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DEGRADATION OF 2-DEOXYALDOSES BY ALKALINE HYDROGEN PEROXIDE*

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ABSTRACT

Reaction of 2-deoxy-D-*arabino*-hexose, 2-deoxy-D-*lyxo*-hexose, and 2-deoxy-D-*erythro*-pentose with alkaline hydrogen peroxide in the presence of magnesium hydroxide afforded the corresponding 2-deoxyaldonic acid, the 1,4-lactone, and the 1-*O*-formyl derivative of the next lower alditol. The 2-deoxyaldonic acids were separated in 60–80% yields, as new, crystalline lithium salts. The 1,4-lactones were obtained under conditions that precluded intermediate formation of the free acids; presumably, the reaction proceeded by way of an intermediate, furanosyl hydroperoxide, which was converted into the lactone by elimination of water. With an excess of alkaline hydrogen peroxide, in the absence of magnesium hydroxide, the substrates were degraded to formic acid, with concurrent decomposition of hydrogen peroxide. It is shown that decomposition of hydrogen peroxide is catalyzed by hydroperoxide anion, and that it takes place by both a chain, and a non-chain, process. The decomposition reactions afford an abundant source of hydroxyl radical capable of oxidizing a wide variety of compounds.

INTRODUCTION

In prior publications, we reported that alkaline hydrogen peroxide degrades aldoses by nucleophilic addition of hydrogen peroxide to the carbonyl group, followed by an α-hydroxy-hydroperoxide cleavage of the adduct, with formation of formic acid and the next lower aldose[3-5]. Repetition of the process results in stepwise degradation of the aldose to formic acid, and finally, to formaldehyde, which is subsequently oxidized to formic acid. It seemed possible that, because the α-hydroxy-hydroperoxide cleavage reaction is relatively rapid, it obscures slower reactions that are important for substances lacking the α-hydroxyl group. Inasmuch as 2-deoxyaldoses lack this important feature, we undertook a study of their reactions with alkaline hydrogen peroxide[2] that resulted in a much clearer understanding of some of the reactions previously investigated. Hence, we have modified and extended

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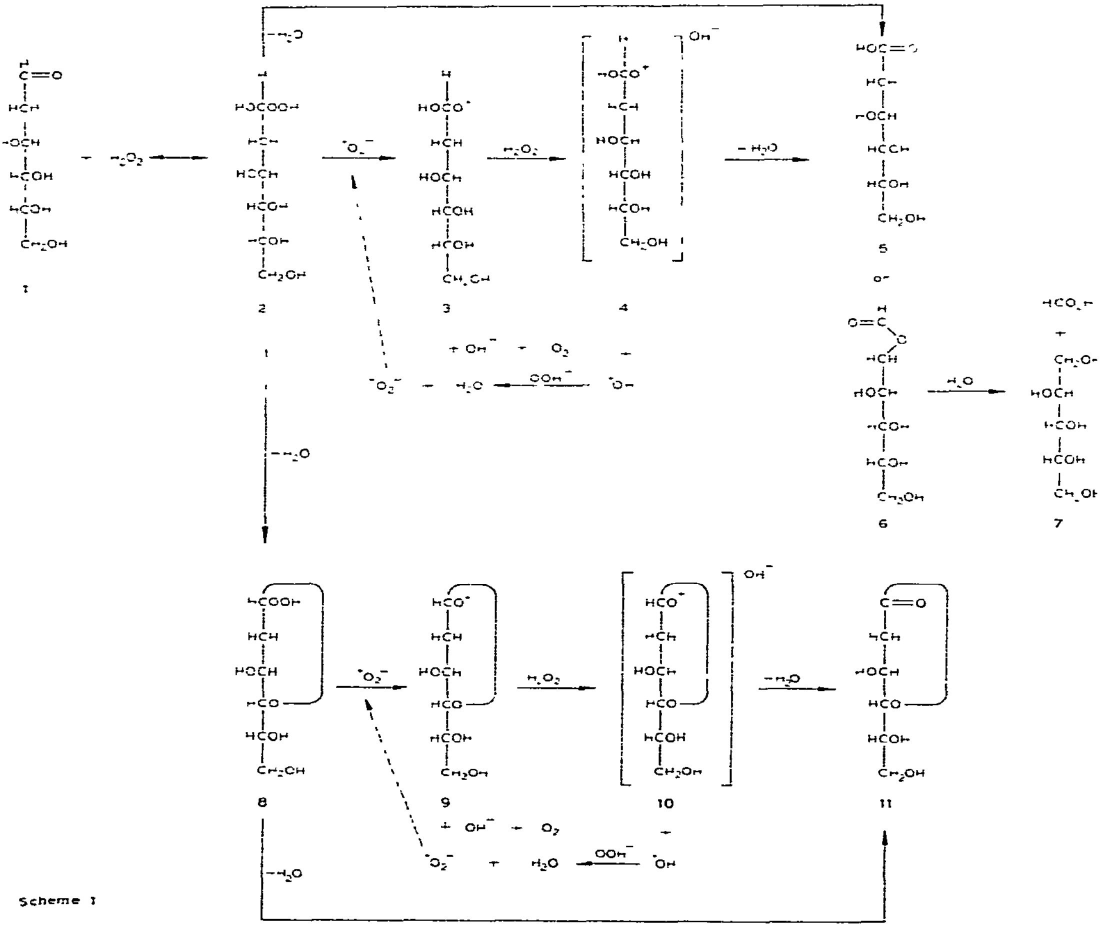
*Reactions of Carbohydrates with Hydroperoxides, Part XIV; for Part XIII, see ref. 1. For a preliminary report, see ref. 2.

some of our earlier concepts regarding degradation reactions with alkaline hydrogen peroxide.

