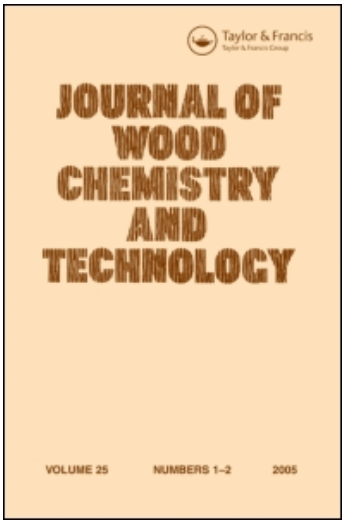

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Alkaline Degradation of 1,5-Anhydro-4-0-β-D-Glucopyranosyl-2,3,4-Tri-O-Methyl-D-Glucitol

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ALKALINE DEGRADATION OF 1,5-ANHYDRO-4-O-β-D-GLUCOPYRANOSYL-2,3,4-TRI-O-METHYL-D-GLUCITOL[1]

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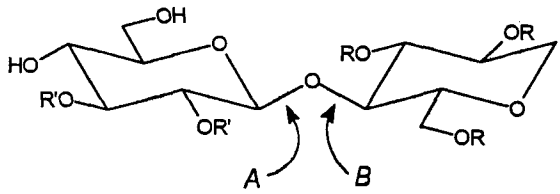
ABSTRACT

The title compound (**2**) was degraded at 150-180°C in oxygen-free 0.5-2.5M aqueous NaOH. Degradation occurred by cleavage of both the glycosyl-oxygen bond (80-95%) and the oxygen-aglycon bond (5-20%). Cleavage of the glycosyl-oxygen bond yielded 1,5-anhydro-2,3,6-tri-O-methyl-D-glucitol (**5**) from the aglycon. The reactive intermediate, 1,6-anhydro-β-D-glucopyranose, was formed from the glycosyl moiety in amounts (50-88%) dependent upon the reaction conditions. Cleavage of the oxygen-aglycon bond resulted in unidentified products, probably acidic and fragmentary in nature and quantified as a mass deficit. Data for cleavage of the glycosyl-oxygen bond is consistent with an S_NicB(2') mechanism while that for oxygen-aglycon bond cleavage is consistent with an S_N1 mechanism.

INTRODUCTION

During alkaline pulping of wood the viscosity of the pulp decreases substantially due to random cleavage of the β-1,4-glucosidic linkages of the cellulose. The cleavage is generally ascribed[3-9] to a base-catalyzed, intramolecular S_NicB(2) mechanism[10] which would result in at least partial formation of 1,6-anhydro-β-D-glucopyranose end groups,[7,11,12] although this has not been demonstrated.

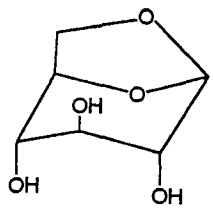
Previously, we reported studies of the degradation of a cellulose model, 1,5-anhydro-4-O-β-D-glucopyranosyl-D-glucitol (**1**, 1,5-anhydrocellobiitol), under alkaline pulping conditions.[13,14] One of the studies also included a limited study of the degradation of 1,5-anhydro-4-O-β-D-glucopyranosyl-2,3,6-tri-O-methyl-D-glucitol (**2**, 1,5-anhydro-2,3,6-tri-O-methyl-cellobiitol).[14] Although **1** and **2** degraded in aqueous alkali by cleavage of both the glycosyl-oxygen bond (**Bond A**) and the oxygen-aglycon bond (**Bond B**), cleavage of the glycosyl-oxygen bond was the dominant mode of degradation for both compounds. However, while only 30-35% of the cleavages of the glycosyl-oxygen bonds of **1** resulted in formation of 1,6-anhydro-β-D-glucopyranose (**3**), 65-75% of such reactions of **2** formed **3**.



1 R = R' = H

2 R = Me ; R' = H

4 R = R' = Me



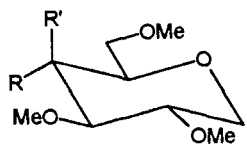
3

The partially methylated disaccharide **2** is a less logical model for cellulose than **1**. However, the high degree of formation of the 1,6-anhydride **3** from **2** and thus, the possible analogy between the mechanism of alkaline degradation of **2** and the mechanism most frequently proposed for cellulose degradation led us to study alkaline reactions of **2** in greater detail. The degradation of **2** was studied at 150-180°C in aqueous, oxygen-free sodium hydroxide (0.5-2.5 M). A limited, auxiliary study of 1,5-anhydro-4-O-(2,3-di-O-methyl-β-D-glucopyranosyl)-2,3,6-tri-O-methyl-D-glucitol (**4**) was made under similar conditions.

RESULTS

Product Analyses

The product distribution for alkaline degradations of **2** depended on the reaction conditions. The stable products identified were 1,5-anhydro-2,3,6-tri-O-methyl-D-glucitol (**5**) (80-97%) and 1,5-anhydro-2,3,6-tri-O-methyl-D-galactitol (**6**) (<0.5%). It was demonstrated that **5** was stable (<3% reaction) over 17 half-lives of the reactant **2**.



