The Autoxidation of 2,3-Dihydroxy-2-propenal (Triose Reductone). The Effects of the pH on the Rate Constants

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The autoxidation of 2,3-dihydroxy-2-propenal (triose reductone) was investigated between pH 2.83 and 13.91 in the presence of disodium dihydrogen ethylenediaminetetraacetate (EDTA 2NA). The reaction obeyed the first-order rate law with respect to the triose reductone and the zeroth-order rate law with respect to oxygen when the oxygen concentration was higher than 0.246 mM (1 mM$=10^{-3}$ mol dm^{-3}) at 30 °C. The pH dependence of the reaction rates showed that the reaction rates are governed by the acid-base equilibrium of triose reductone. The rate constants for neutral and singly- and doubly-charged anions of triose reductone at 30 °C were $(3.6\pm0.1)\times10^{-6}$, $(7\pm1)\times10^{-5}$, and $(1.8\pm0.1)\times10^{-2}$ s^{-1} respectively. The hydrogen peroxide produced as a result of the triose reductone oxidation was also found to oxidize triose reductone.

The 2,3-dihydroxy-2-propenal produced from dextrose by alkaline hydrolysis is called triose reductone because of its strong reducing ability. The stoichiometry of the oxidation of triose reductone with hydrogen peroxide,[1] periodic acid,[2] sodium periodate,[3] iodine,[4] iron(III) chloride,[4] 2,6-dichlorophenolindophenol (DCIP),[4] and selenium oxide[5] has been studied by only a few workers. The first kinetic study of the oxidation was attempted by Arndt *et al.*,[4] but they did not determine the rate constants. Recently, Obata *et al.*[6] studied the reduction of DCIP with triose reductone in the pH range between 2 and 11; they obtained the second-order rate constants. The enzymatic autoxidation of the reductone using oxidase and peroxidase was studied in detail.[7] Although the nonenzymatic autoxidation of triose reductone was well known,[8,9] no one has studied it kinetically. Since triose reductone is an endiol compound whose redox behavior quite resembles that of the physiologically important L-ascorbic acid, we were interested in studying the autoxidation of the reductone.

Experimental

The triose reductone was prepared and purified by the method of Euler and Martius.[10] The formic acid,[11] glyoxylic acid,[12] glycolic acid,[12] glyoxal,[13] and hydrogen peroxide[14] were determined colorimetrically according to the procedures described in the literature.

Kinetic Method. The triose reductone was dissolved in a given volume of a solution, containing 4 mM each of acetic acid, phosphoric acid, and boric acid, and 1 mM of EDTA. The concentrations of the dissolved oxygen were controlled by saturating with argon, air, or oxygen gas so as to be 0.246, and 1.23 mM respectively, based on the known oxygen solubility at a given temperature. An aliquot of an aqueous solution of sodium hydroxide was added to 3 cm^3 of the triose reductone solution in a capped quartz cell, with precaution taken to avoid any change in the oxygen concentration. The oxidation time courses were followed spectrophotometrically with a Hitachi 323 Recording Spectrophotometer by measuring the decreasing absorption at 267 or 293 nm. The temperature was controlled at 30±0.1 °C. The pseudo first-order rate contant, k_{obsd}, was determined from the slope of the linear plots of log OD against time in the usual manner. The pH values of the reaction solutions were measured with a digital pH meter (Toyo Model PT-3D) before and after the reaction; we thus confirmed no appreciable pH change during the reaction. The hydrogen peroxide solution was added to the solution of triose reductone before the injection of the sodium hydroxide solution.

