Kinetic Studies of the Oxidation of 2,3-Dihydroxy-2-propenal (Triose Reductone) by the Peroxodisulfate Ion

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Kinetic studies of the oxidation of 2,3-dihydroxy-2-propenal (triose reductone) by the peroxodisulfate ion ($S_2O_8^{2-}$) were carried out between pH 4.1 and 5.9 at various temperatures (10—30 °C) and for ionic strengths (I) (0.07 to 1.07 M (1 M=1 mol dm^{-3})) which were adjusted using $NaClO_4$. The pH dependence of the reaction rates revealed that the singly-charged anion (RH^-) was chiefly responsible for the reaction, while undissociated reductone was inactive to peroxodisulfate ion. The rate constant (k_2) of RH^- with $S_2O_8^{2-}$ was 0.79 M^{-1} s^{-1} at 25 °C and I=1.07 M (ΔH^{*}=37 kJ mol^{-1}, ΔS^{*}=−123 J deg^{-1} mol^{-1}). A relationship of $\log k_2 = -0.95 + 1.88 I^{1/2}/(1+I^{1/2})$ was found at 30 °C.

The 2,3-dihydroxy-2-propenal produced from dextrose by alkaline hydrolysis is called triose reductone because of its strong reducing ability. The reductone is the simplest in structure of the compounds having an enediol group; the physiologically important L-ascorbic acid is a typical compound of this structure. Thus kinetic studies on the reaction of triose reductone would help to clarify the mechanisms of the physiological activities of enediol compounds. Previously, we studied the kinetics of the autoxidation of triose reductone in an aqueous solution and compared the rate constants with those of L-ascorbic acid.[1] The peroxodisulfate ion is known as a powerful two-electron oxidizing agent which employes an electron-transfer mechanism. The reaction with alcohol gives alcohol radicals and sulfate anion radicals.[2] In an effort to resolve whether the sulfate anion radicals work as an oxidizing species in the present experiment, we have studied the kinetics of the oxidation of triose reductone by aqueous peroxodisulfate ion in the pH range 4.1—5.9 and have compared the kinetic parameters with those for the reaction of L-ascorbic acid.[3]

Experimental

Materials. Triose reductone was prepared and purified by the method described in the literature.[4] Potassium peroxodisulfate and sodium perchlorate of analytical grade of E. Merck were used without further purification. All the other chemicals used were guaranteed reagents of the Wako Pure Chemicals Co. Ltd.

Reaction Solution. The triose reductone solution was prepared by dissolving 2 mg of the compound in 0.5 dm^3 of the aqueous solution saturated with argon (a high-purity argon gas was bubbled through the solution to remove the dissolved oxygen) and containing 50 mM of acetate buffer, 5 mM of disodium dihydrogen ethylenediaminetetraacetate (EDTA), and a given weight of sodium perchlorate; the bubbling of an argon gas was continued to avoid oxygen contamination. The potassium peroxodisulfate solution was prepared by dissolving 0.9 g of the solid in 0.25 dm^3 of water and then the dissolved oxygen was removed by the bubbling of argon through the solution.

Kinetic Method. Since the triose reductone is sensitive to oxygen, the reductone solution was transferred into a quartz cell under replacement with argon gas. The reaction was started by mixing the peroxodisulfate solution with the reductone solution. The pH value, ionic strength, and temperature of the reaction solution were kept constant during the reaction. Kinetic data were obtained spectrophotometrically by using a Hitachi 323 Recording Spectrophotometer. The temperature was controlled by circulating thermostated water around the cell housing. The reaction were followed by measuring the decreasing absorption of triose reductone at a wavelength between 268 and 293 nm. The pH values of the reaction solutions were measured with a Toa Dempa HM-20E digital pH meter immediately after the measurement of the absorption. The activity coefficients f_i for protons at varying ionic strengths (I) were obtained by using $\log f_i = -0.358 z_i^2 I^{1/2}/(1 + 10^8 a_i \times 0.2325 I^{1/2})$ with $a_i = 900$ pm and $z_i = 1$.[5] The activity coefficients used in this paper were 0.83 (0.17), 0.79 (0.57), and 0.76 (1.07): the ionic strength is given in parentheses.

Results and Discussion

Dissociation Constant of Triose Reductone. The first dissociation constants (pK_1) of triose reductone (RH_2) for the equilibrium, $RH_2 \rightleftharpoons RH^- + H^+$, were determined by the spectrophotometric method reported previously[1] at an ionic strength of 1.07 M (with the temperature (°C) in parentheses): 4.83 (10), 4.83 (15), 4.78 (20), 4.74 (25), and 4.70 (30), and at 30 °C (with the I in parentheses): 4.78 (0.57) and 4.88 (0.17).

