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DEGRADATION OF 1,5-ANHYDRORIBITOL AND 1,5-ANHYDROXYLITOL BY OXYGEN IN AQUEOUS SODIUM HYDROXIDE SOLUTIONS

EUGENE C. MILLARD, LELAND R. SCHROEDER*, AND NORMAN S. THOMPSON
The Institute of Paper Chemistry, Appleton, Wisconsin 54911 (U. S. A.)
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ABSTRACT

Degradation of both 1,5-anhydroribitol (**1**) and 1,5-anhydroxylitol (**2**) by oxygen in 1.25M sodium hydroxide at 120° exhibited induction periods and produced hydrogen peroxide. The maximum concentration of hydrogen peroxide was attained at less than 10% reaction of **1** and **2**. An intermediate, organic peroxide was detected in reactions of **2**, but not in reactions of **1**. The rate of degradation of **1** was much greater than that of **2**. The reaction of **1** was second order with respect to **1**, whereas the reaction of **2** displayed complex kinetics indicative of autoinhibition by reactive intermediates. A free-radical mechanism involving intermediate α-hydroxyhydroperoxidic species is proposed for the reactions of **1** and **2**. In contrast to reactions of **1**, the α-hydroxyhydroperoxidic species formed in reactions of **2** are postulated to be stabilized by intramolecular hydrogen-bonding. The augmented stability of the α-hydroxyhydroperoxidic species would increase the importance of peroxy radical–peroxy radical termination-reactions, which produce nonradical products. The termination reactions, by decreasing the rate of the radical chain-reaction, effect autoinhibition. The acidic degradation products formed from **1** and **2** were identical, but were formed in different relative ratios. The major products were formic acid, acetic acid, lactic acid, glycolic acid, glyceric acid, 3-*O*-(carboxymethyl)glyceric acid, and 1,4-anhydro-2-*C*-carboxytetritols. Possible pathways for formation of the products are presented.

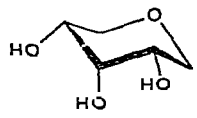
INTRODUCTION

During delignification of wood or pulp by molecular oxygen in alkaline media, degradation of the polysaccharides can be quite severe. The degradation is manifested primarily as a decrease in viscosity caused by depolymerization of the polysaccharides[1–3]. Studies of cellulosic model-compounds[4–11] indicate that the depolymerization is caused by oxidation of hydroxyl groups of the monomeric glycose residues to form carbonyl-containing intermediates, which may undergo base-catalyzed

*To whom correspondence should be addressed.

β-elimination reactions to cleave the glycosidic linkages[12–14]. Oxidation is also postulated to produce α-dicarbonyl intermediates which, on further oxidation, yield dicarboxylic acids[8–9] or which may also undergo ring contraction via a benzilic acid type of rearrangement to form *C*-carboxy-furanoid species[8,9,11,15].

In this paper we report on a study of the degradation of 1,5-anhydroribitol (**1**) and 1,5-anhydroxylitol (**2**) by oxygen in aqueous sodium hydroxide. These model compounds were selected to determine whether the configuration of the hydroxyl groups of a pyranoid ring would affect the rate and mode of its degradation. Since the advent of this investigation, Malinen and Sjöström[11] have reported that methyl α-D-mannopyranoside is degraded more rapidly than methyl α-D-glucopyranoside by oxygen in alkali, a fact that is consistent with the present results.



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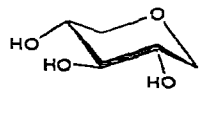

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RESULTS

General. — Degradations of **1** and **2** were studied by using 1.25M sodium hydroxide at 120°, with 75 lb. in.$^{-2}$ partial oxygen pressure (25°), and both 0.01M and 0.1M anhydroalditol. Disappearance of the anhydroalditols was monitored by quantitative g.l.c. analysis of deionized, acetylated samples of the reaction components.

The reactions exhibited short induction-periods that were primarily evident when an initial anhydroalditol concentration of 0.01M was used. These periods were extremely variable[16]. However, the reactions were subsequently very reproducible, as illustrated in Fig. 1.

Extreme variation in the rate of stirring of the solutions had no effect on the rate of anhydroalditol degradation[16]. Thus, as has also been reported for alkali–oxygen reactions of other carbohydrates[17,18], diffusion of oxygen into the reaction solution is evidently not a rate-controlling factor in the degradations of **1** and **2**.

1,5-Anhydroribitol (**1**) was degraded much more rapidly than 1,5-anhydroxylitol (**2**) (for example, see Fig. 1), a fact which must be attributed at least to the difference in the configuration of the hydroxyl group at C-3 of **1** and **2**, and possibly also to the configurational relationship between adjacent hydroxyl groups of **1** and **2**. 1,5-Anhydroribitol has only *cis* 1,2-glycol groups, whereas 1,5-anhydroxylitol has only *trans* 1,2-glycol groups. Similarly, methyl α-D-mannopyranoside is degraded more rapidly than its C-2 epimer, methyl α-D-glucopyranoside, by oxygen in aqueous sodium hydroxide[11].

Kinetic analysis. — To determine the order of the reactions with respect to the anhydroalditol, it was assumed that the concentrations of oxygen and sodium hydroxide remained essentially constant during the reactions. Thus, the basic rate-

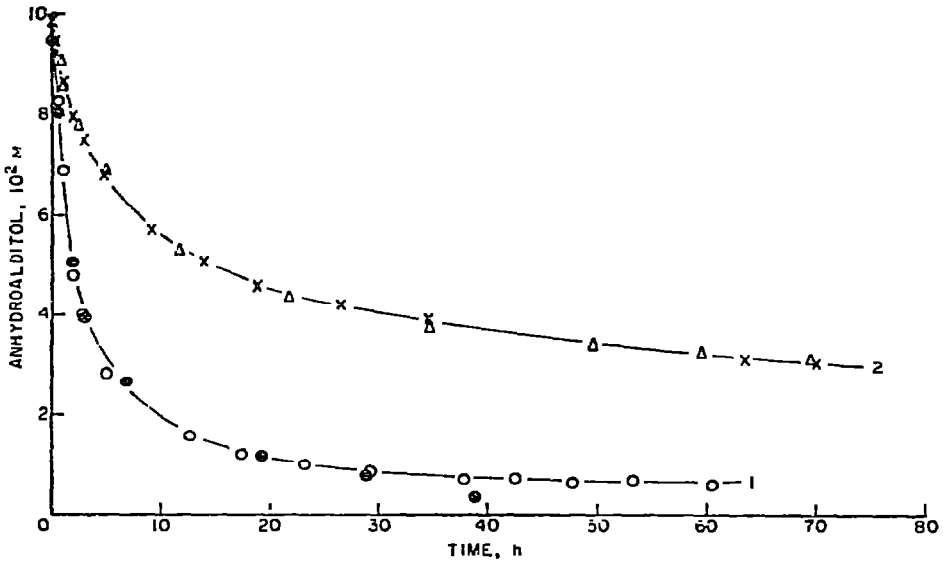


Fig. 1. Duplicate reactions of 0.1M 1,5-anhydroribitol (1) and 0.1M 1,5-anhydroxylitol (2) in 1.25M sodium hydroxide at 125° and 75 lb.in.$^{-2}$ of oxygen (25°).

expression given in equation (*1*) could be expressed as in equation (*2*) or equation (*3*):

$$-\mathrm{d}[A]/\mathrm{d}t = k[A]^a[\mathrm{O_2}]^b[\mathrm{NaOH}]^c, \quad (1)$$

$$-\mathrm{d}[A]/\mathrm{d}t = k'[A]^a, \quad (2)$$

$$\log(-\mathrm{d}[A]/\mathrm{d}t) = \log k' + a\log[A], \quad (3)$$

where A is **1** or **2**; t is time; k is the rate constant; a, b, and c are the orders of the reaction with respect to the indicated reactant; and $k' = k[\mathrm{O_2}]^b[\mathrm{NaOH}]^c$ and is essentially constant.

