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CATALYTIC HYDROGENOLYSIS OF SACCHARIDES

PART I. QUALITATIVE AND QUANTITATIVE METHODS FOR THE IDENTIFICATION AND DETERMINATION OF THE REACTION PRODUCTS

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INTRODUCTION

High pressure, catalytic hydrogenation and hydrogenolysis of saccharides, which can be considered as interesting base materials for the production of polyhydric alcohols, have been studied by several investigators[1-5]. The process has been applied[6] to produce a mixture of polyhydric alcohols for subsequent nitration to give a substitute for nitroglycerine. Similar work has been reported[7], and Korf [8] found that CuO–CeO_2–SiO_2 (95:5:100, w/w) was the most selective catalyst for the conversion of sucrose into glycerol. The hydrogenation experiments were carried out batchwise in rotating autoclaves, and the standard conditions are listed in Table I; the course of the reaction temperature and pressure changes are indicated in Fig. 1. By fractional

TABLE I

REACTION CONDITIONS IN THE STANDARD, AUTOCLAVE EXPERIMENT FOR THE CATALYTIC HYDROGENOLYSIS OF SUCROSE

Sucrose	100 g	Initial pressure of H_2	200 atm.
Methanol–water (75:25, w/w)	150 g	Reaction time	30 min
Catalyst, CuO–CeO_2–SiO_2	10 g	Reaction temperature	215°
Calcium hydroxide	1 g	Autoclave volume	500 ml

distillation of the reaction product, Korf obtained about 45% of glycerol. In continuing this work, we hoped to develop a better understanding of the complex reaction mechanism and of the kinetics of the various chemical reactions that take place simultaneously and consecutively, in order to establish optimal reaction conditions. For these studies, reliable and reproducible analytical methods for the determination of all intermediates and final reaction components are required.

DISCUSSION AND EXPERIMENTAL

Qualitative paper chromatography of the reaction products. — Many solvent systems and spray reagents have been described [9-11] as suitable for the paper chromatography of carbohydrates of low molecular weight. In the present work, the best

separations of the reaction products were achieved with butyl alcohol–ethanol–water (4:1.1:1.9)[10].

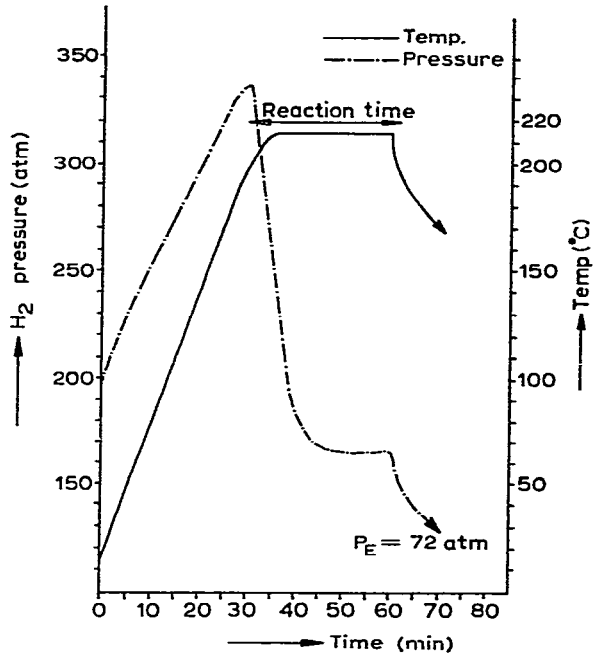

Fig. 1. Hydrogen pressure and reaction temperature as a function of the reaction time for catalytic hydrogenolysis of sucrose under standard, autoclave conditions.

Chromatography was performed at room temperature on Whatman No. 1 paper by the descending technique; the elution time was approximately 20 hours. For the simultaneous detection of saccharides and polyhydric alcohols, anisaldehyde–sulfuric acid–ethanol[12] was originally used; saccharides give, in general, violet spots, whereas polyhydric alcohols, with the exception of glycols, give pale, violet-blue spots. A disadvantage of the reagent is that charring of the paper occurs because of the presence of sulfuric acid. This could be prevented by replacing the sulfuric acid by benzenesulfonic acid. With other acids, the spray reagent is inactive. The composition of the modified reagent was anisaldehyde–benzenesulfonic acid–ethanol (1:2:20, w/w). Development of the spots was effected by heating for 15 min at 85°.

