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 $HClO_4$ has been investigated at $26.0 \pm 0.1°C$ and $I = 1.10M$ ($NaClO_4$). 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[1]. A lot of interest has been shown towards its reactions mainly because of its physiological activities[2]. It has been found to be very active in the treatment of scurvy and as a precursor in the synthesis of collagen[1]. However, definite knowledge of the details of its activities is surprisingly scanty.

In pusuit 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.[3-10] Recent work by lyun et al.[11] on the reaction of ascorbic acid with diaquatetrakis (2,2^1-bipyridine)-μ-oxodiruthenium (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, IO_4^-, 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 periodate ion arises from a desire to gain insight into its behavior especially as a strong oxidant. Most of its reactions with inorganic[12-20] and organic[21] substrates have been reported to occur by inner-sphere mechanism. Most of the reactions have shown evidence for products with transfered groups. Also kinetic evidence for rapid pre-equilibrium formation of intermediate products supported the inner-sphere pathway for some of these reactions[13-16, 18]. It is our hope that data gathered from this reaction will assist in the explanation of some of the complexities that attend the rections of periodate ion.

EXPERIMENTAL

Materials

L-Ascorbic acid (Fischer Reagent Grade) herein after referred to as H_2A was used without

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**Address:- Department of Science Technology*
Federal College of Chemical and Leather Technology,
P.M.B. 1034, Zaria, Nigeria.

**Author for correspondence.*

further purification with its fresh solutions prepared every two days. Solutions of $NaClO_4$ were standardised gravimetrically while those of $HClO_4$ 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 $[IO_4^-]$ was kept constant at 1.0×10^{-4}M and the concentration of ascorbic acid varied between 1×10^{-5} M and 5×10^{-3}M at $[H^+] = 0.001$ M and I=1.10 M ($NaClO_4$).

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 ($NaClO_4$) and $[H^+]$ maintained as 0.01M unless otherwise stated.

Plots of $\log_{(A_\infty - A_t)}$ against time, t, (where A_∞ and A_t 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

$$(A_\infty - A_t) = (A_\infty - A_o)\, e^{k_{obs} \cdot t} \ldots\ldots (1)$$

A_o is the absorbance at the beginning of the reaction. Second order rate constants, k_2, were obtained as ratios of k_{obs} to $[H_2A]$. Rate constant of two runs agreed to within ±2.4%. Reported rate constants are the means of two runs.

RESULTS AND DISCUSSION

Mole ratio determination showed that for ever mole of periodate ion reduced, 3.5 moles o ascorbic acid were oxidised. Plot of A_∞ versu mole ratio (IO_4^-/H_2A) had a sharp break at abou 0.278 corresponding approximately to a mol ratio of 1:3.5. This mole ratio is consistent wit equation (2)

$$2IO_4^- + 7H_2A + 2H^+ \rightarrow 8H_2O + 7A + \ldots\ldots\ldots\ldots (2)$$

Whereas no report of the reaction of H_2A wit oxyanions exists, its reactions with metal ion where dehydroascorbic acid (A) was produced a the main organic product has been reported[9,11] This product is obtained if H_2A acts as a two electron reagent as the above reaction suggests The formation of iodine was indicated by it characteristic yellowish brown colour and it formation of a bluish-black colour when mixe with starch solution. Also the yellowish - brow coloured reaction mixture showed absorption a about 480nm. This is indicative of aqueou iodine[22,23]

Under pseudo-first order conditions with $[H_2A$ at least 20-fold excess over $[10_4^-]$ and at constan ionic strength, pseudo-first order plots showe close linearity for at least 80% extent o reaction. This implies that the order of reactio with respect to $[IO_4^-]$ is unity. Pseudo - firs order rate constants, determined as slopes o these plots, are shown in Table 1. The rate o reaction increases with increase in $[H_2A]$. Als the plot of $\log k_{obs}$ versus log $[H_2A]$ was linea with a slope of 1.09 implying first orde dependence of rate on $[H_2A]$ as shown in Fig. 1 This observation corroborates othe observations[12,13] on the oxidation of some iro (II) and cobalt (II) complexes by periodate. Th rate law for the reaction is given as equation (3

$$-\frac{d[IO_4^-]}{dt} = k_2\,[H_2A]\,[IO_4^-] \ldots\ldots (3)$$

Within the range $0.001 \leq [H^+] \leq 0.1$M a $[H_2A] = 0.02$M and constant ionic strength th rate of reaction increases with increase in $[H^+$ (Table 1). A plot of second order rate constant k_2, against $[H^+]$ in the above acid range wa

