, respectively, at $I = 1.0$ M and $t = 25$ °C. The reactions are supposed to proceed by univalent electron-transfer steps involving $I_2^-\cdot$ as the transient intermediate species. The most likely mechanism consistent with the kinetic data is an outer-sphere electron-transfer mechanism.

Introduction

Kinetic investigations of redox reactions of $Ti(H_2O)_6^{3+}$ as reductant have aroused considerable interest in the last few years. Rate studies of reactions of this ion with ammine complexes of Co(III)[1-9] and Ru(III),[10-12] aquometal ions,[13,14] and aqueous solutions of chlorine[15] have been reported. About 25 years ago, Winstein and Johnson published their findings on the rate of oxidation of this ion by aqueous iodine.[16] Their results were consistent with the rate equation (1). Their

$$\frac{-d[I_2]}{dt} = -\frac{1}{2}\frac{d[Ti(III)]}{dt} = \frac{k_1[Ti^{3+}][I_2]}{[H^+]} + \frac{k_2[Ti^{3+}][I_3^-]}{[H^+]} + \frac{k_1[Ti(III)]}{[H^+]} \qquad (1)$$

investigations were confined to fairly high concentrations of acid, $[H^+] \geq 0.1$ M, and iodide, and the Ti(III) concentrations were varied only fourfold. Apart from their inability to explain the third term in the rate equation (i.e., the iodine-independent term), recent reports on aquotitanium(III) reactions show that a more complex acid dependence than they observed is a common feature of Ti^{3+}(aq) reactions, and the form of dependence they reported is only valid at high acid concentrations. In addition to our continuing interest in halogen redox reaction mechanism, we have reinvestigated the kinetics of the oxidation of aquotitanium(III) ion by iodine and triiodide over a wider range of reactant concentrations. We also extended the studies to include the kinetics of the reduction of iodine and triiodide by $TiEDTA^-$ over a fairly wide pH range.

Experimental Section

Reactant solutions, i.e., Ti^{3+}(aq), $TiEDTA^-$, and I_2 were prepared and analyzed as previously reported.[12,17,18] Lithium chloride, sodium acetate, and hydrochloric acid were all BDH (A.R. grade) and were used without further purification. CF_3SO_3Li was prepared from the reaction of Li_2CO_3 with trifluoromethanesulfonic acid and analyzed as previously described.[12]

Our recent observations[12] on aquotitanium(III) solutions suggest that the tendency of such solutions to form oxo-bridged polynuclear species, particularly at low acid concentration, is inhibited by chloride ions. Therefore, the kinetic studies were conducted in a chloride medium, except during the investigation of the effect of chloride ion when trifluoromethanesulfonate ions replaced the chloride ions. Rate measurements were made on a Unicam SP1750 spectrophotometer for the slow reactions and the Durrum-Gibson stopped-flow spectrophotometer for the faster reactions. The temperature of the reaction was maintained at 25.0 ± 0.1 °C by circulating thermostated water from a bath through the cell compartments of the spectrophotometers. The progress of the reaction was monitored by following absorbance changes due to iodine at λ 468 nm, the isosbestic point for I_2 and I_3^-. All rate measurements were made under pseudo-first-order conditions with titanium(III) concentration at least in 20-fold excess over that of total iodine. Ionic strength was kept constant at 1.0 M with LiCl or CF_3SO_3Li.

Results

Oxidation of Aquotitanium(III) Ion (Ti^{3+}(aq)) by Iodine. Under pseudo-first-order conditions (Ti(III) in excess), plots of log $(A_t - A_\infty)$ vs. time (A_t and A_∞ being the absorbances of iodine at time t and the end of reaction, respectively) were linear to more than 90% reaction. From the slopes of linear plots, the pseudo-first-order rate constant k_{obsd} was determined for different initial concentrations of Ti(III). For $[I_2]_T$ (total iodine) $= (1.0–2.5) \times 10^{-4}$ M, $[I^-] = 4.0 \times 10^{-3}$ M, $[H^+] = 0.10$ M, and $[Ti(III)] = (0.2–6.0) \times 10^{-3}$ M a plot of log k_{obsd} vs. log $[Ti(III)]_0$ was linear and has a slope of 1.01 ± 0.04. The linearity of the pseudo-first-order plot and the slope of unity obtained in the latter plot confirm that the reaction, under the above specified conditions, is strictly first order in Ti(III) and first order in iodine. Thus, at constant iodide and hydrogen ion concentrations, the rate equation for the reaction is