DISCUSSION OF REACTION MECHANISMS

As expected, the degradation of 2-deoxy-D-*arabino*-hexose ("2-deoxy-D-glucose", **1**) proved to be slower and more complicated than that of a normal aldose. The study showed the existence of two successive processes, namely, a primary process beginning with the nucleophilic addition of hydrogen peroxide to the carbonyl form of the sugar, and a secondary process leading to complete degradation of the sugar. The primary process afforded 2-deoxy-D-*arabino*-hexonic acid ("2-deoxy-D-gluconic acid", **5**), 1-*O*-formyl-D-arabinitol (**6**), 2-deoxy-D-*arabino*-hexono-1,4-lactone ("2-deoxy-D-glucono-1,4-lactone", **11**) and a small proportion of formic acid. The secondary process begins with oxidation of one of the hydroxyl groups of the substrate by hydroxyl radical formed by decomposition of hydrogen peroxide. The



Scheme 1

resulting carbonyl compound then undergoes α-hydroxy-hydroperoxide cleavage-reactions, with production of formic acid and carbon dioxide[6]. The relative importance of the two processes depends upon the reaction conditions. At low temperatures, in the presence of magnesium hydroxide, the primary process greatly predominates, whereas, at slightly elevated temperatures, in the absence of magnesium hydroxide, the secondary process prevails.

With reference to the primary process shown in Scheme 1, addition of hydroperoxide anion to the carbonyl form of the sugar is rapid, and takes precedence over other reactions in the medium. Supplementary experiments showed that formation of hydroperoxide **2** from the sugar is reversible. Thus, addition of hydrogen peroxide to an alkaline solution of **1** caused a rapid decrease in optical rotation. Upon acidification of the solution, the optical rotation returned to almost its original value. Deionization, and evaporation of the solution, then gave a crystalline residue consisting in large measure of regenerated **1**, with a small proportion of lactone **11**. Evidently, the concentration of the free sugar was low, because the solution remained colorless, although highly alkaline (pH 13.3). Presumably, acyclic hydroperoxide **2** exists in solution in equilibrium with the free sugar until it decomposes, or undergoes ring-closure, with formation of furanosyl hydroperoxide **8**. The presence of **8** in the reaction medium was shown by separating lactone **11** from the mixture under conditions that precluded intermediate formation of acid **5**.

Conversion of acyclic hydroperoxide **2** and furanosyl hydroperoxide **8** into products may take place in two ways, depending upon the reaction conditions. Under highly alkaline conditions in the absence of a redox catalyst, the hydroperoxide may decompose by a heterolytic process. Thus, heterolytic cleavage of the C-1–H bond and the O–OH bond would yield **5** from **2**, and **11** from **8**. Heterolytic cleavage of the bonds is a relatively high-energy process, and is unimportant in reaction mixtures containing a redox catalyst. In reaction mixtures containing a large excess of alkaline hydrogen peroxide, the decompositions take place, in large measure, by a process analogous to the Haber–Weiss decomposition of hydrogen peroxide[7]. The process may be initiated by any redox catalyst or reagent capable of supplying an electron to the hydroperoxide with formation of hydroxyl ion and an oxy radical[8]. Suitable reagents for this purpose include superoxide radical, hydroperoxide anion, or ferrous ion. Reaction of hydroperoxide **2** or **8** with superoxide radical, for example, affords oxy radical **3** or **9** and a molecule of oxygen. Reaction of **3** or **9** with an oxidant in the solution affords an electron-deficient intermediate, **4** or **10**. This intermediate, shown in brackets, exists as a zwitter-ion in a transition state, that collapses to characteristic products by elimination of a proton and a shift of electrons to the electron-deficient oxygen atom. A shift of electrons from the C–H bond of **4** gives 2-deoxy-D-*arabino*-hexonic acid (**5**), whereas a shift of electrons from the C-1–C-2 bond gives 1-*O*-formyl-D-arabinitol (**6**)*, which, on hydrolysis, affords D-arabinitol (**7**).