Results and Discussion

Dissociation Constants of Triose Reductone. Though the pK_a value for the first dissociation of triose reductone has been reported to be 5.00,[10] 4.93,[15] or 5.12,[16] the value for the second dissociation has not been available in the literature. The UV absorption spectra of triose reductone at pH 3.80, 8.00, and 13.5 under an argon atmosphere are shown in Fig. 1. An acidic solution (pH 1.5—4.1) of triose reductone showed an absorption maximum at 268 nm ($\varepsilon=16300$), neutral and slightly basic solutions (pH 6.8—10.0), at 293 nm ($\varepsilon=24600$), and a strongly basic solution (pH>13.5), at 323 nm

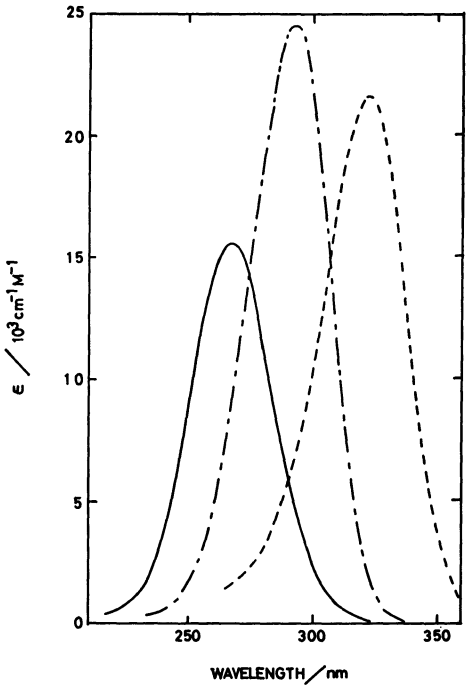
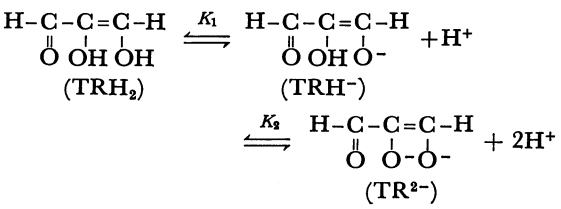


Fig. 1. Absorption spectra of triose reductone.
——: pH 3.80, —·—: pH 8.00, ------: pH 13.5.

(ε=23300). Triose reductone has two dissociable hydrogen atoms according to the following acid-base equilibria:



the three absorption spectra corresponding to the neutral molecule (TRH_2), the monoanion (TRH^-), and the dianion (TR^{2-}). The values of pK_{a1} and pK_{a2} can be calculated by means of Eqs. 1 and 2. The concentrations of TRH_2 and TRH^- in Eq. 1 were

$$pK_{a1} = pH + \log \frac{[TRH_2]}{[TRH^-]} \quad (1)$$

$$pK_{a2} = pH + \log \frac{[TRH^-]}{[TR^{2-}]} \quad (2)$$

computed from the spectra at pH 5—6, and those of TRH^- and TR^{2-} in Eq. 2, from the spectra at pH 12—13. The values of pK_{a1} and pK_{a2} obtained were 5.03 and 13.0 respectively at 30 °C.

Stoichiometry of the Oxidation. In the case of the autoxidation of a concentrated triose reductone solution without buffer capacity and EDTA, hydrogen peroxide was detected in the course of the reaction. However, the hydrogen peroxide disappeared after the triose reductone had been completely consumed. Table 1 shows the yields of the oxidation products from triose reductone. It has been reported that the oxidation of triose reductone with an excess of hydrogen peroxide gave carbon dioxide and formic acid.[1] In a similar way, periodic acid gave formic acid and glyoxylic acid,[2] and selenium oxide gave 2,2-dihydroxypropanedial (dehydroreductone hydrate).[5] Sodium periodate gave formic acid and glyoxylic acid in the first step, and then glyoxylic acid was oxidized to formic acid and carbon dioxide.[3] Formic acid and glyoxylic acid were detected in the present work; further, the total concentration of the two acids was found to amount to twice the triose reductone consumed (Table 1). It may be reasonable to consider that the oxidation of triose reductone with oxygen proceeds *via* a step-by-step oxidation as has been described above. The oxidation also proceeds in a similar way with the hydrogen peroxide produced by the reduction of oxygen.