$$-\frac{1}{2}\frac{d[Ti(III)]}{dt} = -\frac{d[I_2]}{dt} = k_o[Ti(III)][I_2]_T \qquad (2)$$

$$k_o = k_{obsd}/[Ti(III)]$$

In a solution containing I_2 and I^-, a very fast[19] equilibrium (eq 3) is set up. Previous rate studies[18] of iodine reactions have

$$I_2 + I^- \underset{}{\overset{K_{I_3^-}}{\rightleftharpoons}} I_3^- \qquad K_{I_3^-} = 748\ M^{-1}\ {}^{22} \qquad (3)$$

shown that I_2 and I_3^- are reduced at different rates by the same reductant. Thus, k_o was determined at different iodide concentrations at a constant $[H^+]$ and for $[I^-]$ varying from 0.004 to 0.10 M. In this range of iodide concentrations, k_o decreases as $[I^-]$ increases, which implies that I_3^- reacts more slowly than I_2. In order to resolve k_o into the rate constants for iodine and triiodide, we assume eq 4 and 5 to be the activation paths for

$$Ti(III) + I_2 \xrightarrow{k_{I_2}} (\text{activated complex})^* \qquad (4)$$

$$Ti(III) + I_3^- \xrightarrow{k_{I_3^-}} (\text{activated complex})^* \qquad (5)$$

the reaction of I_2 and I_3^- with Ti(III). From eq 3–5, eq 6 is

$$k_o(1 + K_{I_3^-}[I^-]) = k_{I_2} + k_{I_3^-}K_{I_3^-}[I^-] \qquad (6)$$

derived. A plot of the left-hand side of eq 6 vs. $[I^-]$ should be linear with the intercept and slope being k_{I_2} and $k_{I_3^-}K_{I_3^-}$, respectively. Such a plot, which is typical for all the acid concentrations investigated in this work is shown in Figure 1 for three different acid concentrations. k_{I_2} and $k_{I_3^-}$ were determined from least mean squares computation of the intercept and the slope of such a plot, respectively, for 16 different acid

0020-1669/79/1318-3602$01.00/0

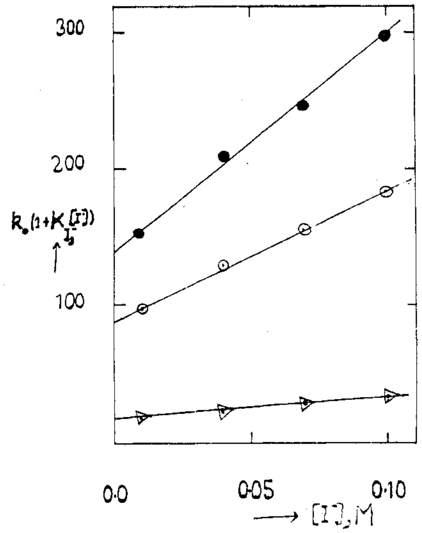

Figure 1. Effect of iodide at different acid concentrations on the $Ti^{3+}(aq) + I_2$ reaction, shown by a plot of $k_o(1 + K_{I_3^-}[I^-])$ vs. $[H^+]$: ●, $[H^+]$ = 0.009 M; ○, $[H^+]$ = 0.0144 M; △, $[H^+]$ = 0.10 M.