The solubility of oxygen in the solution would be low, $\sim 2.5 \times 10^{-3}$M[19], and hence it would not be present in large excess relative to the anhydroalditol. However, as diffusion of oxygen into the solution was not a rate-determining factor, the constant pressure of oxygen maintained over the solution ensured that the concentration of oxygen was constant throughout the reactions.

For reactions with 0.01M anhydroalditol, the concentration of sodium hydroxide (1.25M) was in large excess relative to that of **1** or **2**, and thus its concentration remained essentially constant throughout the reactions. For 0.1M anhydroalditol, the assumption that the concentration of sodium hydroxide remains essentially constant in the reaction would seem at first to be inappropriate, particularly for reactions of **1** that were analyzed to 80–90% completion. However, kinetic analyses of reactions of **1** made using this assumption indicated a second-order dependence on **1** at both

0.01M and 0.1M **1**. This would not be expected if the concentration of sodium hydroxide decreased sufficiently during the period of analysis to drastically affect the rate of reaction.

The reactions were analyzed by the differential method[20] using equation (*3*). The variable induction-periods made it impractical to utilize the differential method involving variation of initial reaction-conditions. However, as the degradation rate attained after the induction period was essentially the same for duplicate experiments (see Fig. 1), the differential method employing single kinetic trials was applicable. Analysis entailed measuring the reaction rate at various reaction times corresponding to a number of reactant concentrations, and plotting the data according to equation (*3*), as illustrated in Fig. 2. The slope of the line is *a*, the order of the reaction with

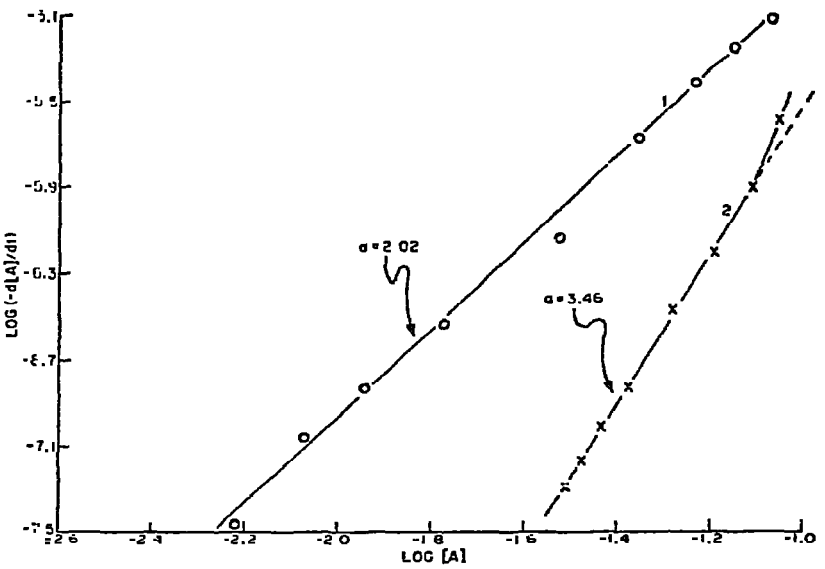


Fig. 2. Determination of the reaction order, *a*, with respect to the anhydroalditol for 0.1M 1,5-anhydroribitol (**1**) and 0.1M 1,5-anhydroxylitol (**2**) in 1.25M sodium hydroxide at 120° and 75 lb $in.^{-2}$ of oxygen (25°).

respect to the anhydroalditol. Values of *a* obtained for reactions of 1,5-anhydroribitol (**1**) were 2.08 and 2.02 at 0.01 and 0.1M **1**, respectively. In contrast, the *a* values for reactions of 1,5-anhydroxylitol (**2**) were 3.03 and 3.46 at 0.01 and 0.1M **2**, respectively. The value of *a* for reactions of **2** also increased at early reaction-times, corresponding to higher concentrations of **2** (see Fig. 2).

Products. — (*a*) *Peroxides.* The concentrations of hydrogen peroxide and organic peroxides formed in reactions of **1** and **2** were determined by a modified colorimetric method[16,21–23]. The procedure is based on the fact that hydrogen peroxide complexes with titanium(IV). Hydrogen peroxide complexes rapidly with the reagent and may thus be differentiated from organic peroxides (which must first

be hydrolyzed to form hydrogen peroxide) by measuring the change in the absorbance in the sample with time. The estimate of the concentration of organic peroxide is probably low, as the extent of their hydrolysis is not known, and organic peroxides may undergo decomposition reactions other than hydrolysis.

As illustrated in Fig. 3A, hydrogen peroxide was formed in reactions of both **1** and **2**. The maximum concentration of hydrogen peroxide was attained at approximately 10% reaction of the anhydroalditol for both reactions, but the maximum concentration of hydrogen peroxide in the reaction of **1** was greater than twice that in the reaction of **2**.

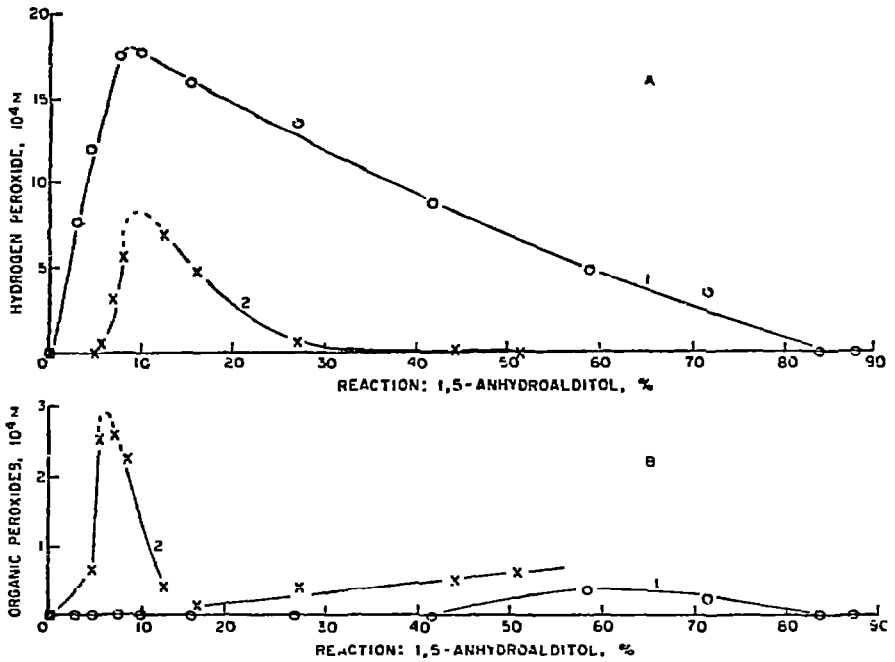
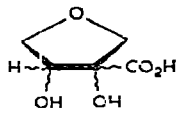


Fig. 3. Hydrogen peroxide (A) and organic peroxide (B) formation in degradations of 0.1M 1,5-anhydroribitol (**1**) and 0.1M 1,5-anhydroxylitol (**2**) in 1.25M sodium hydroxide at 120° and 75 lb.in.$^{-2}$ of oxygen (25°).

The organic-peroxide profile for reactions of **1** and **2** were totally different (see Fig. 3B). No organic peroxides were detectable in the reactions of **1** at early times of reaction. At longer reaction times, some organic peroxides were detected, but the results are inconclusive. In sharp contrast, the concentration of organic peroxide exhibited a maximum early in the reaction of **2**, decreased to a minimum, and then increased. Thus, an intermediate organic peroxide is formed, in significant concentration, early in the degradation of **2**.

