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KINETICS OF ALKALINE DEGRADATION OF MALTOSE IN ETHANOL–WATER SOLUTIONS

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ABSTRACT

The kinetics of the alkaline degradation of maltose in solution in 0.1M sodium hydroxide in ethanol–water of up to 53% (w/w) concentration of ethanol were studied over a temperature range of 30–60°. The isomerization of maltose to maltulose and its further degradation proceeded at approximately the same rate, whereas the isomerization of maltulose to maltose was significantly slower. All these reactions were markedly accelerated with increasing concentration of ethanol in the solvent. At 53% (w/w) concentration of ethanol, the isomerization of maltose and the degradation of maltulose took place 2.0 and 2.4 times as fast as the corresponding reactions in water. The activation energies of these reactions were 115 (isomerization) and 110 (degradation) $kJ.mol^{-1}$, and they were independent of the concentration of the alcohol.

INTRODUCTION

It has recently been shown that the alkali-catalyzed isomerization between D-glucose and D-fructose proceeds much more rapidly in ethanol–water solutions than in pure water[1]. Oligo- and poly-saccharides consisting of (1→4)-linked aldopyranose units undergo this type of isomerization prior to their alkaline, endwise degradation[2]. It was, therefore, considered of interest to clarify the influence of ethanol on the rate of degradation. Maltose was chosen for the experiments, as it possesses a relatively high solubility in ethanol–water mixtures[3], and the reducing D-glucose residue renders possible the direct comparison of the results with the earlier data for the isomerization between D-glucose and D-fructose.

The main reaction-pathways of maltose in alkali are outlined in Scheme 1, where GG, GM, and GF respectively denote maltose, 4-*O*-α-D-glucopyranosyl-D-mannose, and maltulose; GG^-, GM^-, and GF^-, their ionized forms; E^-_{mn}, the enolate ion, where the negative charge is distributed over the oxygen atom at carbon atom *m* and carbon atom *n*; and A, various monomeric degradation-products. The formation of 4-*O*-α-D-glucopyranosyl-D-mannose from maltose and maltulose, as well as the degradation of maltose, can be assumed to be of minor importance, as the corresponding reactions in the cellobiose system are very slow[4]. The degradation of maltulose (or cellobiulose) occurs mainly *via* β-elimination of the (non-

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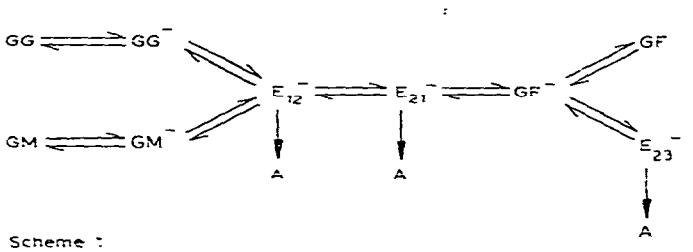

Scheme 1

reducing) D-glucosyl group in enolate ion E_{23}^-. The degradation of enolate ion E_{21}^- is very improbable, because it contains no leaving group. Under these premises, and because the concentrations of enolate ions cannot be determined separately, Scheme 1 is simplified as follows.

$$\mathrm{GG} \overset{K_{GG}}{\rightleftharpoons} \mathrm{GG^-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{GF^-} \overset{K_{GF}}{\rightleftharpoons} \mathrm{GF}, \quad \mathrm{GF^-} \xrightarrow{k_3} \mathrm{A}$$

Scheme 2

Based on Scheme 2, the rates of formation of maltose and maltulose are then expressed by equations *1* and *2*.

$$\mathrm{d}[\mathrm{GG_{tot}}]/\mathrm{d}t = \mathrm{d}([\mathrm{GG}] + [\mathrm{GG^-}])/\mathrm{d}t = -k_1[\mathrm{GG^-}] + k_2[\mathrm{GF^-}] \qquad (1)$$

$$\mathrm{d}[\mathrm{GF_{tot}}]/\mathrm{d}t = \mathrm{d}([\mathrm{GF}] + [\mathrm{GF^-}])/\mathrm{d}t = k_1[\mathrm{GG^-}] - (k_2 + k_3)[\mathrm{GF^-}] \qquad (2)$$