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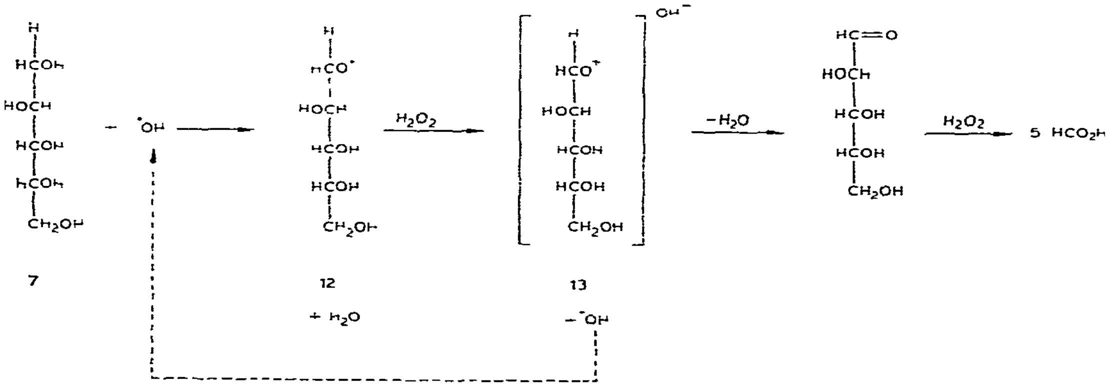
*Formation of the formyl derivative is hypothetical, as only D-arabinitol and formic acid were found experimentally. It is noteworthy, however, that reaction of tetra-*O*-methyl-D-glucose with alkaline hydrogen peroxide gave 1-*O*-formyl-tetra-*O*-methyl-D-arabinose[1].

The reactions shown in Scheme I predominate at low temperatures, especially in the presence of magnesium hydroxide. Treatment of **1** with hydrogen peroxide in the presence of magnesium oxide gave. after removal of cations, a non-volatile acid which. on neutralization with lithium hydroxide, afforded lithium 2-deoxy-D-*arabino*-hexonate, a new crystalline salt. in 80% yield. This procedure is new, and is much simpler than the procedures heretofore used for the preparation of 2-deoxyaldonic acids[9].

In marked contrast to the results obtained in the presence of magnesium hydroxide, treatment of **1** with alkaline hydrogen peroxide at a somewhat elevated temperature (40°) in the absence of magnesium hydroxide resulted in extensive degradation. After several hours. all of the hydrogen peroxide was decomposed, with production of oxygen and from one to five moles of formic acid per mole of **1**, depending on the proportions of hydrogen peroxide and alkali used. The high yield of formic acid cannot be ascribed to the reactions shown in Scheme 1. by which formic acid and D-arabinitol should be formed in equimolar proportions. The yield found requires further oxidation of compounds **5** and **7**. Supplemental experiments showed that these compounds are, in fact, readily degraded by alkaline hydrogen peroxide at slightly elevated temperatures. Presumably, in the degradation process, hydroxyl radical. generated from hydrogen peroxide. attacks one of the hydroxyl groups of the substrate. forming an oxy radical, which is oxidized further. The attack may take place at any point in the molecule. but it occurs most readily at the primary hydroxyl group[6]. In the degradation of alditol **7** depicted in Scheme 2, the initial attack results in oxy radical **12**, which is further oxidized by hydrogen peroxide to the electron-deficient intermediate **13**, with regeneration of hydroxyl radical. The electron deficiency of **13** is relieved by release of a proton, with formation of D-arabinose (**14**). which is then degraded to formic acid by the α-hydroxy-hydroperoxide cleavage-reaction. In the degradation of acid **5**, a similar attack on the primary hydroxyl group leads to 2-deoxy-D-*arabino*-hexuronic acid, which is degraded stepwise to oxalic acid, formic acid. and carbon dioxide[10].

The reactions of 2-deoxy-D-*lyxo*-hexose (**15**) and 2-deoxy-D-*erythro*-pentose (**19**)



Scheme 2

followed essentially the same course as that of 2-deoxy-D-*arabino*-hexose. The primary reaction of **15** afforded 2-deoxy-D-*lyxo*-hexonic acid (**16**), 2-deoxy-D-*lyxo*-hexono-1,4-lactone (**17**), and 1-*O*-formyl-D-lyxitol (**18**). The last compound is the same as 5-*O*-formyl-D-arabinitol. Under the experimental conditions used, the ester was hydrolyzed to D-arabinitol (**7**), which was isolated, and identified by mixed melting-point and comparative i.r. spectra. The nonvolatile acid from **15**, with an equivalent amount of lithium hydroxide, afforded the corresponding new, crystalline salt.

Reaction of 2-deoxy-D-*erythro*-pentose (**19**) with alkaline hydrogen peroxide afforded 2-deoxy-D-*erythro*-pentonic acid (**20**) (separated as the new, crystalline lithium salt), 2-deoxy-D-*erythro*-pentonolactone (**21**), and 1-*O*-formylerythritol (**22**). The last compound was separated by chromatography. Acid hydrolysis of the eluted product afforded crystalline erythritol, which was identified by mixed melting-point and comparative i.r. spectra.