(*b*) *Carboxylic acids*. The acidic products formed in the degradations of **1** and **2** were the same. The major ones were formic acid (**3**), acetic acid (**4**), lactic acid (**5**),

glycolic acid (**6**), glyceric acid (**7**), 2,3-dihydroxybutanoic acid (**8**), 3-*O*-(carboxymethyl)glyceric acid (**9**), and an isomeric mixture of 1,4-anhydro-2-*C*-carboxytetritols (**10**). 3-Hydroxypropanoic acid (**11**), 2-hydroxybutanoic acid (**12**), and 2,4-dihydroxybutanoic acid (**13**) were minor degradation products. Potential pathways for formation of these products are presented later.



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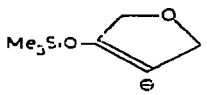
Formic acid and acetic acid were identified as their benzyl esters by comparison of their g.l.c. retention-times with those of authentic materials.

Lactic acid, glycolic acid, and glyceric acid, in combination with 2,3-dihydroxybutanoic acid[24], were identified as their pertrimethylsilyl(Me_3Si) ethers by comparison of their g.l.c. retention-times and g.l.c.–mass spectra with those of authentic materials. 3-*O*-(Carboxymethyl)glyceric acid, 3-hydroxypropanoic acid, 2-hydroxybutanoic acid, and 2,4-dihydroxybutanoic acid were identified as their Me_3Si derivatives by g.l.c.–m.s. Analysis of the mass spectra of the acids relied heavily on the studies of Petersson[25,26].

The isomeric 1,4-anhydro-2-*C*-carboxytetritols (**10**), analogous to the methyl *C*-carboxyglycofuranosides formed in similar reactions of methyl glycosides[8,9,11], were identified as their Me_3Si derivatives by g.l.c.–m.s. The major diagnostic peaks were *m/e* 364 (P^+), 349 ($P^+ - 15$), and 157.



m/e 157

Quantitative analyses of the major products, excluding acetic and formic acid, as a function of the extent of reaction of **1** and **2**, are shown in Fig. 4. Lactic acid and glycolic acid are fairly stable products, as indicated by the fact that their rate of formation was at all times equal to, or greater than, their rate of degradation. In contrast, glyceric acid, 2,3-dihydroxybutanoic acid, and the anhydrotetritols (**10**), all of which contain 1,2-glycol groups, are degraded in the reaction systems. Whether or not 3-*O*-(carboxymethyl)glyceric acid is stable in the reaction media is uncertain.

DISCUSSION

A mechanism proposed for the degradation of **1** and **2** by oxygen in alkaline media is given in equations (*4*) through (*22*), where H–C–OH is a carbinol group of either **1** or **2** and M is a catalytic metal. The mechanism, based on both the present

