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CLEAVAGE OF D-*arabino*-HEXOS-2-ULOSE AND GLYOXAL WITH HYDROGEN PEROXIDE

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ABSTRACT

The kinetics of the cleavage of D-*arabino*-hexos-2-ulose (**1**) and of glyoxal (**2**) with hydrogen peroxide in alkaline water and in 44% (w/w) ethanol–water solutions (pOH 0.5–5) were studied over a temperature range of −25 to +25°. The relative rate of the competing reactions of **1** with the cleavage in 0.03–1M sodium hydroxide was determined from the rate of formation of hydrogen peroxide in the oxidation of D-glucose to **1** with 2-anthraquinonesulfonic acid in the presence of oxygen at 25 and 40°. The cleavages of both **1** and **2** were first-order with respect to hydrogen peroxide, and also to hydroxyl ion at low alkalinities. The rate of cleavage of **1** reached a maximum at pOH ~2.5, whereas the competing reactions of **1** and the cleavage of **2** were constantly accelerated with increasing hydroxyl-ion concentration. Unlike **2**, compound **1** was cleaved more rapidly in ethanol–water than in water. The activation energies of the cleavage of **1** and **2**, and the competing reactions of **1**, were 49, 57, and 65 $kJ.mol^{-1}$, respectively.

INTRODUCTION

Hydrogen peroxide has long been known to cleave α-dicarbonyl compounds, with formation of a pair of carboxylic acids. The kinetic information about the reaction has, however, been inadequate, although the reaction has proved to be first-order with respect to hydrogen peroxide[1] and to be catalyzed by hydroxyl ion[2]. The involvement of a similar cleavage in the oxidation of reducing carbohydrates with oxygen[3], or with a quinone in the presence of oxygen[4], has given rise to the present work, in which the kinetics of the cleavage of D-*arabino*-hexos-2-ulose (**1**) and glyoxal (**2**), in addition to their other, competing reactions, are discussed.

RESULTS

Rate equations. — The rates of cleavage of both **1** and **2** were directly proportional to the substrate concentration and to the concentration of hydrogen peroxide, according to Eq. *1*.

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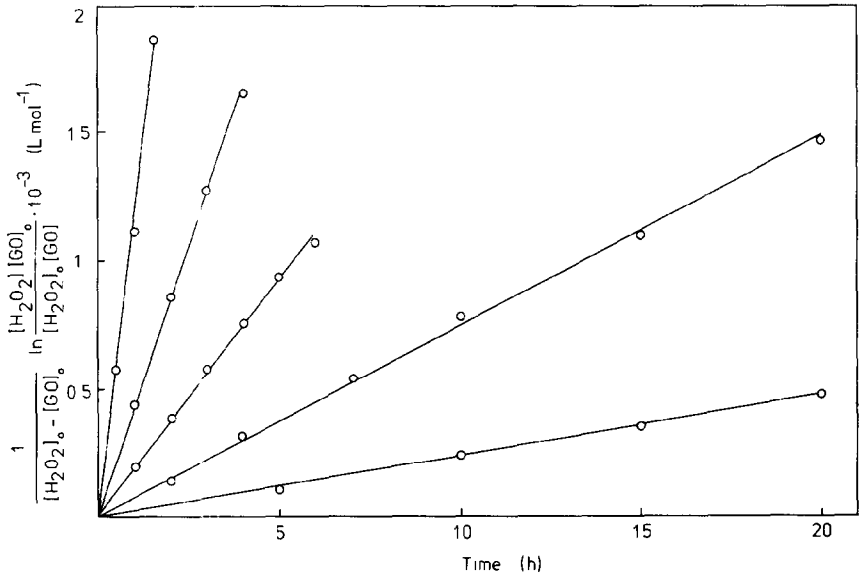

Fig. 1. Cleavage of 0.5mM glyoxal (**2**) with mM hydrogen peroxide at pH 11, 10.5, 10, 9.5, and 9, reading clockwise, at 25°.

$$d[H_2O_2]/dt = -k[GO][H_2O_2], \tag{1}$$

where GO denotes **1**, or **2**. Under the conditions applied, the other, competing reactions were usually relatively slow, and therefore the rate constants could be readily calculated by the integrated form of Eq. *1* (see Eq. *2* and Fig. 1).

$$\frac{1}{[H_2O_2]_0 - [GO]_0} \ln \frac{[H_2O_2][GO]_0}{[H_2O_2]_0[GO]} = kt, \tag{2}$$

where the subscript denotes the initial conditions.

