# Polarographic Studies on the Pulse Radiolytic Oxidation of Ascorbic Acid in Aqueous Solution

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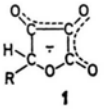
The radicals produced by the oxidation of ascorbic acid in aqueous solution by ionizing radiation have been investigated by pulse radiolytic[1-3] and ESR[4] methods. A relatively long-lived intermediate of this oxidation is the ascorbic acid radical anion **1**.



**1**

Oxidation can occur by the ·OH radicals produced in the radiolysis of aqueous solutions or by $Br^-_2$ radical anions in solutions containing $Br^-$. In the case of the reaction of ·OH radicals, precursors of the ascorbic acid radical anion were shown to have life-times between 5 and 1500 $\mu$sec[3]. By comparison, in $Br^-$ containing solutions, these precursors have very short half-lives (few microseconds). In the present work simultaneous optical absorption and polarographic current measurements were carried out to investigate the polarographic behavior of radical anion **1** and also to obtain additional evidence for the existence of the precursors in ·OH radical reaction with ascorbic acid.

The experimental details of the polarographic technique have been described elsewhere[5-7]. In principle, aqueous solutions of ascorbic acid ($5 \cdot 10^{-4}$ M), saturated with $N_2O$, were pulse irradiated by a 20 ns pulse from a 12 MeV, 6 A Linear Accelerator. Sodium sulphate (0.35 M) was used as the supporting electrolyte. The potential of the hanging mercury drop was measured *vs* a saturated calomel electrode. In some experiments the ascorbic acid solution contained in addition $5 \cdot 10^{-2}$ M $Br^-$ ions. Under these conditions, the radiation produced ·OH radicals react mainly with $Br^-$ to produce $Br_2^-$. The reaction of $Br_2^-$ with ascorbic acid is complete in less than 1 $\mu$sec[3]. As can be recognized from curve 1b obtained in $Br^-$ containing solutions at pH = 10, the optical absorption of the radical anion at 360 nm is present immediately after the pulse and was nearly constant during the time of observation. Curve 1a shows the corresponding polarographic current-time curve at -0.8 V. The shape of the current-time curve (Fig. 1a) depends on several factors which are well explained elsewhere[7-10].

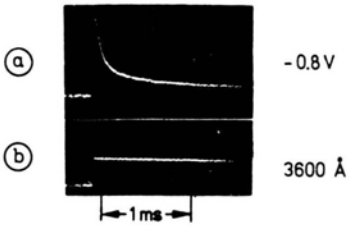



Fig. 1. Current *vs* time-curve and optical absorption *vs* time curve of pulse irradiated ascorbic acid solution containing $Br^-$ at pH = 10 [ascorbic acid]: $5 \cdot 10^{-4}$M, [$Br^-$]: $5 \cdot 10^{-2}$M.

Short time polarograms for $Br^-$ free and $Br^-$ containing solutions are shown by curves b and a in Fig. 2. The cathodic current after 20 $\mu$sec is plotted here *vs* the potential. A polarographic wave is observed in both cases between 0 and -0.7 V (*vs* the saturated calomel electrode) and a plateau between -0.7 to -1.1 V. The half-wave potential values calculated from the curves a and b are nearly similar which shows that the same intermediate which is presumably the radical anion **1** is obtained both by the reation of ·OH radicals and $Br_2^-$ with ascorbic acid. The electrokinetic analysis of the reduction wave of radical anion **1** has been reported elsewhere[7]. The slight increase in current at potentials more negative than -1.1 V of curve a is attributed to hydrogen peroxide produced radiolytically in small yield. The limiting current value between -0.7 and -1.1 V is about 30% smaller in the case of $Br^-$ free solutions, indicating that less ascorbic acid radicals are present here after 20 $\mu$sec than in the $Br^-$ containing solutions. This observation is in agreement with the pulse radiolytic investigation according to which all of the

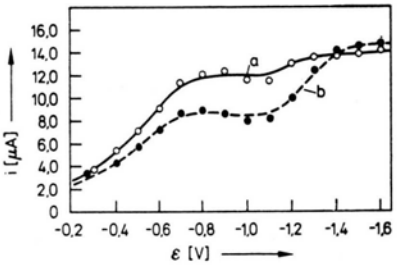



Fig. 2. Short-time polarograms of the ascorbic acid radical anion *1* in $N_2O$ saturated aqueous solutions of ascorbic acid ($5 \cdot 10^{-4}$M) at pH = 10; a. With $5 \cdot 10^{-2}$M $Br^-$; b. without $Br^-$.

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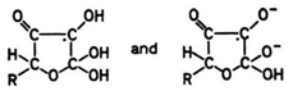
ascorbic acid radicals are formed within only a few microseconds after the pulse from the $Br^-$ containing solutions while about 30% of the radicals will be formed during much longer times after the pulse from the $\cdot OH$ containing precursors[3]. The final plateau above -1.4 V has the same height in both curves 2a and 2b. The increase in current of curve b between -1.1 and -1.4 V is attributed to $H_2O_2$ and the reduction of the longer-lived precursors of the ascorbic acid radical. Apparently, the precursors formed by $\cdot$ OH addition to ascorbic acid such as



are less readily reduced at the mercury electrode than the radical anion **1** itself and will, therefore, contribute to current only at more negative potentials.

Similar studies in $Br^-$ free and $Br^-$ containing ascorbic acid solutions were also carried out at pH = 3.6. Current measurements were made up to -1.2 V. The results are qualitatively in agreement with those obtained in alkaline solutions. The extent to which the limiting current value for $Br^-$ free solutions is lower is even higher than 30%. These studies are also in agreement with the pulse radiolytic investigation[3].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