Table I. Rate Constants for Ti(III) + I_2, I_3^- reactions[a]

$10^3[H^+]$, M	$10^{-2}k_{I_2}$, $M^{-1}\ s^{-1}$	k_{I_3}, $M^{-1}\ s^{-1}$
3.6	1.81	6.8
5.4	1.53	6.7
7.2	1.42	5.0
9.0	1.39	2.2
10.8	1.12	2.4
14.4	0.89	1.3
15.0	0.85	1.2
15.8	0.57	1.4
26.4	0.52	0.70
30.0	0.34	0.67
50.0	0.32	0.46
60.0	0.29	0.39
80.0	0.21	0.23
100.0	0.18	0.21
150.0	0.09	0.14
200.0	0.84	0.12

[a] k_{I_2} and $k_{I_3^-}$ are linear least mean squares analyses of plots of $k_o(1 + k_{I_3^-}[I^-])$ vs. $[I^-]$. I = 1.0 M (LiCl), t = 25 °C, [Ti(III)] = (2.0–200.0) × 10^{-3} M, $[I_2]_T$ = (1.0–4.0) × 10^{-4} M, $[I^-]$ = 0.004–0.16 M.

concentrations in the range $[H^+]$ = 0.0036–0.2 M. The results are presented in Table I. Plots of $k_{I_2}^{-1}$ or $k_{I_3^-}^{-1}$ vs. $[H^+]$ are linear (Figure 2) with finite intercepts, and therefore, the rate constants vary with $[H^+]$ according to eq 7. Values of a and b obtained from least mean squares analysis of the data are

$$k_{I_2} = \frac{1}{a_1 + b_1[H^+]} \tag{7a}$$

$$k_{I_3^-} = \frac{1}{a_2 + b_2[H^+]} \tag{7b}$$

$$a_1 = (1.90 \pm 0.09) \times 10^{-3}\ M\ s$$

$$b_1 = (6.24 \pm 0.01) \times 10^{-1}\ s$$

$$a_2 = (1.46 \pm 0.12) \times 10^{-1}\ M\ s$$

$$b_2 = 43.8 \pm 4.8\ s$$

From eq 2 to 7, the rate equation for the reaction under our experimental conditions is

$$-\frac{d[I_2]_T}{dt} = -\frac{1}{2}\frac{d[Ti(III)]}{dt} = \frac{[Ti(III)][I_2]}{a_1 + b_1[H^+]} + \frac{[Ti(III)][I_3^-]}{a_2 + b_2[H^+])} \tag{8}$$

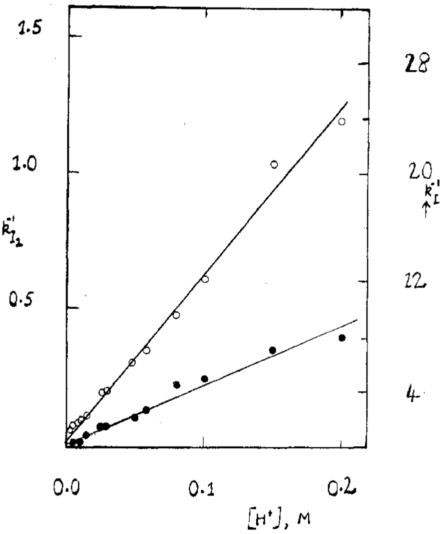

Figure 2. Effect of acid on the rate constants for the $Ti^{3+}(aq) + I_2$, I_3^- reactions, shown by a plot of $k_{I_2}^{-1}$ or $k_{I_3^-}^{-1}$ vs. $[H^+]$: ○, $k_{I_2}^{-1}$; ●, $k_{I_3^-}^{-1}$.

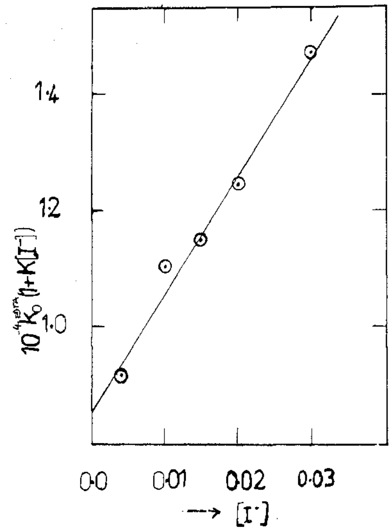

Figure 3. Effect of iodide on the rate constant for the $TiEDTA^-$ + I_2 reaction, shown by a plot of $k_o^{EDTA}(1 + k_{I_3^-}[I])$ vs. $[I^-]$ (I = 1.0 M, t = 25 °C).