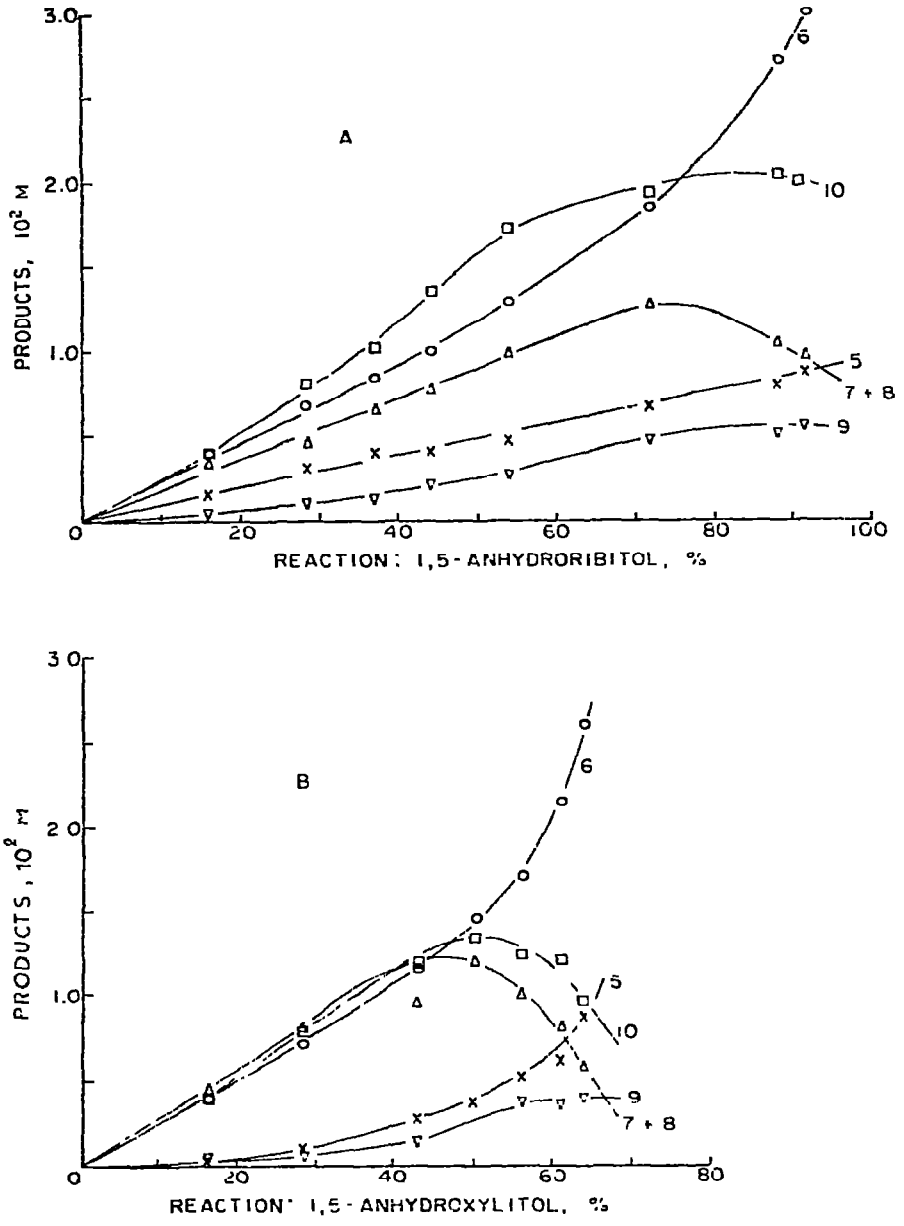
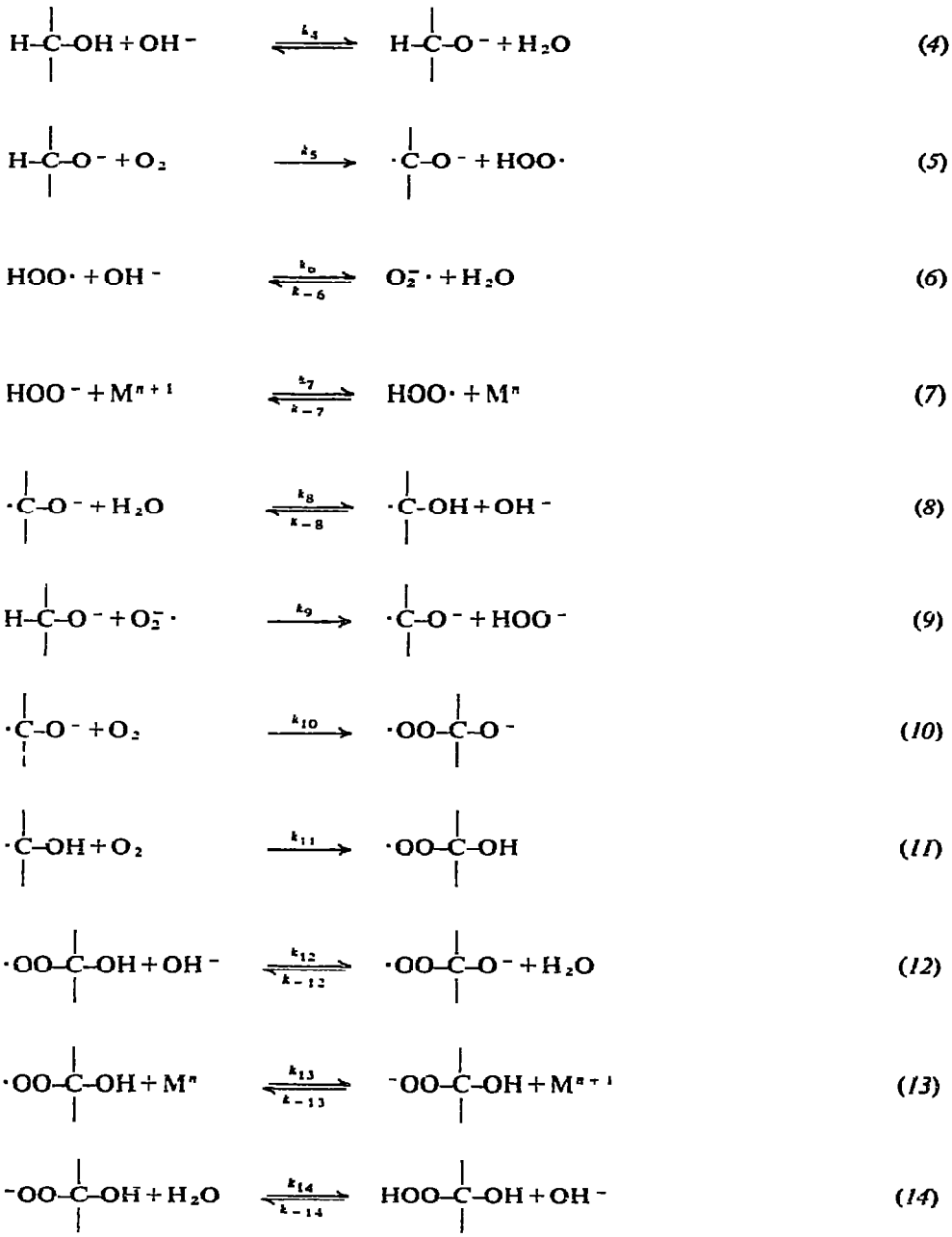
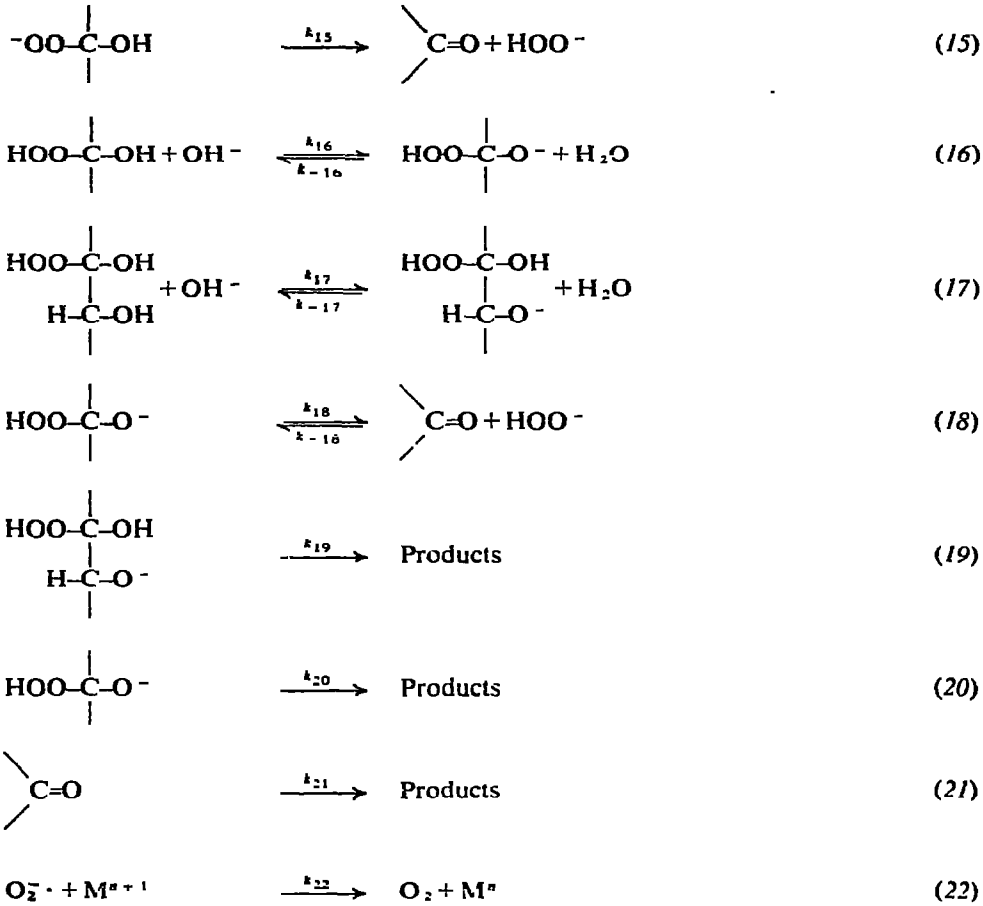


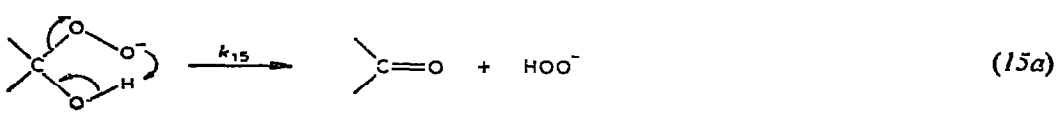
Fig. 4. Major products from degradations of 1,5-anhydroribitol (A) and 1,5-anhydroxylitol (B); lactic acid (5), glycolic acid (6), glyceric acid (7), 2,3-dihydroxybutanoic acid (8), 3-*O*-(carboxymethyl)glyceric acid (9), and 1,4-anhydro-2-*C*-carboxytetritols (10).

results and several studies of other investigators, can account for the observed induction periods, the formation of hydrogen peroxide and an organic peroxide intermediate, the kinetics of the reactions, and the formation of acidic degradation-products.

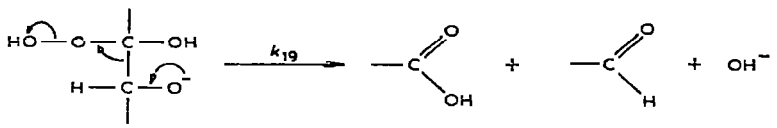




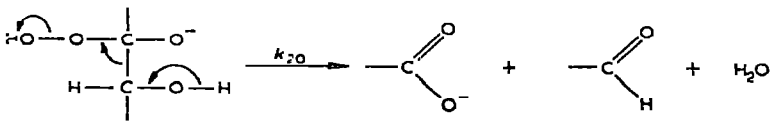
As with other reactions of carbohydrates with oxygen in alkaline media[6,7,10,27], the degradations of **1** and **2** exhibited induction periods during which the concentration of hydrogen peroxide increased. The initial step of the oxidative degradation is believed to be the ionization of a hydroxyl group [reaction (*4*)][6,7,10,11]. Formation of the oxyanion facilitates abstraction of the geminal hydrogen atom by oxygen to form the hydroperoxy radical (HOO·) and the ketyl radical [reaction (*5*)]. The hydroperoxy radical would exist primarily as its conjugate base, the superoxide radical ($O_2^-\cdot$), in the alkaline system [reaction (*6*)][28]. When the concentration of superoxide radical reaches the threshold level, rapid degradation of the anhydroalditols (**1** and **2**) is believed to be propagated by a free-radical chain-reaction involving an α-hydroxyhydroperoxide intermediate [reactions (*6*) through (*18*)]. The α-hydroxyhydroperoxide



would be formed by reaction of oxygen with either the ketyl radical or its conjugate acid [reactions (*10*) and (*11*)] and a subsequent one-electron transfer involving a catalytic metal ion [reaction (*13*)][29]. Carbonyl groups may be formed from either conjugate base of the α-hydroxyhydroperoxide [reactions (*15*) and (*18*)]. Reaction (*15*) is believed to occur by a cyclic process, as indicated in equation (*15a*). The acidic products may be formed from intermediates containing carbonyl groups [reaction (*21*)][4,5,7-15] or directly from an intermediate containing an ionized α-hydroxyhydroperoxy group [reactions (*19*) and (*20*)], as proposed by Isbell[30] and as indicated in equations (*19a*) and (*20a*).