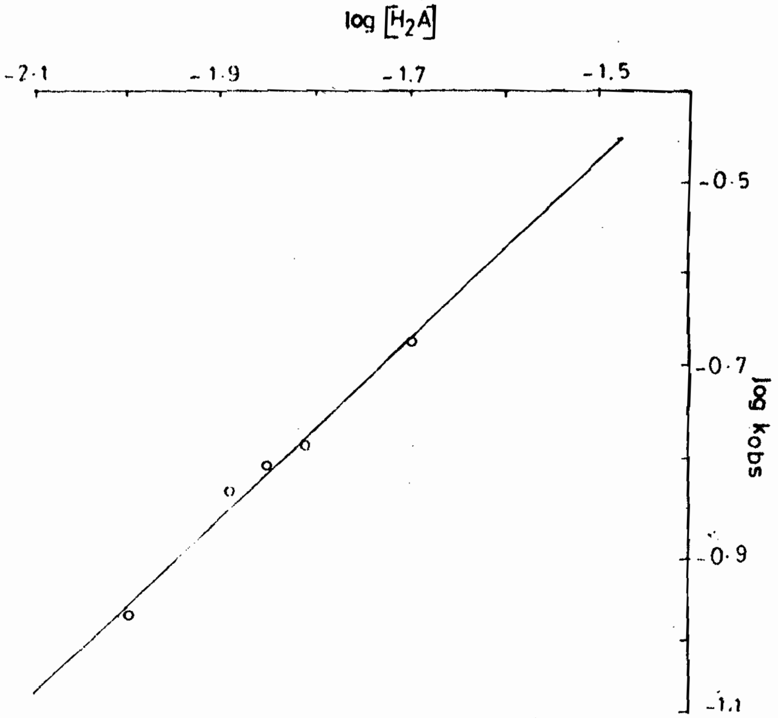

Fig. 1 : Plot of log k_{obs} versus log [H$_2$A] for the reduction of IO$_4^-$ by H$_2$A at λ_{max} = 480nm and T = 26°C

Table 1: Second order rate constants for the reduction of IO$_4^-$ by H$_2$A at [IO$_4^-$] = 1x10^{-3}M λ_{max} = 480nm and T = 26.0 ± 0.1°C.

10^2[H$_2$A], M	10^2[H$^+$], M	I,M(NaClO$_4$)	k_2,M^{-1}s^{-1}
1.0	1.0	1.10	10.82
1.3	1.0	1.10	10.82
1.4	1.0	1.10	1.28
1.5	1.0	1.10	10.71
2.0	1.0	1.10	10.59
2.0	0.5	1.10	8.89
2.0	0.7	1.10	9.90
2.0	1.0	1.10	10.82
2.0	1.5	1.10	11.52
2.0	3.5	1.10	16.12
2.0	0.7	0.05	10.02
2.0	0.7	1.10	9.97
2.0	0.7	1.00	10.00

Table 2: Dependence of second order rate constant on anions and dielectric constant, D, for reduction of IO$_4^-$ by H$_2$A at [H$_2$A] = 2.0 x 10^{-2} M [IO$_4^-$] = 1x10^{-3}M, I=1.10M (NaClO$_4$), λ_{max} = 480nm and T = 26.0 ± 0.1°C.

	10^2[X],M	k_2,M^{-1}s^{-1}
X=CH$_3$COO$^-$	1.0	9.21
	3.0	4.30
	4.0	1.01
	5.0	0.90
	10.0	0.76
	50.0	-----*
X=NO$_3^-$	1.0	8.00
	5.0	2.30
	10.0	1.60
	50.0	1.55
	100.0	1.20
	D	
	81.39	10.48
	77.10	10.36
	72.19	10.71
	66.68	10.13

*(no reaction even after 5 hours).

linear and fitted equation (4)