At high acid eq 8 is essentially the same as eq 1 without the iodine-independent term.

At $[H^+]$ = 0.10 M and constant $[I^-]$, k_o was determined for $[Cl^-]$ = 0.10, 0.4, 0.7, and 1.0 M and I = 1.0 M (LiCl + CF_3SO_3Li). The values of k_o obtained were within 5% of each other and showed no systematic variation with $[Cl^-]$. Thus, as in many other Ti(III) reactions, a chloride medium is "innocent" for the rate studies conducted in this work.

Oxidation of $TiEDTA^-$. This reaction was also found to be first order in [Ti(III)] and also first order in $[I_2]_T$. As in the reactions of the aquo ion, the second-order rate constant k_o^{EDTA} decreases as $[I^-]$ increases at a constant pH. From the plots of $k_o^{EDTA}(1 + K_{I_3^-}[I^-])$ vs. $[I^-]$, at pH 1.0 (Figure 3), the following values of $k^{EDTA}{}_{I_2}$ and $k^{EDTA}{}_{I_3^-}$ were obtained:

$$k^{EDTA}{}_{I_2} = (8.52 \pm 0.28) \times 10^3\ M^{-1}\ s^{-1}$$

$$k^{EDTA}{}_{I_3^-} = (2.63 \pm 0.21) \times 10^2\ M^{-1}\ s^{-1}$$

k_o^{EDTA} was determined as a function of pH in the range pH 0.5–8.0 and at $[I^-]$ = 4.0 × 10^{-3} M. It was found, as shown in Table II, that the dependence of the rate constant on pH is biphasic. Below pH 2.5, the rate is independent of pH, but above this pH, k_o^{EDTA} increases with pH. A similar behavior

Table II. Rate Constants for the $TiEDTA^- + I_2$ Reaction as a Function of pH[a]

pH	$10^{-3}k^{EDTA}$, $M^{-1}\ s^{-1}$	pH	$10^{-3}k^{EDTA}$, $M^{-1}\ s^{-1}$
0.15	2.3	4.85	4.5
0.75	2.3	4.95	4.9
1.70	2.9	5.13	5.3
2.25	2.5	5.46	6.9
2.80	3.0	5.56	7.3
3.43	3.2	5.83	12
3.95	3.6	6.15	61
4.30	3.9	6.80	51
4.40	4.1	7.40	96
4.58	4.13	7.45	130

[a] $[TiEDTA^-] = (2.0\text{-}8.0) \times 10^{-3}$ M; $[I_2]_T = (1.0\text{-}2.0) \times 10^{-4}$ M; $I = 1.0$ M (LiCl + CH_3COONa); $t = 25$ °C.

has also been observed for the oxidation of $TiEDTA^-$ by some cobalt(III)–ammine complexes.[17] The results were fitted into the expression given by eq 9 by using nonlinear least mean

$$k_o^{EDTA} = \frac{p + q[H^+]^{-1}}{1 + r[H^+]^{-1}} \qquad (9)$$

squares[20] with $(1/k_o^{EDTA})^2$ weighting and p fixed[21] at 2500, the mean value of k_o^{EDTA} at pH 2.5. The computed estimates of the parameters obtained are

$$q = 1.43 \times 10^{-2}\ s^{-1} \qquad r = 1.070 \times 10^{-7}\ M$$

By substituting the values of these parameters in eq 9, we calculated k_o^{EDTA} for different pH values, and the results plotted as k_o^{EDTA} vs. pH are presented in Figure 4. For comparison purposes, the experimental data points are also shown in the plot.

