ALKALINE THERMOLYSIS OF PHENYL α- AND β-D-GLUCOPYRANOSIDES

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(Received May 19th, 1972; accepted for publication, June 16th, 1972)

ABSTRACT

Pyrolysis of phenyl α- and β-D-glucopyranosides in the presence and absence of 5% of sodium hydroxide has been investigated by co-ordinated thermal and chemical methods. The resulting thermograms and kinetic data show that the configurational effects observed for aqueous systems also prevail under the pyrolytic condition, and that the thermolysis of the β-D anomer under alkaline conditions is facilitated by anchimeric assistance of the *trans*-hydroxyl group at C-2, to provide a quantitative yield of 1,6-anhydro-β-D-glucopyranose.

INTRODUCTION

It has been known for many years that vacuum pyrolysis of starch and cellulose results in thermal cleavage of the glycosidic bonds and formation of 1,6-anhydro-β-D-glucopyranose[1,2]. The mechanism of this reaction, however, still remains to be established, and theories that have been advanced include both homolytic and heterolytic cleavage[2]. In the latter case, 1,2-anhydro and 1,4-anhydro compounds have been suggested as reaction intermediates, by analogy with the formation of 1,6-anhydro-β-D-glucopyranose from the alkaline hydrolysis of phenyl β-D-glucopyranoside through anchimeric assistance of the *trans*-hydroxyl group at C-2[3,4].

Recent studies in this laboratory have shown that thermal cleavage of glycosidic bonds occurs more generally than has been recognized previously, and pyrolysis of a variety of carbohydrates, including phenyl D-glucopyranosides and D-xylopyranosides, results in release of the aglycon, condensation of the glycosyl units, and decomposition of the sugar moiety through a combination of acid- and alkali-catalyzed degradation pathways[5–10]. These investigations have also shown that cleavage of the glycosidic bonds proceeds by a heterolytic reaction. However, the exact mechanism and the type of intermediates involved still remain to be established. One of the obstacles to resolving the various possibilities is that virtually no experimental data are available about the magnitude of the conformational and configurational effects under pyrolytic conditions, when the energy barrier could be more readily surmounted.

In this study, the thermal behaviors of phenyl β-D-glucopyranoside and phenyl

α-D-glucopyranoside have been compared, before and after treatment with alkali, in order to gain further information about the nature of the pyrolytic reactions and the influence of the configurational variation.

RESULTS AND DISCUSSION

Thermograms of phenyl β-D-glucopyranoside and the α-D anomer are shown in Figs. 1 and 2. As discussed previously[6], the β-D form shows three major events corresponding to the loss of crystallization water, melting, and decomposition (Fig. 1). A closely similar pattern is shown by the α-D form, except that it has no crystallization water and displays a single d.t.g. peak for weight loss (Fig. 2).

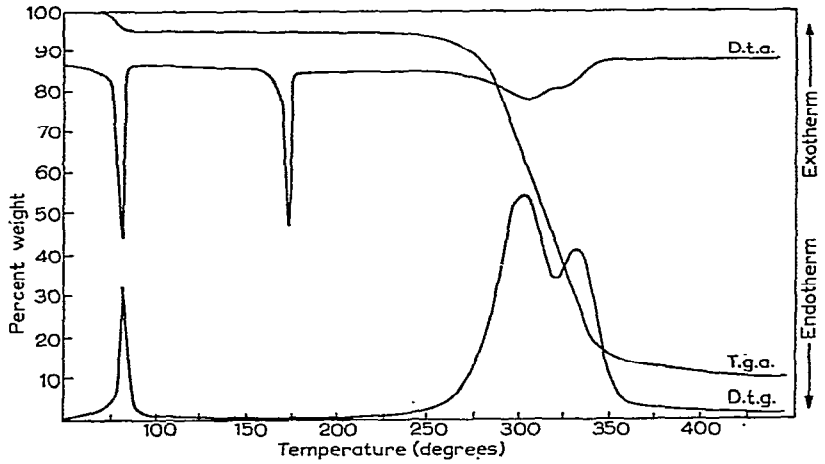

Fig. 1. Thermogram of phenyl β-D-glucopyranoside.

