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Kinetics of the Polymerization of Aldohexoses*

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SUMMARY

Thermogravimetric procedures are used to obtain the kinetic parameters for the intermolecular condensation of the anomers of D-glucose, D-mannose, and D-galactose. The condensation rates in the temperature range 176-220°C are found sufficiently rapid compared to the rates of mutarotation that significant differences between anomers can be observed.

Comparison of the specific rate constants for the intermolecular condensation show α-D-galactose to be most reactive, followed by β-D-galactose, α-D-mannose, β-D-mannose, α-D-glucose, and β-D-glucose in decreasing order. Within the initial 60% of the condensation, where it is observed that the condensation primarily involves the loss of reducing end groups, the reaction is essentially bifunctional and probably self-catalyzed, resulting in a third-order reaction rate. The activation energies are 83, 75, and 77 kcal/mole for β-D-glucose, α-D-mannose, and α-D-galactose, respectively. It is suggested that the reactivity of the aldohexoses is correlated with the position of the axial hydroxyl groups on the pyranose ring.

INTRODUCTION

Kinetics of the Polymerization of Aldohexoses

In a previous investigation [1] it was shown that correlated differences existed in the products formed in the polycondensation of

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the anomers of the aldohexoses in the molten state provided that the reaction was not carried to completion. Further, catalysts and trace impurities which tend to act as catalysts had to be avoided and a temperature range of 176-220°C was required so that intramolecular condensation was negligible while mutarotation was secondary to the intermolecular condensation reaction.

The purpose of the present investigation was to see whether differences in structure of the various aldohexoses could be reflected in possible differences in the rates of polycondensation and whether these differences could be correlated with the structure of the monomer. Because polycondensation is accompanied by the formation of a small molecule, water, thermogravimetry appeared to be a technique well suited to this investigation provided that only the product of condensation was removed. Preliminary experiments showed that in vacuo conditions caused a significant loss of monomer. The use of an atmosphere of argon avoided this complication. To ensure that the product of condensation was removed as rapidly as it was formed, a large surface/volume ratio for the reacting mass was maintained. Also, the flow of argon was kept in a range where the reaction rates were independent of the rate of flow. The nonisothermal method of Freeman and Carroll [2] was used to determine the kinetic parameters.

The requirement for condensation [1] is a reducing end group which can react with the primary hydroxyl group or any axial hydroxyl group on the pyranose ring. For the reaction to go to completion a maximum weight loss of 10.0% can be expected. A differential equation for the reaction may be written as

$$d[H_2O]/dt = k[OH]^n \tag{1}$$

where [OH] is the concentration of unreacted end group at time t and n is the order of reaction. Equation (1) may be rewritten as

$$dW/dt = k'W_t^n \tag{2}$$

where dW/dt is the rate of formation of H_2O and W_t is the weight of unreacted reducing end groups at time t. Since a linear heating rate is used, t is proportional to the temperature T and Eq. (2) may be shown to lead to

$$\frac{\Delta \log (dW/dT)}{\Delta \log W_t} = \frac{E_A}{2.303R} \times \frac{\Delta(1/T)}{\Delta \log W_t} + n \tag{3}$$

if the Arrhenius equation for the energy of activation, E_A, is assumed. A plot of

$$\frac{\Delta \log (dW/dT)}{\Delta \log W_t} \text{ versus } \frac{\Delta (1/T)}{\Delta \log W_t}$$

the data being taken from the thermogravimetric curve, leads to a value for both E_A and n. Substitution of the latter value in Eq. (2) permits evaluation of the rate constants k′.

EXPERIMENTAL

Apparatus

An Ainsworth vacuum-semimicro automatic recording balance (Model RV-AU-2) along with the auxiliary equipment described earlier [1] were used to measure the weight loss associated with the intermolecular condensation reactions of the aldohexoses. The slopes of the thermogravimetric curves were measured at specific temperatures with a mechanical differentiator [3].

The preparation and purification of the anomers of D-glucose, D-mannose, and D-galactose have been described in a previous publication [1].

