

**KINETICS AND MECHANISM OF THE REDUCTION OF DICHLOROTETRAKIS
(2,2'-BIPYRIDINE)-μ-OXODIRUTHENIUM(III) ION
BY Ti(III)-EDTA IN AQUEOUS ACIDIC MEDIUM**

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ABSTRACT. The kinetics and mechanism of the reduction of dichlorotetrakis-(2,2'-bipyridine)-μ-oxo-diruthenium(III) ion by the Ti(III)-edta complex has been studied in aqueous acidic media. At I = 0.5 M (LiCl) and T = 25.0 ± 0.1 °C, the data obtained is consistent with the rate law: $-d/dt[(bipy)_2ClRuORuCl(bipy)_2^{2+}] = k_0^{edta}[Ti(III)-edta]$ $[(bipy)_2ClRuORuCl(bipy)_2^{2+}]$. The second-order rate constant, k_0^{edta} , showed two mechanistic components with k_0^{edta} independent of pH for $pH \geq 3$ and increasing with pH for $pH < 3$. This has been interpreted in terms of the changing identity of the Ti(III)-edta species as a function of the pH of the reaction medium. Least-square analysis was used to fit k_0^{edta} into an expression of the form,

$$k_0^{edta} = \frac{k_2 + k_2K_1[H^+]^{-1} + k_3K_1K_2[H^+]^{-2}}{1 + K_1[H^+]^{-1} + K_1K_2[H^+]^{-2}}$$

with K_1 and K_2 fixed as earlier determined as 9.55×10^{-3} M and 2.29×10^9 M respectively, k_2 and k_3 were determined as

$$k_2 = (2.96 \pm 0.13) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$$

$$k_3 = (3.20 \pm 0.56) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$$

respectively. On the basis of the data obtained, the outer-sphere mechanism has been suggested.

INTRODUCTION

The interest in titanium(III) aquoion as the reductant in electron transfer reactions has recently been extended to the Ti(III)-edta complex (1-10). Sykes and Thompson (11) reported some rate studies of the oxidation of Ti(III)-edta by some cobalt(III) ammine complexes for $pH < 2$. We have also investigated the kinetics of the oxidation of Ti(III)-edta complex (12), by iodine (13) and bromine (14) over a wider range of pH. The rates of the latter reactions showed two mechanistic components as a function of pH. This parallels the dependence of the half-wave potential of the Ti(IV)-edta/Ti(III)-edta couple on pH as reported in the polarographic studies of Maveric and Pecsok (15). As in the case of the latter report, the two mechanistic components have been interpreted in terms of differing reactivities of Ti(III)-edta species in solution. Hereafter, Ti(III)-edta is used to represent any type of complex formed between Ti(III) and ethylenediammine tetraacetate ion regardless of whether the ligand acts as a penta- or hexa-coordinate or its hydrolysed or unhydrolysed form. Individual species are indicated by $TiOH_2(edta)$, $TiOH_2(Hedta)$ and $TiOH(edta)^{2-}$. As a continuation of our interest in the reactions of Ti(III)-edta, we now report

our kinetic investigation of the oxidation of the Ti(III)-edta complex by the dichlorotetrakis(2,2'-bipyridine)- μ -oxo-diruthenium(III) ion in acidic media.