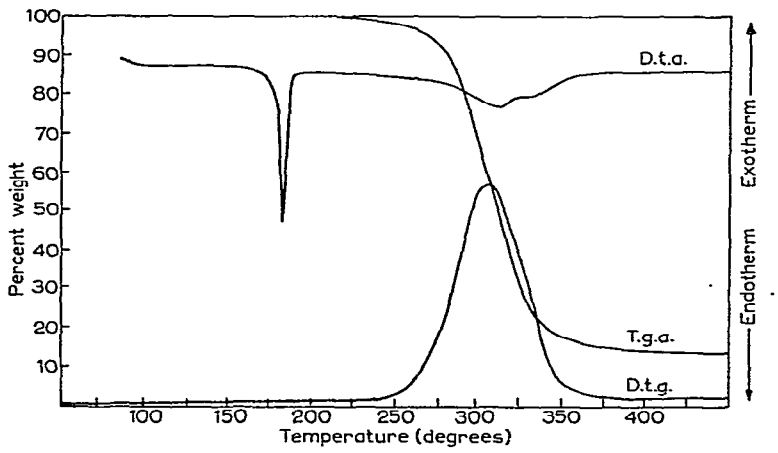

Fig. 2. Thermogram of phenyl α-D-glucopyranoside.

After treatment with 5% of sodium hydroxide, the crystallinity of both samples is destroyed, and thermal analysis (Figs. 3 and 4) does not show the sharp endotherms for dehydration and melting which are observed for the pure crystalline compounds. Other than the solid-state changes, however, the alkaline treatment produces only a slight effect on the decomposition behavior of the α-D form (Fig. 4), whereas it substantially alters the decomposition pattern of the β-D form (Fig. 3). By comparison of Figs. 1 and 3, it may be seen that the alkali treatment has lowered the decomposition endotherm of phenyl β-D-glucopyranoside from ~310° to 230°, and two new exothermic peaks appear at ~275° and 320°.

It has been already shown that, in the absence of alkali, heating of the β-D-glycoside results in cleavage of the glycosidic group and condensation of the sugar moiety to a mixture which contains very little 1,6-anhydride and is decomposed on

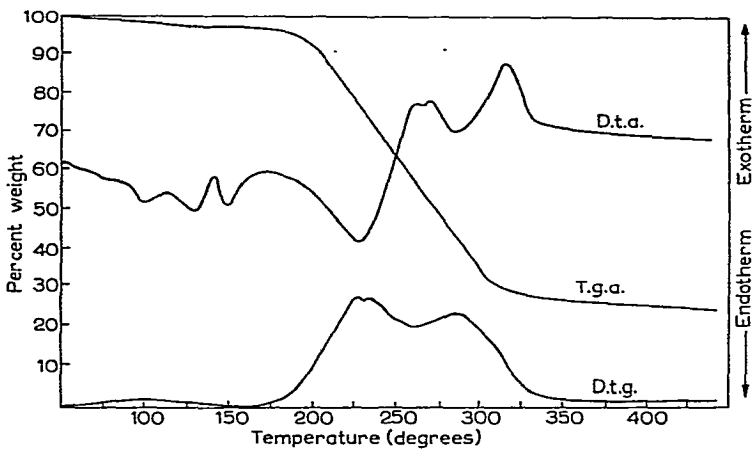

Fig. 3. Thermogram of phenyl β-D-glucopyranoside+5% of sodium hydroxide.

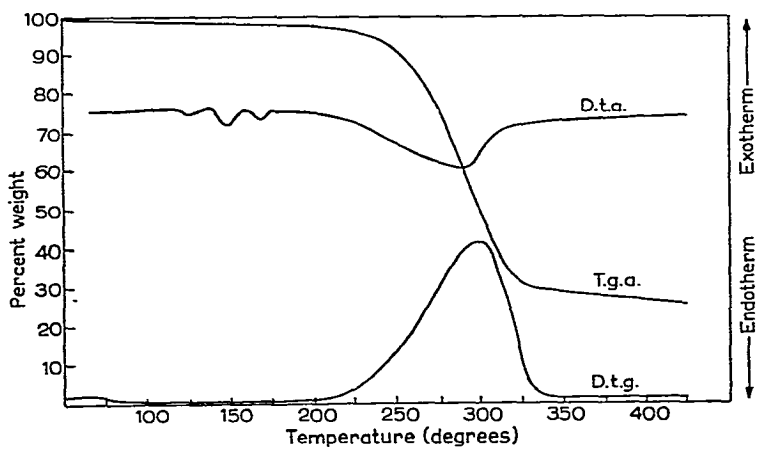

Fig. 4. Thermogram of phenyl α-D-glucopyranoside+5% of sodium hydroxide.