(*19a*)



(*20a*)

Termination of the radical chain-reaction may be effected by the reverse of reaction (*7*) and reaction (*22*).

A rate expression for the disappearance of the anhydroalditols (*A*) was derived on the basis of the reaction mechanism, proposed by making steady-state approximations for the radical species and the catalytic metal ions[16].

$$-\mathrm{d}[A]/\mathrm{d}t = K_4 k_5 [A][\mathrm{OH}^-][\mathrm{O}_2] + K_4^2 k_5 k_9 [A]^2 [\mathrm{OH}^-]^2 [\mathrm{O}_2]/k_{22}[\mathrm{M}^{n+1}] \qquad (23)$$

The first term of the rate expression describes the induction period, which would exhibit a first-order dependence on the anhydroalditol, sodium hydroxide, and oxygen. The concentration of metal ion in the denominator of the second term, being very small, makes this term large relative to the first one. Thus, equation (*23*) indicates that, after the induction period, the reactions of **1** and **2** should exhibit a second-order dependence on the anhydroalditol. This was found to be the case for 1,5-anhydroribitol (**1**), but 1,5-anhydroxylitol (**2**) exhibited higher orders of reaction (see Fig. 2). A potential explanation for the difference between **1** and **2** is given later.

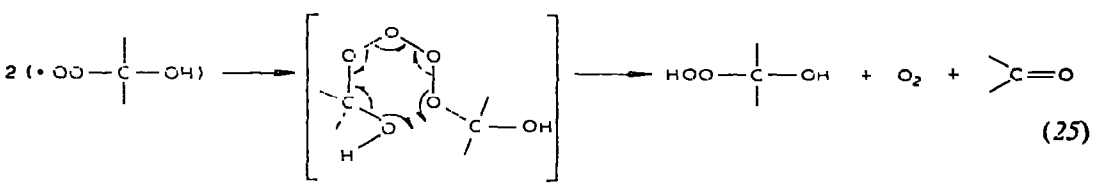
Based on equation (*23*), the reactions of the anhydroalditols would be expected to exhibit also a second-order dependence on the concentration of sodium hydroxide. This was not tested experimentally. Previously, it was reported that the reaction of methyl β-D-glucopyranoside with oxygen in aqueous sodium hydroxide exhibited an approximately first-order dependence on the alkali concentration[7,10]. However, there

are indications that the order of the reaction of methyl β-D-glucopyranoside with respect to the hydroxide concentration may be variable, attaining a higher order as the alkali concentration is increased[31].

When the hydroxyl radical (HO·) was also considered to be a reactive species in the anhydroalditol degradations, a rate expression similar to equation (*23*), but including a third term indicative of the role of the hydroxyl radical, was generated[16]. The additional term has a first-order dependence on the anhydroalditol. As the degradation of **1** was found to be second order with respect to **1**, it can be inferred that the hydroxyl radical does not play a major role in the reaction. This is consistent with the supposition that the hydroxyl radical would not be an important chain-propagating radical in oxidations in which the concentration of metal ion is extremely small[32].

Reactions of 1,5-anhydroxylitol (**2**) exhibited higher reaction orders with respect to the alditol than reactions of 1,5-anhydroribitol (**1**). This is attributed to autoinhibition of reactions of **2** by a reactive intermediate, which would make the reaction order in **2** as a function of time, as determined, greater than the order in **2** with respect to the initial concentration or true order[20]. The inhibitor is postulated to be a species containing a stabilized, α-hydroxyhydroperoxy free-radical. The mechanisms of degradation of **1** and **2** are considered to be the same except that radical chain-termination by reactions (*24*) and (*25*)*, which involve α-hydroxyhydroperoxy radicals, are proposed to play a major role in reactions of **2**. Because these reactions produce only nonradical products, they would cause the radical chain-reaction to slow down and thereby retard the rate of degradation of **2**.

(*24*)



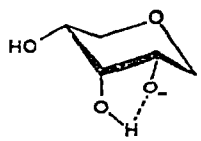
(*25*)

In order for reactions (*24*) and (*25*) to be important in reactions of **2** and not in reactions of **1**, the concentration of species containing α-hydroxyhydroperoxy radicals must be substantially greater in reactions of **2** than in reactions of **1**. The

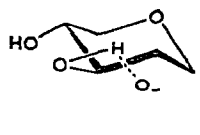
*Reaction (*25*) is proposed to occur through the decomposition of a tetraoxide intermediate via a cyclic transition-state[33]. Tetraoxides derived from tertiary peroxy radicals have been shown to be quasi-stable species at low temperature[34].

reaction of **1** produced essentially no detectable organic peroxides, whereas the concentration of organic peroxides in the reaction of **2** exhibited a maximum early in the reaction, decreased to a minimum, and subsequently increased (see Fig. 3). The curve for organic peroxide in the reaction of **2** can be rationalized as a build up and subsequent degradation of α-hydroxyhydroperoxides in conjunction with a slower build up of dialkyl peroxides. A potential explanation for the difference in the concentration of α-hydroxyhydroperoxidic species in reactions of **1** and **2** is given in the ensuing discussion.

Equatorial hydroxyl groups of **1** and **2** should ionize preferentially, as the resulting oxyanions, being less hindered than their axial counterparts, are more readily solvated[35]. The anions, A^-, would also be stabilized by hydrogen bonding to the hydroxyl group on the adjacent carbon atom[36]. Thus, for **1**, ionization of OH-2 or OH-4 would occur preferentially with the molecule in the $^4C_1$(D) conformation,



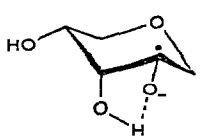
A^- (1)



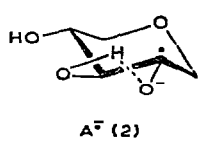
A^- (2)

whereas ionization at OH-3 would be favored in the $^1C_4$(D) conformation*. For **2**, all of the hydroxyl groups are equatorial in the $^4C_1$(D) conformation. For simplicity, only reactions initiated by ionization of OH-2 of **1** and **2** in the $^4C_1$(D) conformation will be discussed. However, the same stereochemical implications apply to any of the equatorial hydroxyl groups of **1** or **2**.