To calculate the concentrations of the ionized sugars, the ionization constants of maltose (K_{GG}) and of maltulose (K_{GF}) are required. These are given by Eqs. *3* and *4*.

$$K_{GG} = \frac{[\mathrm{GG^-}]}{[\mathrm{GG}][\mathrm{HO^-}]} \qquad (3)$$

$$K_{GF} = \frac{[\mathrm{GF^-}]}{[\mathrm{GF}][\mathrm{HO^-}]} \qquad (4)$$

If the initial concentration of maltulose is zero, the isomerization rate of maltose to maltulose (*cf.*, Eq. *2*) after an infinitesimal reaction-time is obtained from Eq. *5*.

$$\mathrm{d}[\mathrm{GF_{tot}}]/\mathrm{d}t = k_1[\mathrm{GG^-}] = k_1 \cdot \frac{K_{GG}[\mathrm{HO^-}]}{1 + K_{GG}[\mathrm{HO^-}]} \cdot [\mathrm{GG_{tot}}], \qquad (5)$$

where the expression for the concentration of ionized maltose is derived from Eq. *3*.

The countervalue of the sum of Eqs. *1* and *2* gives the rate of degradation of maltulose, shown by Eq. *6*.

$$d[A]/dt = -d([GG_{tot}] + [GF_{tot}])/dt = k_3[GF^-] = k_3 \cdot \frac{K_{GF}[HO^-]}{1 + K_{GF}[HO^-]} [GF_{tot}] \quad (6)$$

When maltose is allowed to react in alkali for a sufficiently long time, the ratio between the concentrations of maltose and maltulose finally levels off to a certain value. Then, the relative rates of disappearance of maltose and maltulose are equal, or

$$\frac{d[GG_{tot}]/dt}{[GG^-]} = \frac{d[GF_{tot}]/dt}{[GF^-]}. \quad (7)$$

By substituting Eqs. *1* and *2* in Eq. *7*, the following expression (*8*) is obtained for the isomerization rate-constant of maltulose.

$$k_2 = \{k_1(1 + [GG^-]/[GF^-]) - k_3\}/(1 + [GF^-]/[GG^-]) \quad (8)$$

RESULTS AND DISCUSSION

As shown in Fig. 1, both the formation of maltulose and the disappearance of disaccharides are greatly accelerated with increasing ethanol concentration. The fact that the maximum concentration of maltulose remains almost constant, apart from the changes in the ethanol concentration and temperature, indicates only slight changes between the relative isomerization and degradation rates.

In Fig. 2, the rates of disappearance of the disaccharides are plotted against the concentration of maltulose. As might be expected on the basis of Eq. *6*, straight lines are obtained. The slopes of these lines give the rate constants for the degradation of maltulose (k_3), which well obey the Arrhenius equation, with an activation energy of 110 kJ.mol^{-1} (see Fig. 3). A somewhat higher activation energy was found for the isomerization of maltose (k_1 = 115 kJ.mol^{-1}). The present value of the activation energy for the degradation of maltulose is close to that calculated from the results of Green *et al.*[5] for cellobiose (118 kJ.mol^{-1}), whereas significantly lower values have been found for hydrocellulose[6] and amylose[7] (103 and 89 kJ.mol^{-1}, respectively).