Experimental Procedure

Thermogravimetric procedure consisted of advancing the temperature of the sample at a rate of 6.5°C/min under a continuous flow of argon at a rate of 0.08 ft^3/hr. The initial weight of the samples was fixed at 100 mg. The buoyancy correction was obtained by simply recording the weight change of an empty crucible as a function of temperature using the same conditions as prevailed during a thermogravimetric run. This procedure was considered adequate since the weight as well as volume of the reacting mass was one or two orders of magnitude smaller than that of the crucible. The temperature of the sample was determined as a result of a series of separate experiments where thermocouple I was embedded in the sample and the recorded weighings were discarded. An additional thermocouple II was positioned below the heated crucible and the sample temperature (I) was then determined as a function of temperature (II). During a thermogravimetric experiment temperature (II) only was recorded and appropriate corrections were applied.

Analysis was performed on a reaction mass when a weight loss equivalent to 50-60% completion of the condensation occurred. The method described by Nussenbaum and Hassid [4] was used to determine the per cent reducing end groups remaining in the reaction mass.

RESULTS

Thermogravimetric Results for the Monosaccharides Heated in Argon

The thermogravimetric curves in Fig. 1 represent the experimental weight loss associated with the condensation reactions of the anomers of D-glucose, D-mannose, and D-galactose. It is apparent that appreciable differences exist between the various monosaccharides. The spread of the thermogravimetric curves at about the half-lives for the condensation is about 20 degrees. It is 195°C for α-D-galactose and 215°C for β-D-glucose with reproducibility better than ±1.0°C.

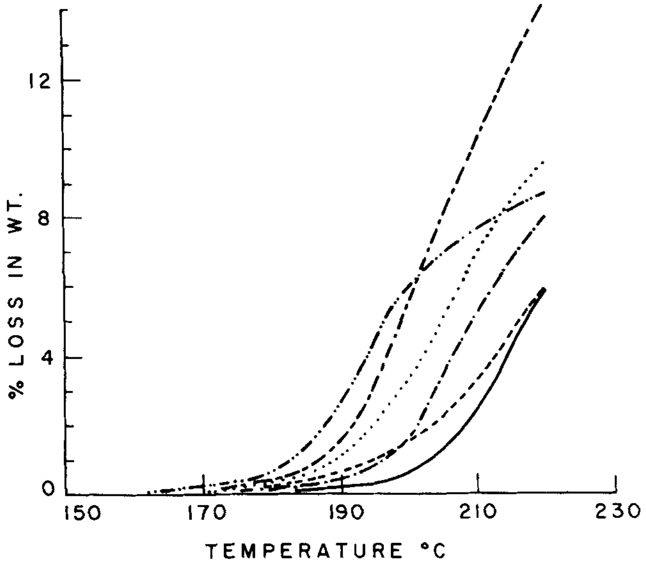

Fig. 1. Thermogravimetric curves for the polycondensation of the anomers of D-glucose, D-mannose, and D-galactose. Per cent loss in weight vs. temperature (°C). Heating rate = 6.5°C/min. Anomers heated under an atmosphere of argon. ————, β-D-glucose; — — — —, α-D-glucose; - . - . - . -, β-D-mannose; . . . . , α-D-mannose; — — — — —, β-D-galactose; -. . -. . -, α-D-galactose.

For five out of the six anomers studied the percentages of reducing end groups remaining in the reaction mixture, after approximately 55% of the condensation, agrees within the experimental error

Table 1. Comparison of Observed and Estimated Percentage of Reducing End Groups in Reaction Mixtures

	Observed[a]	Estimated[b]
α-D-galactose	30	45
β-D-galactose	38	44
α-D-mannose	51	47
β-D-mannose	48	44
α-D-glucose	45	47
β-D-glucose	53	48

[a] According to the method described by Nussenbaum and Hassid [4].

[b] Estimated from thermogravimetric measurements by assuming that for every molecule of water formed one end group has reacted.

with that estimated from the results of the thermogravimetric measurements (see Table 1).

