Detection of Free Radical Intermediate during the Oxidation of Ascorbic acid by Cyclic Voltammetry

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Ascorbic acid undergoes oxidation in two stages in non aqueous medium. In the first step, dehydroascorbic acid is formed as the product. The first oxidation step takes place in two steps on Pt electrode. The formation of radical intermediate in this first step is confirmed by *in-situ* esr - electrochemical experiments. The radical intermediate could not be identified on a GC electrode. The details of the second stage of oxidation are not very clear.

The elecctrochemical oxidation of L-ascorbic acid reported sofar [1-8] has shown the overall oxidation to be a 2e, $2H^+$ step giving dehydroascorbic acid as the product. Study of the oxidation of ascorbic acid at platinum, tantalum, gold and mercury electrodes in aqueous solution in esr cavity has given evidence for a relatively long lived radical intermediate species [9]. So far, all the investigations have been carried out only in aqueous medium. Though there have been indications for free radical formation [10], it is not yet shown from conventional electrochemical studies that such radical is the primary reduction product. To get a direct evidence for the generation of a radical anion in electrochemical reactions in an aprotic solvent, the study of electrochemical oxidation of ascorbic acid in DMF was taken up for the first time. In this present study, an attempt has been made to detect the radical intermediate formation on the voltammetric time scale and confirm the same through *in-situ* esr - electrochemical studies under the same conditions.

EXPERIMENTAL

The cyclic voltammograms were recorded in a medium containing DMF and tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. Ascorbic acid (GR) was used for the investigations. A three compartment cell was used for the studies. Working electrode was either GC (BAS, MF) or Pt (BAS, MF 2013). A Pt foil was used as the counter electrode; Ag/AgCl was the reference electrode. The solutions were deaerated with nitrogen gas for an hour.

Cyclic voltammograms were recorded using a potentiostat (LB 75 M, Wenking) coupled to a scan generator (Wenking VSG 72) and a X-Y/t recorder (Rikadenki, Japan). *In-situ* esr - electrochemical studies were carried out in a thin layer quartz cell, where Pt gauze served as the working electrode, Ag wire as the reference electrode and tungsten as the counter electrode. The esr spectrum was recorded in a Varian (112 x/q) band spectrometer.

J.Electrochem Soc. India Vol 43 - 4 (1994) 227-231

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RESULTS

Investigations with GC electrode

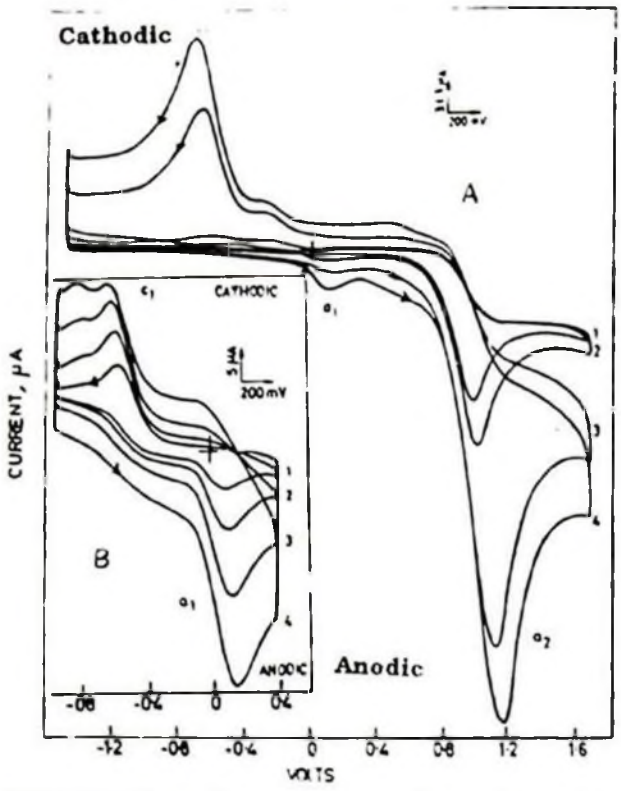


Fig.1 Cyclic voltammograms of ascorbic acid (9.09 mm) on GC electrode in the medium DMF/TBAP

