[CONTRIBUTION FROM THE INDUSTRIAL RESEARCH INSTITUTE, UNIVERSITY OF CHATTANOOGA]

THE REACTION OF SUCROSE WITH ETHYLENE OXIDE[1]

J. W. LEMAISTRE[2] AND RAYMOND B. SEYMOUR

Received June 14, 1948

Although the addition of ethylene oxide to starch (3) and cellulose (2) has been reported, no instance of a reaction of this type with sugars of low molecular weight has been found in the literature. We have, therefore, studied the action of ethylene oxide on sucrose.

Sucrose and ethylene oxide did not react appreciably in neutral aqueous solution or in liquid ethylene oxide but reacted readily at room temperature in aqueous sodium hydroxide solution. Reactions were carried out with molar ratios of ethylene oxide to sucrose of 1, 2, 3, 4, and 11. In all cases the ethylene oxide was entirely converted to non-volatile products and only in the first case could any unchanged sucrose be recovered from the reaction mixtures. The products were gummy or glassy mixtures whose sweetness decreased with increasing ethylene oxide content. Attempts to separate these mixtures into their components were not very successful. One crystalline substance was isolated in small yield by utilizing as seeds a few crystals which appeared spontaneously in some of the mixtures. The composition of this material agreed essentially with that calculated for a bis-(β-hydroxyethyl)sucrose. Figure 1 shows a photomicrograph of the crystals.

The products of these reactions were gums which were soluble in water, methanol, and pyridine and insoluble in ether, chloroform, and acetone. Their solubility in ethanol and dioxane increased with the proportion of ethylene oxide. They were hygroscopic in about the same degree as glycerol. They did not depress the surface tension of water except when the molar ratio of ethylene oxide to sucrose was 4:1 or over and then the effect was small. In this respect the addition products resembled sucrose (1).

Since it did not appear feasible to isolate the individual components of the reaction mixtures, indirect evidence was obtained that these were addition products and not mixtures of sucrose with polyethylene glycols. The reacted mixtures had about the same observed optical rotations as the original sucrose solutions, but acid hydrolysis of the former gave final values of rotation that differed significantly from those obtained by inverting the sucrose solutions. These inverted solutions also differed from those of sucrose in their reaction with phenylhydrazine. As the ratio of ethylene oxide to sucrose increased, the yield of D-glucose phenylosazone decreased. When the molar ratio exceeded two to one, orange-red oils only were obtained rather than crystalline osazone. Further, the acetylation of the reaction products gave acetates whose saponification

[1] Presented in part before the Division of Sugar Chemistry at the 112th National Meeting of the American Chemical Society, New York, N. Y., September 17, 1947.

[2] Present address Chattam Chemical Co., Chattanooga, Tennessee.

equivalents agreed with the values calculated for sucrose-ethylene oxide addition products.

The results of the work indicate that the major reaction of ethylene oxide with sucrose proceeds in the expected manner by addition of the epoxide at hydroxyl groups of the sugar.

Figure 1. Addition Product of Sucrose and Ethylene Oxide (x 60).

PROCEDURE

Reaction of sucrose with ethylene oxide. A solution of 34.3 g. of sucrose in 150 g. of 0.25 *N* aqueous sodium hydroxide was treated with ethylene oxide gas until the desired weight had dissolved. Alternatively, liquid ethylene oxide could be added to the cold sucrose solution. The flask was stoppered and left at room temperature for twenty-four hours. The solution was then run slowly through a 2 x 50 cm. column of Amberlite IR-100-H[3] to remove sodium hydroxide. Yields of crude reaction product determined at this point by evaporating aliquot samples over anhydrous calcium sulfate *in vacuo* were quantitative when molar ratios of ethylene oxide to sucrose up to 4:1 were used. When the molar ratio was 11:1, the

[3] Resinous Products and Chemical Co.

crude yield was 92.5%, indicating 87% conversion of ethylene oxide to non-volatile products.

The reaction products were obtained by concentrating their solutions, prepared as above, *in vacuo*, dehydrating by distillation of the residues with five volumes of dioxane or pyridine, and removing the solvent *in vacuo*. The resulting gums could not be crystallized although many attempts were made using various solvents. One crystalline substance was obtained as follows: The dehydrated product from 17.6 g. of ethylene oxide (0.4 mole) and 34.3 g. of sucrose (0.1 mole) was dissolved in hot dioxane and cooled. The gum (6.5 g.) which separated was dissolved in 6 g. of methanol and seeded with crystals which had appeared spontaneously in a sample of the original crude addition product. After a few hours, there was filtered off 1.3 g. of white needles, m.p. 205–207°. After recrystallization from methanol, the melting point was 215°; $[\alpha]_D^{25}$ −38.7° (0.295 g., made up to 10 ml. with water, gave $\alpha_D^{25} = -1.14°$, 1 dm. tube).