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

Where a and b were determined by the method of least mean squares to be 8.3 $M^{-1}s^{-1}$ and 2.9 x 10^4 $M^{-3}s^{-1}$ respectively at 26.0 ± 0.1°C and I = 1.10M ($NaClO_4$). Substituting the expression for K_2 into equation (3) gives equation (5)

$$-\frac{[IO_4^-]}{dt} = (a + b[H^+]^2)\,[IO_4^-]\,[H_2A] \ldots\ldots\ldots\ldots\ldots (5).$$

This relationship is similar to the kinetic pattern of the reation of IO_4^- with 12-tungstocobaltate (III)[20] and oxo-bridged ruthenium dimer[24]. Whereas most reactions of ascorbic acid show inverse acid dependence except in strong acid media[9-10], reactions of IO_4^- show direct acid dependence as the rate of oxygen exchange is dependent on concentration of hydrogen ion[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 not unconnected with the various equilibria established by IO_4^- in aqueous solution; species like H_5IO_6, $H_4IO_6^-$, $H_3IO_6^{2-}$ and IO_4^- have been reported to exist in aqueous solutions of IO_4^-. The species IO_4^- and H_5IO_6 are known to predominate in acidic IO_4^- solutions at 25°C with the proportion of H_5IO_6 increasing with decreasing pH[27]. 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^o 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^o as main reductants[9,11].

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

$$IO_4^- + H^+ + 2H_2O \overset{k_1}{\rightleftharpoons} H_5IO_6 \ldots\ldots\ldots (6)$$

$$H_2A + H \overset{k_2}{\rightleftharpoons} H_3A^+ \ldots\ldots\ldots\ldots\ldots (7)$$

$$H_5IO_6 + H_3A^+ \overset{k_3}{\rightleftharpoons} [H_5IO_6, H_3A^+] \ldots\ldots (8)$$

$$[H_5IO_6, H_3A^+] \overset{k_4}{\rightleftharpoons} 4H_2O + A + IO_2^o \ldots (9)$$

$$IO_2^o + 4H_2A \overset{k_5}{\rightleftharpoons} 4HA^o + 2H_2O + I^o \ldots (10$$

$$IO_4^- + H_2A \overset{k_6}{\rightleftharpoons} OH^- + A + HIO_3 \ldots\ldots (11$$

$$HIO_3 + H_2A \overset{k_7}{\rightleftharpoons} 2H_2O + HIO_2^o + A^o \ldots (12$$

$$HIO_2^o + 2HA^o + H^+ \overset{k_8}{\rightleftharpoons} H_2O + \tfrac{1}{2}I_2 + 2A \ldots\ldots\ldots (13)$$

$$2HA^o + A^o \overset{k_9}{\rightleftharpoons} 2H^+ + 3A \ldots\ldots\ldots (14)$$

$$OH^- + H^+ \rightarrow H_2O \ldots\ldots\ldots\ldots (15)$$

$$I^o \rightarrow \tfrac{1}{2}I_2 \ldots\ldots\ldots\ldots\ldots\ldots (16)$$

$$\text{Rate} = k_4[H_5IO_6, H_3A^+] + k_6[IO_4][H_2A] \ldots (17$$

Where $[H_5IO_6, H_3A^+] =$
$k_3[H_5IO_6][H_3A^+] \ldots\ldots\ldots\ldots (18)$

and $[H_3A^+] = k_2[H^+][H_2A] \ldots\ldots\ldots\ldots (19)$

and $[H_5{}^+IO_6] = k_1[IO_4^-][H^+] \ldots\ldots\ldots\ldots (20)$

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

$\text{Rate} = k_1k_2k_3\ [H_2A][IO_4^-][H^+]^2 + k_6[IO_4^-$
$[H_2A] \ldots\ldots\ldots\ldots\ldots\ldots$

$= (k_3k_2k_1k_4\ [H^+]^2 + k_6)\ [IO_4^-][H_2A] \ldots (21)$

Equation (21) is similar to equation (5) where a $= k_6$ and $b = k_3k_2k_1k_4$.

The possibility of the formation of ascorbate cation, H_3A^+ (of eqn (7)) at pH 6.05 has been reported for the reaction of $[Mn^{III}(salen)H_2O]^+$ with H_2A[9]. At this point the existence of HA^- is thought to be improbable. The reaction between H_2A and pertechnate ion in strong acid media was also observed to involve H_3A^+. The reaction also had second order dependence on hydrogen ion concentration[10]. 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 only showed 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 neglible negative intercept[33]. 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.

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