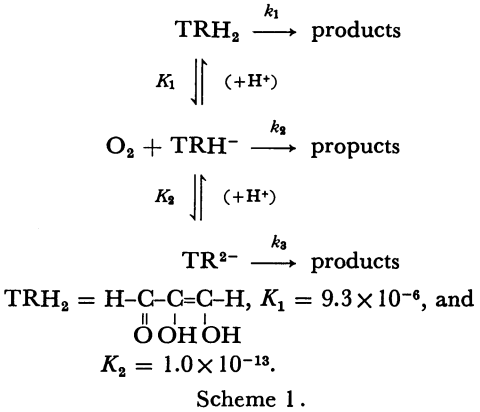
Table 1. Autoxidation of aqueous solution of triose reductone

Product	Yield/%[a]
Hydrogen peroxide	0 (12)[b]
Glyoxylic acid	30
Glycolic acid	0
Formic acid	167
Glyoxal	0

a) The yield presented is based on the assumption that 1 mol of triose reductone yields 1 mol of each of the products. b) The yield in parentheses is a value observed in the course of the reaction.

Effect of pH on Rate of Autoxidation. The UV spectra of a triose reductone solution saturated with oxygen or air were identical with those shown in Fig. 1 below pH 10. However, above pH 10 it was not clear whether or not these spectra were identical due to the fast degradation of the reductone.

The first-order rate constants (k_{obsd}/s^{-1}) were obtained from the slopes of the linear $\log[TR]_t$ *vs.* time plots, where t denotes the total analytical concentration. The pH-rate profile for the autoxidation of triose reductone at 30 °C is sigmoid (Fig. 2). For the effect of the oxygen concentration on the rate, no difference in k_{obsd} was observed in the oxygen concentration range between 0.246 and 1.23 mM. Since no oxidant other than oxygen was involved in the reaction system, the reaction rates should depend on the oxygen concentration. However, the rates were practically constant and independent of the oxygen concentration when it was over 0.246 mM. The pH-rate profile clearly reflects the involvement of various triose reductone species. We may envisage the reaction scheme shown in Scheme 1.



Scheme 1.

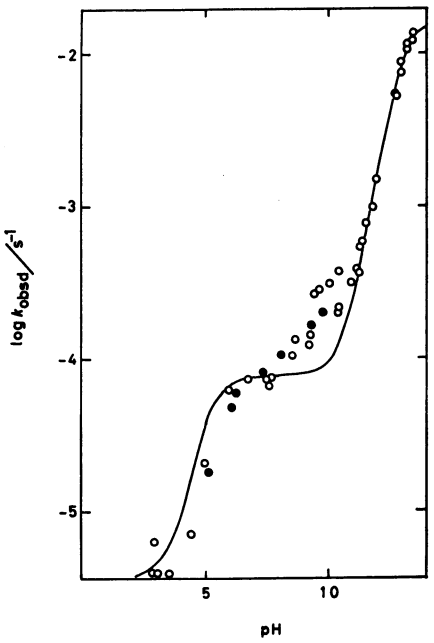


Fig. 2. Relation between log k_{obsd} and pH for the autoxidation of triose reductone at 30 °C.
○: Oxygen saturated, ●: air saturated. The solid line reflects log k_{calcd} according to Eq. 10.

Thus, at a constant acidity, the simplest rate expression is given by Eq. 3:

$$\text{rate} = k[\text{TR}]_t. \quad (3)$$

At various pH values:

$$[\text{TR}]_t = [\text{TRH}_2] + [\text{TRH}^-] + [\text{TR}^{2-}] \quad (4)$$

$$[\text{TRH}_2] = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}[\text{TR}]_t$$

$$[\text{TRH}^-] = \frac{[\text{H}^+]K_1}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}[\text{TR}]_t, \text{ and}$$

$$[\text{TR}^{2-}] = \frac{K_1K_2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}[\text{TR}]_t. \quad (5)$$

Hence, the rate equation becomes:

$$-\frac{\text{d}[\text{TR}]_t}{\text{d}t} = \frac{k_1[\text{H}^+]^2 + k_2[\text{H}^+]K_1 + k_3K_1K_2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}[\text{TR}]_t. \quad (6)$$