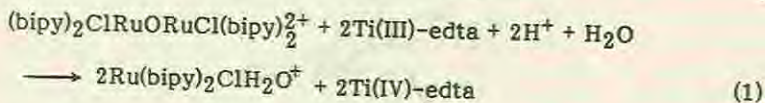
EXPERIMENTAL

Solutions of the Ti(III)-edta complex were prepared by adding predetermined amounts of $Ti(H_2O)_6^{3+}$ solutions to a reaction medium containing the required amount of LiCl, sodium acetate, HCl and NaHEDTA. Ti(III) solutions in trifluoromethanesulfonic acid were prepared and analysed for titanium(III) and acid content as previously reported (8, 10). The quantity of NaHEDTA contained in the solution was always in slight excess of what is required for a 1:1 Ti-edta complex. Sodium acetate, HCl, LiCl (BDH, Analar Grade) were used without further purification and $Na_2H_2EDTA \cdot 2H_2O$ (BDH) was used after two recrystallizations. The dichlorotetrakis(2,2'-bipyridine)- μ -oxo-diruthenium(III) ion was prepared and characterized as previously reported (16). Solutions of the dimer in water were kept in the freezer and were stable over at least two days after which a new solution was always prepared.

Kinetics. All rate measurements were made on the Durrum-Gibson stopped-flow spectrophotometer. The rates of the reaction were monitored under pseudo-first-order conditions by following the decrease in absorbance at $\lambda = 648$ nm characteristic of the oxobridged complex. First-order rate constants obtained from the slopes of plots of $\ln(A_t - A_\infty)$ against time (A_t and A_∞ are the absorbance at the time t and infinity respectively) gave a first-order dependence on reductant and hence a second-order rate constant k_0 . Any reported rate constant is an average of duplicate runs. Rate constants obtained from such runs agree within 5%. The ionic strength was maintained constant at 0.5 M for all runs with $CF_3SO_3Li^+$. The temperature was kept constant at $25.0 \pm 0.1^\circ C$ for all runs by circulating water through the reaction chambers of the spectrophotometer. All solutions were properly flushed with argon before each run.

RESULTS AND DISCUSSION

Stoichiometry. The stoichiometry of the reaction was determined by spectrophotometric titrations under an inert atmosphere of argon to be 2.01 ± 0.03 moles of Ti(III)-edta consumed per mole of the oxobridged dimer. The reduced ruthenium product under this condition is $Ru(bipy)_2H_2OCl^+$ as evidenced by the appearance of the visible spectrum of this ion (17). The reaction of interest can therefore be represented by the following equation:



Order of the reaction.

The rate of the reaction was measured with the concentration of Ti(III)-edta at least 20 times that of the oxobridged dimer. Pseudo-first-order plots were linear to more than 90% completion of reaction. The linearity of these plots demonstrate that this reaction is first-order in $[(bipy)_2ClRuORuCl(bipy)_2^{2+}]$.

Pseudo-first-order rate constants were determined at different initial concentrations of the Ti(III)-edta complex. A plot of $\log k_1$ (k_1 is the pseudo-first-order rate constant) against $\log [Ti(III)\text{-edta}]$ was linear with a slope of 0.97 ± 0.07 confirming that the reaction of interest is strictly first

order in [Ti(III)-edta]. Hence at constant $[H^+]$ and ionic strength of 0.5 M, the rate equation is:

$$\frac{-d[(bipy)_2ClRuORuCl(bipy)_2]^{2+}}{dt} = k_o^{edta}[Ti(III)-edta][(bipy)_2ClRuORuCl(bipy)_2]^{2+} \quad (2)$$

The second-order rate constants k_o^{edta} (Table 1) were determined as

$$k_o^{edta} = k_1/[Ti(III)-edta] \quad (3)$$

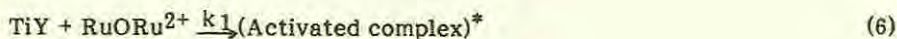
Table 1. Second-order rate constants of the reaction of $(bipy)_2ClRuORuCl(bipy)_2^{2+}$ with the Ti(III)-edta complex $[(bipy)_2ClRuORuCl(bipy)_2]^{2+} = 1.75 \times 10^{-5} M, T = 25.0 \pm 0.1 \text{ } ^\circ C, I = 0.5 M.$