further heating[6]. The reactions which take place in the presence of alkali were investigated by isothermal heating of a treated sample at 175°, which corresponds with the initiation of the degradation reactions in Fig. 3. As the degradation proceeded at this temperature, aliquots of the reaction mixture were trimethylsilylated and analyzed by g.l.c.[11] for the remaining glycoside and the yield of 1,6-anhydride. The results, summarized in Table I, showed almost quantitative formation of 1,6-anhydro-β-D-glucopyranose from the degraded glycoside. This indicates that the d.t.a. and d.t.g. peaks at ~230° in Fig. 3 correspond with cleavage of the glycosidic group, formation of 1,6-anhydride, and evaporation of the aglycon. The next two d.t.a. peaks at ~275° and 320° and the d.t.g. peak at ~290° were assigned to decomposition of 1,6-anhydro-β-D-glucopyranose in the presence of alkali, since essentially the same decomposition patterns were produced by detailed thermal analysis of the 1,6-anhydride treated with 5% of sodium hydroxide (Fig. 5).

TABLE I

COMPOSITION OF THE ALKALINE THERMOLYSIS PRODUCTS

Starting material	*Temp. (degrees)*	*Time (min)*	*Remaining D-glucoside (%)*	*1,6-Anhydro-β-D-glucopyranose*	
				Analyzed (%)	*Calc. (%)*
Phenyl β-D-glucopyranoside	175	8	83.8[a]	7.4[a]	10.2[a]
		15	68.1	18.8	20.2
		20	59.5	22.0	25.6
		30	48.8	28.1	32.5
		30	47.1	32.7	33.5
Phenyl α-D-glucopyranoside	200	5	92.0	5.1	
		10	85.2	4.0	
		30	77.4	4.2	
		70	56.5	7.3	
1,6-Anhydro-β-D-glucopyranose	200	10		90.3	
		20		86.5	
		30		83.4	
		60		77.5	
		90		68.3	

[a]Based on the original weight.

Comparison of Figs. 2 and 4, however, indicates only a slight shift in the decomposition peak of the α-D form from ~305° to ~290°, after the treatment, which is in contrast with the results obtained with the β-D form. The contrasting effects of the alkali treatment were confirmed by isothermal heating of the α-D form in the presence of alkali at 200° which corresponds to the temperature of the degradation threshhold in Fig. 4. Analysis of the reaction mixture, as before, showed that considerably less 1,6-anhydride is produced from cleavage of the α-D-glycoside (see Table I). Since the latter experiment was conducted at a higher temperature, it may be argued that the difference is due to the high rate of decomposition of the 1,6-anhydride

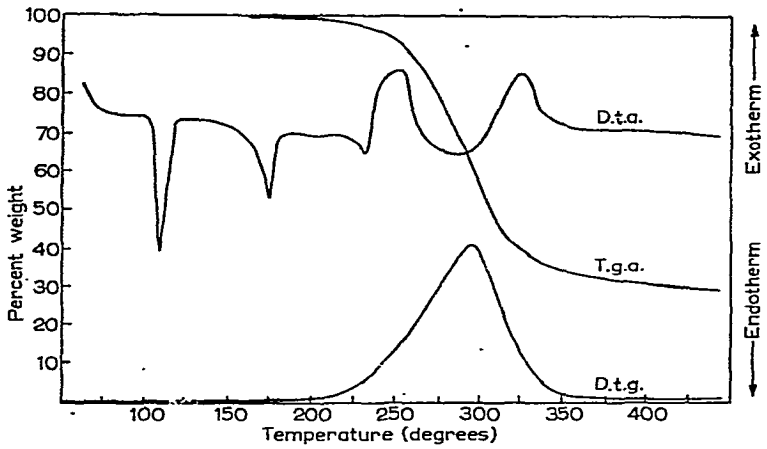

Fig. 5. Thermogram of 1,6-anhydro-β-D-glucopyranose + 5% of sodium hydroxide.

at 200°. However, as can be seen from the data in Table I, this possibility was eliminated by isothermal experiments with 1,6-anhydro-β-D-glucopyranose under identical conditions.