5 R = OH, R' = H

6 R = H, R' = OH

1,6-Anhydro-β-D-glucopyranose (**3**) was identified as a reactive intermediate, confirming the previous study of **2**.[14]

As reported previously,[14] a difference (up to 20%) in the moles of stable products formed from the aglycon (1,5-anhydro-2,3,6-tri-O-methyl-D-glucitol moiety) of **2** and the moles of **2** reacted was observed. The deficit is presumed to result from formation of either ionic or fragmentation products which would not be detected with the analytical techniques employed. In the following discussion this deficit is referred to as the unidentified products (**U**).

Kinetic Analyses

The degradations of **2** and **4** were followed by quantitative g.l.c. analyses of deionized, acetylated samples of the reactions.

Since the sodium hydroxide concentration was very large relative to the concentration of **2** and **4**, pseudo-first-order kinetics were observed. For convenience, the disappearance of reactant and appearance of products from the aglycon were analyzed by parallel-first-order kinetics (Equations 1, 2, and 3; Figure 1).[15]

$$\ln(X_{r,t}) = -k_r t \tag{1}$$

$$\ln(X_{i,\infty} - X_{i,t}) = -k_r t + \ln(X_{i,\infty}) \tag{2}$$

$$k_i = k_r X_{i,\infty} \tag{3}$$

where $X_{r,t}$ is the mole fraction of reactant at time t, $X_{i,t}$ is the mole fraction of product i at time t, $X_{i,\infty}$ is $X_{i,t}$ at completion (the relative proportion of product i formed), k_r is the pseudo-first-order rate constant for reactant disappearance, and k_i is the pseudo-first-order rate constant for formation of product i ($\Sigma k_i = k_r$).

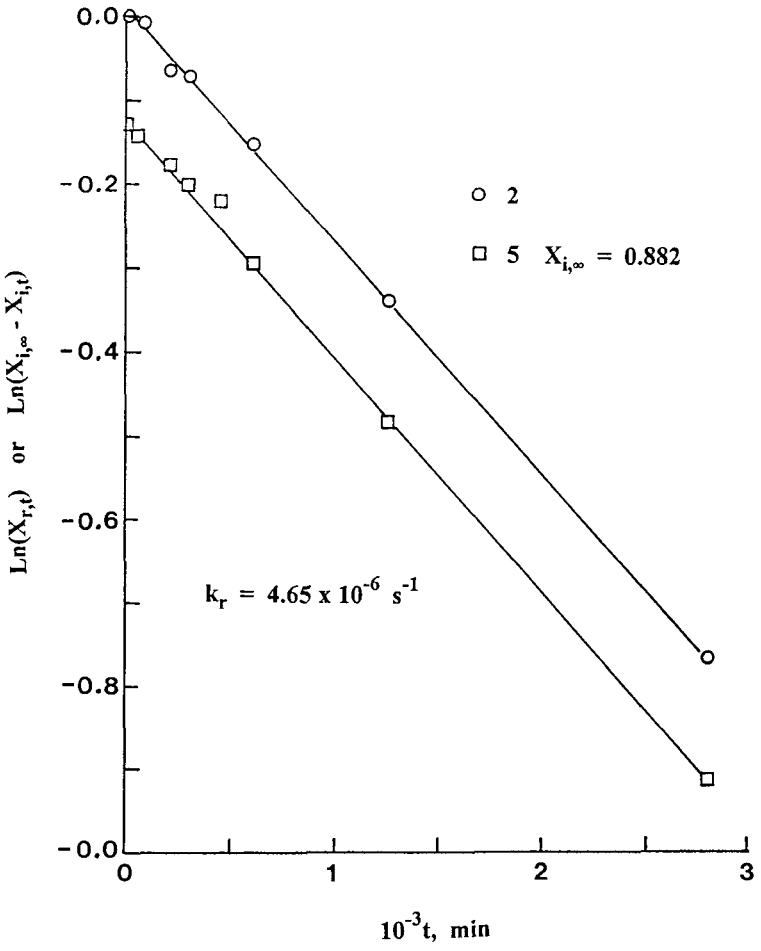


Figure 1. Parallel-first-order kinetic analysis of the degradation of 1,5-anhydro-2,3,6-tri-O-methyl-cellobiitol (**2**) in 2.5M NaOH at 161.9°C.

Rate constants and product mole fractions for degradations of **2** and **4** under various conditions are reported in Table 1. Rate constants for product formation can be calculated from the data in Table 1 using Equation 3. The mole fraction of unidentified