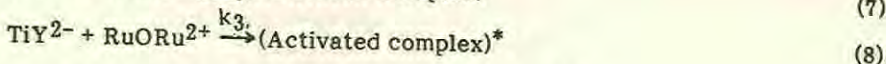
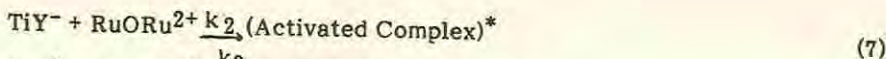
$10^3[Ti(III)-edta]M$	pH	$[X^-]mM$	$10^{-5}k_o^{edta}M^{-1}s^{-1}$
0.20	2.9	-	3.1
0.50	2.9	-	3.2
0.74	2.9	-	3.2
1.11	2.9	-	3.3
1.50	2.9	-	3.1
X = Cl			
1.11	2.9	10	3.1
1.11	2.9	50	3.2
1.11	2.9	100	3.2
1.11	2.9	150	3.1
1.11	2.9	200	3.1
X = NCS			
0.74	3.3	0.5	3.4
0.74	3.3	1.0	3.2
0.74	3.3	5.0	3.2
0.74	3.3	10	3.1
0.74	3.3	15	3.1
0.74	3.3	20	3.2
0.74	3.3	100	3.2

pH dependence.

The second-order rate constants of the oxidation of Ti(III)-edta complex by the oxobridged dimer were measured as a function of pH while the concentrations of the reactant ions and the ionic strength were kept constant. Formate or acetate buffers were used to maintain a constant pH where necessary. pH values were determined by using a pH meter in a medium containing equal volumes of the reactant solutions. The plot of rate constants against pH (Fig. 1) showed two mechanistic components. Such a dependence has been previously observed in the reactions of the Ti(III)-edta complex with aqueous solutions of bromine (14) and iodine (13) and some cobalt(III) ammine complexes (12).

In these reactions, the rate is pH independent in the range $pH < 3$ but in the range $pH > 3$ the rate increases with pH. Such a dependence of rate on pH can be attributed to differing reactivities of the Ti(III)-edta complex species present in solution (17). These are $Ti(H_2O)(Hedta)$, $Ti(H_2O)edta^-$ and $Ti(OH)(edta)^{2-}$. This interpretation is consistent with the findings of the polarographic studies (15), that, at $pH < 3$, $Ti^{III}-edta$ exist as $Ti(H_2O)(edta)$ and $Ti(H_2O)edta^-$ and at $pH > 3$ it exists as the $Ti(OH)(edta)^{2-}$. The principal activation paths for this reaction can therefore be proposed as:





where $\text{Y} = \text{edta}$, $\text{RuORu}^{2+} = (\text{bipy})_2\text{ClRuORuCl}(\text{bipy})_2^{2+}$.

The above scheme gives,

$$k_{\text{o}}^{\text{edta}} = \frac{k_1 + k_2 K_1 [\text{H}^+]^{-1} + k_3 K_1 K_2 [\text{H}^+]^{-2}}{1 + K_1 [\text{H}^+]^{-1} + K_1 K_2 [\text{H}^+]^{-2}} \quad (9)$$

From the titration studies of Ti(III)-edta solutions reported by Podlahova and Podlaha (17) $\text{Ti}(\text{H}_2\text{O})(\text{Hedta})$ and $\text{Ti}(\text{H}_2\text{O})\text{edta}^-$ were identified at $\text{pH} < 3$. The result of this investigation suggests that the above two species react with similar rates, i.e. $k_1 = k_2$. This is also consistent with the result of recent investigations (11, 12). Thompson and Sykes (11) noted that the rate constant for the $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ oxidation of the Ti(III)-edta complex remained unaffected by pH for $\text{pH} < 2$. They therefore suggested that the reactions were insensitive as to whether the free carboxylate of the edta is protonated or not.