Hence, from Eq. 3 we obtain:

$$k = \frac{k_1[\text{H}^+]^2 + k_2[\text{H}^+]K_1 + k_3K_1K_2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}. \quad (7)$$

In the pH range of 2.8—7.7, Eq. 7 can be simplified to Eq. 8, since there is triose reductone in TRH_2 and TRH^-:

$$k = \frac{k_1[\text{H}^+]^2 + k_2[\text{H}^+]K_1}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}. \quad (8)$$

By substituting the observed values for k and $[\text{H}^+]$ in Eq. 8, k_1 and k_2 were obtained as $(3.6\pm0.1)\times10^{-6}$ and $(7\pm1)\times10^{-5}\ \text{s}^{-1}$ respectively. Similarly, Eq. 7 can be simplified to Eq. 9 in the pH range of 10.4—13.4:

$$k = \frac{k_2[\text{H}^+]K_1 + k_3K_1K_2}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}. \quad (9)$$

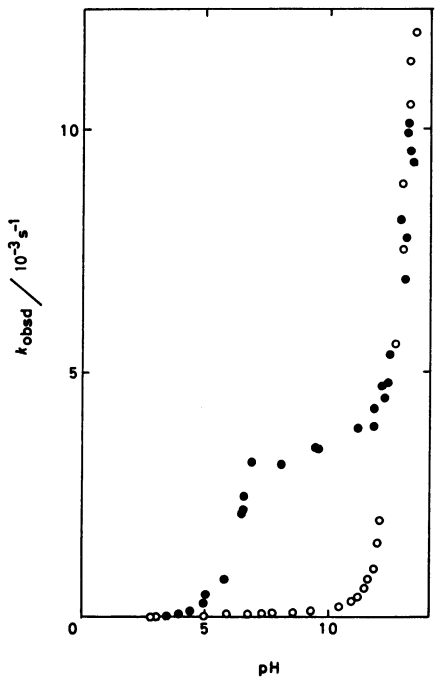


Fig. 3. Relation between k_{obsd} and pH for the autoxidation of triose reductone in the presence and absence of EDTA at 30 °C.
○: In the presence of EDTA, ●: in the absence of EDTA.

The k_3 value thus obtained was $(1.8\pm0.1)\times10^{-2}\ \text{s}^{-1}$, while k_2 was not constant. This fact suggests that the monoanion of triose reductone might be consumed by side reactions at these pHs. Considering the detection of hydrogen peroxide in the course of the autoxidation, the side reaction must be the oxidation of triose reductone with the hydrogen peroxide produced (see below). The solid line in Fig. 2 represents the theoretical plot of log k, calculated using Eq. 7, against the pH. The calculated values of k agree well with the observed k values below pH 8 and above pH 11.

The autoxidation rate constants of L-ascorbic acid at 20 °C have been reported as $8.3\times10^{-7}\ \text{s}^{-1}$ for the monoanion and $8.3\times10^{-2}\ \text{s}^{-1}$ for the dianion; furthter

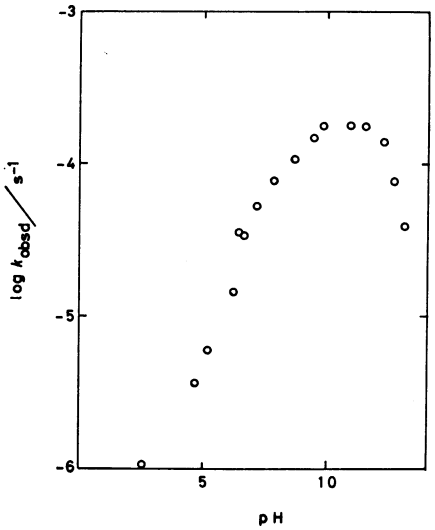


Fig. 4. Relation between log k_{obsd} and pH for the oxidation of triose reductone with hydrogen peroxide in the absence of oxygen at 30 °C.