TABLE II

ALKALINE THERMOLYSIS OF PHENYL D-GLUCOPYRANOSIDES AT DIFFERENT TEMPERATURES

Temp. (degrees)	*Time (min)*	*Remaining D-glucoside (%)*[a]	*Temp. (degrees)*	*Time (min)*	*Remaining D-glucoside (%)*[a]
α-D Anomer			*β-D Anomer*		
150	45	98.44	145	10	96.5
	60	97.48		30	96.0
	90	97.00		45	93.5
	135	93.90		75	89.7
165	20	98.12	165	5	95.0
	50	96.00		15	78.7
	70	93.20		30	72.0
	100	91.70		45	60.0
	180	87.50	195	3	69.5
175	5	98.45		6	65.0
	10	97.92		10	35.5
	15	97.00		15	22.9
	30	94.50			
	60	88.50			
185	5	96.6			
	15	91.8			
	30	85.0			
	60	74.0			
195	5	93.8			
	10	90.8			
	15	83.8			
	20	76.6			

[a]Calculated from the analysis of phenol in the pyrolysis mixture.

Further information on the thermal cleavage of the phenyl glycosides under alkaline conditions was obtained by isothermal kinetic studies. The thermal reaction was followed by colorimetric determination of the liberated phenol, within the

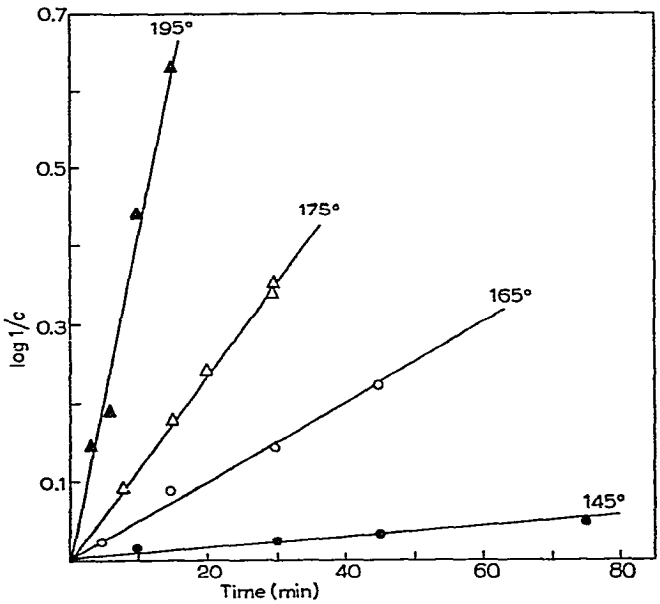

Fig. 6. Isothermal rates of pyrolysis for phenyl β-D-glucopyranoside +5% of sodium hydroxide

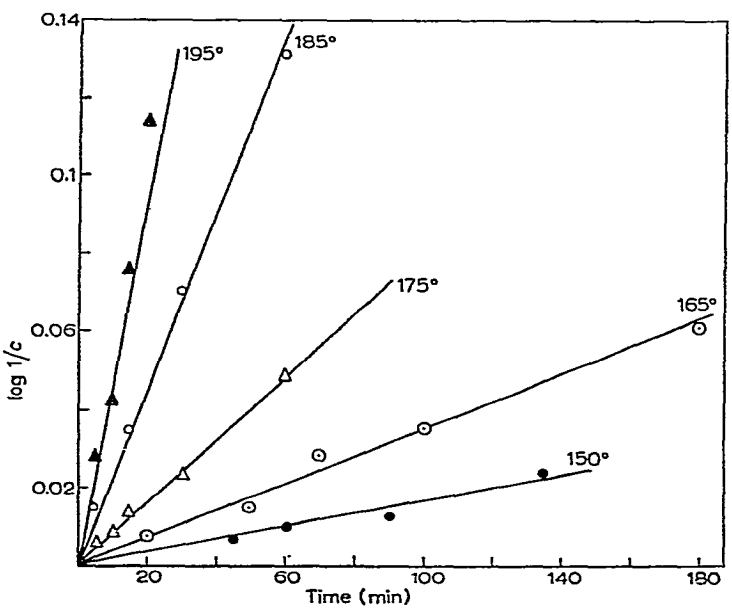

Fig. 7. Isothermal rates of pyrolysis for phenyl α-D-glucopyranoside +5% of sodium hydroxide.

