KINETICS AND MECHANISM OF THE REDUCTION OF TETRAOXOIODATE (VII) ION BY L-ASCORBIC ACID IN PERCHLORIC ACID MEDIUM

P.O. Ukoha* and J.F. Iyun
Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.

ABSTRACT

The stoichiometry, kinetics and mechanism of the reduction of tetraoxoiodate (VII) ion by L-ascorbic acid in aqueous HClO₄ has been investigated at 26.0 ± 0.1°C and I = 1.10M (NaClO₄). The reaction displayed a 1:3.5 stoichiometry and follows the empirical rate law:

$$-d[IO_4^-]/dt = (a+b[H^+])^2 [IO_4^-] [H_2A]$$

The rate of the reaction was unaffected by variation of the ionic strength and dielectric constant of the medium. Also free radical intermediates have been implicated as active intermediates in this reaction. The reaction has been rationalised on the basis of ion-pair complex with outer-sphere character and also a possible inner-sphere route.

INTRODUCTION

L-Ascorbic acid is a naturally occurring compound found in fairly high concentrations in cells of citrus fruits and fresh vegetables. A lot of interest has been shown towards its reactions mainly because of its physiological activities. It has been found to be very active in the treatment of scurvy and as a precursor in the synthesis of collagen. However, definite knowledge of the details of its activities is surprisingly scanty.

In pursuit of the desire to gain full knowledge of the reaction patterns of L-ascorbic acid, its complexes with various transition metals have been prepared and its electron transfer reactions with metal ions studied. Recent work by Iyun et al. on the reaction of ascorbic acid with diaquatetrakis (2,2'-bipyridine)-μ-oxo-dichromium (III) ion indicated a 2:1 oxidant: reductant stoichiometry and an inverse acid dependence.

Some kinetic information has also been published on the oxidation of L-ascorbic acid by various metal complexes but not much has been known about its reactions with non-metallic species. It is our interest in this work to probe its electron transfer reactions with a typical non-metallic species, the oxyanion, IO₄⁻, with a view to compare this reaction with well-documented reactions of ascorbic acid with metal ions and enhance the understanding of the redox reactions of ascorbic acid.

In addition, interest in the reaction of permanganate ion arises from a desire to gain insight into its behavior, especially as a strong oxidant. Most of its reactions with inorganic and organic substrates have been reported to occur by inner-sphere mechanism. Most of the reactions have shown evidence for products with transferred groups. Also kinetic evidence for rapid pre-equilibrium formation of intermediate products supported the inner-sphere pathway for some of these reactions. It is our hope that data gathered from this reaction will assist in the explanation of some of the complexities that attend the reactions of permanganate ion.

EXPERIMENTAL

Materials
L-Ascorbic acid (Fischer Reagent Grade) herein after referred to as H₂A was used without
further purification with its fresh solutions prepared every two days. Solutions of \( \text{NaClO}_4 \) were standardised gravimetrically while those of \( \text{HClO}_4 \) were standardised titrimetrically. All other chemicals were of reagent grade and were used as received.

**Stoichiometry**

The stoichiometry was determined by the mole ratio method using spectrophotometric titration at 480nm by monitoring the production of iodine. The \( [\text{IO}_4^-] \) was kept constant at 1.0 \( \times \) 10\(^{-4}\)M and the concentration of ascorbic acid varied between 1x10\(^{-5}\) M and 5x10\(^{-5}\)M at \([\text{H}^+] = 0.001\) M and \(I=1.10\) M (\(\text{NaClO}_4\)).

**Kinetics**

Using Milton Roy Spectronic 21 spectrophotometer, the wavelength of maximum absorption of iodine in aqueous solution was determined to be 480nm. This value agrees closely with what has been reported by other workers\(^{22,23}\). Having certified that neither of the reactants absorbs significantly at this wavelength, kinetic measurements were conducted at this wavelength by monitoring the increase in absorbance of the reaction mixture as the reaction progressed. The reaction was carried out under pseudo-first order conditions with ascorbic acid concentrations in at least 20-fold excess over that of the oxidant. Ionic strength of the reaction was kept constant at 1.10 M (\(\text{NaClO}_4\)) and \([\text{H}^+]\) maintained as 0.01M unless otherwise stated.

Plots of \( \log (A_n - A_0) \) against time, \( t \), (where \( A_n \) and \( A_0 \) are the absorbances at the end of the reaction and at time, \( t \), respectively) were linear for greater than 80% extent of reaction. Pseudo-first order rate constants, \( k_{obs} \), were determined as the slopes of the above plots as given by the equation

\[
( A_n - A_0 ) = ( A_n - A_0 ) e^{k_{obs} \cdot t} \quad \ldots \ldots \ldots (2)
\]

\( A_0 \) is the absorbance at the beginning of the reaction. Second order rate constants, \( k_2 \), were obtained as ratios of \( k_{obs} \) to \([\text{H}_2\text{A}]\). Rate constant of two runs agreed to within \( \pm 2.4\% \). Reported rate constants are the means of two runs.