DECOMPOSITION OF HYDROGEN PEROXIDE BY HYDROPEROXIDE ANION

Many reactions depend upon hydroxyl and hydroperoxide radicals formed by decomposition of hydrogen peroxide. To obtain a better understanding of the reactions, we have studied the decomposition of hydrogen peroxide in considerable detail. It is generally assumed that the decomposition takes place by a process described by Haber and Weiss[7] in 1934. These authors advanced the hypothesis that catalytic decomposition of hydrogen peroxide by ferrous ion involves the production of hydroxyl and hydroperoxide radicals by the reactions shown in eq. *1* and *2*.

Under alkaline conditions, hydrogen peroxide undergoes ionization, affording

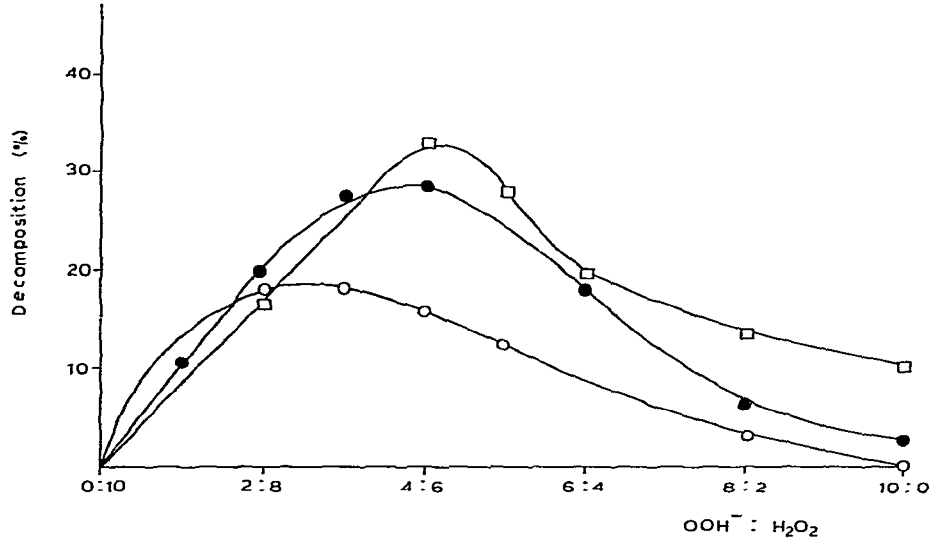


Fig. 1. Decomposition of alkaline hydrogen peroxide by hydroperoxide anion. (Key: □ at 0°; ● at 25°; ○ at 40°.)

$$H_2O + Fe^{2+} \longrightarrow {}^{\cdot}OH + OH^{-} + Fe^{3+} \qquad 1$$

$$OOH^{-} + Fe^{3+} \longrightarrow {}^{\cdot}OOH + Fe^{2+} \qquad 2$$

$$H_2O_2 + OH^{-} \longrightarrow OOH^{-} + H_2O \qquad 3$$

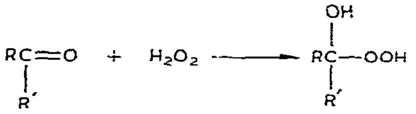
$$H_2O_2 + OOH^{-} \longrightarrow {}^{\cdot}OH + H_2O + {}^{\cdot}O_2^{-} \qquad 4$$

$${}^{\cdot}OH + {}^{\cdot}O_2^{-} \longrightarrow OH^{-} + O_2 \qquad 5$$

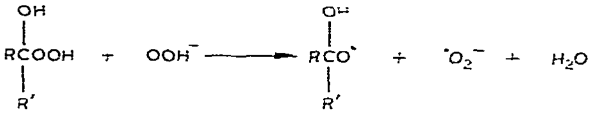
$$H_2O_2 + {}^{\cdot}O_2^{-} \longrightarrow {}^{\cdot}OH + OH^{-} + O_2 \qquad 6$$

$$OOH^{-} + {}^{\cdot}OH \longrightarrow H_2O + {}^{\cdot}O_2^{-} \qquad 7$$

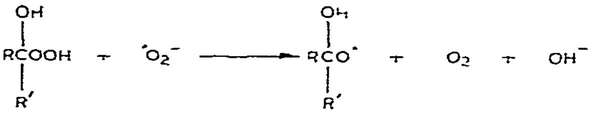
$$3\,H_2O_2 \longrightarrow 2\,{}^{\cdot}OH + 2\,H_2O + O_2 \qquad 8$$