temperature range of 145–195°. The resulting data (Table II), as seen in Figs. 6 and 7, fit the equation $\ln(1/c) = kt$ for pseudo-first-order kinetics; where c is the mole fraction of unreacted phenyl glucosides after reaction time t, and k is the pseudo-first-order rate constant. The rate constants calculated from these data (Table III) were, in turn, least-square fitted in the Arrhenius equation to give activation energies of 34.5 ± 3 and 30 ± 4 kcal.mole^{-1} for alkaline pyrolysis of the β- and α-D forms, respectively.

TABLE III

RATE CONSTANTS OF THE ALKALINE THERMOLYSIS OF PHENYL D-GLUCOPYRANOSIDES

Temp. (*degrees*)	$k \times 10^3$ (min^{-1})	
	α-D *Anomer*	β-D *Anomer*
145		1.2
150	0.5	
165	0.7	10.7
175	1.0	24.9[a]
185	4.8	
195	13.8	99.5

[a]Calculated from the yield of 1,6-anhydro-β-D-glucopyranose.

The above data show that, under alkaline conditions, the β-D form is pyrolyzed ~10 times more rapidly than the α-D form, and that the configurational effect which has been observed in aqueous systems[3,4,12–14] still prevails under the pyrolytic conditions involving considerably higher temperatures.

The kinetic studies and quantitative formation of 1,6-anhydro-β-D-glucopyranose from the β-D form under alkaline conditions are consistent with the established mechanism[3,4] for the alkaline hydrolysis of the glycosidic group through anchimeric assistance of the *trans*-hydroxyl group at C-2.

The exact mechanisms for the thermolyses of the α-D form under alkaline conditions and the α- and β-D forms under normal conditions have not been established, but it is interesting to note that they all proceed at higher temperatures, give low yields of 1,6-anhydride, and produce similar thermograms (Figs. 4, 2, and 1, respectively) which are substantially different from the decomposition pattern of the alkali-treated β-D form (Fig. 3). One of the inferences from these data is that, if formation of 1,6-anhydro-β-D-glucopyranose from cellulose[2] involves participation of the *trans*-hydroxyl group at C-2, then one should expect lower yields and rates of reaction with starch, which has the opposite glycosidic configuration. This subject will be discussed in another paper.

EXPERIMENTAL

Preparation of samples. — Phenyl α- and β-D-glucopyranosides were prepared as described previously[6,15]. Samples of these compounds were dissolved in a solution

of sodium hydroxide in methanol calculated to add 5% of alkali after evaporation of the solvent. The mixtures were dried *in vacuo* at 50° and kept under anhydrous conditions. A sample of 1,6-anhydro-β-D-glucopyranose containing 5% of sodium hydroxide was prepared in the same manner.

Analytical methods. — The thermal analysis and g.l.c. of carbohydrates were carried out by the same method and equipment that were described in previous publications in this series[6,7]. The u.v. spectra were obtained with a Hitachi EPS-3, Coleman recording-spectrophotometer.

Thermolysis of phenyl D-glucoside samples. — Small amounts of the samples (~5 mg) were weighed and sealed in ampoules (5 ml) under a nitrogen atmosphere. The ampoules were then heated in a constant-temperature oil-bath for different periods, rapidly cooled in cold water, and opened.

For determination of 1,6-anhydride and the unreacted glycosides, the reaction mixtures were trimethylsilylated[11] and analyzed by g.l.c., using D-glucitol as an internal standard. The resulting data are given in Table I.

In the kinetic experiments, the reaction mixtures were dissolved in 5 ml of distilled water and 1-ml samples of the solution were diluted with 10 ml or 20 ml of M sodium hydroxide. The amounts of liberated phenol in the final solution were determined colorimetrically by the u.v. absorption[16]: λ_{max} 287 (ε 2,600). This gave the amounts of unreacted phenyl D-glucosides summarized in Table II. A Wang 600 Series programmed-calculator was used for computation of the kinetic data from the experimental results.

ACKNOWLEDGMENTS

The authors thank the U. S. Public Health Service, Food and Drug Administration, and the U. S. Forest Products Laboratory, Madison, Wisconsin, for their financial support and interest.

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