At pH 0.75 and $I = 1.0$ M, k_o^{EDTA} was determined for acetate concentrations, 0.05, 0.10, 0.15, and 0.2 M, and it was found that k_o^{EDTA} is independent of acetate.

Discussion

In the reaction of the aquo ion, our results differ from those of Winstein and Johnson in three respects, viz., (i) our rate equation (eq 8) contains no iodine-independent term, (ii) the acid dependence equation is more complex than theirs, but approximates to theirs at high acid, and (iii) the rate constants k_{I_2} and $k_{I_3^-}$ obtained in this work are higher than values that could be obtained from their data.[23]

In order to ascertain that these differences are not due to impurities, we measured, for comparison purposes, the rate constant for the $Ti^{3+} + Ru(NH_3)_6^{3+}$ reaction. The results were $[Ru(NH_3)_6^{3+}] = 1.34 \times 10^{-3}$ M, $[Ti^{3+}] = 1.25 \times 10^{-5}$ M, $[H^+] = 0.2$ M, $t = 25$ °C, $I = 1.0$ M, and $k = 0.90\ M^{-1}\ s^{-1}$. This rate constant is in excellent agreement with 0.855 $M^{-1}\ s^{-1}$ at $[H^+] = 0.206$ M obtained by Davies and Earley under similar experimental conditions.[10]

We prefer to accept our data on the $Ti(H_2O)_6^{3+} + I_2$ reactions because (a) our investigations were carried out over a wider range of reactant and acid concentrations (Ti(III) was for over a 22-fold variation in titanium(III) concentrations), (b) our work was carried out in the acid range 0.0036–0.2 M while Winstein's was for only 0.10–0.50 M, and (c) k_{I_2} and $k_{I_3^-}$ were determined in Winstein's work for only three different acid concentrations and at very high concentrations of iodide.[23] Since, at such high iodide concentrations (0.1–0.5 M), the iodine is present predominantly as I_3^-, $k_{I_3^-}$ determined from such data is likely to have a greater error than $k_{I_3^-}$ determined from the data at the iodide concentrations employed in our studies. A similar disagreement has been reported between earlier rate constants reported for the $Ti^{3+}(aq) + Co(NH_3)_5Cl^{2+}$ reaction[24] and the results of more recent investigations.[2]

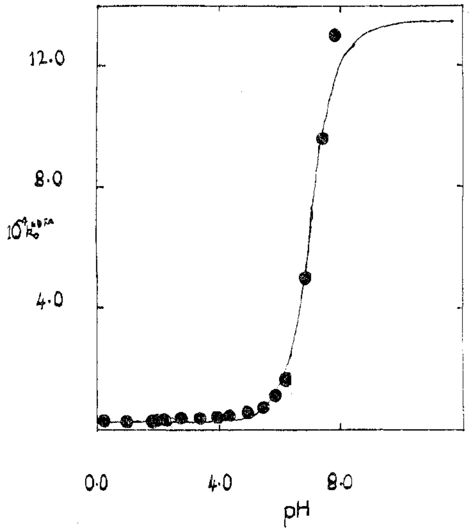

Figure 4. Effect of pH on the rate constant for the $TiEDTA^- + I_2$ reaction, shown by a plot of k_o^{EDTA} vs. pH. The solid line represents the calculated values of k_o^{EDTA} according to eq 9 while the points represented by ● are the experimentally determined values of k_o^{EDTA}.

In the oxidation of $Ti^{3+}(aq)$ by iodine, the form of the rate equation (eq 8) implies two kinetic components, one involving a bimolecular reaction between Ti(III) and I_2 and the other a reaction between Ti(III) and I_3^-. In both cases, as in many other reactions of aquotitanium(III), the Ti(III) is partitioned between a kinetically inactive acidic form (having an acidity constant of K_a) and an active basic form (this accounting for the observed H^+ dependence). Thus, the important net activation processes for the reactions are

$$Ti^{3+}(aq) \xrightleftharpoons{K_a} TiOH^{2+} + H^+ \qquad (10)$$

$$TiOH^{2+} + I_2 \xrightarrow{k_1} \text{(activated complex)*} \qquad (11)$$

$$TiOH^{2+} + I_3^- \xrightarrow{k_2} \text{(activated complex)*} \qquad (12)$$

From the above, the rate equation (13) can be readily derived.