Kinetics of the Reactions. The kinetic runs were carried out over the pH range from 4.1 to 5.9. In this pH range, the thermal decomposition of either peroxodisulfate or triose reductone was so slow under 30 °C that the decomposition could be neglected.[2] When pseudo-first-order conditions ($[TR]_0 \ll [S_2O_8^{2-}]_0$) were adopted, plots of ln A_t *vs.* t were linear for at least 60% of the whole reaction; here $[TR]_0$ indicates the initial concentrations of all the forms of triose reductone ($[TR]_0$ can be put as $[RH_2]_0 + [RH^-]_0$ in the present pH range), $[S_2O_8^{2-}]_0$ indicates the initial concentration of peroxodisulfate ion, and A_t indicates the absorbance of triose reductone at time t. The observed first-order rate constants were proportional to the concentration of peroxodisulfate ion. When second-order conditions ($[TR]_0 = [S_2O_8^{2-}]_0$) were employed, the second-order plots were also linear; *i.e.* the plots of $[TR]^{-1}$ *vs.* t were rectilinear. Thus, the empirical rate equation may be written as follows:

$$-\frac{d[TR]}{dt} = k_0[TR][S_2O_8^{2-}], \tag{1}$$

where k_0 is the observed second-order rate constant. The conventional treatment of the reaction involving the acid dissociation equilibrium gives k_0 as in Eq. 2.

$$k_0 = k_1 + (k_2 - k_1)\frac{K_1}{[H^+] + K_1}, \tag{2}$$

$$RH_2 \overset{K_1}{\rightleftharpoons} RH^- + H^+, \tag{3}$$

where K_1 is the first dissociation constant of triose reductone, and k_1 and k_2 are rate constants of the reaction of RH_2 and RH^- with $S_2O_8^{2-}$, respectively. The plots of k_0 *vs.* $K_1/(K_1+[H^+])$ showed a proportional relationship; the plots are given in Figs. 1 and 2. The k_1 values calculated from the experimental data are considered to be zero within the experimental errors. Hence, the rate equation becomes:

$$-\frac{d[TR]}{dt} = \frac{k_2K_1[TR][S_2O_8^{2-}]}{[H^+] + K_1}. \tag{4}$$

The k_2 values are listed in Table 1. The rate equation 4 can be simplified to Eq. 5:

$$-\frac{d[TR]}{dt} = k_2[RH^-][S_2O_8^{2-}]. \tag{5}$$

Equation 5 shows that the reactive species of triose reductone against peroxodisulfate is the monoanion of the reductone in the present pH range.

Mechanism of the Reaction. The presence of $RH^{\bullet}$ radical in the autoxidation of triose reductone catalyzed by peroxidase has been confirmed by ESR measurements.[6] For the purpose of examining whether the present reaction occurs *via* successive one-electron transfers involving the $RH^{\bullet}$ radical, the acrylonitrile (2×10^{-4} dm^3) was added as a radical scavenger to the reaction solution (3×10^{-3} dm^3) at the start of the reaction. The observed second-order rate constant decreased to only 90% of the value in the absence of acrylonitrile. No observable white sediment of polyacrylonitriles was found in the reaction solution in the course of reaction. Although there are some possibilities that the sulfate anion radicals produced in Eq. 6 oxidize triose reductone by chain reactions, the effect of the radical scavenger is not so strong as to indicate the importance of $RH^{\bullet}$ radical. This fact suggests that the reaction occurs *via* a two-electron oxidation instead of successive one-electron oxidations. But it is reasonable to suppose that triose reductone radical and sulfate anion radical are produced by a one-electron oxidation once in a cage, then they react rapidly to consume the radicals. The following scheme can be written to account for the experimental results:

$$RH^- + S_2O_8^{2-} \xrightarrow{k_2} (RH^{\bullet} + SO_4^{-\bullet} + SO_4^{2-}), \tag{6}$$

$$\xrightarrow{\text{very fast}} 2SO_4^{2-} + DR + H^+, \tag{7}$$

where DR represents dehydroreductone hydrate, 2,2-dihydroxypropane-1,3-dial. Dehydroreductone is known as an unstable product in the oxidation of triose reductone by many oxidizing agents to give formic acid,

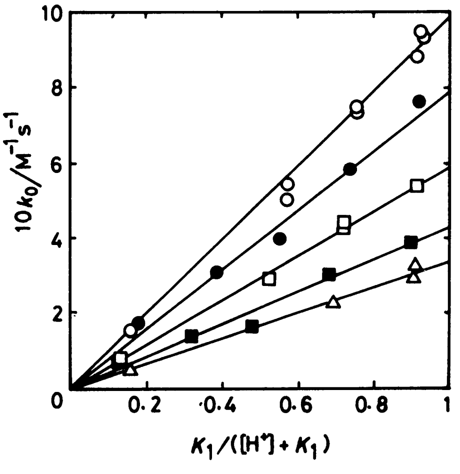

Fig. 1. Relation between k_0 and $K_1/([H^+]+K_1)$ for the oxidation of triose reductone with peroxodisulfate at ionic strength 1.07 M and various temperatures. ○: 30 °C, ●: 25 °C, □: 20 °C, ■: 15 °C, △: 10 °C.

