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ABSORPTION SPECTRUM OF THE 2,3-DIHYDROXY-2-PROPENAL (TRIOSE REDUCTONE) RADICAL

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Absorption spectrum of 2,3-dihydroxy-2-propenal (triose reductone) radical was observed upon the oxidation by anion radicals $(SCN)_2^{-\cdot}$ and $Br_2^{-\cdot}$ in pulse-irradiated solutions. The triose reductone radical was found to decay by a bimolecular reaction.

2,3-Dihydroxy-2-propenal (triose reductone) is one of most simple reductones and shows strong reducing ability as in the case of L-ascorbic acid. Triose reductone has been found to yield in biological systems.[1-3] We have studied the oxidations of triose reductone by oxygen and hydrogen peroxide,[4] and peroxodisulfate ion[5] kinetically in which a scheme involving the triose reductone radical has been proposed.

The enzymatic oxidation of triose reductone has been reported to produce the free radical,[6] the electron spin resonance spectrum of which has been observed. We have studied the oxidation of triose reductone in aqueous solution by the oxidizing anion radicals $X_2^{-\cdot}$ (X: SCN, Br), using the pulse radiolysis technique. Pulses of 10-MeV electrons of 0.5 - 3 μs duration were delivered from an electron linear accelerator to a N_2O saturated solution of 2×10^{-2} M (1 M = 1 mol dm^{-3}) in KSCN and 3×10^{-4} M in triose reductone at pH 9.4 adjusted with sodium hydroxide solution. A transient absorption was observed at wavelengths longer than those at which the triose reductone and its permanent reaction products absorb. The optical densities at the end of the pulse were measured at wavelengths 350-460 nm with doses of about 840 rads. Figure 1 shows the spectrum which shows an absorption maximum at 400 nm. The same spectrum was obtained in a N_2O-saturated solution of 2×10^{-2} M in KBr and 3×10^{-4} M in triose reductone at pH 9.6. The reaction scheme of the oxidation of triose reductone is described as follows (TRH_2 = triose reductone):

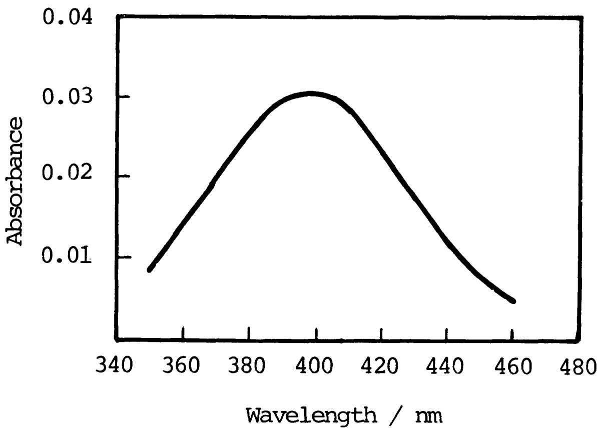

Fig. 1. Absorption spectrum of the triose reductone radical.

$$H_2O \rightsquigarrow H,\ e^-_{aq},\ OH,\ H_2O_2,\ H_2 \qquad (1)$$

$$N_2O + e^-_{aq} + H_2O \longrightarrow N_2 + OH + OH^- \qquad (2)$$

$$X^- + OH \longrightarrow X\cdot + OH^- \qquad (3)$$

$$X\cdot + X^- \longrightarrow X_2^{-\cdot} \qquad (4)$$

$$(X = SCN,\ Br)$$

$$TRH_2 \rightleftharpoons TRH^- + H^+ \qquad (5)$$

$$pK_1 = 5$$

$$TRH^- + X_2^{-\cdot} \longrightarrow TRH\cdot (\text{or } TR^{-\cdot} + H^+) + 2X^- \qquad (6)$$

N_2O scavenges e^-_{aq} and converts it into the OH radical. All the OH radicals react with X^- (X = SCN, Br) and produce oxidizing anion radicals $X_2^{-\cdot}$. Then, they oxidize the triose reductone to yield the triose reductone radical. The decay of the radical was of second-order with doses ranging from 300 to 1700 rads. The decay rate value of $2k/\varepsilon$, where 2k is the bimolecular reaction rate constant for the triose reductone radical and ε is the molar extinction coefficient at 400 nm, is 5.9×10^4 and 6.7×10^4 cm s^{-1} for KSCN and KBr systems mentioned above. The total yield of the triose reductone radical was assumed to be $G_{e^-_{aq}} + G_{OH} = 2.7 + 2.8 = 5.5$ from the above reaction scheme. Then, the extinction coefficient was determined to be 6200 M^{-1} cm^{-1} at 400 nm. The same spectrum as that shown in Fig. 1 was observed in a pulse-irradiated N_2O saturated solution of 1×10^{-4} M triose reductone, but the yield of the radical was evaluated about half the G value of the OH radical from the optical densities. We are continuing studies to clarify the reason for the result and the reaction mechanism.

References

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