NOTE

Radiolysis of Ascorbic Acid in Aqueous Solution

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1. Introduction

A number of studies on the radiation-induced decomposition of several vitamins have been reported in connection with the application of ionizing radiation to the sterilization of foods and drugs. Ascorbic acid, a biologically important substance as vitamin C, was found to be highly sensitive to radiation¹⁻⁴.

The present paper reports the effect of ⁶⁰Co γ -radiation on ascorbic acid in deaerated aqueous solution with no additives which are ordinarily used to avoid the spontaneous oxidation of the solute during the irradiation. The reactivity of H atoms toward ascorbic acid was also determined by the scavenger method.

2. Experimental

Ascorbic acid (Merck reagent grade) was used in its original state. Alkaline permanganate aqueous solution was distilled three times and the obtained water was used to prepare the solution in every run. Five ml of aqueous solution of ascorbic acid was placed in a glass tube 13 mm i.d. which served as a irradiation cell. A break-seal was attached to the top of the tube when the gas analysis was required. The material connected with a vacuum line was outgassed by means of freeze-thaw cycles. The all irradiations were made at 17°C with ⁶⁰Co gamma rays at a dose rate of $1.44 \times 10^{18} \text{ eV m}^{-2} \text{ h}^{-1}$. After irradiation, methaphosphoric acid was added to the solution to avoid the spontaneous oxidation of the solute during the course of the analysis. Ascorbic acid was

determined by titration with 2,6-dichlorophenol indophenol. Dehydroascorbic acid was determined spectrophotometrically with 2,4-dinitrophenyl hydrazine. The determination of hydrogen radiolysed from the solution was carried out by gas chromatography using a molecular sieve 5A column with argon as a carrier.

3. Results

Figure 1 presents our results of the radiolysis of deaerated 1 mM ascorbic acid solution at its natural pH (3.6). The radiolytic yield of ascorbic acid, AH_2 , expressed in G value is 3.6. Yields of dehydroascorbic acid, $G(\text{A})$, and hydrogen, $G(\text{H}_2)$, are 1.9 and 0.49, respectively. As observed in Fig. 2, $G(-\text{AH}_2)$ and $G(\text{H}_2)$ are constant within the range of concentration from 0.5 to 10 mM for doses up to

Fig. 1 Radiolysis of 1 mM ascorbic acid in deaerated system.
○: ascorbic acid (AH_2) radiolysed,
△: dehydroascorbic acid (A),
●: hydrogen

$6 \times 10^{18} \text{ eV ml}^{-1}$, the highest dose used. It is also shown in Fig. 2 that the addition of HPO_3 (6%) does not affect the hydrogen yield in the solution.

Fig. 2 Radiolytic yield as a function of initial concentration.

○: aqueous solution,
●: 6% HPO_3 solution,
△: N_2O (3~10 mM) presented.

4. Discussion

The active species initially produced during the absorption of ionizing radiation in water are usually hydrated electrons, H atoms and OH radicals. It has been proposed by Rao⁴⁾ that H atom abstracts the hydrogen atom from ascorbic acid to form hydrogen by the following reaction.

Since $G(\text{H}_2)$ in the present experiment is nearly equal to the molecular yield of hydrogen, G_{H_2} , from irradiated water and independent of the concentrations of solute and hydrogen ion, it is unlikely that reaction (1) could be responsible for the formation of hydrogen. As to the fate of H atoms, an addition reaction onto an unsaturated bond, $-\text{C}(\text{OH})=\text{C}(\text{OH})-$, in ascorbic acid molecule may occur as follows.

To determine the rate constant of reaction (2), 2-propanol was added to the solution containing nitrous oxide (10 mM) which converts e_{aq}^- to OH radical very efficiently. If H atoms also react with 2-propanol according to reaction (3), equation (1) should describe the dependence of difference in hydrogen yield

($\Delta G(\text{H}_2)$) in the solution containing nitrous oxide without and with 2-propanol on solute composition.

$$\frac{1}{\Delta G(\text{H}_2)} = \frac{1}{G_{\text{H}}} \left\{ 1 + \frac{k_2(\text{AH}_2)}{k_3(2\text{-propanol})} \right\} \quad (1)$$

Figure 3 shows this to be the case and consequently $k_2/k_3 = 4.5$ and $G_{\text{H}} = 0.56$ which agree well with the accepted values⁵⁾. Taking $3.9 \times 10^7 \text{ M}^{-1} \cdot \text{sec}^{-1}$ for k_3 ⁶⁾, k_2 is to be $2 \times 10^8 \text{ M}^{-1} \cdot \text{sec}^{-1}$.

Fig. 3 Competition for H atom between ascorbic acid and 2-propanol plotted according to eq. (1).

Since the reactivity of H atoms, the typical reducing species, towards AH_2 is fairly high as demonstrated above, it may be reasonable to assume that e_{aq}^- reacts with AH_2 in the same way as H atom does.

It has been found by us that N_2O does not affect $G(-\text{AH}_2)$. This should be due to that OH and e_{aq}^- have nearly equal reactivity towards AH_2 . The reaction of OH with AH_2 has been proposed as follows.

The rate constant of reaction (5) is $7.2 \times 10^9 \text{ M}^{-1} \cdot \text{sec}^{-1}$ by pulse radiolysis⁷⁾ and this large value is undoubtedly due to the fact that AH_2 has easily oxidizable functional group.

As to the fate of these oxidized and reduced intermediates such as AH and AH_3 , the following reactions are taken into consideration.

If e_{aq}^- , H and OH would radiolyse AH_2 as in reaction (2), (4) and (5), $G(-\text{AH}_2)$ will be about 6, which corresponds to the total radical yield ($G_{\text{e}_{\text{aq}}^-} + G_{\text{H}} + G_{\text{OH}}$). However, our observed $G(-\text{AH}_2)$ (=3.6) is much lower than the total yield and this should be due to the reproduction of AH_2 through reaction (6) and (8). The product AH_4 is not yet identified but probably corresponds to gulono- γ -lactone which is oxidized to AH_2 by means of Fenton's reagent according to Berends, et al.⁸⁾ The formation of dehydroascorbic acid, A, as was illustrated in Fig. 1, depends on the disproportionation by reaction (6) and on reaction (7). $G(-\text{AH}_2)$ and $G(\text{A})$ cannot be estimated on the kinetic basis, because we cannot determine the proportion of rate constants of reaction (6), (7) and (8).

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