A) Scan range -1.2 V to +1.7 V
Scan rates (mV/s) 1) 20 (2) 40 (3) 200 (4) 400

B) Scan range -1.2 V to +0.4 V;
Scan rates (mV/s) 1) 50 (2) 100 (3) 200 (4) 400

Fig. 1A represents the cyclic voltammogram in the medium DMF/TBAP on GC electrode at different scan rates in the scan range - -1.2 V to +1.7 V. As the scan rate is increased, the peaks become better defined. The peak values are presented in Table 1. Two anodic peaks (a1 and a2) are observed. The peaks are at 0 mV and +920 mV respectively at a scan rate of 50 mV/s. On the reverse scan at this scan rate, a single cathodic peak c1, occurs at - 760 mV.

Fig. 1B represents the cyclic voltammogram in the restricted potential range -1 V to +0.4 V to cover the anodic peak a1 alone. Comparing Fig. 1A and B, it is observed that the peak c1 is the cathodic peak corresponding to the anodic peak a1.

Fig. 2A represents the cyclic voltammograms of ascorbic acid in the medium DMF/TBAP on platinum electrode in the scan range -1.2 V to +1.7 V at different scan rates. On the anodic side, there are three anodic peaks -a1, a'1 and a2; two peaks are observed on the cathodic side. It was observed from the figure that the potentials of all the above peaks vary with scan rate. Peak a1 occurs

Table 1

Peak Potentials and Currents in Cyclic Voltammograms of Ascorbic acid

GC electrode; Potential range -1.2 V to +1.7 V;
Medium DMF/TBAP; Conc. of ascorbic acid 9.09 mM;

Scan rate	Peak Potentials (mV)			Peak Currents (μA)		
mV/s	a1	a2	c1	a1	a2	c1
20	-	960	-	-	133.2	-
40	60	980	-700	9.9	176.5	26.6
200	100	1100	-720	19.0	362.9	103.2
400	100	1140	-740	23.3	399.6	156.5

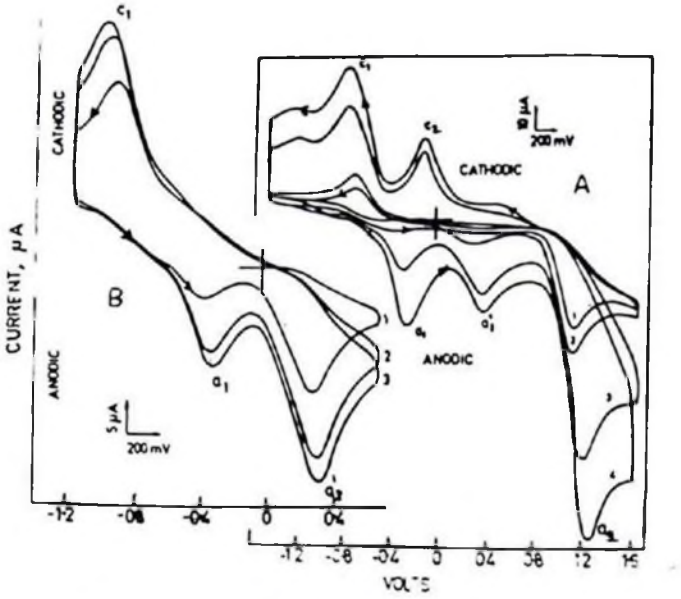


Fig2. Cylic voltammograms of ascorbic acid (9.09 mm) in the medium DMF/TBAP on Pt electrode

A) Scan range -1.2 V to +1.7 V; scan rates (mV/s) 1) 20 (2) 40 (3) 200 (4) 400

B) Scan range -1.2 V to +0.6 V; scan rates (mV/s) 1) 200 (2) 400 (3) 500

at a potential of -0.3 V and a2 at +1.260 V at scan rate of 200 mV/s. c2 occurs only at higher scan rates (> 200 mV/s). At 200 mV/s, c2 occurs at a potential of -0.1 V and c1 at a potential of - 0.92 V.