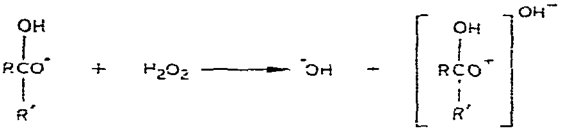
$$R'RC{=}O + H_2O_2 \longrightarrow R'RC(OH)OOH \qquad 9$$



$$R'RC(OH)OOH + OOH^{-} \longrightarrow R'RC(OH)O^{\cdot} + {}^{\cdot}O_2^{-} + H_2O \qquad 10$$



$$R'RC(OH)OOH + {}^{\cdot}O_2^{-} \longrightarrow R'RC(OH)O^{\cdot} + O_2 + OH^{-} \qquad 11$$



$$R'RC(OH)O^{\cdot} + H_2O_2 \longrightarrow {}^{\cdot}OH + \left[R'RC(OH)O^{+}\right]OH^{-} \qquad 12$$

$$Mg(OH)_2 + {}^{\cdot}O_2^{-} \longrightarrow Mg(OO^{\cdot})(OH) + OH^{-} \qquad 13$$

$$Mg(OO^{\cdot})(OH) + {}^{\cdot}OH \longrightarrow MgO + O_2 + H_2O \qquad 14$$

hydroperoxide anion (eq. *3*). Reaction of this anion with hydrogen peroxide affords hydroxyl radical, superoxide radical, and water (eq. *4*). Reaction of hydroxyl radical and superoxide radical affords hydroxyl ion and oxygen (eq. *5*). Thus, one mole of hydrogen peroxide is decomposed by one mole of hydroperoxide anion in a non-chain process (eqs. *4* and *5*). Alternatively, decomposition of hydrogen peroxide may take place by a chain reaction that begins with superoxide radical. This radical, a reducing agent, reacts with hydrogen peroxide, forming hydroxyl radical, hydroxyl ion, and oxygen (eq. *6*). Reaction of hydrogen peroxide anion with hydroxyl radical (eq. *7*) egenerates the superoxide radical, affording a chain reaction (eqs. *3*, *6*, and *7*), hereby hydrogen peroxide is converted into water and oxygen.

To ascertain whether decomposition of hydrogen peroxide does, in fact, roceed by both a chain, and a non-chain process, we studied the decomposition by he method of continuous variation in solutions containing increasing proportions f alkali. The results (see Fig. 1) show that, with increasing proportions of alkali, he decomposition of hydrogen peroxide in a fixed period of time increases to a aximum and then decreases. At low temperatures, the maximum occurs at a point here the ratio $OOH^- : H_2O_2$ is $\sim 0.7 : 1$. At higher temperatures, the maximum shifts, nd the ratio becomes less. Decomposition of hydrogen peroxide by the non-chain rocess of eqs. *4* and *5* would show a maximum when the ratio $OOH^- : H_2O_2$ is $1 : 1$, hereas decomposition involving the chain reaction of eqs. *3*, *6*, and *7* would show maximum at a lower ratio that depends on the length of the chain. The shift in the osition of the maximum in the curves in Fig. 1 indicates that the contribution of the hain reaction to the overall process increases with increase in temperature. The hain may be started by traces of a catalyst, and may be terminated by the reaction f eq. *5* or by decomposition of either radical by any other process.

NHANCEMENT OF THE OXIDATIVE POWER OF ALKALINE HYDROGEN PEROXIDE BY CARBOYDRATES, AND INHIBITION BY MAGNESIUM HYDROXIDE

The sum of the reactions of eqs. *3*, *4*, and *6*, given in eq. *8**, shows that deomposition of hydrogen peroxide by hydroperoxide anion provides an abundant urce of hydroxyl radical, one of the strongest oxidants known[11]. In a prior paper[12], e ascribed the previously known enhancement of the oxidative power of alkaline ydrogen peroxide by L-ascorbic acid to a chain reaction leading to a supply of ydroxyl radical. Enhancement of the oxidative power of alkaline hydrogen peroxide y carbohydrates in general may also be ascribed to reactions leading to the production hydroxyl radicals. Thus, with an excess of alkaline hydrogen peroxide, a carbonyl mpound forms an adduct (eq. *9*) that exists in solution until decomposed by the actions of either eq. *10* or *11*. Reaction *10* affords an oxy radical and a superoxide dical, both of which, with additional hydrogen peroxide, afford hydroxyl radical qs. *6* and *12*). Fig. 2 illustrates the acceleration in the decomposition of alkaline ydrogen peroxide by the addition of 2-deoxy-D-*arabino*-hexose, and the inhibition the decomposition by magnesium hydroxide.

The discovery that magnesium carbonate retards the degradation of cellulose the oxidative bleaching of wood pulp[13–15] has stimulated much research on the fect of magnesium compounds on the reactions of carbohydrates with oxygen and drogen peroxide under alkaline conditions. Several hypotheses have been advanced account for this effect, but the cause is still largely unknown. We assumed, as a

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n our Preliminary Communication[2], eq. *4* on p. c9 thereof does not enter into the summation, en here as eq. *8*.