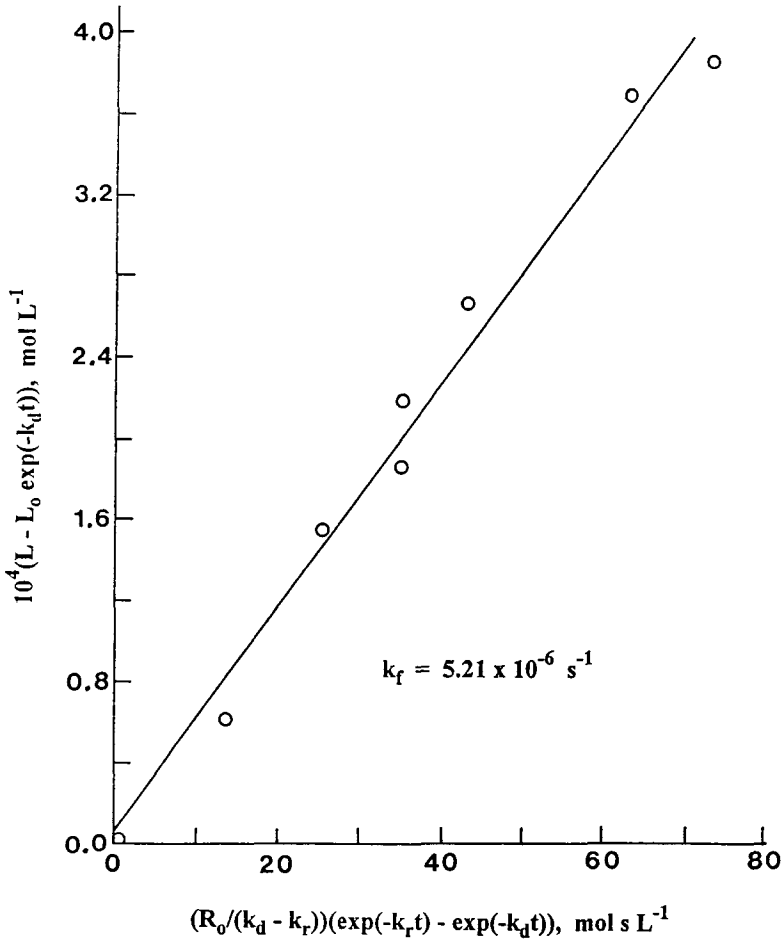


Figure 2. Determination of the rate constant (k_f) for formation of 1,6-anhydro-β-D-glucopyranose (**3**) in a degradation of 1,5-anhydro-2,3,6-tri-O-methyl-cellobiitol (**2**) in 2.5M NaOH at 171°C.

products was calculated as: $X_{U,\infty} = 1 - X_{5,\infty}$. The concentration of **6** was too low to be measured routinely.

Rate constants (k_f) for formation of 1,6-anhydro-β-D-glucopyranose (**3**) from **2** were calculated from the linear relationship (Equation 4, Figure 2) describing the concentration of **3** as a function of time.[13,14]

$$L - L_0 e^{-k_d t} = k_r R_0 (e^{-k_r t} - e^{-k_d t}) / (k_d - k_r) \qquad (4)$$

where L is the concentration of **3** at time t, L_o is the initial concentration of **3**,[18] R_o is the initial concentration of **2**, k_r is the rate constant for degradation of **2**, and k_d is the pseudo-first-order rate constant for degradation of **3**. The values of k_d were determined previously.[14]

The mole fractions of **3** formed in degradations of **2** ($X_{3,\infty}$, Table 1) were calculated as the ratio, k_f/k_r. Since **3** degrades at these reaction conditions, $X_{3,\infty}$ is actually zero. Conceptually, however, $X_{3,\infty}$, as calculated, is the mole fraction of **2** which degrades *via* **3** without reference to the subsequent fate of **3**.

DISCUSSION

As reported previously,[14] degradation of **2** results primarily from cleavage of the glucosyl-oxygen bond of the glycosidic linkage, but cleavage of the oxygen-aglycon bond also occurs to a significant extent. Cleavage of the glucosyl-oxygen bond is characterized by exclusive formation of 1,5-anhydro-2,3,6-tri-O-methyl-D-glucitol (**5**) from the aglycon and partial formation of 1,6-anhydro-β-D-glucopyranose (**3**) from the glucosyl moiety. Since cleavage of the glycosyl-oxygen bond yields only **5** from the aglycon, and **5** is stable under the degradation conditions, the lack of a mole balance between **5**

TABLE 1

Rate Constants and Product Mole Fractions for Degradations of 1,5-Anhydro-2,3,6-tri-O-methyl-cellobiitol (2) and 1,5-Anhydro-2,2',3,3',6-penta-O-methyl-cellobiitol (4)

No.	Reactant	Temp., °C	NaOH, M	NaOTs,[a] M	$10^6 k_r$,[b] sec^{-1}	$X_{5,\infty}$,[c]	$X_{U,\infty}$,[c]	$X_{3,\infty}$,[c]	$10^6 k_{go}$,[d] sec^{-1}	$Y_{3,\infty}$,[e]
1	2	151.4	2.50	----	1.66	0.831	0.169	0.633	1.38	0.76
2	2	161.9	2.50	----	4.65	0.882	0.118	0.585	4.10	0.66
3	2	171.3	2.50	----	9.85	0.924	0.076	0.529	9.10	0.57
4	2	182.1	2.50	----	26.4	0.951	0.049	0.477	25.1	0.50
5	2	171.3	0.50	----	4.33	0.798	0.202	0.531	3.46	0.67
6	2	171.6	0.50	2.00	3.28	0.803	0.197	0.707	2.63	0.88
7	2	171.2	0.75	1.75	4.47	0.857	0.143	0.660	3.83	0.77
8	2	170.8	1.50	1.00	6.22	0.913	0.087	0.568	5.68	0.62
9	4	171.4	2.50	----	0.995	0.337	0.663	----	0.335	----