The next step in the radical chain-reaction is abstraction of the hydrogen atom geminal to the oxyanion by the superoxide radical to form the ketyl radical, $A^{\cdot-}$ [reaction (*9*)]. Abstraction of the hydrogen atoms is facilitated by the increased electron density provided by the oxyanion. The hydrogen bonding and solvation



$A^{\cdot-}$ (1)



$A^{\cdot-}$ (2)

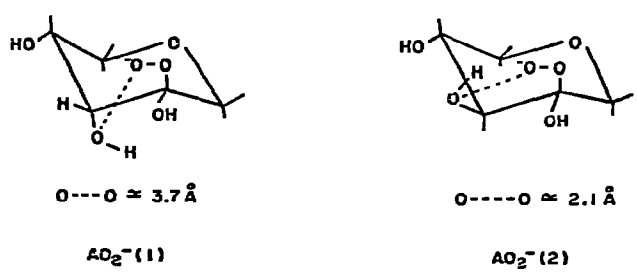
effects would help stabilize the ketyl radical, $A^{\cdot-}$, toward inversion, particularly in $A^{\cdot-}$ (1). Thus, subsequent reaction of $A^{\cdot-}$ with oxygen [reaction (*10*)] would selectively form the conjugate base of the α-hydroxyhydroperoxy radical ($^-AO_2\cdot$) in which the

*The ratios of the $^4C_1$(D) to the $^1C_4$(D) conformer for **1** and **2** in water at 25° have been estimated to be 74:26 and 95:5, respectively[37].

$^{-}AO_2^{\cdot}$ (1) $^{-}AO_2^{\cdot}$ (2)

configuration of the hydroxyl groups of $A^{\cdot-}$ is retained. In addition, reaction (*10*) would be expected to have an essentially zero activation energy[38-40]. Thus, once $A^{\cdot-}$ is formed it would react very rapidly with oxygen in its vicinity. This would also aid in making reaction (*10*) stereoselective.

A species containing an α-hydroxyhydroperoxy radical ($AO_2^{\cdot}$) or an α-hydroxyhydroperoxy anion (AO_2^{-}) is subsequently formed from $^{-}AO_2^{\cdot}$ [reactions (*12*) and (*13*)]. Unlike its counterpart in the reaction of **1**, the AO_2^{-} produced in the reaction of **2** can form an effective intramolecular hydrogen-bond between the peroxyanion and the hydroxyl group on the adjacent carbon atom. The pertinent minimum oxygen–oxygen distances for AO_2^{-} of **1** and **2** are 3.7 and 2.1 Å, respectively, as shown in Fig. 5. These oxygen–oxygen distances would be the same, respectively, for any α-hydroxyhydroperoxy anion formed at a carbon atom having an equatorial hydroxyl group in **1** and **2**. In solution, the oxygen–oxygen distance is critical in determining the strength of a hydrogen bond. Based on neutron-diffraction studies on ice[41], the optimum oxygen–oxygen distance for hydrogen bonding is approximately 2.8 Å. Oxygen atoms that can theoretically approach each other at distances less than 2.8 Å may also move apart to attain the optimum distance for hydrogen bonding. Thus, only α-hydroxyhydroperoxy anions formed from 1,5-anhydroxylitol (**2**) are capable of being stabilized through effective hydrogen-bonding.



O---O ≃ 3.7 Å O----O ≃ 2.1 Å

AO_2^{-}(1) AO_2^{-}(2)

Fig. 5. Minimum oxygen–oxygen distances for α-hydroxyhydroperoxides formed at C-2 in 1,5-anhydroribitol (**1**) and 1,5-anhydroxylitol (**2**) in the $^4C_1$ (D) conformation. Distances were determined from Dreiding molecular models.

It is also probable that α-hydroxyhydroperoxy radicals ($AO_2^{\cdot}$) formed from **2**, but not those from **1**, can hydrogen-bond with hydroxyl groups on adjacent carbon atoms in a manner similar to the anions (AO_2^{-}). Rust and Youngman[42], in a study of autoxidation of pentanediols, concluded that intramolecular hydrogen-bonding

enhances the stability of a peroxy radical and hence increases the importance of self-termination reactions.

Thus, intramolecular hydrogen-bonding may increase the stability of both the α-hydroxyhydroperoxy radical (AO_2) and the α-hydroxyhydroperoxy anion (AO_2^-) that are formed in reactions of **2**, and hence increase their concentrations in the system. In addition, hydrogen bonding in AO_2^- would decrease product formation by such ionic pathways as reactions (*15a*), (*18*), and (*20a*). Therefore, as AO_2^- and $AO_2^{\cdot}$ are interconvertible [reaction (*13*)], the net result is that the $AO_2^{\cdot}$ concentration is effectively increased to the point where the bimolecular radical-termination reaction [reaction (*25*)] becomes important and effects autoinhibition of the degradation of **2**.

Based on the preceding discussion, the inhibiting effects of $AO_2^{\cdot}$ should increase as its concentration increases. It is evident from Fig. 3 that the concentration of

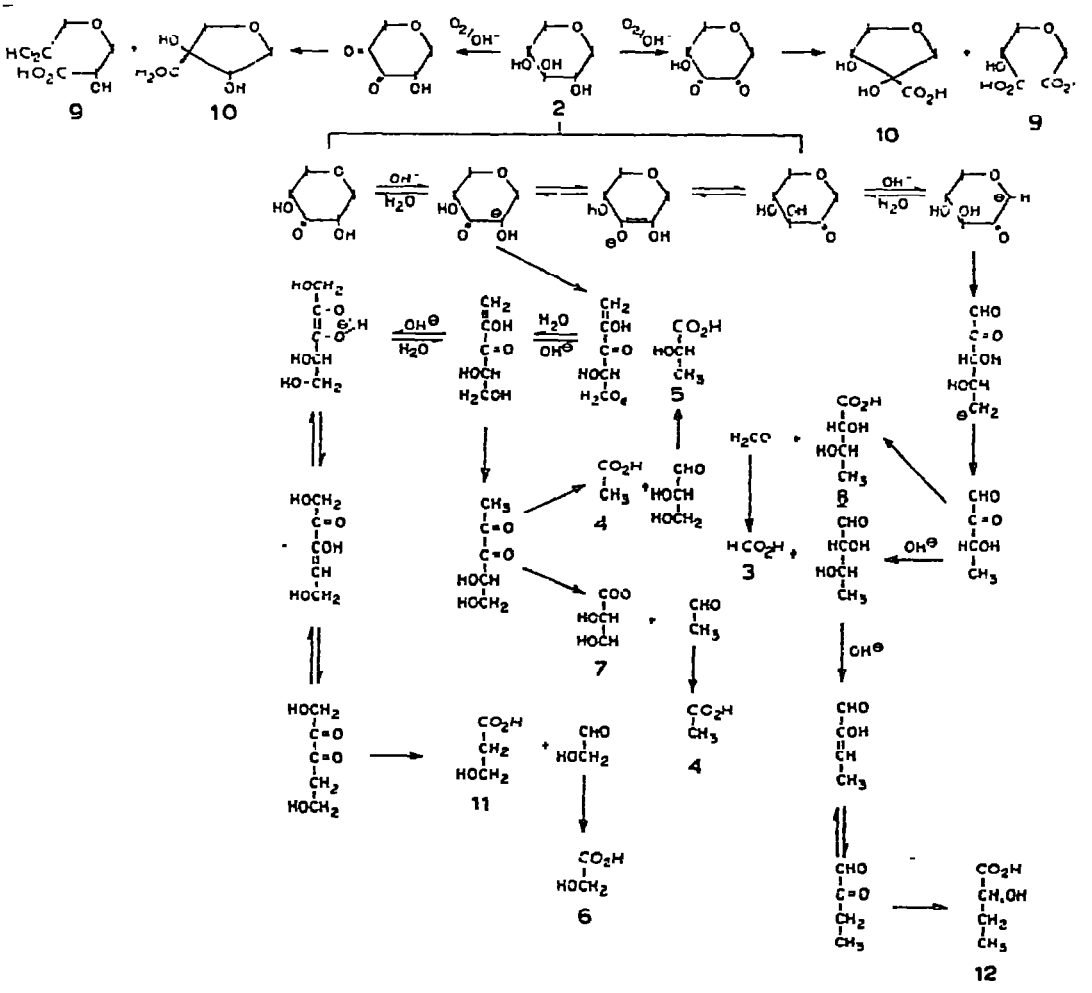


Fig. 6. Potential pathways for product formation in degradations of 1,5-anhydroalditols (**1** and **2**).

hydroperoxidic species is greatest early in the reaction of **2**. Fig. 2 shows that the apparent reaction-order with respect to **2** increases at early reaction-times corresponding to the highest concentration of hydroperoxides.