The paper chromatogram of the reaction product of the standard, autoclave experiment showed, besides traces of unreacted sucrose, the presence of hexitols, pentitols, tetritols, glycerol, and unknown compounds (red spots) having R_F values between 0.70 and 0.90. The unknown compounds are probably furan derivatives.

Quantitative analysis of the reaction products by gas–liquid chromatography. — Quantitative g.l.c. analyses were required for the determination of reaction products ranging from volatile alcohols to the high-boiling polyhydric alcohols. It was also important to have accurate analyses for water, since water is consumed during the hydrolysis step, and formed in the destructive hydrogenation of the polyhydric alcohols.

Because of the marked difference in volatility of the individual compounds, it was not possible to analyse the reaction product in one operation. A preliminary, fractional distillation was therefore performed to give the following fractions: (*a*) methanol–water (b.p. 95°); (*b*) water–glycol (b.p. 125°/10 mm); (*c*) glycerol–hexitol (b.p. > 125°/10 mm).

G.l.c. was performed with an F & M Model 720 chromatograph, provided with a dual-column system, temperature programming, and independent heating of the detector and injection blocks. The detector was a double, thermal-conductivity cell.

(*a*) *Methanol–water fraction.* G.l.c. of highly polar compounds (alcohols and water) is complicated by the phenomenon of tailing[13]. Deactivation of such supports as diatomaceous earth with hexamethyldisilazane (HMDS) or trimethylchlorosilane[14], or use of very inactive supports, such as Teflon[15], enables tailing to be suppressed, and water may then be determined[16].

The methanol–water fraction (*ca.* 90% methanol) was analysed with a 25-cm column of 20% diglycerol on Chromosorb W (60–80 mesh; HMDS). The conditions are listed in Table II, and the chromatogram is shown in Fig. 2.

TABLE II

CONDITION OF THE G.L.C. ANALYSES

	Methanol–water	*Water–glycol*	*Glycerol–hexitol*
Analytical column	25 × 0.4 cm Cu-tube (HMDS)	1 m × 4 mm Cu-tube (HMDS)	3 m × 4 mm S.S.-tube (HMDS)
Compensating column	—	—	1.5 m S.S.tube (HMDS)
Column filling	20% diglycerol/ Chromosorb 60–80 (HMDS)	15% diglycerol/ Chromosorb 60–80 (HMDS)	20% silicone rubber/ Chromosorb 60–80 (HMDS)
Column temperature (°)	60–80	70–135	125–280
Programming (°/min)	10	5	7.5
Temp. of injection block (°)	210	210	285
Temp. of detector (°)	320	320	320
Flow rate of H_2 (l/h)	3.0	3.0	6.0 and 3.6
Bridge current (mamp)	150	150	150
Injected amount (μl)	5	5	25

Alcohols may be detected in the methanol–water fraction by using a 12-m column of 10% benzyldiphenyl on Chromosorb W (60–80 mesh; HMDS), at 80°. With a flame-ionisation detector (F & M Model 1609), the water signal can be suppressed. In an analysed, methanol–water fraction, less than 0.1% of isopropyl alcohol was present.

(*b*) *Water–glycol fraction.* Similar difficulties to those above were encountered in the quantitative determination of water in this fraction. G.l.c. of glycols has been reported by several investigators[17]. The water–glycol fraction contains *ca.* 60% of water, 20% of ethylene glycol, 20% of propane-1,2-diol, and small percentages of