**RESULTS AND DISCUSSION**

Mole ratio determination showed that for every mole of periodate ion reduced, 3.5 moles of ascorbic acid were oxidised. Plot of \( A_n \) versus mole ratio (\( \text{IO}_4^- / \text{H}_2\text{A} \)) had a sharp break at about 0.278 corresponding approximately to a mole ratio of 1:3.5. This mole ratio is consistent with equation (2)

\[
2\text{IO}_4^- + 7\text{H}_2\text{A} + 2\text{H}^+ \rightarrow 8\text{H}_2\text{O} + 7\text{A} + \text{I}_2 \\
\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)
\]

Whereas no report of the reaction of \( \text{H}_2\text{A} \) with oxyanions exists, its reactions with metal ions where dehydroascorbic acid (A) was produced as the main organic product has been reported\(^{11}\). This product is obtained if \( \text{H}_2\text{A} \) acts as a two-electron reagent as the above reaction suggests. The formation of iodine was indicated by its characteristic yellowish brown colour and its formation of a bluish-black colour when mixed with starch solution. Also the yellowish - brown coloured reaction mixture showed absorption at about 480nm. This is indicative of aqueous iodine\(^{22,23}\).

Under pseudo-first order conditions with \([\text{H}_2\text{A}]\) at least 20-fold excess over \([\text{IO}_4^-] \) and at constant ionic strength, pseudo-first order plots showed close linearity for at least 80% extent of reaction. This implies that the order of reaction with respect to \([\text{IO}_4^-] \) is unity. Pseudo - first order rate constants, determined as slopes of these plots, are shown in Table 1. The rate of reaction increases with increase in \([\text{H}_2\text{A}]\). Also the plot of \( \log k_{obs} \) versus \( \log [\text{H}_2\text{A}] \) was linear with a slope of 1.09 implying first order dependence of rate on \([\text{H}_2\text{A}]\) as shown in Fig. 1. This observation corroborates other observations\(^{12,17}\) on the oxidation of some iron (II) and cobalt (II) complexes by periodate. The rate law for the reaction is given as equation (3)

\[
\frac{d[\text{IO}_4^-]}{dt} = k_2 [\text{H}_2\text{A}] [\text{IO}_4^-] \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3)
\]

Within the range \(0.001 \leq [\text{H}^+] \leq 0.1\)M at \([\text{H}_2\text{A}] = 0.02\)M and constant ionic strength the rate of reaction increases with increase in \([\text{H}^+] \) (Table 1). A plot of second order rate constant, \( k_2 \), against \([\text{H}^+] \) in the above acid range was
Figure 1: Plot of log $k_{obs}$ versus log $[H_2A]$ for the reduction of $IO_3^-$ by $H_2A$ at $\lambda_{max} = 480\text{nm}$ and $T = 25^\circ\text{C}$.

Table 2: Dependence of second order rate constants on anions and dielectric constant, $D$, for reduction of $IO_3^-$ by $H_2A$ at $[H_2A] = 2.0 \times 10^{-5}\text{M}$ $[IO_3^-] = 1 \times 10^{-6}\text{M}$, $l = 1.10\text{M}$ (NaClO$_4$), $\lambda_{max} = 480\text{nm}$ and $T = 26.0 \pm 0.1^\circ\text{C}$.

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<tr>
<th>$10^3[H_2A], M$</th>
<th>$10^3[H^+], M$</th>
<th>$I, M$(NaClO$_4$)</th>
<th>$k_2, M^{-1}s^{-1}$</th>
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*(no reaction even after 5 hours).

linear and fitted equation (4)

\[ k_2 = a + b[H^+]^2 \] ................. (4)

Where a and b were determined by the method of least mean squares to be 8.3 M^{-1}s^{-1} and 2.9 \times 10^4 M^{-1}s^{-1} respectively at 26.0 ± 0.1°C and J = 1.10 M (NaClO_3). Substituting the expression for \( k_2 \) into equation (3) gives equation (5)

\[ \frac{[IO_3^-]}{d[P_2 A]} = (a + b[H^+]^2) \times [IO_3^-] \times [P_2 A] \]

\[ = \text{(5).} \]

This relationship is similar to the kinetic pattern of the reaction of \( IO_4^- \) with 12-tungstocobaltate (III)\(^{20}\) and o xo-bridged ruthenium dimer\(^{28}\). Whereas most reactions of ascorbic acid show inverse acid dependence except in strong acid media\(^{30}\), reactions of \( IO_4^- \) show direct acid dependence as the rate of oxygen exchange is dependent on concentration of hydrogen ions\(^{25}\). The protons, as has been reported\(^{26}\), enhance the cleavage of the bond between the oxide ions and the central atom. The hydrogen ion dependence of the rate of reaction is also unconnected with the various equilibria established by \( IO_4^- \) in aqueous solution; species like \( HIO_6^- \), \( H_2IO_6^- \), \( H_3IO_6^2^- \) and \( IO_4^- \) have been reported to exist in aqueous solutions of \( IO_4^- \). The species \( IO_4^- \) and \( H_2IO_6^- \) are known to predominate in acidic \( IO_4^- \) solutions at 25°C with the proportion of \( H_3IO_6^2^- \) increasing with decreasing pH\(^{25}\). The involvement of protonated species which are likely to be more reactive than \( IO_4^- \) supports the influence of acidity on the reaction. However, at constant \([H^+]\) and keeping other parameters constant, variation of ionic strength did not affect the rate of reaction as depicted by Table 1. This observation is typical of reactions occurring between cation and neutral species or anion and neutral species\(^{28}\). Since periodate is negatively charged, the main reductant species have to be HA\(^+\) or \( H_2A \). This is in accordance with the observed effect on the rate of reaction of variation of the dielectric constant, \( D \), of the medium. The rate constant was independent of \( D \) within the dielectric constant range 66.68 - 81.39 as shown in Table 2. Earlier reports on reactions of \( H_2A \) equally implicated \( H_2A \) and \( HA^+ \) as main reductants\(^{8,11}\).

