MECHANISMS AND APPLICATIONS OF THERMAL AND OF ALKALINE DEGRADATION OF SUCROSE — A SUMMARY REPORT

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ABSTRACT

Novel hypotheses are presented for the detailed mechanisms responsible for the first steps in alkaline degradation and thermal degradation of sucrose. The understanding of the mechanism of the latter process has led to the development of new methods using sucrose for synthesis of fructosides and of “grafted” polysaccharides. These products may be industrially useful and thus present a new avenue for non-food uses of sucrose.

INTRODUCTION

In normal manufacture and use, sucrose is subject to three distinct types of degradation which can result in losses and in formation of undesirable products such as color and ash. The modes of degradation are respectively acid hydrolysis, alkaline degradation and thermal degradation. The first process is mechanistically simple and well understood, whereas the latter two processes have remained virtually an unknown area in mechanistic terms and these will be dealt with in turn. Oxidative degradation is not normally a problem in normal usage and will not be dealt with here, although we are investigating aspects of its future potential application. This paper aims to summarize very briefly our recent progress in understanding the exact chemistry of thermal and of alkaline degradation and some possible applications of this chemistry.

Alkaline degradation in aqueous solution is a much slower reaction than acid hydrolysis, but can cause significant losses and color under conditions of alkalinity and high temperature which may be encountered in manufacture. The predominant final product is lactic acid (up to 70% ultimate yield) and the deliberate alkaline degradation of sucrose has been considered as a possible method of manufacture of this acid, although the economics of the process make it unlikely to compete effectively with alternative sources of the acid.

The mechanism of alkaline degradation of sucrose has not previously been determined. An assumption is sometimes made that the initial step is a scission of
sucrose into glucose and fructose by some unspecified mechanism, followed by "normal" alkaline degradation of the monosaccharides. Such an initial reaction does not in fact occur and the aim of our investigation has been to explain the surprising sensitivity of sucrose to alkali (as compared e.g. with relevant model compounds). The approach described below leads to the hypothesis that the peculiar arrangement of hydroxyl groups in sucrose is an essential feature which leads to a facile displacement reaction in alkaline solution. The initial products are reducing disaccharides which are much more reactive to alkali and degrade mainly to lactic acid.

The thermal degradation of sucrose occurs very slowly in the crystal lattice and very rapidly when the crystal melts. Such reactions may be of importance when non-crystalline dry sucrose is subjected to heat and this circumstance may arise at the surface of the stalk when cane is burnt in the field. Thermal degradation, in addition to acid hydrolysis and alkaline degradation may possibly also occur in hot sucrose syrups. We have attempted to determine the mechanisms of the first steps in this degradation; the later stages in the process are very complex and include polymerization and elimination reactions, finally yielding highly colored polymers and subsequently a carbonaceous char. The approach described below leads to the hypothesis that the first step is a facilitated scission of the glycosidic linkages of sucrose to yield glucose and fructose carbonium ion (F+). The latter can reach with glucose and with unchanged sucrose to form polymers. We have been able to exploit this hypothesis to use that F+ (generated from sucrose) in simple synthesis of fructosides and of "grafted" polysaccharides which could not readily be produced by other methods.

METHODS

Most of the procedures used in these studies have been described in detail in earlier reports (O'Donnel, Richards). The detailed description of some procedures such as the proofs of positions of methyl groups in sucrose derivatives are novel but would require more space than is available in a summary paper such as this. They will be described in subsequent detailed scientific reports.

RESULTS AND CONCLUSIONS

(a) Mechanisms of Alkaline Degradation

Under alkaline conditions which degrade sucrose quite rapidly, octa-O-methyl-sucrose and several other "models" of sucrose are quite stable (Fig. 1) (Bollman and Schmidt-Berg). Some of the hydroxyl groups are therefore involved in the reaction. When a mixture of mono-O-methyl sucroses is degraded under the same conditions (curve B, Fig. 1), some of the monomethyl sucroses degraded at the same rate as sucrose but others are relatively resistant to degradation. By nuclear magnetic resonance and gas chromatographic analysis we have shown that two monomethyl sucroses are relatively stable. These are 1,2-O-methyl-sucrose and probably 3,4-hydroxyl groups are involved in the initial (rate determining) steps of the degradation. This leads us to the hypothesis shown in Fig. 2. This shows two competing first steps in the degradation. In one case the ionized
FIGURE 1. Degradation of sucrose and some derivatives in 4. ON sodium hydro-oxide solution at 100°.