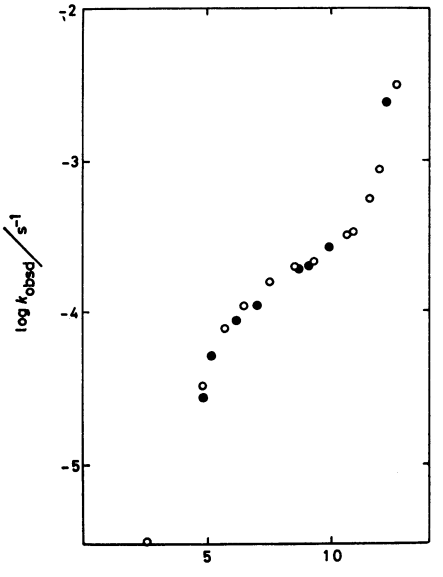


Fig. 5. Relation between log k and pH for the oxidation of triose reductone with hydrogen peroxide in the presence of oxygen at 30 °C.
○: Observed, ●: calculated.

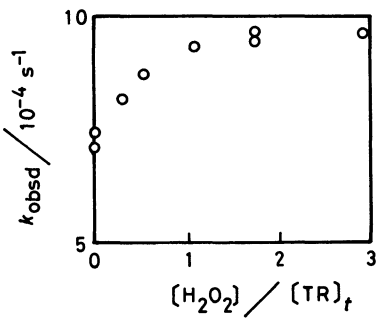


Fig. 6. Relation between k_{obsd} and ratio of hydrogen peroxide to triose reductone in the presence of oxygen at pH 6.6±0.2 and 30 °C.

the reaction rates of the monoanion are independent of the oxygen concentration.[17] Although the reaction rates of triose reductone with DCIP are slower than those of L-ascorbic acid with DCIP throughout the pH range,[6] the autoxidation rate constants are faster than those of L-ascorbic acid in the acidic and neutral pH ranges, but slower in the alkaline range.

Effect of EDTA. The autoxidation of a triose reductone solution without EDTA also obeyed the first-order rate law. Figure 3 shows the pH-rate profile of the autoxidation of triose reductone with and without EDTA. Although the effect of EDTA on rate constants was not appreciable below pH 4 or above pH 12.5, the rate constants for the autoxidation without EDTA were fifty times larger than those with EDTA at pH 7—10. The study of the inhibition of a copper catalyst on the autoxidation of L-ascorbic acid with EDTA[18] suggests that a trace amount of a metal cation may also have a catalytic effect on the autoxidation of triose reductone.

Reaction of Triose Reductone with Hydrogen Peroxide. A triose reductone solution prepared in a manner similar to the solution for the oxygen autoxidation was deoxygenated with argon. This solution was treated with a 2—3-times excess of hydrogen peroxide at 30 °C. The reaction obeyed the first-order rate law with respect to triose reductone. A plot of log k_{obsd} *vs.* pH (Fig. 4) resulted in a bell-shaped curve with a rate maximum at pH 11. On the other hand, when the solution was saturated with air instead of argon, a plot of log k_{obsd} *vs.* pH resulted in a broadly sigmoid curve (Fig. 5) resembling that in Fig. 2. For the effect of the hydrogen peroxide concentration on the rates for the system saturated with air at pH 6.48—6.80, $k_{obsd}-7.4\times10^{-4}$ was proportional to the hydrogen peroxide concentration until the latter reached the mole of triose reductone. However, k_{obsd} was constant, independently of the hydrogen peroxide concentration, when the concentration was larger than that of triose reductone (Fig. 6).

If the oxidation rate constant also depends on the dissociation of both triose reductone and hydrogen peroxide, the relationship of log k_{obsd} and pH (3—13) should be a sigmoid curve and not a bell-shaped curve. Therefore, some reactions to consume hydrogen peroxide in a higher pH range other than reduction with triose reductone might occur in the reaction system. Although the oxidation of triose reductone with hydrogen peroxide has not been explained kinetically, the reaction-rate constants for the oxidation of triose reductone with hydrogen peroxide in the presence of an oxygen molecule agreed with the sum of the reaction-rate constants for the oxygen molecule and those for hydrogen peroxide in the absence of oxygen at the same pH (Fig. 5).

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