The present experiments afforded no accurate kinetic data for the isomerization of maltulose (k_2), mainly because of the fact that this reaction was slow. The level-off value of the ratio between the concentrations of ionized maltose and maltulose is ~1/2 (*cf.*, Fig. 1). Based on this value, and the data for k_1 and k_3 (*cf.*, Fig. 3) the value of k_2 computed from Eq. *8* is ~0.2 times k_1. In the D-glucose–D-fructose system, practically no differences were found[1] between k_1 and k_2. Although the rate of isomerization of maltose is twice that of D-glucose, no appreciable difference exists between their rates of enolization, because the sums of k_1 and k_2 are roughly equal. The present data concerning the rates of isomerization are in good agreement

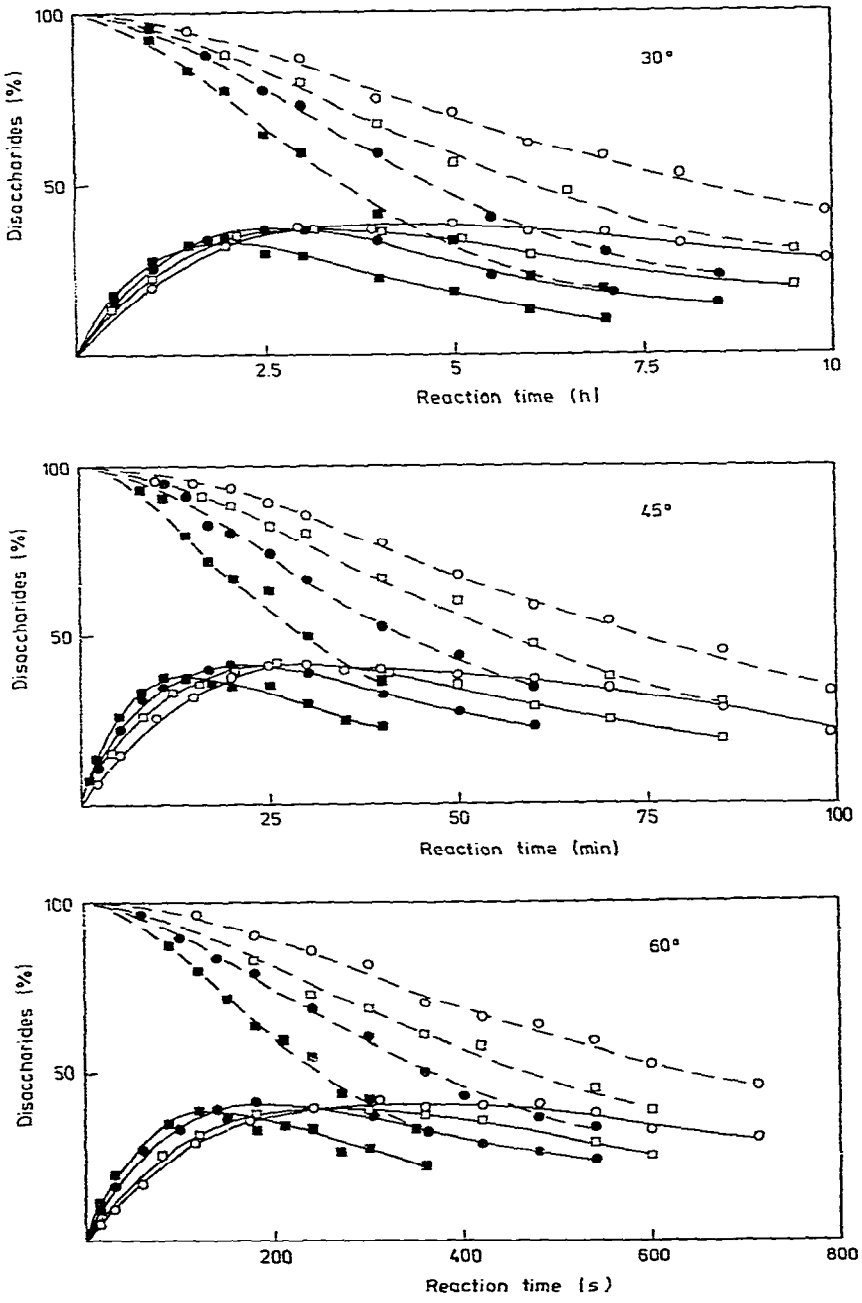

Fig. 1. The degradation of maltose in 0.1M sodium hydroxide in 0 (○), 17 (□), 34 (●), and 53% (■) (w/w) ethanol at 30, 45, and 60°. (The broken lines refer to the total amount of maltose and maltulose, and the full lines, to the amount of maltulose as calculated on the starting material.)