$$\text{rate} = -\frac{d[Ti(III)]}{dt} = \frac{k_1K_a[Ti(III)][I_2]}{[H^+] + K_a} + \frac{k_2K_a[Ti(III)][I_3^-]}{[H^+] + K_a} \qquad (13)$$

Since eq 8 and 13 are identical, $a_1 = 1/k_1$, $b_1 = 1/k_2K_a$, $a_2 = 1/k_2$, and $b_2 = 1/k_2K_a$. From these the values of k and K_a computed are $k_1 = 5.3 \times 10^2\ M^{-1}\ s^{-1}$, K_a (from a_1 and b_1) = 3.0×10^{-3} M, $k_2 = 6.9\ M^{-1}\ s^{-1}$, and K_a (from a_2 and b_2) = 3.3×10^{-3} M, and the mean value of K_a is 3.2×10^{-3} M. The mean value estimated for K_a in this work is in very good agreement with 3.5×10^{-3} M similarly obtained by Orhanovic[7] for outer-sphere reactions of $Ti^{3+}(aq)$ ion with cobalt(III) complexes.[7] Other workers have also fitted their data with 1.6×10^{-3} and 4.6×10^{-3} M for outer-sphere reactions,[2,4] involving $Ti^{3+}(aq)$ as the reductant. The experimental value of K_a as determined[25] by independent workers, although not under identical conditions, put its value in the range (1.6–6.9) $\times 10^{-3}$ M. However, the kinetically and experimentally derived values are much lower than the 0.01–0.16 M often obtained for reactions in which a binuclear intermediate, i.e., an inner-sphere mechanism, is involved[12] in $Ti^{3+}(aq)$ redox reactions.

In the oxidation of $TiEDTA^-$ by I_2, the biphasic nature of the acid dependence replicates the acid dependence of the half-wave potential as reported by Pecsok and Maverick.[26] The interpretation they gave their results was that below pH 2.5 the Ti(IV) species exists as TiEDTA, while above pH 2.5 it exists as $TiO(EDTA)^{2-}$. Thus, as in the oxidation of $Ti^{3+}(aq)$ to TiO^{2+}, *a prior* hydrolysis of $TiEDTA^-$ to $TiOH(EDTA)^{2-}$ must precede the electron-transfer step in the oxidation of $TiEDTA^-$ above pH 2.5. Therefore, it follows that in the oxidation of $TiEDTA^-$ by I_2, the net activation processes in the pH range investigated in this work are

$$\mathrm{TiEDTA^- + H_2O} \xrightleftharpoons{K_a^{\mathrm{EDTA}}} \mathrm{HOTiEDTA^{2-} + H^+} \quad (14)$$

$$\mathrm{TiEDTA^- + I_2} \xrightarrow{k_1^{\mathrm{EDTA}}} \text{(activated complex)*} \quad (15)$$

$$\mathrm{HOTiEDTA^{2-} + I_2} \xrightarrow{k^{\mathrm{EDTA}}{}_{\mathrm{OH}}} \text{(activated complex)*} \quad (16)$$

Equations 14 to 16 lead to the rate equation

$$-\frac{d[I_2]}{dt} = \frac{k_1^{\mathrm{EDTA}} + k^{\mathrm{EDTA}}{}_{\mathrm{OH}}K_a^{\mathrm{EDTA}}[H^+]^{-1}}{1 + K_a^{\mathrm{EDTA}}[H^+]^{-1}}\{[\mathrm{Ti(III)}][I_2]\} \quad (17)$$

and hence

$$k_o^{\mathrm{EDTA}} = \frac{k_1^{\mathrm{EDTA}} + k^{\mathrm{EDTA}}{}_{\mathrm{OH}}K_a^{\mathrm{EDTA}}[H^+]^{-1}}{1 + K_a^{\mathrm{EDTA}}[H^+]^{-1}} \quad (18)$$