FIGURE 2. Hypothesis for computing first step in alkaline degradation of sucrose.
hydroxyl at position 1\(^1\) of the fructose moiety displaces the glycosidic linkage and in the other case the ionized hydroxyl at position 3\(^1\) (O'Donnel and Richards\(^2\)) of the fructose moiety undergoes the same sequence. In each case the sucrose is converted to a new disaccharide which can be regarded as a glucosyl derivative of fructose. These derivatives will be very much more sensitive to alkaline degradation than sucrose itself (Kenner and Richards\(^3\)) and will immediately degrade mostly to lactic acid.

(b) Mechanism of Thermal Degradation

Thermal degradation of sucrose occurs more readily in anhydrous dimethyl sulphoxide (DMSO) solution, than in the melt (Fig. 3), but in each case is a first order reaction. The reaction is inhibited by hydrogen-bonding solvation, either by other sucrose molecules or by water. It is also inhibited by methylation of the hydroxyl groups (Fig. 3). When the degradation is carried out in the presence of another alcohol such as benzyl alcohol, this reacts with the first reactive intermediate in the sucrose degradation and the two anomeric benzyl fructofuranosides are formed, together with a-D-glucopyranose.

Curve A: sucrose melt at 190°
Curve B: 4% sucrose in DMSO at 90°
Curve C: 4% octa-O-methyl sucrose in DMSO at 90°, also 4% sucrose + 5% water in DMSO at 90°

**FIGURE 3.** Thermal degradation of sucrose.
These observations lead to the hypothesis shown in Fig. 4. This shows an initial scission of the sucrose into α-D-glucopyranose and fructose carbonium cation (F⁺). The latter (F⁺) reacts with an alcohol to produce the anomeric fructosides. In the melt F⁺ is most likely to react with glucose or another sucrose molecule to produce a complex mixture of disaccharides and trisaccharides (including the kestoses) and subsequently higher polymers. The processes may be summarized as follows:

(i) G−F→α−G+F⁺ (initial, rate-determining step)  
(sucrose)  

(ii) F⁺ + ROH→F−O−R (in presence of added alcohol)  

(iii) F⁺ + G−F⁺F−G−G−F−F (in melt)  

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\begin{align*}
\text{HOCH}_2 \text{O} & \quad \text{G} \quad \text{Hea} \quad \text{HOHOO}_2^+ \\
\text{OH} & \quad \text{CH}_2\text{OH} \\
\text{Sucrose} & \\
\text{ROH} & \quad \text{F} - \text{O} - \text{R} \\
\text{HOCH}_2 \text{O} & \quad \text{OR} \quad \text{CH}_2\text{OH} \\
\text{Fructofuranosides} & \quad \text{CH}_2\text{OH} \\
\end{align*}
\]

**FIGURE 4.** Hypothesis for thermal degradation of sucrose and reaction of the fructose carbonium ion with an alcohol.

In addition F⁺ may be subject to a small extent to an internal cyclization to form 2,6-anhydro fructofuranose (Bohlmann and Schmidt – Berg⁴), but this compound is relatively stable and does not normally react further. The F⁺ may also undergo complex, less specific modes of degradation and is a probable source of much of the hydroxymethylfurfural which is a significant product in such reactions. In degradations carried out in DMSO solution, the glucose may be recovered in almost theoretical yield.

(c) **Applications of Thermal Degradation of Sucrose**

The general reaction (ii) summarized above may be applied in theory to any alcohol. We have demonstrated its feasibility with benzyl alcohol and propose to


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**RESUMEN**

Unas modernas hipótesis se presentan para el detallado mecanismo responsable en los primeros pasos en la degradacion termal y la degradacion alcalina de sucrose. El conocimiento del mecanismo en el procedimiento ultimo ha conducido al desarrollo de nuevos metodos usando sucrose para sintesis de fructosides y de polysaccharides "injertadas". Estos productos pueden ser industrialmente utiles y asi presentan una nueva avenida en el empleo de sucrose fuera de usos comestibles o alimenticios.