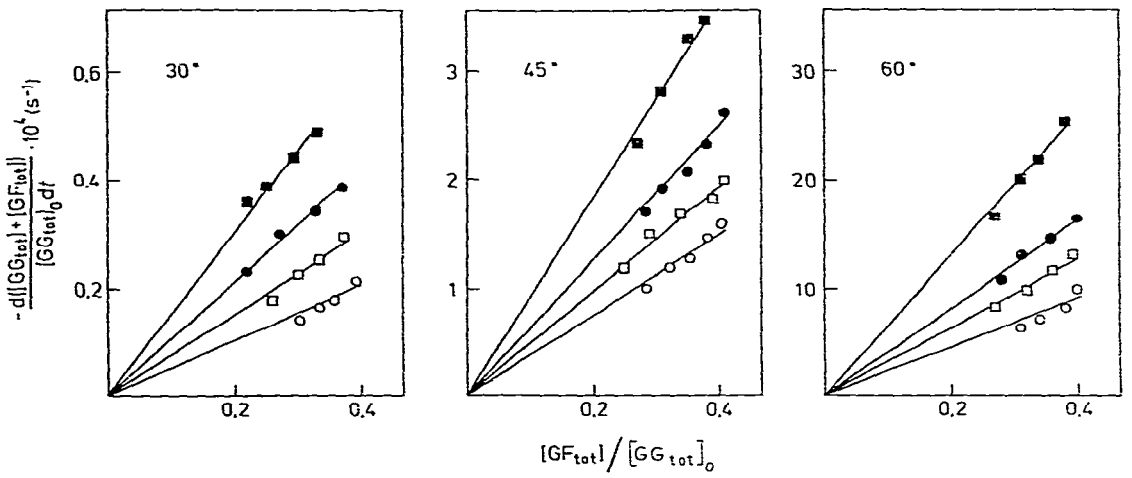

Fig. 2. The overall rate of disappearance of maltose and maltulose in 0.1M sodium hydroxide in 0 (○), 17 (□), 34 (●), and 53% (■) (w/w) ethanol at 30, 45, and 60° as a function of the concentration of maltulose.

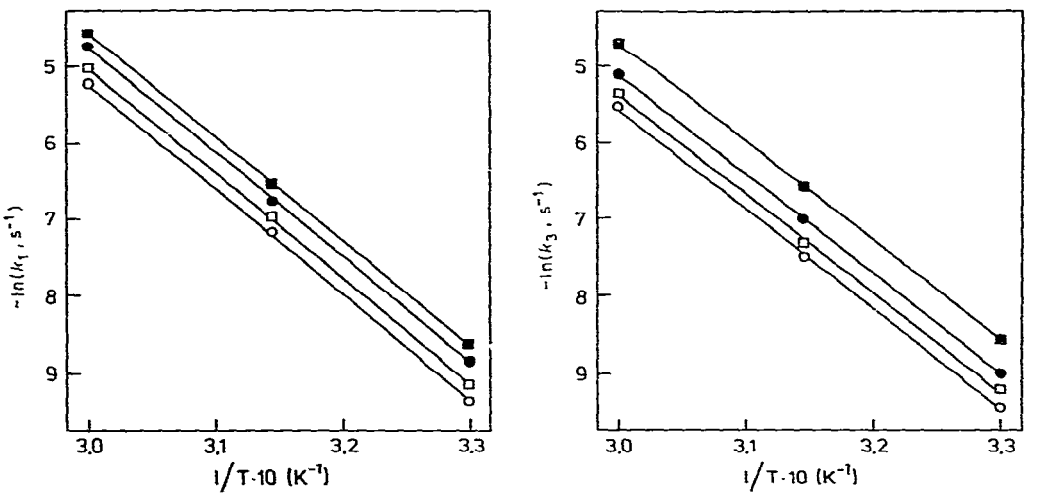

Fig. 3. The isomerization rate-constant of maltose (k_1) and the degradation rate-constant of maltulose (k_3) in 0 (○), 17 (□), 34 (●), and 53% (■) (w/w) ethanol between 30 and 60°.

with those reported by MacLaurin and Green[4] for cellobiose, cellobiulose, D-glucose, and D-fructose.