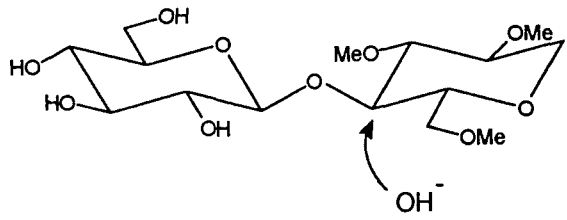
[a]Sodium p-toluenesulfonate; [b]Rate constant for overall degradation; [c]Product mole fraction: 1,5-anhydro-2,3,6-tri-O-methyl-D-glucitol (5), 1,6-anhydro-β-D-glucopyranose (3), and unidentified products (U); [d]Rate constant for glycosyl-oxygen bond cleavage; and [e]Mole fraction of 1,6-anhydro-β-D-glucopyranose (3) based only on glycosyl-oxygen bond cleavage.

formed and **2** degraded substantiates oxygen-aglycon bond cleavage. The unidentified products (**U**) result from such cleavage.

Oxygen-Aglycon Bond Cleavage

The methylated hydroxyl groups of the aglycon in **2** preclude mechanisms for oxygen-aglycon bond cleavage involving intramolecular displacement of the glucopyranosyloxy anion by any of the aglycon hydroxyl groups or their conjugate bases. For compounds undergoing primary degradation by such mechanisms, methylation of the participating hydroxyl group essentially stops the neighboring group reaction.[11,19,20]

An S_N2 mechanism involving nucleophilic attack at C-4 by hydroxide ion to displace the glucopyranosyloxy anion would result in formation of 1,5-anhydro-2,3,6-tri-O-methyl-D-galactitol (**6**) from the aglycon. Thus, since **6** was only formed in trace amounts, the S_N2 mechanism is not important in oxygen-aglycon bond cleavage.



The most logical mechanism for oxygen-aglycon bond cleavage in **2** is an S_N1 mechanism (Figure 3) in which heterolysis of the bond would form the 1,5-anhydro-2,3,6-tri-O-methyl-4-deoxy-D-xylo-hexitol-4-cation (**7**) and the β-D-glucopyranosyloxy anion (**8**). The anion **8** would degrade rapidly to acidic products.[21] The carbocation **7** could potentially undergo rearrangements or reaction with hydroxide ion or water.

Reaction of **7** with hydroxide ion or water to form **5** and **6** apparently is not important. If such reactions occurred, they would

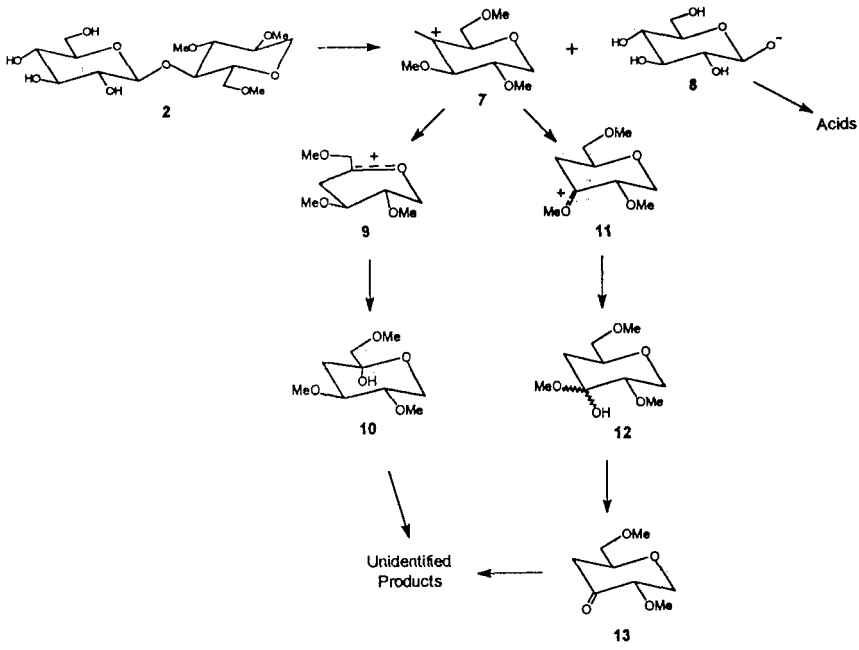


Figure 3. Proposed S_N1 mechanism for oxygen-aglycon bond cleavage with some of the potential routes for product formation.

have to be fast relative to other reactions of **7** and, thus, it would be expected that the galactitol **6** would be the dominant product because of a shielding effect of the departing anion **8**. Since **6** was formed in only trace amounts, these reactions of **7** are of negligible importance.

Rearrangements of **7** involving hydride shifts to form more stable cations would be feasible[22] and could account for the unidentified products **U**. For example, rearrangement of **7** involving a shift of H-5 would generate the more stable carboxonium ion **9** (Figure 3). Reaction of **9** with water or hydroxide ion would form 3-deoxy-1,4,5-tri-O-methyl-D-threo-hexulopyranose (**10**) which would undergo elimination and fragmentation reactions to account for **U**. Alternatively, **7** could form the carboxonium ion **11** by a shift of H-

3. Reaction of **11** with water or hydroxide ion would form the hemiketal **12** and subsequently 1,5-anhydro-4-deoxy-2,6-di-O-methyl-D-erythro-3-hexulose (**13**). The ketose **13** would degrade to also account for **U**.

