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KINETICS OF THE THERMAL REACTIONS OF SOME DISACCHARIDES

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ABSTRACT

The kinetics of the early stages of pyrolysis of several disaccharides have been examined thermogravimetrically. Cleavage of the glycosidic bond has been postulated as the rate-determining step for these thermal reactions. This step is followed primarily by the formation of anhydrohexopyranoses with the elimination of water. The kinetic parameters for these disaccharides have been compared with the literature values for aqueous acid hydrolyses of these same compounds

INTRODUCTION

Pyrolyses of disaccharides have been conducted in both the presence and absence of acid catalysts. Prominent among the products of the early stages of the reaction are some 1,6-anhydrohexopyranoses, some 1,6-anhydrohexofuranoses, some monosaccharides, and some polymeric material. If the first step is cleavage of the glycosidic bond with the formation of a carbonium ion at the anomeric carbon, then subsequent steps can proceed in several ways. An attack of the oxygen of the primary hydroxymethyl group at the anomeric carbon will yield one of the previously mentioned 1,6-anhydrohexopyranoses; the addition of a molecule of previously liberated water followed by the loss of a proton can lead to a monosaccharide. An attack of the carbonium ion on one of the oxygens of another sugar will lead to the formation of an oligo- or polysaccharide.

One interesting facet of these reactions is that some of the products of the heating of dry sugars are similar to those obtained in the reaction of disaccharides in aqueous solutions. While one usually considers only hydrolysis to monosaccharides under these conditions, there are other possibilities. The reaction of methyl-α-D-altropyranoside in aqueous acid produces a very significant yield of the 1,6-anhydroaltropyranose [1]. While polymers are not commonly produced under the conditions of acid hydrolysis, such conditions are used to produce D-isomaltose [2].

In spite of the large amount of interest and work done with disaccharides, the kinetics of the pyrolytic reactions of the disaccharides has not been

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previously established. In this current investigation, the kinetics have been studied over the first 20% of the reaction based on the elimination of water, the only volatile product of the early stages of the pyrolysis. The upper temperature range was 182°C in the case of D-maltose to 238°C for the case of D-cellobiose, where the reactions would be less complex than those encountered on prolonged heating at higher temperatures, and where primary products are being converted to secondary and tertiary compounds.

EXPERIMENTAL

Equipment and materials

The Ainsworth Model RU-AUI semimicro, automatic, recording balance was used in all the thermogravimetric measurements. All the disaccharides were reagent grade chemicals. To insure purity, they were chromatographed through charcoal—celite columns using ethanol—water mixtures as irrigants. They were checked for purity by means of paper chromatography using 6 : 4 : 3 (v/v) 1-butanol—pyridine—water, with detection by the silver nitrate method of Trevelyan et al. [3].

Methods

A 0.556 mmole sample was used in all cases. The furnace was flooded with argon which was under a constant flow rate of 2.3 l min^{-1} during the entire process. The temperature was advanced at a uniform rate of 6.2° min^{-1}. A more detailed description of the experimental procedure has been published [4].

The method of calculating the kinetic parameters was a differential difference one [5]. In the current investigation, it was assumed, as a result of preliminary measurements, that each disaccharide yields a maximum of one molecule of H_2O over the above-mentioned temperature range. Thus for the dehydration reaction to go to completion, a 10% loss of weight was incurred. The kinetic equation used was

$$\frac{\Delta \ln(-\mathrm{d}W/\mathrm{d}T)}{\Delta \ln W} = \frac{E_a}{R}\,\frac{\Delta(1/T)}{\Delta \ln W} + n$$

where T is the absolute temperature, E_a the activation energy, n the order of reaction, W the weight fraction of the reactant remaining at T, and $-\mathrm{d}W/\mathrm{d}T$ the rate of fractional weight loss. A plot of $\Delta \ln(-\mathrm{d}W/\mathrm{d}T)/\Delta \ln W$ versus $\Delta(1/T)/\Delta \ln W$ was used in Fig. 1 to obtain the activation energy and the order of reaction.

Three of the four disaccharides were initially hydrates; the fourth was anhydrous. All of the disaccharides also contained small quantities of adsorbed moisture, but it was a simple matter to discern the point at which the disaccharides became strictly anhydrous during the course of the experiment. All reaction parameters were calculated on the basis of the anhydrous disaccharide.

