Influence of Acid and Temperature on the Rate of Inversion of Sucrose

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ABSTRACT

The optical rotation, at acid pH, of inverted sucrose solutions was found to be independent of the type of acid. Since it was clear that, under these conditions, the anion had no influence on optical rotation, it was possible to devise a simple mathematical model to predict reaction velocity as measured by polarimetry.

INTRODUCTION

The inversion ef sucrose is of fundamental scientific importance and of economic importance. The inversion reaction has been studied for many years, serving as a basis for devisirig the laws of mass action and as a primary example of a first order kinetic reaction. Sucrose inversion (Fig. 1) occurs when the glycosidic linkage of the disaccharide is hydrolyzed, releasing the monosaccharide units. The term inversion is derived from observing the reaction by polarimetry. Sucrose solutions are dextrorotatory, but after hydrolysis the resulting equilibrium syrups have a levorotatory value. Thus, the sign of the rotatory power has been inverted or transposed.

A review of the literature indicated that the reaction is dependent on solution pH, temperature, sucrose concentration, and hydrolyzing reagent. The influence of reagent was difficult to understand because, by currently

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accepted theory, reactions such as inversion will be catalyzed by hydronium ions. It is an objective of this paper to clarify the subject.

An exhaustive study was made by Jackson & Gillis (1920). They examined factors which affect the Clerget analyses for determination of sucrose concentration and purity. Their findings indicated that not only the concentration but also the type of acid used influenced saccharimeter readings. Browne & Zerban (1941) believe that this is partially due to the changeability of the optical rotatory power of fructose. For example, as the concentration of HC1 increases, the optical rotation of fructose becomes more negative (Fig. 2). Jackson & Gillis (1920) also found that invert syrups formed with H_3PO_4 were not stable enough for absolute sugar determinations. Organic acids did not seem to have the same effect as the mineral acids and their action on specific rotation was unpredictable. However, Jackson and Gillis were able to quantify the variability in the saccharimeter readings for invert sugar due to the acids by the formulas:

(Here -42.00° S is the rotation of an aqueous invert solution at 20°C and m is the weight of the acid per 100 ml).

Despite these anomalies, it was felt by researchers that the ultimate factor which is responsible for inversion is the effective hydronium ion

Fig. 2. Influence of HCl concentration on the specific rotation of fructose.

concentration. In this paper we examine the effects of acid concentration and temperature on the reaction velocity of acidic sucrose inversion.

METHODS

Equilibrium invert syrups

Normal solutions of HCl, H_3PO_4 and H_2SO_4 were prepared to correspond to a calculated pH 1. These were used to prepare $10-50\%$ (w/v) solutions of sucrose. The solutions were kept at 38°C until 99.99% inversion was reached (1.5 days), then brought to 23° C for polarimetric readings.

Concentrated sucrose solutions

Concentrated sucrose solutions at pH 1.5 were stored at 18, 23 and 35°C. Aliquots were removed and the time recorded. 2 grams were placed into a 1 liter volumetric flask, diluted to volume, and brought to 23°C for polarimetric readings.

pH Determinations

The pH of the samples was determined using a glass electrode on Corning Instrument Division pH/Ion Meters (No. 150) calibrated to pH 2.

Polarimetry

The polarimeter employed was an Autopol III Automatic Polarimeter from Rudolf Research, Fairfield, NJ, USA, equipped with digital readout. The polarimeter tube was a 2 dm jacketed tube.

RESULTS AND DISCUSSION

The graph of $\lceil \alpha \rceil_0^2$ vs initial sugar concentration (Fig. 3) shows that there is no difference between the optical rotations of the solutions due to the acid employed. Our conclusion was that indeed the hydronium ion concentration alone is responsible for the equilibrium specific rotation, rather than the acid type.

The main interest of Jackson & Gillis (1920) was to eliminate all possible sources of variability within the Clerget method. They were striving to increase the reliability and accuracy of the acidic method by finding the most

Fig. 3. Optical rotation of various concentrations of sucrose solutions at $pH1$ using different acids: $-\blacksquare$ -- Phosphoric, $-\spadesuit$ - sulfuric, $-\square$ - hydrochloric.

stable polarimeter reading possible in order to approach that of the invertase method. Our interest was in the general effect of the acid and we have thus found there is no variability due to the acid type.

After deducing the major factor of the acid in sucrose inversion, we examined the interactions in the time/temperature relationship at set pH and set sucrose concentration. A narrow (18-40°C) temperature range was used in order to minimize fluctuations in specific rotation. Using data for pH 1 and 2 from Jackson & Gillis (1920) along with our data at pH 1.5, it was found that at a given pH, the time required to 99.99% inversion is reciprocally related to, and is, for all practical purposes, linear within, a 20°C temperature range (Fig. 4).

Fig. 4. Kinetic plot of sucrose inversion with respect to temperature: \blacksquare pH 2-0, \blacklozenge pH 1-5, \blacksquare pH 1.0.

From this data, linear regression yields the following equation:

 log_{10} (hours to 99.99% inversion) = (pH - 0.5) + (39.0) (temperature)⁻¹

Thus, a pH 1.5 solution at 30°C requires about 200h to reach 99.99% inversion.

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