The possibility appeared to exist that **7** could also initiate a series of intramolecular reactions involving participation of the methoxyl groups and culminating in the formation of various partially methylated 1,5-anhydroalditols.[23,24] However, the absence of detectable quantities of 1,5-anhydroalditols other than **5** and **6** indicates that participation of the neighboring methoxyl group in reactions of **7** is unimportant. In addition, it indicates that formation of **5** does not accompany oxygen-aglycon bond cleavage.

Glycosyl-Oxygen Bond Cleavage

Since **5** is the sole product from the aglycon in glycosyl-oxygen bond cleavage in **2**, and is not formed from oxygen-aglycon bond cleavage, the rate constant for glycosyl-oxygen bond cleavage, k_{go}, can be calculated from Equation 5 and the data in Table 1. The k_{go} values are reported in Table 1.

$$k_{go} = k_5 = k_r X_{5,\infty} \qquad (5)$$

Similarly, since the 1,6-anhydride **3** can only be formed as a result of glycosyl-oxygen bond cleavage, the mole fraction of **3** based on the overall degradation of **2** ($X_{3,\infty}$) could be misleading. Therefore, the $X_{3,\infty}$ values have been converted to mole fractions based only on glycosyl-oxygen bond cleavage ($Y_{3,\infty}$, Table 1).

The results of the study are consistent with an $S_N$icB(2') mechanism being operative in cleavage of the glycosyl-oxygen bond in alkaline degradation of **2**. As indicated in Figure 4, a rapid equilibrium between OH-2' and its conjugate base would precede the rate-determining step in which, with the glucopyranosyl moiety in the $^1C_4$ conformation, a nucleophilic attack by the C-2' oxyanion at

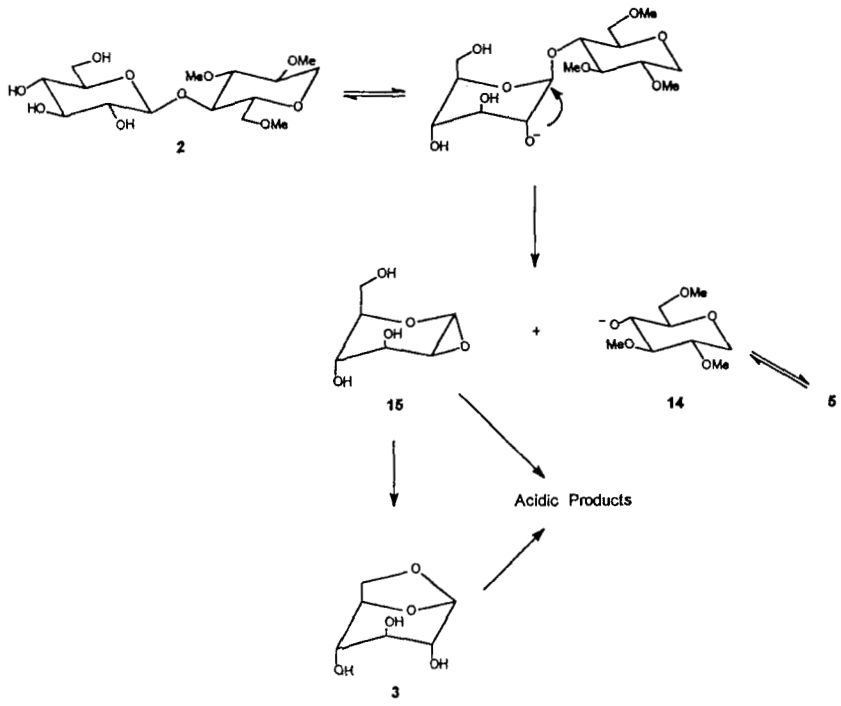


Figure 4. Proposed $S_N$icB(2') mechanism for glycosyl-oxygen bond cleavage.

C-1 would displace the conjugate base of 1,5-anhydro-2,3,6-tri-O-methyl-D-glucitol (**14**) with concomitant formation of 1,2-anhydro-α-D-glucopyranose (**15**). The 1,2-anhydride **15** would subsequently form the 1,6-anhydride **3** by intramolecular nucleophilic attack by the C-6 oxyanion at C-1, or react in several ways to yield acidic products *via* a reducing sugar.

The most compelling pieces of evidence for an $S_N$icB(2') mechanism for cleavage of the glycosyl-oxygen bond of **2** are the fact that etherification of OH-2' drastically reduced the rate of reaction and the substantial amounts of 1,6-anhydro-β-D-glucopyranose (**3**) formed.

The rate constant (k_{go}) for glycosyl-oxygen bond cleavage in 1,5-anhydro-4-O-(2,3-di-O-methyl-β-D-glucopyranosyl)-2,3,6-tri-O-methyl-D-glucitol (**4**, Reaction 9, Table 1) was approximately 3.7% of that for **2** under similar conditions (Reaction 3). Similar rate reductions on etherification of OH-2 have been reported for p-nitrophenyl β-D-galactopyranoside,[19] p-nitrophenyl β-D-xylopyranoside,[20] and phenyl β-D-glucopyranoside,[11] all of which degrade by $S_N$icB(2) mechanisms.