The kinetic study of the condensations was limited to the initial 60% because the reaction mixtures were found to be completely soluble under these conditions. Thus the analysis of the reaction mixture for per cent of reducing end groups could be carried out. Also, Puddington's work [9] on D-glucose shows that for the initial 6% weight loss the predominant reaction product liberated is water. This is equivalent to a 60% completion of reaction.

The initial 60% of the condensation of β-D-glucose, α-D-galactose, and α-D-mannose is replotted in Fig. 2A, B, and C in accordance with Eq. (3). The two sets of points which were obtained from two independent thermogravimetric experiments in the case of β-D-glucose (see Fig. 2A) are an indication of the reproducibility of the derived kinetic parameters. The calculated activation energies and order of reaction are given in Table 2. The resulting order of the condensation reaction was used to calculate the relative rate constants as given in Eq. (2). This was done using the slopes of the thermogravimetric curves at 196°C, where precision was optimum. The results for the six aldohexoses are shown in Table 3.

DISCUSSION

It had been suggested previously [1] that the condensation reaction below 220°C is a bifunctional reaction involving a reducing end group and a hydroxyl group.

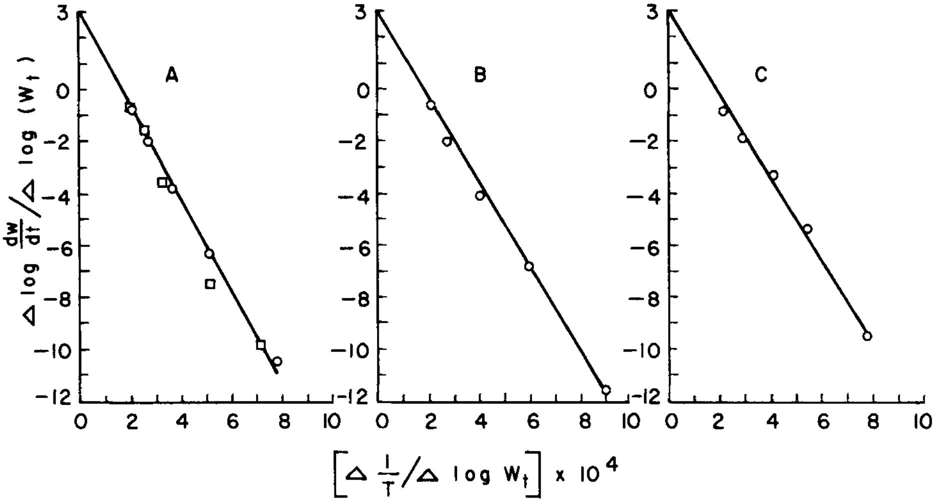

Fig. 2. Plot of thermogravimetric data:

$$\frac{\Delta \log (dw/dt)}{\Delta \log W_t} \text{ vs. } \frac{\Delta(1/T)}{\Delta \log W_t}$$

for polycondensation reaction: A, β-D-glucose; B, α-D-galactose; C, α-D-mannose. The two sets of points for β-D-glucose represent data for two independent experiments.

The agreement between the observed and estimated reducing end groups remaining in the reaction mixtures of the anomers of D-glucose, D-mannose, and D-galactose shows that it is the reducing end groups which are primarily involved in the condensation. The reasons for the poor agreement in the case of α-D-galactose (see Table 1) are not clear.

Table 2. Energy of Activation and Order of Reaction Obtained from the Slopes and Intercepts of Lines in Fig. 2

Monomer	Energy of activation, kcal/mole	Order of reaction
β-D-glucose	83	3.0
α-D-galactose	77	3.0
α-D-mannose	75	3.0

Table 3. Relative Rate Constants for the Polycondensation Reaction of the Anomers of D-Glucose, D-Galactose, and D-Mannose at 196°C

Monosaccharide	Relative third-order rate constant
β-D-glucose	0.085
α-D-glucose	0.241
β-D-mannose	0.362
α-D-mannose	1.16
β-D-galactose	3.37
α-D-galactose	5.75

The results obtained from Fig. 2 and listed in Table 2 clearly indicate a third-order reaction, which suggests that the condensations are self-catalyzed by the ionization of the reducing end group. These findings are not entirely unexpected in view of the work of Flory [5] on the kinetics of acid-catalyzed polyesterification reactions. When such reactions are run with bifunctional monomers in the presence of an added acid, second-order kinetics are found. When, however, the hydrogen ion is furnished by one of the reactants, third-order kinetics is observed.