Equation (9) therefore becomes,

$$k_{\text{o}}^{\text{edta}} = \frac{k_2 + k_2 K_1 [\text{H}^+]^{-1} + k_3 K_1 K_2 [\text{H}^+]^{-2}}{1 + K_1 [\text{H}^+]^{-1} + K_1 K_2 [\text{H}^+]^{-2}} \quad (10)$$

Using values of $\text{p}K_1$ and $\text{p}K_2$ as measured by Podlahova and Podlaha (18) i.e.

$$\text{p}K_1 = 2.02 \pm 0.01$$

$$\text{p}K_2 = 8.64 \pm 0.02$$

non-linear least-square computer fitting (19) of the obtained data using an iterative programme with $(1/k_{\text{o}}^{\text{edta}})^2$ weighting gave values of k_2 and k_3 as:

$$k_2 = (2.96 \pm 0.13) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$$

$$k_3 = (3.10 \pm 0.56) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$$

The value of $k_2(\text{calc}) = (2.96 \pm 0.13) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ is similar to the value of $k_2(\text{expt}) = 2.8 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ the average value of $k_{\text{o}}^{\text{edta}}$ for $\text{pH} \leq 3$.

$k_{\text{o}}^{\text{edta}}$ was calculated as a function of pH on the basis of the proposed mechanism. Fig. 1 shows the rate constant/pH profile for $k_{\text{o}}^{\text{edta}}(\text{expt})$ and $k_{\text{o}}^{\text{edta}}(\text{calc})$ as a function of pH. A fit with a correlation coefficient of 0.99 was obtained

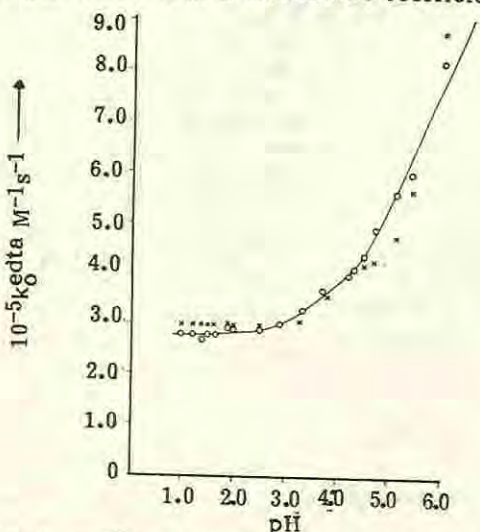


Fig. 1. Plot of $k_{\text{o}}^{\text{edta}}(\text{expt})$ and $k_{\text{o}}^{\text{edta}}(\text{calc})$ versus pH for the $(\text{bipy})_2\text{ClRuORuCl}(\text{bipy})_2^{2+} + \text{Ti}(\text{III})\text{-edta}$ reaction.

$\circ = k_{\text{o}}^{\text{edta}}(\text{expt})$ and $\times = k_{\text{o}}^{\text{edta}}(\text{calc})$.

between $k_{\text{O}}^{\text{edta}}$ (calc) and $k_{\text{O}}^{\text{edta}}$ (expt) confirming the proposed mechanism. However, it is worth noting that the difference between the calculated and observed rate constant in the range $1.0 \leq \text{pH} \leq 6.0$ does not show a systematic trend. Many factors could be responsible for the discrepancy including uncertainty in the nature of the titanium-edta species present in solution and the limitation of the computer programme.

Table 2. Observed and calculated second-order rate constants, $k_{\text{O}}^{\text{edta}}$ for the $\text{Ti(III)-edta}^- \text{-(bipy)}_2\text{ClRuORuCl(bipy)}_2^{2+}$ reaction in the pH range 1.0-6.0
 $[\text{Ti(III)-edta}] = 3.4 \times 10^{-6} \text{ M} - 6.1 \times 10^{-4} \text{ M}$,
 $[(\text{bipy})_2\text{ClRuORuCl(bipy)}_2^{2+}] = 1.0 \times 10^{-5} \text{ M}$,
 $I = 0.5 \text{ M}$, $T = 25.0 \pm 0.1^\circ\text{C}$.