Since eq 9 and eq 18 are identical, it follows that $k_1^{\mathrm{EDTA}} = 2.5 \times 10^3\ M^{-1}\ s^{-1}$, $k^{\mathrm{EDTA}}{}_{\mathrm{OH}} = 1.3 \times 10^5\ M^{-1}\ s^{-1}$, and $K_a^{\mathrm{EDTA}} = 1.1 \times 10^{-7}$ M. The magnitude of K_a^{EDTA} is in close agreement with 1.5×10^{-7} M obtained[17] from the kinetics data for the oxidation of $TiEDTA^-$ by $CO(NH_3)_6^{3+}$.

In the oxidation of either $Ti^{3+}(aq)$ or $TiEDTA^-$ by I_2 or I_3^-, it is assumed that, as in most of the reactions of halogens with reducing ions,[15,18] the electron transfer proceeds by way of univalent changes, and the immediate product of the rate-determining bimolecular electron-transfer steps is the dihalogen radical ion, $I_2^{-}\cdot$. Our results in this work show the subsequent reactions of this transient species add no complications to the rate behavior of the systems being investigated.

As regards whether the reactions of interest proceed by either the inner- or the outer-sphere mechanism, the only convincing kinetic evidence for the outer-sphere mechaism is in the magnitude of the rate constant for the oxidation of $TiEDTA^-$ by I_2 above pH 2.5. The rate constant obtained for this reaction is much higher (about 100-fold) than the substitution-controlled electron-transfer rates in the inner-sphere reactions[17] of $TiEDTA^-$ with $Co(NH_3)_5SCN^{2+}$ or $Co(NH_3)_5N_3^{2+}$. By comparison with available results on the choice of mechanism by aquotitanium(III), two *less* convincing pieces of evidence seem to support an outer-sphere mechanism for reactions reported in this work. These are (i) the fact that inner-sphere reactions of $Ti^{3+}(aq)$ with metal complexes are accompanied by more complex acid dependence behavior[12] than can be explained by merely invoking hydrolysis of the aquotitanium(III) and (ii) that inner-sphere reactions of $Ti^{3+}(aq)$ have only been established for complexes where the "lead-in" ligands are typically Pearson's hard bases, whereas complexes with relatively soft bases like iodide react by the outer-sphere mechanism.[3]

Acknowledgment. We are grateful to Professor Earley of Georgetown University, who while A.A. was working in his laboratory initiated the idea of investigating the kinetics and mechanism of oxidation of $TiEDTA^-$ by various metal complexes.

Registry No. $Ti(H_2O)_6^{3+}$, 17524-20-8; $TiEDTA^-$, 67816-26-6; I_2, 7553-56-2.