The only remarkable deviations from Eq. *2* were observed at high hydroxyl-ion concentrations (>0.01M), where the rearrangement of glyoxal (**2**) became significant. In that case, the disappearance of **2** was expressed by Eq. *3*, which, in combination with Eq. *1*, gave the relative rate of cleavage (see Eq. *4*).

$$d[GO]/dt = -k'[GO] - k[GO][H_2O_2] \tag{3}$$

$$\frac{d[H_2O_2]}{d[GO]} = \frac{k[H_2O_2]}{k' + k[H_2O_2]} \tag{4}$$

The ratio between the rate constants of the rearrangement and cleavage was obtained when the final concentration of hydrogen peroxide (after complete conversion of **2**) was substituted in the integrated form of Eq. *4* (see Eq. *5*).

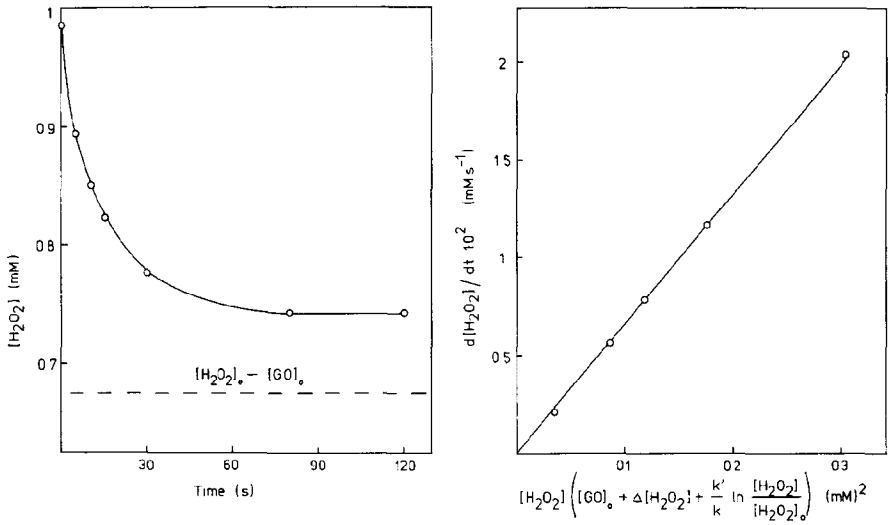

Fig. 2. Cleavage of 0.3mM glyoxal (**2**) with mM hydrogen peroxide in 0.01M sodium hydroxide at 25°.

$$[GO] - [GO]_0 = [H_2O_2] - [H_2O_2]_0 + \frac{k'}{k} \ln \frac{[H_2O_2]}{[H_2O_2]_0} \tag{5}$$

After that, the concentration of glyoxal at any reaction time could be calculated from the same equation. The rate of disappearance of hydrogen peroxide was, in turn, determined as the slope of the plot of the concentration of hydrogen peroxide against the reaction time. The rate constant of the cleavage was, consequently, given by Eq. *6* (see Fig. 2).

$$d[H_2O_2]/dt = -k[H_2O_2]\left([GO]_0 + [H_2O_2] - [H_2O_2]_0 + \frac{k'}{k} \ln \frac{[H_2O_2]}{[H_2O_2]_0}\right) \tag{6}$$

On treatment with 2-anthraquinonesulfonic acid (AMS), D-glucose yielded **1** as the primary oxidation-product[1]. The reduced AMS was readily re-oxidized by oxygen, with formation of an equimolar amount of hydrogen peroxide, which, in turn, was consumed in the cleavage of **1** according to Eq. *4*. The formation of hydrogen peroxide was thus expressed by Eq. *7*, or, after integration, by Eq. *8*.

$$\frac{d[H_2O_2]}{d[G]} = 1 - \frac{k[H_2O_2]}{k' + k[H_2O_2]}, \tag{7}$$

where G denotes D-glucose.

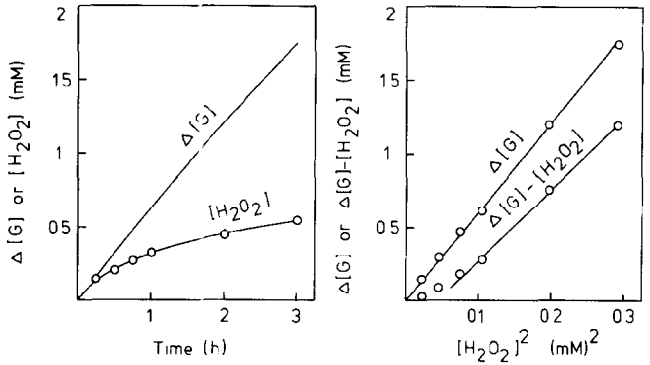

Fig. 3. Formation of hydrogen peroxide in the oxidation of 10mM D-glucose with mM AMS in 0.1M sodium hydroxide in the presence of oxygen at 25°.