pH	$10^5 k_{\text{O}}^{\text{edta}}(\text{expt})\text{M}^{-1}\text{s}^{-1}$	$10^{-5} k_{\text{O}}^{\text{edta}}(\text{calc})\text{M}^{-1}\text{s}^{-1}$
1.0	2.8	3.0
1.2	2.8	3.0
1.4	2.7	3.0
1.5	2.8	3.0
1.6	2.8	3.0
1.9	2.9	3.0
2.0	2.9	3.0
2.5	2.9	3.0
2.9	3.0	3.0
3.3	3.3	3.1
3.7	3.7	3.6
4.2	4.0	4.0
4.3	4.1	4.1
4.5	4.4	4.2
4.7	4.9	4.3
5.1	5.6	4.8
5.4	6.0	5.7
6.0	8.2	8.8

Previous works have shown (17) that although the three species employed in our model, $\text{Ti(H}_2\text{O)Hedta}$, $\text{Ti(H}_2\text{O)edta}^-$ and Ti(OH)edta^{2-} are the dominant species, other less identifiable polymerized species are also present. In our calculations the kinetic significance of such species has not been quantified.

As to whether the reduction of the oxobridged dimer by Ti(III)-edta proceeds by the outer- or the inner-sphere mechanism, the only evidence of mechanism is that the rate constant $k_{\text{O}}^{\text{edta}} = 10^5 \text{ M}^{-1}\text{s}^{-1}$ obtained is much higher than the substitution controlled rate for inner-sphere reactions of $\text{Ti}^{\text{III}}\text{-edta}$ with $\text{Co(NH}_3)_5\text{SCN}^{2+}$ and $\text{Co(NH}_3)_5\text{N}_3^{2+}$ (12) and also much greater than the substitution rate constant, $k = 10^{-2}\text{--}10^{-3} \text{ M}^{-1}\text{s}^{-1}$ obtained for $(\text{bipy})_2\text{ClRuORuCl(bipy)}_2^{2+}$ (18). This suggests that this reaction most probably occur by the outer-sphere mechanism.

As in the case of $\text{Cr(edta)H}_2\text{O}^-$ (19, 20, 21) and $\text{Ru(edta)H}_2\text{O}^-$ (22) and as observed in earlier reactions of $\text{Ti(edta)H}_2\text{O}^-$ (11, 13), edta appears to have a strong labilizing effect on the complexed H_2O . It has also been observed (6, 23) that early first row transition-metal ions exhibit a reluctance to use halide ions as bridging ligands in reactions that occur by the inner-sphere mechanism. Hence the observed lack of dependence of rate on $[\text{Cl}^-]$ and $[\text{NCS}^-]$ in the range investigated suggests that species Ti(III)-edtaCl^- or Ti(III)-edtaNCS^- which might result in the chloride or thiocyanate medium probably react by the same mechanism and at the same rate as the parent Ti(III)-edta complex. We suggest this mechanism to be outer-sphere.

Our result also corroborates earlier reports (11, 13, 14) that the Ti(III)-edta complex is a more effective reductant than the Ti(III) aquoion. The rate constant for the Ti(III) reduction of $(\text{bipy})_2\text{ClRuORuCl(bipy)}_2^{2+}$ ion (24) is $6.2 - 60.3 \text{ M}^{-1}\text{s}^{-1}$ in the acid range $0.01 \leq [\text{H}^+] \leq 0.15$ and the reduction potentials, E° , are respectively $\text{TiO}^{2+}\text{-edta/Ti(III)-edta}$, 0.03V (15), and $\text{TiO}^{2+}/\text{Ti}^{3+} = 0.1\text{V}$ (25).

Although thermodynamics predicts the correct order of electron-transfer between these ions, the relatively low rate observed for the Ti(III) aquoion reduction of the oxobridged ion may be due to the drastic structural rearrangement accompanying the conversion of an aquoion to an oxocation.

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