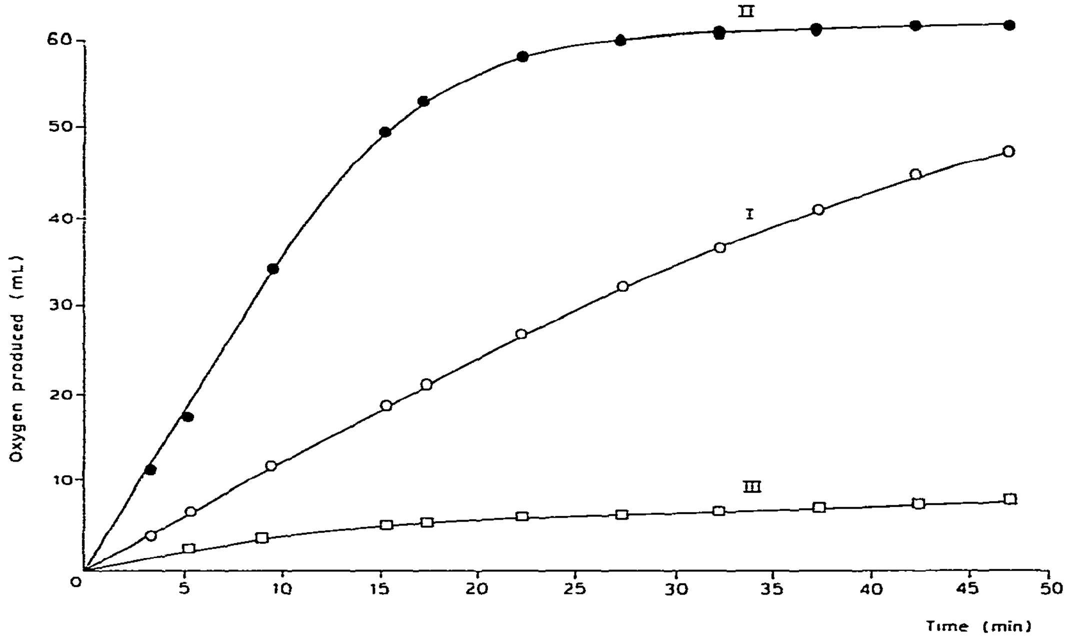

Fig. 2. Effect of a carbonyl compound and of magnesium hydroxide on the decomposition of hydrogen peroxide at 40°. [Curve I. KOH (1 mL; 3M), H_2O (1 mL), and H_2O_2 (1 mL, 30%). Curve II. Same as curve I, plus 2-deoxy-D-*arabino*-hexose (164 mg). Curve III. Same as curve I, plus $MgSO_4$ (25 mg).]

working hypothesis[8], that the superoxide radical forms a magnesium–superoxide complex (eq. *13*). This complex would immobilize, and possibly precipitate, the superoxide radical. Removal of superoxide radical by any means would inhibit production of hydroxyl radical, and thus lessen the oxidative capacity of the reaction mixture. The complex may also act as a scavenger for hydroxyl radicals by the reaction shown in eq. *14*. The hypothesis does not explain why magnesium hydroxide is much more effective than other hydroxides. Obviously, more experimental work is necessary for a clear understanding of the inhibiting effect.

EXPERIMENTAL

General. — Evaporations were conducted under diminished pressure at a bath temperature of less than 40°. Melting points (uncorrected) were determined with a Kofler apparatus. Specific rotations were measured with a Perkin–Elmer Model 141 photoelectric polarimeter. Infrared spectra were recorded, either for Nujol mulls or KBr pellets, with a Perkin–Elmer Model 137 spectrophotometer. The following solvents were used for paper chromatography: (*A*) 4:1:1 1-butanol–ethanol–water, and (*B*) 3:2:1:1 butyl acetate–acetic acid–ethanol–water. Whatman No. 1 paper was used for qualitative, and No. 3MM for preparative, chromatography. Detection was effected with silver nitrate and sodium hydroxide. A.C.S.-certified-grade reagents and solvents were used as purchased. Commercial "2-deoxy-D-glucose", "2-deoxy-D-galactose", and "2-deoxy-D-ribose" were recrystallized to give chromatographically pure sugars.

General procedure for isolation of products. — Reaction mixtures were prepared from the 2-deoxy-D-aldoses, ice-cold potassium hydroxide solutions, and hydrogen peroxide with, and without, the addition of magnesium sulfate or magnesium oxide. The mixtures were placed in lightly stoppered test-tubes, and maintained, with agitation, at the temperatures cited. After the desired reaction-period, the excess of hydrogen peroxide was decomposed by the addition, to each tube, of 0.1 g of activated carbon (Norit) followed by heating in a hot-water bath until evolution of oxygen ceased. Each suspension was then filtered, and the filtrate diluted to a definite volume. Aliquots were used for determining optical rotation, chromatographic behavior, formic acid, 2-deoxyldonic acids, alditols, and organic peroxides.

In preliminary studies with 2-deoxy-D-*arabino*-hexose, the reaction products were separated into a "neutral fraction" and an "acid fraction". The separation was not sharp, because of interconversion of acid **5** and its lactone **11**. Omission of the separation step in the oxidation of all three deoxy sugars, and preparation of the lithium salts directly, gave, under optimum conditions, 2-deoxyaldonic acids in yields of up to 80%.