References and Notes

(1) (a) J. P. Birk, *Inorg. Chem.*, **14**, 1724 (1975); (b) A. Bakac and M. Orhanovic, *Inorg. Chim. Acta*, **21**, 173 (1977).
(2) M. Orhanovic and J. E. Earley, *Inorg. Chem.*, **14**, 1478 (1975).
(3) G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **15**, 638 (1976).
(4) A. H. Martin and E. S. Gould, *Inorg. Chem.*, **14**, 873 (1975).
(5) A. Adegite and J. F. Ojo, *Inorg. Chem.*, **16**, 477 (1977).
(6) A. Bakac and M. Orhanovic, *Inorg. Chim. Acta.*, **21**, 173 (1977).
(7) A. Bakac, R. Marcec, and M. Orhanovic, *Inorg. Chem.*, **16**, 3133 (1977).
(8) N. Akinyugha, J. Ige, J. F. Ojo, O. Olubuyide, and R. Simoyi, *Inorg. Chem.*, **17**, 219 (1978).
(9) M. Hery and K. Wieghardt, *Inorg. Chem.*, **17**, 1130 (1978).
(10) P. Chalilpoyil, K. M. Davies, and J. E. Earley, *Inorg. Chem.*, **16**, 12 (1977).
(11) K. M. Davies and J. E. Earley, *Inorg. Chem.*, **17**, 3350 (1978).
(12) A. Adegite, J. E. Earley, and J. F. Ojo, *Inorg. Chem.*, **18**, 1535 (1979).
(13) T. P. Logan and J. P. Birk, *Inorg. Chem.*, **12**, 580, 2464 (1973).
(14) J. D. Ellis and A. G. Sykes, *J. Chem. Soc., Dalton Trans.* 537, 2553 (1973).
(15) A. Adegite and S. Edeogu, *J. Chem. Soc., Dalton Trans.*, 1203 (1975).
(16) C. E. Johnson and S. Winstein, *J. Am. Chem. Soc.*, **73**, 2601 (1951).
(17) A. Adegite and P. Agaba, *Inorg. Chem.*, in press.
(18) A. Adegite and H. Egboh, *Inorg. Chim. Acta.*, **2**, 1 (1977).
(19) D. H. Turner, G. W. Flynn, N. Sutin, and J. V. Beitz, *J. Am. Chem. Soc.*, **94**, 1554 (1972).
(20) We are very grateful to Dr. Watson on secondment from the Department of Physics, Carleton University, Ottawa, Canada, to Ahmadu Bello University, Zaria, who wrote the program for this computation.
(21) When *p* in eq 9 was not fixed, but treated as an unknown, the following values were computed for the three parameters: $p = 2936\ M^{-1}\ s^{-1}$, $q = 1.299 \times 10^{-2}\ s^{-1}$, $r = 9.20 \times 10^{-8}$ M. These values compare favorably with the estimates obtained when "*p*" is fixed at $2500\ M^{-1}\ s^{-1}$.
(22) M. Davies and E. Gwyne, *J. Am. Chem. Soc.*, **74**, 2748 (1952).
(23) Since Johnson and Winstein[16] did not analyze their data in such a way as to obtain values for k_{I_2} and $k_{I_3^-}$ at the various acid concentrations, we did this with their data by plotting $k_o(1 + K_{I_3}[I^-])$ vs. $[I^-]$. From least mean squares analysis, k_{I_2} and $k_{I_3^-}$ were obtained from the slope and intercept, respectively. This was possible for only three different acid concentrations (because of inadequacy of data) and the results are as follows: $[H^+] = 0.10$ M, $k_{I_2} = 7.4\ M^{-1}\ s^{-1}$, $k_{I_3^-} = 0.009\ M^{-1}\ s^{-1}$; $[H^+] = 0.177$ M, $k_{I_2} = 3.69\ M^{-1}\ s^{-1}$, $k_{I_3^-} = 0.008\ M^{-1}\ s^{-1}$; $[H^+] = 0.329$ M, $k_{I_2} = 1.82\ M^{-1}\ s^{-1}$, $k_{I_3^-} = 0.005\ M^{-1}\ s^{-1}$. At these three acid concentrations, only three iodide concentrations could be employed, viz., $[I^-] = 0.098$, 0.179, and 0.342 M. Beyond $[I] = 0.342$ M, $k_o(1 + K_{I_3^-}[I^-])$ does not vary with $[I^-]$.
(24) V. W. Cope, R. G. Miller, and R. T. M. Fraser, *J. Chem. Soc. A*, 301 (1967).
(25) Directly measured values of k_a as reported in the literature are as follows: 2.8×10^{-3} M, $I = 3.0$ M KBr, M. R. Paris and C. L. Gregoire, *Anal. Chim. Acta*, **42**, 439 (1968); 1.6×10^{-3} M, H. Krentzien and F. Brito, *Chem. Abstr.*, **73**, 78656 (1970); 6.9×10^{-3} M, $I = 0.25$–1.5 M (KBr), R. L. Pecsok and A. N. Fletcher, *Inorg. Chem.*, **1**, 155 (1962).
(26) R. L. Pecsok and E. F. Maverick, *J. Am. Chem. Soc.*, **76**, 358 (1954).
(27) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley, New York, 1967, p 113.