$$\Delta[G] - [H_2O_2] = \frac{k}{2k'} [H_2O_2]^2 \qquad (8)$$

In the beginning of the reaction, hydrogen peroxide was formed more rapidly than Eq. *8* requires; this resulted from the reduction of AMS in competing reactions of **1**. To compensate for this deviation, $\Delta[G]$ in Eq. *8* was replaced by $\Delta[G] + [H_2O_2]$, which roughly corresponded to the total amount of α-dicarbonyl compounds formed, because the portion of **1** that did not undergo cleavage consumed ~1 equivalent of AMS. The resulting equation (see Eq. *9*) was obeyed throughout the reaction conditions used, and this was considered to justify its application.

$$\Delta[G] = \frac{k}{2k'} [H_2O_2]^2 \qquad (9)$$

In separate experiments, it was shown that the formation of hydrogen peroxide in the oxidation of D-glucose with oxygen (see Fig. 3) follows similar kinetics, which clearly demonstrated that the equilibrium reaction between **1**, hydrogen peroxide, and their addition product (which is formed primarily with oxygen) was much more rapid than the cleavage.

Effect of reaction conditions. — The influence of hydroxyl-ion concentration on the cleavage of 1 gave support for the participation of the hydroperoxide anion in the formation of the intermediate addition-product. At low alkalinities, the rate of cleavage was roughly proportional to the first power of the hydroxyl-ion concentration, and it reached its maximum at pOH ~2.5, which corresponds to the pK value of hydrogen peroxide[5] (see Fig. 4). At higher concentrations of alkali, the cleavage was retarded to some extent in water solution, whereas, in ethanol–water, the maximum rate remained constant. In ethanol–water, the cleavage was faster than in water.

For some reason, no maximum was observed in the rate of cleavage of glyoxal (**2**), but it accelerated constantly with increasing hydroxyl-ion concentra-

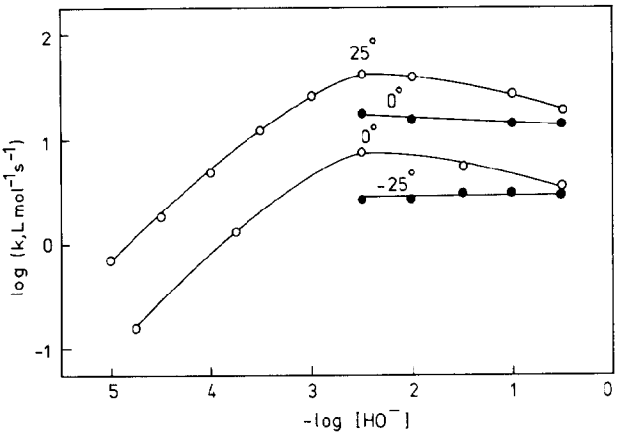

Fig. 4. Effect of hydroxyl-ion concentration on the rate of cleavage of **1** with hydrogen peroxide in water (○) and 44% (w/w) ethanol–water (●).

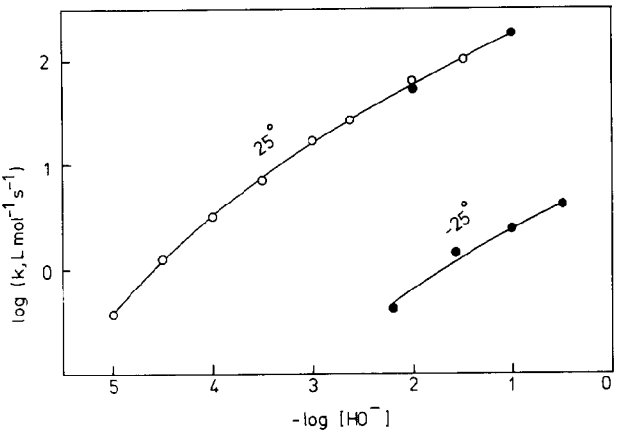

Fig. 5. Effect of hydroxyl-ion concentration on the rate of cleavage of **2** with hydrogen peroxide in water (○) and 44% (w/w) ethanol–water (●).

tion (see Fig. 5). Addition of ethanol had no influence on the cleavage of **2**, although its rearrangement was clearly retarded.

The relative rate of cleavage of both **1** and **2** decreased with increasing alkalinity of the solution (see Fig. 6). In the absence of hydrogen peroxide, the rate of disappearance of **2** was proportional to the second power of the hydroxyl-ion concentration, in accordance with the literature[6]. The rate of disappearance of **1**, instead, increased more slowly than the hydroxyl-ion concentration.