Phenyl β-D-glucopyranoside which is believed to degrade solely by an $S_N$icB(2) mechanism under comparable reaction conditions yielded >80% 1,6-anhydro-β-D-glucopyranose (**3**).[11] It has been suggested previously[13,14] that other nucleophiles can also degrade the 1,2-anhydride (**15**, Figure 4) before it can form the 1,6-anhydride (**3**). Thus, the large amounts of **3** formed in degradations of **2** are consistent with the glycosyl-oxygen bond cleavage occurring by an $S_N$icB(2') mechanism.

Apparent thermodynamic functions of activation, calculated from the pseudo-first-order rate constants for glycosyl-oxygen bond cleavage (k_{go}, Reactions 1-4, Table 1) for 170°C, are also consistent with an $S_N$icB(2') mechanism. The entropy, $\Delta S^{\ddagger}$ (-13.8 J $^{\circ}K^{-1}$ mol^{-1}), is similar but somewhat more negative than $\Delta S^{\ddagger}$ for phenyl β-D-glucopyranoside (-5.4 J $^{\circ}K^{-1}$ mol^{-1}). The enthalpy, $\Delta H^{\ddagger}$ (147 kJ mol^{-1}), is somewhat greater than $\Delta H^{\ddagger}$ for phenyl β-D-glucopyranoside (118 kJ mol^{-1}) but this is to be expected since **2** has a poorer leaving group (**14**, Figure 4) than the phenoxy anion in phenyl β-D-glucopyranoside.

The negative salt effect of 24% (k_{go}, Reaction 6 *vs* Reaction 5, Table 1) for reactions of **2** is also consistent with an $S_N$icB(2') mechanism for glycosyl-oxygen bond cleavage. This would be anticipated since the localized charge on the C-2' oxyanion becomes delocalized over a three-atom system in the transition state of the $S_N$icB(2') reaction. The higher ionic strength (Reaction 6) at the same hydroxide concentration would tend to favor the reactant with its localized charge, hence a slower rate of reaction.

The alkaline degradation of **2** exhibited a positive dependence of k_{go} on the hydroxide ion concentration at constant ionic strength

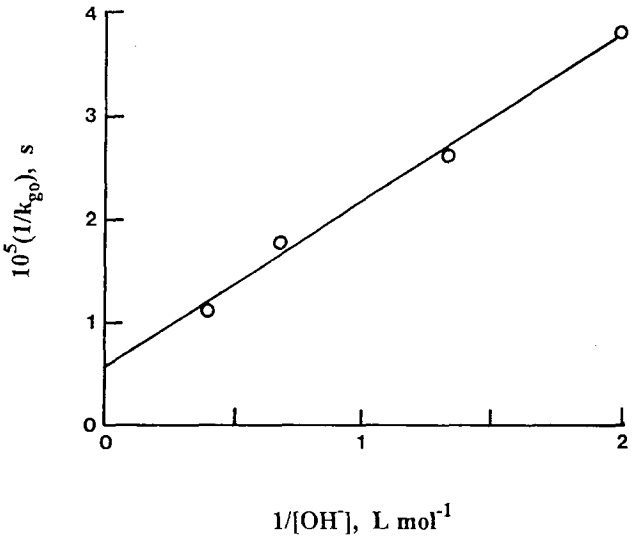


Figure 5. Reciprocal plot for glycosyl-oxygen bond cleavage in alkaline degradation of 1,5-anhydro-2,3,6-tri-O-methyl-cellobiitol (**2**)at 2.5M ionic strength.

(Reactions 2,6,7, and 8, Table 1). Lai[25] has shown that theoretically if cleavage of a glycosidic linkage occurs by an $S_N$icB mechanism the observed rate constant, e.g. k_{go}, should be related to the hydroxide ion concentration by Equation 6.

$$1/k_{go} = 1/k + 1/kK[OH^-] \quad (6)$$

where K is the equilibrium constant for formation of the conjugate base of the appropriate hydroxyl group and k is the specific rate constant for conversion of the ionized glycoside to products.

The linear correlation of $1/k_{go}$ versus $1/[OH^-]$ (Figure 5) is consistent with the alkaline cleavage of the glycosyl-oxygen bond in **2** occurring by an $S_N$icB(2') mechanism.

An S_NicB(2')-ro mechanism, as suggested by Schroeder and Henderson[26] for the alkaline degradation of 1,5-anhydro-4-O-β-D-*mannopyranosyl*-D-mannitol (1,5-anhydromannobiitol) and subsequently by Kaylor, et al.[27] for 1,5-anhydro-4-O-(4',6'-O-benzylidene-β-D-glucopyranose)-D-glucitol, could account for the decrease in the degradation rate on etherification of OH-2', the $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values, the negative salt effect, and the linear reciprocal plot, but not the large amount of 1,6-anhydro-β-D-glucopyranose **3** that is formed from **2**.[11] Thus, the S_NicB(2') mechanism is the most logical pathway for alkaline glycosyl-oxygen bond cleavage in **2**.