Potential reaction-pathways for formation of the acidic products identified in reactions of **1** and **2** are illustrated in Fig. 6. Once a carbonyl group is introduced into the alditol ring, rapid alkaline rearrangements can shift the carbonyl moiety to any carbon atom containing a hydroxyl group. The ring can then be opened by elimination reactions and the resultant, acyclic dicarbonyl intermediates can form the carboxylic acids[43–45]. In addition, such products as lactic acid (**5**) and glycolic acid (**6**) must also be formed from other products (see Fig. 4). Before ring cleavage occurs, a second carbonyl group may be introduced adjacent to the first one. The α-dicarbonyl intermediate may undergo carbon–carbon bond cleavage to form dibasic acids (**9**) or undergo a benzilic acid type of rearrangement to produce the 1,4-anhydro-2-*C*-carboxy-tetritols[8,9,15] (**10**).

EXPERIMENTAL

Analytical methods. — Melting points were determined on a calibrated Thomas–Hoover capillary apparatus. Optical rotations were determined with a Perkin–Elmer 141 MC polarimeter. Colorimetric analyses were performed with a Beckman DU spectrophotometer. Atomic-absorption spectra were determined with a Perkin–Elmer 305 instrument.

G.l.c. analyses were performed with a Varian Aerograph 1200 instrument equipped with a hydrogen flame-ionization detector and a Honeywell Electronic 16 recorder with a Disc integrator. The columns were housed in 0.125-in. stainless-steel tubing and were arranged for on-column injection. The following columns and operating conditions were employed: (*A*) 10% SE-30 on 60–80 mesh DMCS-AW Chromosorb W (5 ft); nitrogen, 15 ml min^{-1}; column, 165°; injector, 260°; and detector, 260°; (*B*)10% SE-30 on 60–80 mesh DMCS-AW Chromosorb W (5 ft): nitrogen, 8 ml min^{-1}; column, 185°; injector, 260°; and detector, 260°; (*C*) 3% OV-17 on 80–100 mesh Supelcoport (10 ft); nitrogen, 30 ml min^{-1}; column, 120°; injector, 160°; and detector, 190°; and (*D*) 3% OV-17 on 80–100 mesh Supelcoport (10 ft); nitrogen, 15 ml.min^{-1}; column, 70° for 22 min, then programmed at 4°.min^{-1} for 17 min, and subsequently at 1°.min^{-1} to completion; injector, 265°; and detector, 265°.

Mass spectra were determined with a DuPont Instruments 21-491 spectrometer interfaced with a Varian Aerograph 1440 gas chromatograph. G.l.c. conditions *D* with helium as the carrier gas were used.

1,5-Anhydroribitol (**1**). — 2,3,4-Tri-*O*-benzoyl-β-D-ribopyranosyl bromide[46] was hydrogenated in the presence of 10% palladium on carbon[47]. The product mixture was debenzoylated with sodium methoxide in 20:1 (v/v) methanol–chloroform, refluxed with 0.1M sodium hydroxide for 2 h, deionized with Amberlite MB-3 resin, decolorized, and isolated as a clear syrup. Crystallization from the syrup in 1:1

ethanol–ethyl acetate gave **1** (80% yield); m.p. 128–129°, $[\alpha]_D$ 0° (water) [lit.[46] m.p. 128–129°, $[\alpha]_D$ 0° (water)].

1,5-Anhydroxylitol (**2**). — Phenyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside[48] was reduced with W-2 Raney nickel in ethanol[49]. The product mixture was deacetylated with sodium methoxide in methanol, treated with 0.1M sodium hydroxide, deionized with Amberlite MB-3 resin, decolorized and isolated as a syrup. Crystallization from the syrup in abs. ethanol gave **2** (77% yield); m.p. 115–116°, $[\alpha]_D$ 0° (water) [lit.[49] m.p. 116–117°, $[\alpha]_D$ 0° (water)].

Kinetic analyses. — Sodium hydroxide solutions for kinetic experiments were freshly prepared from a carbonate-free 50% (wt) stock solution of sodium hydroxide by diluting the stock solution with carbon dioxide-free, triply-distilled water under a nitrogen atmosphere[16].

The reactor system, described in detail elsewhere[16], consisted of a 250-ml capacity, Teflon-lined brass reactor that could be sampled while hot and under pressure, and an oil-bath assembly that controlled the reactor temperature at 120 ±0.2°.

The reactor was loaded and assembled in a nitrogen atmosphere, connected to the sampling system and the oil-bath apparatus, lowered into the heated oil bath, and allowed to equilibrate thermally. A zero-time sample was then taken and the reaction was initiated by pressurizing the reactor to a partial oxygen pressure of 75 lb. in.$^{-2}$ (25°). The size of the samples and the amount of internal standard solution added to the samples were determined gravimetrically. 1,6-Anhydro-β-D-glucopyranose and methyl β-D-xylopyranoside were used as the internal standards for reactions of **1** and **2**, respectively.

Samples (~1.5 ml) of the reaction solution containing the internal standard were deionized on a column (6–8 ml) of Amberlite MB-3 (H^+,OH^-) resin, evaporated *in vacuo*, and the residues acetylated with acetic anhydride (0.25 ml) in pyridine (0.75 ml) for 18 h. The acetylation mixtures were diluted with distilled water, shaken for 0.5 h, and extracted with chloroform (2 × 5 ml). The chloroform extracts were washed with M hydrochloric acid (15 ml) and water (10 ml), dried (sodium sulfate), and evaporated *in vacuo*. The dried samples were dissolved in chloroform (~0.2 ml) and analyzed by g.l.c., with conditions *B* for reactions of **1** and conditions *A* for reactions of **2**.

Product analyses. — Peroxide analyses were performed in conjunction with all kinetic experiments by using 0.1M carbohydrate. The peroxide concentrations were determined by a modification of the colorimetric method, using titanium sulfate reagent[16,23]. A sample of the reaction solution (1.0 ml) was neutralized with 0.25M sulfuric acid to pH 6–7, treated with titanium sulfate reagent (0.2 ml), and diluted to volume (10.0 ml) with water. At that point, the solution had pH ~1. The concentration of hydrogen peroxide was estimated from the initial absorbance (420 nm) of the solution. The concentration of organic peroxide was estimated from the maximum increase in the absorbance during the succeeding 36 h. The procedure was calibrated by using hydrogen peroxide solutions of known concentration. A sample of the

reaction-mixtures that were monitored for peroxides was also analyzed by atomic absorption for cadmium, cobalt, copper, chromium, iron, magnesium, manganese, nickel and zinc.

Formic and acetic acids were identified as products as their benzyl esters[50] by comparison of the g.l.c. retention-times (T_r) of the esters with those of authentic materials. A sample (~3.0 ml) of the solution was eluted with distilled water (15 ml) through a column (5 ml) of Amberlite IR-120 (H^+) resin. The eluate was titrated to pH ~8 with 0.03M tetrabutylammonium hydroxide and concentrated *in vacuo* to a syrup. The syrup was dissolved in anhydrous acetone (3 ml) and allowed to react with benzyl bromide (0.5 ml) for 2 h. The acetone solution was analyzed directly by g.l.c. under conditions *C*.