The voltammograms taken in the restricted potential range to cover only peaks a1 and a'1 (Fig 2B) does not show the peak c2. This indicats that c2 is the reverse peak for a2. Typical values of potential current values are given in Table 2.

DISCUSSION

It can be inferred from the results that the oxidation of ascorbic acid occurs in two stages corresponding to two peaks a1, a2 (Fig. 1). In the case of Pt, the first stage of oxidation takes place in two steps and hence three anodic peaks (a1, a'1 and a2) are obtained (Fig.2). The value of n was determined to be 2 from the peak current values of a1 (Fig.1A). Spectral study shows the product formed at the peak a1 to be dehydroascorbic acid. In the case of Pt electrode, the peak a1 is split into two peaks as a1 and a'1; the product obtained at a'1 was found to be dehydroascrobic acid. Hence peak a1 at Pt electrode represents a 1e, electro-oxidation giving a radical anion which undergoes a second irreversible one electron oxidation to dehydroascorbic acid.

Table 2

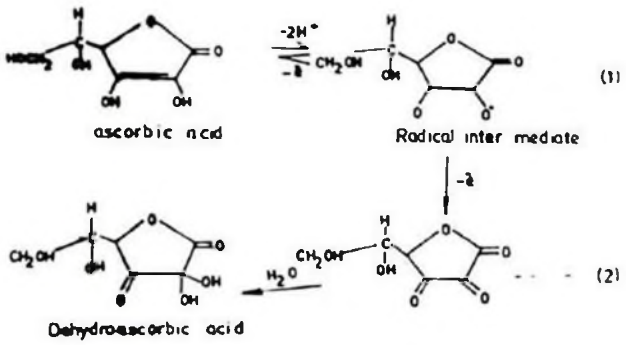
Peak Potential and Current in Cyclic voltammograms of Ascorbic acid

Electrode Pt; Medium DMF/TBAP; Potential range -1.0 V to +1.7 V; Concentration of ascorbic acid 9.09 mM

Scan rate	Peak Potentials (mV)					Peak Currents (μA)			
mV/s	a1	a1	a2	c1	c2	a1	a1	a2	c1
20	*	*	1160	-920	*	*	*	38	12
40	-400	300	1180	-940	*	*	*	47	17
200	-380	380	1260	-1000	-120	16	20	80	35
400	340	400	1320	-1020	-120	35	17	105	47

* indicates that the peak could not be resolved at the current sensitivity level employed.

In the case of GC electrode, the oxidation to dehydroascorbic acid occurs in a single step. On the Pt electrode, the formation of radical intermediate could be clearly seen. The peak potential of the radical formation is -400 mV. When the scan range is restricted upto -400 mV, the reverse peak c1 appears at -920 mV indicating that c1 is the corresponding peak for a1. This indicates that L-ascorbic acid and its 1 e radical oxidation product do not form a reversible couple as given in literature reports [8]. The peak potential also coincides with that reported in the literature. Hence the mechanism of oxidation at Pt electrode is as given below:



The participation of hydrogen ions during the oxidation step was proposed in analogy to the literature reports [6,7,11]. The reactions 1 and 2 can be seperately identified on a platinum electrode, but it could not be sensed on a GC electrode. This must be due to the inherent slow electron transfer rate [12] on the GC compared to Pt.

Controlled potential electrolysis was performed at Pt gauze electrode in DMF/ TBAP medium in a quartz electrochemical cell at -400 mV and *in-situ* esr signal was recorded (Fig.3). The free radical signal occurs at a field of 3360 G. The line width is 2.5 G. The radical formation was thus confirmed by esr spectra taken during electrolysis. The intensity of the spectrum remains unchanged with increase in time of electrolysis indicating that the product does not get occumulated. The radical formed reacts immediately to give further products. Hence the intensity remains the same. The signal obtained was similar to that observed earlier by Aldaz et.al. [9]. However further resolution of the spectrum was not possible with the instrumentation available.