The ionization of the monosaccharides apparently occurs at the hydroxyl group on the C_1 position. A comparison of the reported constants [6] for the ionization of D-glucose with those of methyl-α-D-glucoside and methyl-β-D-glucoside show that the replacement of the hydroxyl group on the C_1 position with a methoxy group lowers the ionization constant for D-glucose by a factor of approximately 30. The ionization constants are 6.6×10^{-13}, 1.97×10^{-14}, and 2.64×10^{-14} for D-glucose, methyl-α-D-glucoside, and methyl-β-D-glucoside, respectively. In addition, a comparison of the reported values for the ionization of D-mannose with D-manitol indicates that reducing the aldehyde group of D-mannose to an alcohol group results in the lowering of the ionization constant, again by a factor of approximately 30.

Previous work [1] suggests two reaction mechanisms for the condensations of the anomers of D-galactose, D-mannose, and D-glucose. One mechanism is that the intermolecular condensation occurs between the hydroxyl group on the C_6 position and the carbonyl group. In this case, the primary alcohol group is considered more reactive than the other hydroxyl groups on the pyranose ring. This has been shown to be the case for D-glucose [1]. Thus the linear polymers formed from the condensation of the anomers of D-glucose are mainly composed of 1, 6 ether linkages.

It is interesting to note that the 1, 6 ether linkage predominates in the polyglucose formed as a result of the condensation of D-glucose in the presence of an acid catalyst [7].

The other possible mechanism for the intermolecular condensation reaction involves hydroxyl groups on the pyranose ring which are comparable in reactivity to the primary alcohol group. This appears to be the case for the anomers of D-galactose and D-mannose based upon a comparison of their relative rate constants with that of the anomers of D-glucose (see Table 3).

If the anomers of D-galactose, D-mannose, and D-glucose are assumed to exist in the C_1 configuration [8], the anomers of D-galactose and D-mannose differ from the anomers of D-glucose in that they contain an axial hydroxyl group on the C_4 and C_2 positions of the pyranose ring, respectively. Since the relative rate constants for the condensation of the anomers of D-galactose and D-mannose were found to be higher than those for the glucose anomers, it may be postulated that the axial hydroxyl groups with respect to the pyranose ring increases their availability. This hypothesis is also supported by the fact that the relative rate constants for the condensations of the α anomers of D-galactose, D-mannose, and D-glucose were observed to be higher than for the β anomers, as is shown in Table 3.

The location of the axial hydroxyl groups on the pyranose ring also appears to affect their reactivity. The relative rate constants for the condensation of the anomers of D-galactose were found to be larger than those for the anomers of D-mannose, even though their activation energies are about the same (see Table 2). Apparently, the close proximity of the axial hydroxyl groups on the C_1 position tends to inhibit the reactivity of the axial hydroxyl on the C_2 position to some extent. Thus the 1, 4 and 1, 6 ether linkages should predominate in the linear polymers resulting from the condensation of the anomers of D-galactose, and the 1, 2 and 1, 6 ether linkages should predominate in the mannose polymer. Because the rate constants for the condensation of the anomers of D-galactose are larger than those for the anomers of D-mannose, one may expect more 1, 4 ether linkages in the galactose polymers than 1, 2 ether linkages in the mannose polymers.

The literature does not appear to contain information regarding the values for the activation energies for the polymerization of saccharides other than that reported by Puddington [9]. Using an isothermal method and vacuum conditions, the initial stage of the thermal reaction of cellobiose was reported as 62 kcal/mole, a value not very far removed from those given in Table 2. In the case of D-glucose the initial 60% of the condensation was lost while the reaction was being brought to temperature. A value of 29 kcal/mole was reported for the final stage of the reaction. In view of the fact that Puddington makes no mention of distillable unreacted glucose, it is probable that the glucose contained sufficient trace impurities to have the reaction proceed rapidly enough to prevent the glucose from distilling.

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