The other acidic products were analyzed by g.l.c. as their pertrimethylsilyl ethers. The products were identified by comparison of their retention times with those of authentic materials when possible, and by g.l.c.–m.s. analysis[16]. A sample (~3.0 ml) of the solution was eluted with distilled water (15 ml) through a column (5 ml) of Amberlite IR-120 (H^+) resin. The eluate was concentrated *in vacuo* to a syrup. The syrup was dried by adding 1,2-dichloroethane and evaporating the mixture *in vacuo*. The syrup was dissolved in dimethyl sulfoxide (0.3 ml), and Tri-Sil Concentrate (0.5 ml) was added to the solution. The mixture was shaken for 24 h and then the top layer of the two-phase system was analyzed by g.l.c. under conditions *D*. For semiquantitative analysis of the products, a solution of an internal standard (methyl β-D-xylopyranoside) was added to the solution prior to the ion-exchange procedure. Response factors were determined for lactic, glycolic, and glyceric acids by subjecting them to the analytical procedure. The response factors used for the 1,4-anhydro-2-*C*-carboxytetritols and 3-*O*-(carboxymethyl)glyceric acid were estimates based on their molecular weights.

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REFERENCES

1 A. ROBERT, P. RÉROLLE, A. VIALLET, AND O. MARTIN-BORRET, *A.T.I.P. Bull.*, 18 (1964) 151–176.
2 A. ROBERT AND A. VIALLET, *A.T.I.P. Rev.*, 25 (1971) 237–241.
3 G. L. AKIM AND A. YA. FRANK, *Cellulose Chem. Technol.*, 7 (1973) 441–450, and references cited therein.
4 R. D. BROOKS AND N. S. THOMPSON, *Tappi*, 49 (1966) 362–366.
5 O. SAMUELSON, *Das Papier*, 24 (1970) 671–678.
6 J. L. MINOR AND N. SANYER, *J. Polymer Sci. C*, 36 (1971) 73–84.
7 J. D. SINKEY AND N. S. THOMPSON, *Paperi Puu*, 56 (1974) 473–486.
8 B. ERICSSON, B. O. LINDGREN, AND O. THEANDER, *Cellulose Chem. Technol.*, 8 (1974) 363–385; B. ERICSSON, B. O. LINDGREN, O. THEANDER, AND G. PETERSSON, *Carbohydr. Res.*, 23 (1972) 323–325.
9 B. ERICSSON AND R. MALINEN, *Cellulose Chem. Technol.*, 8 (1974) 327–338.
10 J. T. MCCLOSKEY, L. R. SCHROEDER, J. D. SINKEY, AND N. S. THOMPSON, *Pap. Puu*, 57 (1975) 131–145.

11 R. MALINEN AND E. SJÖSTRÖM, *Cellulose Chem. Technol.*, 9 (1975) 231–238.
12 J. F. HASKINS AND M. J. HOGSED, *J. Org. Chem.*, 15 (1950) 1264–1274.
13 A. MELLER, *Holzforschung*, 14 (1960) 129–139.
14 O. THEANDER, *Tappi*, 48 (1965) 105–110.
15 R. MALINEN, *Pap. Puu*, 57 (1975) 193–204.
16 E. C. MILLARD, Doctoral Dissertation. The Institute of Paper Chemistry, Appleton, Wis., June 1976.
17 W. B. GLEASON AND R. BARKER, *Can. J. Chem.*, 49 (1971) 1425–1432.
18 H. G. J. DEWILT AND B. F. M. KUSTER, *Carbohydr. Res.*, 19 (1971) 5–15.
19 G. BRUHN, J. GERLACH, AND F. PAWLEK, *Z. Anorg. Chem.*, 337 (1965) 68–79.
20 K. J. LAIDLER, *Reaction Kinetics*, Vol. 1, MacMillan, New York, 1963.
21 C. N. SATTERFIELD AND A. H. BONNELL, *Anal. Chem.*, 27 (1955) 1174–1175.
22 H. PROBINER, *Anal. Chem.*, 33 (1961) 1423–1426.
23 S. MARKLUND, *Acta Chem. Scand.*, 25 (1971) 3517–3531.
24 F. W. BACHELOR AND G. A. MIANA, *Can. J. Chem.*, 47 (1969) 4089–4091.
25 G. PETERSSON, *Tetrahedron*, 26 (1970) 3413–3428.
26 G. PETERSSON, *Org. Mass Spectrom.*, 6 (1972) 577–592.
27 O. SAMUELSON AND L. STOLPE, *Svensk Papperstidn.*, 72 (1969) 662–666.
28 D. BEHAR, G. CZAPSKI, J. ROBINI, L. M. DORMAN, AND H. A. SCHWARZ, *J. Phys. Chem.*, 74 (1970) 3209–3213.
29 C. WALLING AND A. GOOSEN, *J. Am. Chem. Soc.*, 95 (1973) 2987–2991.
30 H. S. ISBELL, *Adv. Chem. Ser.*, 117 (1973) 70–87.
31 J. T. MCCLOSKEY, Doctoral Dissertation, The Institute of Paper Chemistry, Appleton, Wis., January, 1971.
32 C. WALLING, *Free Radicals in Solution*, John Wiley and Sons, New York, 1957, pp. 427–430, 565–575.
33 G. A. RUSSELL, *J. Am. Chem. Soc.*, 79 (1957) 3871–3877.
34 R. HIATT, in D. SWERN (Ed.), *Organic Peroxides*, Vol. II, Wiley-Interscience, New York, 1971, p. 88.
35 E. L. ELIEL, N. L. ALLINGER, S. J. ANGYAL, AND G. A. MORRISON, *Conformational Analysis*, Interscience, New York, 1965, p. 274.
36 J. A. RENDLEMAN, JR., *Adv. Chem. Ser.*, 117 (1973) 51–69.
37 L. J. PITZNER AND R. H. ATALLA, *Spectrochim. Acta*, 31A (1975) 911–929.
38 K. U. INGOLD, *Chem. Rev.*, 61 (1961) 563–589.
39 G. A. RUSSELL, A. G. BEMIS, E. J. GEELS, E. G. JANZEN, AND A. J. MOYE, *Adv. Chem. Ser.*, 75 (1968) 174–201.
40 A. FISH, in D. SWERN (Ed.), *Organic Peroxides*, Vol. I, Wiley-Interscience, New York, 1970, p. 143.
41 S. W. PETERSON AND H. A. LEVY, *Acta Crystallogr.*, 10 (1957) 70–79.
42 F. F. RUST AND E. A. YOUNGMAN, *J. Org. Chem.*, 27 (1962) 3778–3781.
43 B. LINDBERG AND O. THEANDER, *Acta Chem. Scand.*, 22 (1968) 1782–1786.
44 B. ERICSSON, B. O. LINDGREN, AND O. THEANDER, *Cellulose Chem. Technol.*, 7 (1973) 581–591.
45 R. MALINEN AND E. SJOSTROM, *Pap. Puu*, 54 (1972) 451–468.
46 R. W. JEANLOZ, H. G. FLETCHER, JR., AND C. S. HUDSON, *J. Am. Chem. Soc.*, 70 (1948) 4052–4054.
47 S. JACOBSEN AND C. PEDERSEN, *Acta Chem. Scand.*, 27 (1973) 3111–3117.
48 C. B. PURVES, *J. Am. Chem. Soc.*, 51 (1929) 3619–3627.
49 H. G. FLETCHER, JR., AND C. S. HUDSON, *J. Am. Chem. Soc.*, 69 (1947) 921–924.
50 P. O. BETHGE AND K. LINDSTRÖM, *Analyst*, 99 (1974) 137–142.