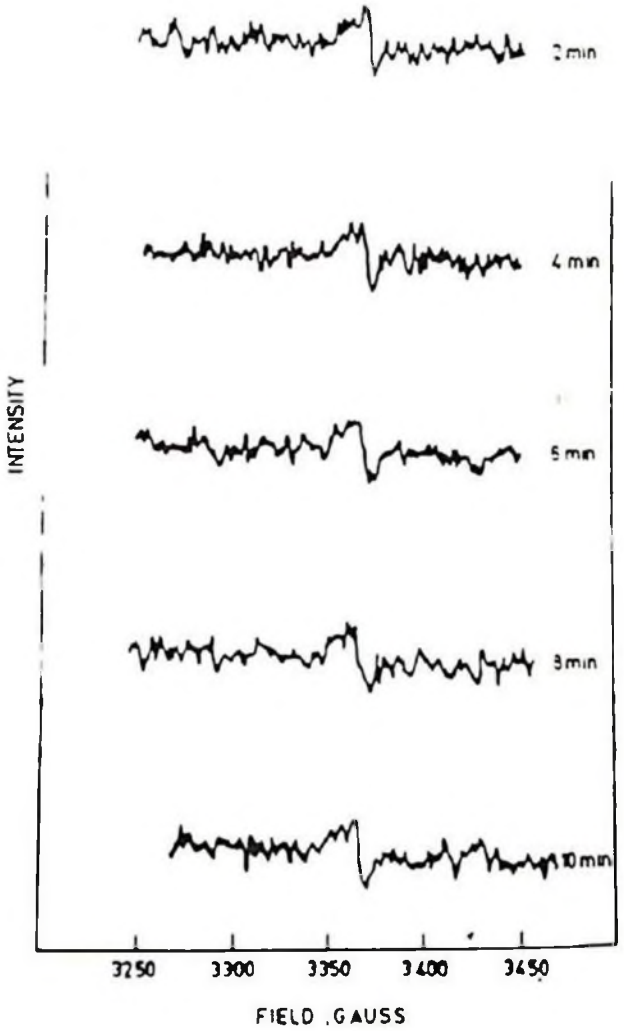
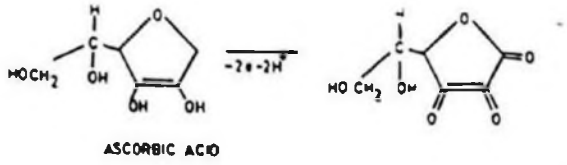
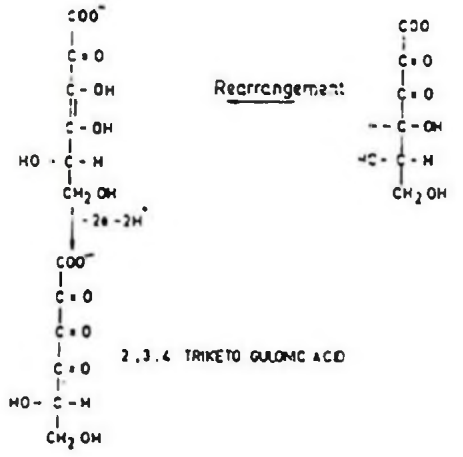


Fig3. ESR spectrum of the radical intermediate obtained during oxidation on Pt electrode in DMF/TBAP

The second stage of oxidation is represented by the peak a2. The reverse peak of a2 is seen at high scan rates (c2) around 0 V, (Fig.2). From the peak current value, n was found to be 2. The products of oxidation could be 2,3,4 triketogulonic acid as given below:



ASCORBIC ACID



2,3,4 TRIKETO GULONIC ACID

The exact details of this mechanism could not be confirmed in the present investigation.

ACKNOWLEDGEMENT

The authors wish to thank Prof. S. Subramanian, Head, RSIC, IIT, Madras for his permission to do the *in-situ* esr electrochemical experiments at RSIC, IIT, Madras.

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