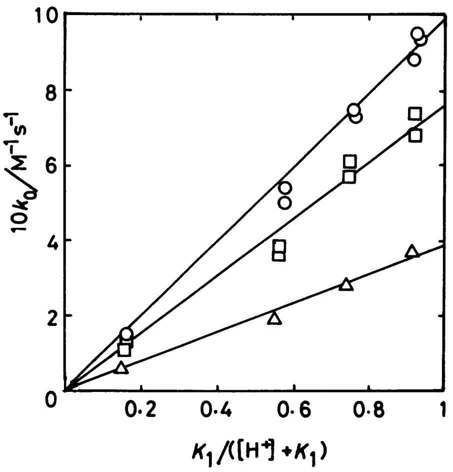

Fig. 2. Relation between k_0 and $K_1/([H^+]+K_1)$ for the oxidation of triose reductone with peroxodisulfate at 30 °C and various ionic strengths. ○: 1.07 M, □: 0.57 M, △: 0.17 M.

Table 1. The second-order rate constant, k_2 in Eq. 2, and the kinetic parameters[a)]

Temp	Ionic strength	$10k_2$
°C	M	$M^{-1}s^{-1}$
10	1.07	3.4±0.1
15	1.07	4.3±0.2
20	1.07	5.9±0.1
25	1.07	7.9±0.3
30	1.07	9.9±0.2
30	0.57	7.6±0.2
30	0.17	3.9±0.2
$\Delta H_2^{\ddagger}$	37±1 kJ mol^{-1}	
$\Delta S_2^{\ddagger}$	−123±5 J deg^{-1} mol^{-1}	

a) The initial concentrations are 6.0×10^{-5} M for triose reductone and 4.5×10^{-4} M for potassium peroxodisulfate, 5×10^{-3} M in EDTA, 0.05 M in sodium acetate, and the given concentrations of acetic acid and sodium perchlorate.

glyoxylic acid, and carbon dioxide.[7—9] Therefore, DR produced in this reaction may also be decomposed by the following equations.

$$\mathrm{DR} + 2\mathrm{H_2O} + \mathrm{S_2O_8}^{2-} \xrightarrow{\text{very slow}} \mathrm{HCOCOOH} + 2\mathrm{SO_4}^{2-} + \mathrm{HCOOH} + 2\mathrm{H}^+, \quad (8)$$

$$\mathrm{HCOCOOH} + \mathrm{H_2O} + \mathrm{S_2O_8}^{2-} \xrightarrow{\text{very slow}} \mathrm{HCOOH} + 2\mathrm{SO_4}^{2-} + \mathrm{CO_2} + 2\mathrm{H}^+. \quad (9)$$

Although the reaction of triose reductone with peroxodisulfate is complicated by competitive and successive reactions with the peroxodisulfate, it is reasonably supposed that the decomposition reactions of DR, Eqs. 8 and 9, occur very slowly compared with Eq. 6, since the experimental rate law for the reaction scheme (Eqs. 6—9) is in agreement with Eq. 5.

Temperature Dependence. The activation parameters correspnding to the specific rate constants are shown in Table 1. Both $\Delta H_2^{\neq}$ and $\Delta S_2^{\neq}$ values in the reaction of triose reductone (37 ± 1 kJ mol^{-1} and -123 ± 5 J deg^{-1} mol^{-1}) are smaller than those (45 ± 1 kJ mol^{-1} and -102 ± 4 J deg^{-1} mol^{-1}, respectively) obtained in the reaction of L-ascorbic acid with peroxodisulfate ion.[3] The k_2 values in the reaction of triose reductone are larger than those obtained in the reaction of L-ascorbic acid over the temperature range of 10—30 °C. Although it has no practical significance, it is worth mentioning that the k_2 for triose reductone should become smaller than the k_2 for L-ascorbic acid at temperatures higher than 108 °C.

Ionic-strength Dependence. Although the ionic-strength values employed in this work lie outside the Debye-Hückel region, the plots of $\log k_2$ *vs.* $I^{1/2}/(1+I^{1/2})$ showed a straight line, with a relationship of $\log k_2 = -(0.95 \pm 0.07) + (1.88 \pm 0.17) I^{1/2}/(1+I^{1/2})$. This dependence is of a kind which is expected for the reaction between two ions of the same sign; the positive value of 1.88 is in good agreement with that of 2.04 which is obtained from the theoretical term of $1.02 z_a z_b \times I^{1/2}/(1+I^{1/2})$ with $z_a = -1$ for RH$^-$ and $z_b = -2$ for $\mathrm{S_2O_8}^{2-}$. The ionic-strength dependence suggests that the reaction between RH$^-$ and $\mathrm{S_2O_8}^{2-}$ (Eq. 6) is the rate-determining step.

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