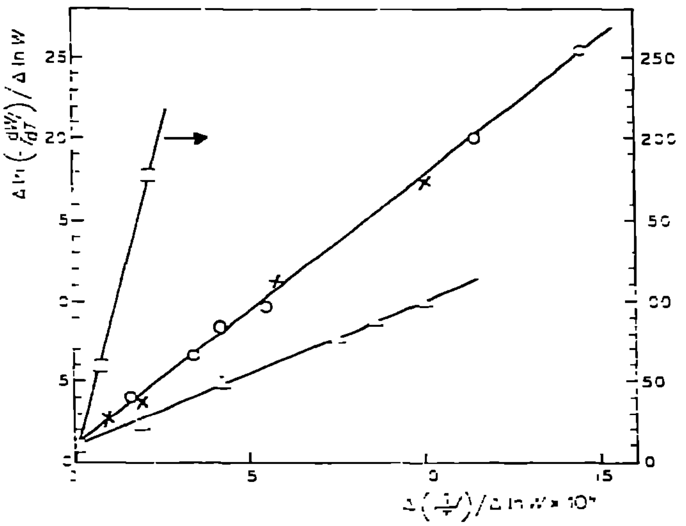

Fig. 1. A plot of $\Delta \ln(-dW/dT)/\Delta \ln W$ vs. $\Delta(1/T)/\Delta \ln W \times 10^4$. The slopes are equal to E_a/R and the intercept is the order of reaction. □, Melibiose; ○, lactose; ×, cellobiose; △, maltose.

RESULTS AND DISCUSSION

Table 1 shows an estimate of the relative thermal stability of the disaccharides based on the total loss of H_2O during the progress of the thermogravimetric measurements. More quantitative estimates of the thermal stability are the rate constants observed at the same temperature. Values for three of these are given in Table 2; the value for maltose is not included in Table 2 because the dehydration reaction for this disaccharide goes to completion at a temperature below the initiation temperature of reaction of the other three.

The energy of activation and the order of the thermal reaction of the disaccharides are obtained from Fig. 1 and are listed in Table 3. It is of interest to note that the hydrolysis parameters for the same four sugars in aqueous acid solutions are quite uniform, yielding values of $E_a = 33 \pm 1$ kcal for

TABLE 1

Temperatures at which disaccharides lose fixed percentages of weight

Disaccharide	Temp (°C) for loss of weight of		
	5%	10%	20%
Maltose	168	175	182
Melibiose	212	215	219
Lactose	215	221	230
Cellobiose	218	227	238

TABLE 2

Rate constants

	Loss of water at 215°C $k_{215} \times 10^3$ sec^{-1}	Aqueous acid hydrolysis * $k_{80} \times 10^5$ sec^{-1}
Melibiose	17.0	20.3
Lactose	2.4	18.0
Cellobiose	1.4	9 08

* Conducted in 0.5 M H_2SO_4 at 80°C (see ref. 6).

TABLE 3

Activation energy, E_a, and order of reaction, n, for thermal reaction of disaccharides

	E_a (kcal)	n
Maltose	18	1.0
Lactose	33	1.0
Cellobiose	33	1.0
Melibiose	160	$\sim$1

first-order reactions [6]. Acid hydrolysis and thermogravimetry yield identical E_a values for lactose and cellobiose [6]. This may be fortuitous in view of the fact that the E_a values for maltose and especially for melibiose obtained from thermogravimetry differ markedly from the values obtained from aqueous acid hydrolysis [6]. The reason for the very high value for melibiose in the molten state is not clear at this time.

The justification for comparing the aqueous hydrolysis of the disaccharides with the thermal reactions in the present investigation is the assumption that in both cases the cleavage of the glycosidic bond, yielding the carbonium ion, is the rate-determining step.

Indeed, one may speculate about the order of magnitude of the rate constants for the aqueous acid hydrolysis if they had been conducted at 215°C and in the presence of a hydrogen ion concentration from water instead of 0.5 M H_2SO_4. A calculated rate constant * for lactose under these conditions is $\sim 0.5 \times 10^{-3}$, which is roughly of the same order of magnitude as the 2.4×10^{-3} determined by thermogravimetry.

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* The extrapolation of a rate constant of an acid hydrolysis conducted at 80°C in 0.5 M H_2SO_4 to a reaction in a molten state at 215°C and a calculated hydrogen ion concentration for water at 215°C involves a number of assumptions and an extrapolation over some ten orders of magnitude. The fact that the rate constant is roughly of the same order of magnitude as the molten state reaction does, however, give some credence to the suggestion that the initial breaking of the glycosidic bond is the rate-governing step.

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