The amount of 1,6-anhydro-β-D-glucopyranose (**3**, Figure 4) formed in the alkaline degradation of **2** was quite dependent on the reaction conditions. At 2.5M NaOH increasing the temperature from 150 to 180°C caused a progressive decrease in the amount of **3** formed ($Y_{3,-}$, Reactions 1-4, Table 1). Similarly, at constant temperature, increasing the hydroxide ion concentration either with constant ionic strength (Reactions 6,7,8, and 3) or without ionic strength control (Reactions 3 and 5) caused a progressive decrease in the amount of **3** formed. However, at 0.5M NaOH, increasing the ionic strength caused the amount of **3** formed to increase. These results are probably indicative of a shift in the product-determining reactions of the intermediate 1,2-anhydro-α-D-glucopyranose (**15**, Figure 4). However, the relative constancy of formation of **3** with changing reaction conditions in the degradation of phenyl β-D-glucopyranoside[11] may also indicate that these changes reflect partial incursion of other reaction mechanisms.[14]

EXPERIMENTAL

Materials

Sodium p-toluenesulfonate was recrystallized from ethanol:water (9:1, vol) and dried *in vacuo* at 50°C.

1,5-Anhydro-4-O-β-D-glucopyranosyl-2,3,6-tri-O-methyl-D-glucitol (**2**), $[\alpha]_D$ +15.3° (H_2O, 25°C) was prepared as described previously.[14]

1,5-Anhydro-2,3,6-tri-O-methyl-D-glucitol (5)

2,3,6-Tri-O-methyl-D-glucopyranose[28] was acetylated with pyridine-acetic anhydride[29] using a modified work-up in which all aqueous phases were extensively back-extracted with chloroform. The sirupy acetate (45 g) was dissolved in 1,2-dichloroethane (80 mL) and treated with hydrogen bromide in acetic acid (30-32%, 50 mL) for 1 h. The solution was diluted with chloroform (300 mL); stirred with ice and water (700 mL) for 0.5 h; washed with water (200 mL), saturated sodium hydrogen carbonate (200 mL), and water (200 mL); dried with calcium chloride; and concentrated *in vacuo* to yield crude 4-O-acetyl-2,3,6-tri-O-methyl-α-D-glucopyranosyl bromide as an oil. The bromide was dissolved in chloroform (150 mL) and methanolic potassium hydroxide (0.5N, 300 mL) containing thiophenol (22 mL) was added to the solution. The mixture was refluxed for 1.5 h, washed with water (2 x 200 mL) and 2N sodium hydroxide (3 x 100 mL), dried ($CaCl_2$), and concentrated in vacuo to a sirup (30 g, 57%). Purification by chromatography on silica gel (60-200 mesh) using chloroform-ethyl acetate (2:1, vol) eluent and crystallization from isopropyl ether yielded phenyl 4-O-acetyl-2,3,6-tri-O-methyl-1-thio-β-D-glucopyranoside (**16**); m.p. 62.5-63°C, $[\alpha]_D$ -46.5° (c 2, $CHCl_3$, 22°C). (Found: C, 57.2; H, 6.9; S, 9.0%. $C_{17}H_{24}O_6S$ requires: C, 57.3; H, 6.8; S, 9.0%).

Compound **16** (10 g) was dissolved in absolute ethanol and Raney nickel W-2 catalyst[30] (20 g) was added. The mixture was maintained at ca. 50°C for 48 h. Additional catalyst (5 g) was added at 4, 8, 24, and 32 h. Silica gel t.l.c. with chloroform-ethyl acetate (3:1, vol) eluent was used to monitor the reaction. After the catalyst settled from the cooled mixture, the supernatant was decanted, and the catalyst was washed with hot ethanol (3 x 200 mL). The alcohol solutions were combined, filtered (Celite), and concentrated *in vacuo* to an oil. The oil was deacetylated with methanolic sodium methoxide.[31] Purification of the product by silica gel (60-200 mesh) chromatography using chloroform-methanol (15:1, vol) eluent and subsequent vacuum distillation yielded 1,5-anhydro-2,3,6-tri-O-methyl-D-glucitol (**5**) as an oil (4.1 g, 61.3%), $[\alpha]_D$ +54.1° (c 2.4, H_2O, 22°C). Literature:[14] m.p. 32-32.5°C, $[\alpha]_D$ +53.8° (c 2.4, H_2O, 25°C).

Phenyl 1-Thio-β-Cellobioside (17)

Phenyl hepta-O-acetyl-1-thio-β-cellobioside (**18**) was prepared from hepta-O-acetyl-α-cellobiosyl bromide[14] as described for the preparation of **16**. Deacetylation of **18**[31] and crystallization of the product from ethanol yielded **17** (35% yield); m.p. 227-230°C, $[\alpha]_D$ -56.8° (c 2, H_2O, 22°C). Literature:[32] m.p. 230°C, $[\alpha]_D$ -59.2° (H_2O).