Oxidation of 2-deoxy-D-aldoses with alkaline hydrogen peroxide under mild conditions. — (*a*) *Preparation of lithium 2-deoxy-*D-arabino-*hexonate.* A reaction mixture consisting of **1** (3 mmol), 3M potassium hydroxide (6 mL), magnesium oxide (150 mg), and 30% hydrogen peroxide (12 mL) was prepared with ice-cold reagents. The mixture was kept, with gentle agitation, for 2 h in a waterbath at room temperature, and for 18 h at 40°. Norit (150 mg) was then added, and, when the evolution of gas had ceased, the mixture was filtered. Paper chromatography revealed a single spot. The filtrate was then passed through Amberlite IR-120 (H^+) resin (25 mL). The acid effluent was evaporated under diminished pressure, and the residue dehydrated by successive addition and evaporation of three 5-mL portions of toluene. The dry residue (0.4515 g) was dissolved in 0.1M lithium hydroxide (28.0 mL), and, after concentration, the solution afforded fine, needle-like crystals. The lithium 2-deoxy-D-*arabino*-hexonate was recrystallized from water with the addition of methanol, and dried over calcium chloride under diminished pressure; yield 80%; $[\alpha]_D^{25}$ +4.3° (*c* 4, H_2O). This salt, prepared from the pure lactone, was reported in our preliminary publication[2], but direct preparation of the salt is simpler.

Anal. Calc. for $C_6H_{11}LiO_6$: C, 38.73; H, 5.96; Li, 3.73. Found: C, 38.64; H, 6.08; Li, 3.69.

(*b*) *Preparation of lithium 2-deoxy-*D-lyxo-*hexonate.* Application of the method described in section (*a*) to the preparation of the lithium salt of **16** afforded a dry residue (0.4256 g, 87%) of crude lithium 2-deoxy-D-*lyxo*-hexonate. The new salt was recrystallized from water, with addition of methanol to incipient turbidity; $[\alpha]_D^{25}$ −2.2° (*c* 2, H_2O).

Anal. Calc. for $C_6H_{11}LiO_6$: C, 38.73; H, 5.96; Li, 3.73. Found: C, 38.64; H. 6.08: Li, 3.59.

*(c) Preparation of lithium 2-deoxy-*D-erythro-*pentonate.* The oxidation method described in section (*a*) was applied to 2-deoxy-D-*erythro*-pentose, and the nonvolatile acid was neutralized with lithium hydroxide. Upon concentration of the neutral solution, and treatment with methanol, the lithium salt slowly crystallized in 80% yield. The compound was recrystallized from water by addition of methanol to incipient turbidity; $[\alpha]_D^{25}$ −1.0° (*c* 2, H_2O).

Anal. Calc. for $C_5H_9LiO_5$: C, 38.48: H, 5.81: Li, 4.45. Found: C, 38.52: H, 5.92: Li, 4.38.

*Oxidation of 2-deoxy-*D-arabino-*hexose at low temperatures.* — An ice-cold mixture consisting of **1** (1 mmol), 2M potassium hydroxide (1 mL), 0.01M magnesium sulfate (1 mL), and 30% hydrogen peroxide (1 mL) was kept at 0–5°. The mixture remained colorless, with little or no evolution of gas, for six months. The excess of hydrogen peroxide was then removed by addition of 50 mg of Norit, followed by warming of the mixture at 40° until evolution of oxygen ceased, and filtration; the filtrate gave the following results: pH 12.9, 0.86 mmol of formic acid, a negative test for **1**, and a qualitative test for an organic peroxide. When treated as described in section (*a*), the reaction mixture afforded the new lithium salt in 75% yield.

*Isolation of 2-deoxy-*D-arabino-*hexono-1,4-lactone.* — A reaction mixture consisting of **1** (3 mmol), water (3 mL), 3M potassium hydroxide (3 mL), magnesium oxide (150 mg), and 30% hydrogen peroxide (3 mL) was prepared from ice-cold reagents, and kept for 5 days at room temperature. Norit was then added, and, when evolution of gas had ceased, the mixture was filtered. The filtrate was cooled in an ice-bath and mixed with mixed cation- and anion-exchange resins (30 mL). The resulting, salt-free suspension was filtered immediately, and the filtrate was evaporated to dryness under diminished pressure. The residue (0.273 g) was extracted with acetone, and the extract evaporated to a syrup (0.180 g, 36.5%) which, in the course of several days, afforded crystalline 2-deoxy-D-*arabino*-hexono-1,4-lactone. Recrystallization from 1,4-dioxane–ether afforded pure lactone **11**; m.p. 97–98°, $[\alpha]_D^{25}$ +68° (*c* 4, H_2O); lit.[16] m.p. 95–97°, $[\alpha]_D$ +68° (*c* 2, H_2O).