The activation energies of the cleavage of both **1** and **2** were lower than those of their other, competing reactions [49, 57, 65, and 76 (ref. 6) kJ.mol^{-1}, respectively]. The ionic strength had a very limited influence on the cleavage reactions, and also on the other reactions of **1**.

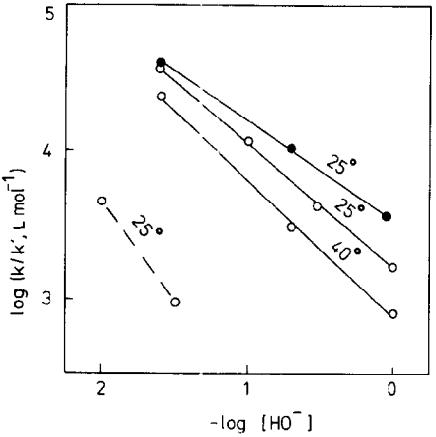

Fig. 6. Effect of hydroxyl-ion concentration on the relative rate of cleavage of **1** (full line) and **2** (dashed line) with hydrogen peroxide in water (○) and 44% (w/w) ethanol–water (●).

EXPERIMENTAL

Cleavage of D-arabino-*hexos-2-ulose*[7,8] (**1**) *and glyoxal* (**2**) *with hydrogen peroxide.* — The stock solutions consisted of 0.5M **1** in methanol, 0.5M **2**, and 0.5M hydrogen peroxide that contained 0.05M magnesium sulfate as a stabilizer. The alkali solutions were mixtures of 0.1M sodium hydrogencarbonate, 0.05M sodium carbonate, and 0.1–1M sodium hydroxide. The pOH values of the hydrogencarbonate–carbonate solutions were calculated as the difference[9] of pK_w and the measured pH values.

After thermostating, 0.5M hydrogen peroxide (20–50 μL) and 0.5M **1** or **2** (5-20 μL) were introduced into alkali solution (10 mL) in a polyethylene vessel under vigorous stirring. The reaction was stopped by adding 2M sulfuric acid (2.5 mL), and then the concentration of hydrogen peroxide was determined by iodometric titration[10].

Consumption of AMS in the oxidation of D-*glucose.* — To a de-aerated and thermostated (35°) solution of 10mM AMS in 0.1M sodium hydroxide (10 mL) was added M D-glucose (100 μL) under a nitrogen atmosphere. After 40 min, the solution was shaken in the presence of air until the red color of the reduced AMS had disappeared. The hydrogen peroxide liberated was determined by iodometric titration[10]. The relative consumption of AMS was obtained as the molar ratio of hydrogen peroxide formed and D-glucose disappeared[1] (2.22 and 2.25 mol/mol, in duplicate determinations).

Oxidation of D-*glucose with AMS in the presence of oxygen.* — To a thermostated solution of AMS (1–2mM) in sodium hydroxide (0.03–1M) in a polyethylene vessel were added M D-glucose (1–5 mL) with 0.1M magnesium sulfate (to prevent the catalytic decomposition of hydrogen peroxide) under a stream of oxygen. The total volume of the solution was 100 mL. The formation of hydrogen peroxide was

monitored by iodometric titration[10], until ~20% of the D-glucose had been consumed[1].

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REFERENCES

1 T. VUORINEN, *Carbohydr. Res.*, 116 (1983) 61–69.
2 C. A. BUNTON, *Nature*, 163 (1949) 444.
3 B. ERICSSON, B. O. LINDGREN, AND O. THEANDER, *Cellul. Chem. Technol.*, 7 (1973) 581–591.
4 T. VUORINEN AND E. SJOSTROM, *J. Wood Chem. Technol.*, 2 (1982) 129–145.
5 A. TEDER AND D. TORMUND, *Sven. Papperstidn.*, 83 (1980) 106–109.
6 P. SALOMAA, *Acta Chem. Scand.*, 10 (1956) 311–319.
7 N. K. RICHTMYER, *Methods Carbohydr. Chem.*, 2 (1963) 127–131.
8 S. BAYNE, *Methods Carbohydr. Chem.*, 2 (1963) 421–423.
9 R. C. WEAST (Ed.), *CRC Handbook of Chemistry and Physics*, 61st edn., CRC Press, Boca Raton, FL, 1980, p. D-168.
10 I. M. KOLTHOFF AND E. B. SANDELL, *Textbook of Quantitative Inorganic Chemistry*, 3rd edn., Macmillan, New York, 1952, p. 574.