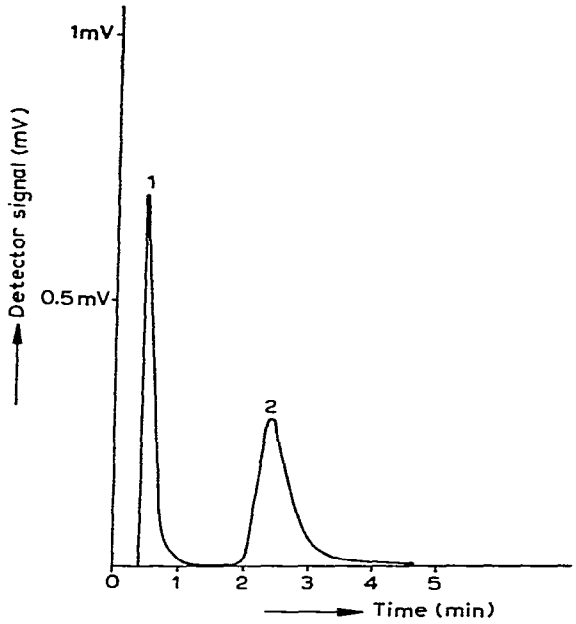

Fig. 2. G.l.c. of the methanol–water fraction.
1, methanol; 2, water.

butane-2,3-diol and methanol. Analysis was effected on a 1-m column of 15% diglycerol on Chromosorb W (60–80 mesh; HMDS). The conditions are given in Table II, and the chromatogram is shown in Fig. 3.

(*c*) *Glycerol–hexitol fraction.* This mixture is not sufficiently volatile to allow direct analysis by g.l.c., and must be converted into more volatile derivatives (ethers or acetates)[18]. Acetylation of the glycerol–hexitol fraction, followed by g.l.c., gave the best results. The following procedure was used for the acetylation. A portion (2.5 g) of the fraction was treated for 2 h with a boiling mixture of acetic anhydride and pyridine (50 ml; 1:2). Most of the acetic anhydride and pyridine was subsequently removed at 45°/15 mm, since these compounds caused tailing during g.l.c. The residue was then dissolved in anhydrous chloroform, and analysed rapidly so that no crystallisation of the hexa-acetates occurred.

Two liquid phases were investigated : (*i*) *Versamid 900* (polar), usable to 350°; and (*ii*) *Silicone gum rubber (methyl) GE-SE-30* (non-polar), usable to 400°. A good separation of the acetates was effected on a 3-m stainless-steel column (HMDS) of 20% Versamid 900 on Chromosorb W (60–80 mesh; HMDS). The isomeric pairs, erythritol–threitol, arabinitol–xylitol, and glucitol–mannitol, were separable by this system. The column, however, aged rapidly resulting in a change and a reduction of the retention volumes. The use of such a column is therefore limited to qualitative analysis.

The more stable, non-polar column (*ii*) gave better quantitative results, although the selectivity was less. The analyses were performed with a 3-m column of 20%

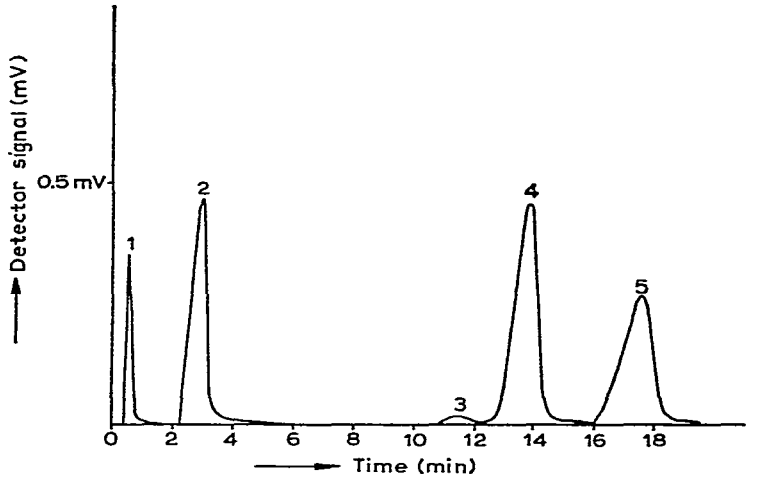

Fig. 3. G.l.c. of the water–glycol fraction.
1, methanol; 2, water; 3, butane-2,3-diol; 4, propane-1,2-diol; 5, ethylene glycol.

silicone gum rubber on Chromosorb W (60–80 mesh; HMDS). The conditions are listed in Table II, and the chromatogram is shown in Fig. 4.