Anal. Calc'd for $C_{12}H_{22}O_{11}\cdot 2C_2H_4O$: 3, 44.7; H, 7.02.
Found:[1] C, 44.8; H, 6.79.

Chemical properties of addition products

Inversion. Neutralized reaction mixtures of one and two moles of ethylene oxide per mole of sucrose and a sucrose solution of the same concentration as that in the reaction

TABLE I

SAPONIFICATION EQUIVALENTS OF ACETYLATED ADDITION PRODUCTS

MOLAR RATIO OF ETHYLENE OXIDE TO SUCROSE[a]	EQUIVALENT WEIGHT, CALC'D FOR OCTAACETATE	FOUND
1	90.45	90.9
2	96.0	96.8
3	101.45	100.7
4	107.0	103.8

[a] Proportions of reactants used to make the addition product.

products were each made 0.1 *N* in hydrochloric acid by adding standard acid to equal volumes of the solutions. The molar ratios of ethylene oxide to sucrose and the initial and final observed rotations (Na_D line, 1 dm. tube, 25°) were: 0:1, +10.7°, −3.2°; 1:1, +10.4°, −2.0°; 2:1, +10.2°, −1.1°.

Reaction with acetic anhydride. Addition products prepared from 0.01 mole of sucrose and dehydrated by distilling with pyridine were treated with 25 ml. of acetic anhydride and heated on a boiling water-bath for three hours. After the acetic acid and anhydride were distilled off *in vacuo*, the residual oils were taken up in ethyl ether, washed first with 10% sodium carbonate solution, and then to neutrality with water. The ether layers were dried over anhydrous calcium sulfate and evaporated to give colorless, viscous oils, yields 4.5–5.5 g. The acetates were insoluble in water, soluble in methanol, ethanol, chloroform, and ethyl ether. Their saponification equivalents, determined by refluxing for one hour with excess 1 *N* sodium hydroxide in 95% ethanol and titrating the excess alkali, are shown in Table I.

Reaction with phenylhydrazine. Aqueous solutions of sucrose and of addition products each containing 1.0 g. of equivalent sucrose in 7.0 ml. were made 0.1 *N* in hydrochloric acid and warmed at 50° for two hours. To each was added a solution of 1.25 g. of phenylhydrazine hydrochloride and 1.5 g. of anhydrous sodium acetate in 10 ml. of water. The solutions were heated on a boiling water-bath. Their behavior was: sucrose, precipitation in

[1] Microanalysis by Oakwold Laboratories, Arlington, Va.

five minutes; 1:1 addition product, precipitation in 10 minutes; 2:1 addition product, precipitation in 15 minutes; 3:1 addition product, turbidity in 30 minutes, precipitation of orange-red oil on cooling. The sucrose solution yielded 1.2 g. of D-glucose phenylosazone, m.p. 208°; the 1:1 addition product, 0.9 g. of impure D-glucose phenylosazone, m.p. 197°, mixed melting point, 203°; the 2:1 addition product, 0.9 g. of crystals contaminated with oily material, recrystallization of which gave 0.4 g. of D-glucose phenylosazone. From the 3:1 and higher addition products no crystalline osazones could be isolated.

We wish to express our gratitude to the Sugar Research Foundation for a grant in support of this work.

SUMMARY

1. Ethylene oxide was found to react with sucrose in aqueous alkaline solution at room temperature.

2. The products were gums which could not be separated into their components. These gums are considered to be mixtures of hydroxyethyl ethers of sucrose. They were hygroscopic and had little surface activity.

3. One crystalline product was isolated. Its composition indicated it to be a bis-(hydroxyethyl)sucrose.

CHATTANOOGA, TENN.

REFERENCES

(1) BROWNE AND ZERBAN, "Sugar Analysis," John Wiley and Sons, New York, **1941**, p. 547.
(2) NIKITIN AND RUDEVNA, *J. Appl. Chem.* (*U.S.S.R.*), **8**, 1023 (1935) *Chem. Abstr.*, **30**, 5408[6], (1936).
(3) ZIESE, *Z. physiol. Chem.* **229**, 213 (1934); **230**, 235 (1935).