Isolation of D-*arabinitol.* — The mother liquor from the crystallization of lactone **11** was combined with the acetone-insoluble material. The solvent was evaporated, and the solid material (0.0787 g, 17%) was dissolved in 3M potassium hydroxide (1 mL). The solution was kept for 18 h at 40°, to decompose residual lactone, treated with mixed ion-exchange resin (10 mL), and evaporated, whereupon D-arabinitol (0.05 g) crystallized. The m.p. (103°) and i.r. spectrum were identical to those of authentic D-arabinitol. Acetylation (acetic anhydride–pyridine) afforded crystalline D-arabinitol pentaacetate, m.p. 74–75°, $[\alpha]_D^{25}$ +37° (*c* 2, $CHCl_3$); lit.[17] m.p. 74–75°, $[\alpha]_D^{20}$ +37.2° (*c* 7, $CHCl_3$).

Isolation of erythritol. — A mixture of 2-deoxy-D-*erythro*-pentose (3 mmol), water (3 mL), 3M potassium hydroxide (3 mL), and 30% hydrogen peroxide (1 mL) was kept for one day at 0° and two days at room temperature. After addition of

Norit (150 mg), the mixture was kept for 18 h at 40°, to decompose the excess of hydrogen peroxide and to hydrolyze the formic ester and lactone present. The mixture was treated with mixed ion-exchange resin (25 mL), and evaporation of the salt-free solution afforded a partially crystalline residue (0.160 g) which, on acetylation (acetic anhydride–pyridine), gave crystalline erythritol tetraacetate, m.p. 87°; lit.[18] m.p. 89°. The product was identical with erythritol tetraacetate prepared from commercial erythritol.

Oxidation with alkaline hydrogen peroxide in large excess at 40° in the presence, and absence, of magnesium hydroxide. — (*a*) *Oxidation of 2-deoxy-*D-arabino-*hexose.* A solution of **1** (0.164 g, 1 mmol) and magnesium sulfate (5 mg) in water (1 mL) was kept, under agitation, in a water-bath at 40°. At 15-min intervals, 3M potassium hydroxide (0.5 mL) and 30% hydrogen peroxide (0.5 mL) were added during 2 h, and the solution was kept for 18 h at 40°: analysis then showed the presence of the following compounds: formic acid (0.54 mmol, 9%), 2-deoxy-D-*arabino*-hexonic acid (**5**; 0.7 mmol, 70%), D-arabinitol (**7**; 0.15 mmol, 15%), and a small amount of unreacted **1**.

On repetition of the experiment, but without the addition of magnesium sulfate, chromatography showed that all of the **1** had been oxidized. The solution contained, by analysis, 5.48 mmol (91%) of formic acid.

(*b*) *Oxidation of* D-*arabinitol.* Oxidation of **7** (0.152 g, 1 mmol) by alkaline hydrogen peroxide was conducted as just described for compound **1**. After the solution had been kept for 20 h at 40°, analysis showed 0.78 mmol (15.6%) of formic acid per mmol of **7**. By treatment of the reaction mixture with ion-exchange resins, and evaporation of the solution, 0.776 mmol (77.6%) of **7** was recovered.

The experiment was repeated without the addition of magnesium sulfate. The solution then afforded 4.5 mmol (90%) of formic acid per mmol of **7**, and no unreacted **7**.

(*c*) *Oxidation of lithium 2-deoxy-*D-arabino-*hexonate.* The experimental procedure just described was applied to the oxidation of lithium 2-deoxy-D-*arabino*-hexonate. The product obtained from the experiment conducted in the presence of magnesium sulfate showed, by analysis, 0.4 mmol of formic acid per mmol of substrate, whereas the product obtained in the absence of magnesium sulfate contained 3.81 mmol of formic acid per mmol.

*Interconversion of lithium 2-deoxy-*D-arabino-*hexonate and 2-deoxy-*D-arabino-*hexono-1,4-lactone.* — A sample of pure lithium 2-deoxy-D-*arabino*-hexonate was treated with a cation-exchange resin, and the effluent was evaporated, and the residue dehydrated. Paper chromatography showed, not only lactone **11** and acid **5**, but also a small amount of a slow-moving constituent that has not yet been identified. Heating of the lactone or acid with glacial acetic acid caused partial conversion into a compound showing a high R_F value in chromatography. Neither compound has been investigated further.

Decomposition of alkaline hydrogen peroxide by hydroperoxide anion. — The data for the curves shown in Fig. 1 were obtained from measurements of the decomposition of hydrogen peroxide in solutions containing increasing proportions of potassium hydroxide. Mixtures prepared from 2M hydrogen peroxide (5 mL) and water (10 mL, containing 0 to 10 mmol of potassium hydroxide) were kept at 0, 25, or 40°. After 6 days for the solutions at 0°, 6 h for those at 25°, and 2 h for those at 40°, the remaining hydrogen peroxide was determined by titration with potassium permanganate in the usual way[19]. The ratios of hydroperoxide anion to hydrogen peroxide were calculated on the assumption that one mole of potassium hydroxide affords one mole of hydroperoxide anion. The results showed maxima at OOH^- : H_2O_2 ratios of 0.28, 0.56, and 0.69, respectively, for the measurements conducted at 40, 25, and 0°. A non-chain reaction of hydrogen peroxide and hydroperoxide anion would show a maximum at a ratio of 1 : 1.

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