At the highest concentration of ethanol used (53% by weight), the rate of isomerization of maltose and the rate of degradation of maltulose were 2.0 and 2.4 times the corresponding values in solution in water (see Fig. 4). At higher concentrations of alcohol, the sugars started to separate as a heavy, oily phase, and reliable data could not be obtained.

On the basis of the present and previous[1] data, the isomerization, as well as the degradation, reactions of reducing sugars are accelerated when ethanol–water

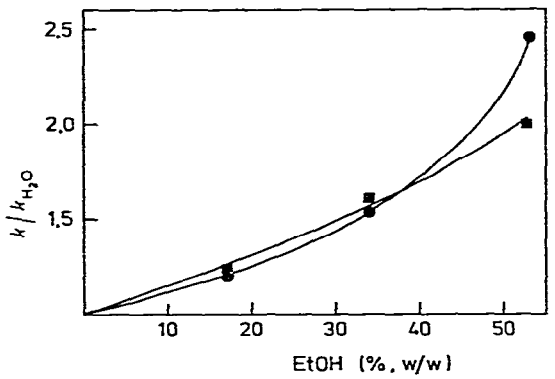

Fig. 4. The ratio of the isomerization rate-constant of maltose (k_1, ■) and the degradation rate-constant of maltulose (k_3, ●) in ethanol–water solutions to the corresponding values in water. (The values are averages from determinations conducted at 30, 45, and 50°.)

mixtures are used as the solvent. Because enolate ions are involved as intermediate products, both in the isomerization and degradation reactions, it seems plausible that the effect of the solvent is primarily directed at the rates of enolization.

EXPERIMENTAL

Determination of reaction rates. — The reactions and analyses were conducted by using the micro technique described earlier[1]; however, a Dowex 50W-X8 (H^+) cation-exchange resin (50–100 mesh) was used to neutralize the alkali in the samples. The disaccharides were analyzed, as their per(trimethylsilyl)ated oximes, by g.l.c. The initial concentrations of sodium hydroxide, maltose, and lactitol (the internal standard) in the reaction mixture were 100, 5, and 5mM, respectively. The amount of maltulose formed from maltose was plotted against the reaction time, and the isomerization rate-constant was calculated from the initial slope of the curve, using Eq. *5*.

To determine the degradation rate of maltulose, the overall concentration of maltose and maltulose was plotted as a function of the reaction time, and the rate of disappearance of the disaccharides was determined as the slope of the curve, and was plotted against the concentration of maltulose. The degradation rate-constant for maltulose was obtained from the slope of the line according to Eq. *6*. The ionization constants obtained earlier[1] for D-glucose and D-fructose were used for maltose and maltulose, respectively.

Gas–liquid chromatographic analysis of disaccharides. — The per(trimethylsilyl)ated sugar oximes were prepared as described earlier[1]; however, more-drastic conditions of oximation were used (40 min at 80°). The products were separated in an OV-101–fused silica, capillary column (0.20 mm i.d. × 10 m). The oven-temperature profile was 1 min at 125°, 30°/min from 125 to 285°, and 5 min at 285°. The injection port and the manifold were kept at 305°. Other chromatographic conditions

were the same as described earlier[1]. Maltulose gave two well-resolved peaks having retention times of 9.55 and 9.67 min, and maltose gave two having retention times of 9.89 and 10.07 min. The retention time of the lactitol, used as the internal standard, was 9.26 min.

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