On the basis of the results obtained in this investigation, the mechanism below is proposed for the title reaction.

\[ k_1 \]

\[ IO_4^- + H^+ + 2H_2O \rightarrow \rightarrow HIO_6^- \] \( \equiv \) \( \text{(6).} \)

\[ k_2 \]

\[ H_2A + H \rightarrow \rightarrow H_2A^+ \] \( \equiv \) \( \text{(7).} \)

\[ k_3 \]

\[ H_2IO_6^- + H_2A^+ \rightarrow \rightarrow \{H_2IO_6^-, H_3A^+\} \] \( \equiv \) \( \text{(8).} \)

\[ k_4 \]

\[ \{H_2IO_6^-, H_3A^+\} \rightarrow \rightarrow 4H_2O + A + IO_4^- \] \( \equiv \) \( \text{(9).} \)

\[ k_5 \]

\[ IO_4^- + 4H_2A \rightarrow \rightarrow 4HA^+ + 2H_2O + 4\] \( \equiv \) \( \text{(10).} \)

\[ k_6 \]

\[ IO_4^- + H_2A \rightarrow \rightarrow OH^- + A + 2HIO_6^- \] \( \equiv \) \( \text{(11).} \)

\[ k_7 \]

\[ HIO_2^- + 2HA^+ + H^+ \rightarrow \rightarrow H_2O + 2H_2 + 2A \] \( \equiv \) \( \text{(12).} \)

\[ k_8 \]

\[ 2HA^+ + A^+ \rightarrow \rightarrow 2H^+ + 3A \] \( \equiv \) \( \text{(13).} \)

\[ k_9 \]

\[ H_2O + 2H^+ \rightarrow \rightarrow H_2O \] \( \equiv \) \( \text{(15).} \)

\[ k_10 \]

\[ \frac{[H_2IO_6^-]}{[H_2A^+]} = k_{10} \] \( \equiv \) \( \text{(17).} \)

Where \( [H_2IO_6^-, H_3A^+] = k_{10} [H_2IO_6^-][H_2A^+] \) \( \equiv \) \( \text{(18).} \)

and \( [H_2A^+] = k_9[H^+][H_2A] \) \( \equiv \) \( \text{(19).} \)

and \( [H_2IO_6^-] = k_9[IO_4^-][H^+] \) \( \equiv \) \( \text{(20).} \)

Substituting eqns (18-20) into eqn (17) gives that

\[ \text{Rate} = k_{10}k_{11} \] \( \equiv \) \( \text{(21).} \)

Equation (21) is similar to equation (5) where \( a = k_6 \) and \( b = k_7 k_8 k_9 k_{10} \).

The possibility of the formation of ascorbate cation, \( H_2A^+ \) (of eqn (7)) at pH 6.05 has been reported for the reaction of \([Mt^{III} \text{ (salen)} \ H_2O]^+\) with \( H_2A^+ \). At this point the existence of HA\(^-\) is thought to be improbable. The reaction between \( H_2A \) and perethenate ion in strong acid media was also observed to involve \( H_2A^+ \). The reaction also had second order dependence on hydrogen ion concentration\(^9\). Equation (8) implicates the role of ion-pair complexes with outer-sphere character. This is probably responsible for the lack of dependence of reaction rate on ionic strength and dielectric constant of the medium. Scanning of the reaction mixture at various intervals of the reaction confirmed the absorption due to presence of \( I_2 \) in solution. The presence of free radicals was indicated by the positive polymerization test on adding acrylamide to the reaction mixture in the presence of excess methanol.

Based on the above findings, the mechanism of reaction has been rationalised on the basis of both outer-sphere and inner-sphere reaction mechanism. This is supported by the Michaelis Menten plot of \( 1/k_{obs} \) versus \( 1/[H_2A] \) which gave negligible negative intercept\(^9\). This indicates that intermediates with appreciable equilibrium constants are non-existent in the reaction. Also, addition of anions, \( NO_3^- \) and \( CH_3COO^- \), did not catalyse the reaction but retarded it (Table 2).

At \([CH_3COO^-]\) of 0.5M no reaction was observed even after five hours. With \( NO_3^- \) the reaction was equally very slow. This is probably due to interaction of these ions with the reactants at transition state.

REFERENCES


accepted 21/7/99

received 23/4/99