Phenyl 4',6'-O-Benzylidene-1-thio-β-cellobioside (19)

Compound **17** (44 g) was shaken with anhydrous benzaldehyde (150 mL) and anhydrous zinc chloride (70 g) for 48 h. The mixture was poured into 10% sodium hydrogen carbonate solution (2 L) and stirred for 1 h. The precipitated product was filtered, washed with petroleum ether (b.p. 30-60°C, 200 mL), and dried *in vacuo* to yield crude **19**. Two crystallizations from absolute ethanol yielded pure **19**; m.p. 198-199°C, $[\alpha]_D$ -65.3° (c 0.5, MeOH, 22°C). Found: C, 57.6; H, 5.6; S, 6.2%. $C_{25}H_{30}O_{10}S$ requires: C, 57.5; H, 5.8; S, 6.1%. δ (DMSO-d_6) 7.25-7.46 (m, SC_6H_5 and CC_6H_5, 10 H) and 5.59 (s, benzylidene methine proton).

Phenyl 4',6'-O-Benzylidene-2,3,6,2',3'-penta-O-methyl-1-thio-β-cellobioside (20)

Compound **19** (32 g) was dissolved in tetrahydrofuran (500 mL) containing powdered sodium hydroxide (70 g). Dimethyl sulfate (50 mL) was added dropwise to the stirred mixture over 1 h. Stirring was continued for 24 h with the mixture at *ca.* 40°C. The mixture was diluted with benzene (250 mL) and water (300 mL), and stirred for an additional 2 h. The organic phase was concentrated *in vacuo* to a white residue which was crystallized from diisopropyl ether to yield **20** (72% yield); m.p. 148-149°C, $[\alpha]_D$ -43.2° (c 1.0, $CHCl_3$, 22°C). Found: C, 61.0; H, 7.0; and S, 5.1%. $C_{30}H_{40}O_{10}S$ requires C, 60.8; H, 6.8; and S, 5.4%. δ ($CDCl_3$) 7.23-7.49 (m, SC_6H_5 and CC_6H_5, 10 H); 5.54 (s, benzylidene methine proton, 1 H); and 3.64, 3.60 (6 H), 3.58, and 3.40 (5 x MeO).

Phenyl 2,3,6,2',3'-Penta-O-methyl-1-thio-β-cellobioside (21)

Compound **20** (22 g) was dissolved in chloroform (100 mL) and methanol (300 mL) and refluxed with Amberlite IR-120 (H^+) resin for 11 h. The resin was filtered and rinsed with methanol (100 mL). The combined filtrates were concentrated *in vacuo* to a sirup which was crystallized from diisopropyl ether to yield **21** (83% yield); m.p. 130-131°C, $[\alpha]_D$ -34.1° (c 1.3, $CHCl_3$, 22°C). Found: C,54.9; H, 7.0; and S, 6.0%. $C_{23}H_{36}O_{10}S$ requires C, 54.8; H, 7.1; and S, 6.4%. δ ($CDCl_3$) 7.23-7.53 (m, SC_6H_5, 5H) and 3.63, 3.60 (6H), 3.54, and 3.38 (5 x MeO).

1,5-Anhydro-2,2',3,3',6-penta-O-methyl-cellobiitol (4)

Compound **21** was dissolved in absolute ethanol (500 mL) and freshly prepared W-2 Raney nickel catalyst (30 g) was added to the solution. The mixture was maintained at *ca.* 45°C for 8 h and filtered through Celite. The residue was washed with hot absolute ethanol (3 x 50 mL). The combined filtrates were concentrated *in vacuo* to a sirup which was crystallized from diisopropyl ether. Two recrystallizations of the product from diisopropyl ether yielded **4** (64.5% yield), m.p. 120-121°C, $[\alpha]_D$ +29.6° (c 1.5, H_2O, 22°C). Found: C, 51.7 and H, 8.1%. $C_{17}H_{32}O_{10}$ requires C, 51.5 and H, 8.1%.

Kinetic Analyses

The reactor system, the techniques for preparing reaction solutions, and loading and sampling the reactor are described in detail elsewhere.[13]

The sample size (*ca.* 1 g) and the amounts of internal standard solutions (n-propyl β-D-xylopyranoside[33] for monosaccharides and cyclohexyl β-cellobioside[14] for disaccharides) added to the sample were determined gravimetrically. The amount of each internal standard solution added to the sample was varied according to the amount of mono- and disaccharide estimated to be present.

The samples were deionized by passing them through a column (10 mm) containing Amberlite MB-3 (H^+, OH^-)(10-15 mL) and eluting

with distilled water (20 mL). The eluate was concentrated to dryness *in vacuo* at <45°C. The residue was acetylated for 18 h with acetic anhydride (1 mL) in pyridine (1 mL). Distilled water (8 mL) was added and the mixture was shaken mechanically for 0.5 h. The mixture was extracted with chloroform (3 x 5 mL) and the combined extracts were washed with 2M HCl saturated with NaCl (15 mL), 10% NaCl saturated with $NaHCO_3$ (15 mL), and water (10 mL). Each wash solution was back-extracted with fresh chloroform (5 mL). The chloroform solutions were then combined, dried (Na_2SO_4), and concentrated *in vacuo* to dryness. The residue was dissolved in chloroform (*ca.* 0.5 mL) and analyzed by g.l.c. Response factors were determined by subjecting known mixtures of the necessary compounds to the analysis procedure.

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