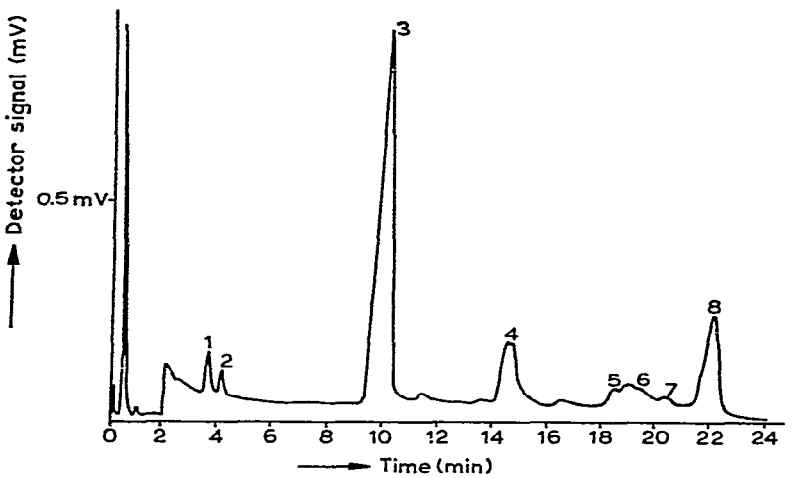

Fig. 4. G.l.c. of the glycerol–hexitol fraction (as acetates).
1, ethylene glycol; 2, propane-1,2-diol; 3, glycerol; 4, tetritols; 5, pentitols; 6, methyl α- and β-D-glucopyranosides; 7, dehydrated hexitols; 8, hexitols.

Because of the high temperature of the column, decomposition of the acetates might be expected. However, a synthetic, acetylated mixture of glycerol, erythritol, and glucitol gave only three peaks, and it is concluded that no decomposition occurs.

Calculations. — The analytical methods described above permit a detailed and reliable analysis of the mixture of reaction products. After measurement of the peak

areas with a planimeter, the composition of the sample can be calculated with the aid of relative, calibration factors[19]. A detailed analysis of the reaction products of the standard, autoclave experiment is shown in Table III; the relative errors are < 5%.

TABLE III

DETAILED ANALYSIS OF THE REACTION PRODUCT FORMED DURING CATALYTIC HYDROGENOLYSIS OF SUCROSE

Components	*Weight (%)*	*Components*	*Weight (%)*
Ethylene glycol	10.0	Methyl D-glucopyranosides	6.5
Propane-1,2-diol	13.2	Dehydrated hexitols	1.6
Butane-2,3-diol	0.4	Hexitols	17.5
Glycerol	35.1	Unknown	2.2
Tetritols	7.7	Lost product	3.2
Pentitols	2.6	Total	100.0

SUMMARY

The numerous, chemical reactions (hydrolysis, cracking, hydrogenation), occurring during the catalytic hydrogenolvsis of saccharides, result in a multicomponent mixture, consisting mainly of polyhydric alcohols. These alcohols, in general, have high boiling points and a poor thermostability. Separation of the individual components by high-vacuum distillation requires a relatively high temperature that causes dehydration, condensation, and charring. Qualitative paper chromatographic and quantitative gas–liquid chromatographic methods of analysis have therefore been developed; these provide useful tools for further studies on reaction mechanisms and reaction kinetics of the hydrogenolysis of saccharides.

REFERENCES

1 W. H. ZARTMAN AND H. ADKINS, *J. Am. Chem. Soc.*, 55 (1933) 4559.
2 G. NATTA, R. RIGAMONTI, AND E. BEATI, *Ber.*, 76 (1943) 641.
3 C. W. LENTH AND R. N. DU PUIS, *Ind. Eng. Chem.*, 37 (1945) 152.
4 I. T. CLARK, *Ind. Eng. Chem.*, 50 (1958) 1125.
5 V. I. SHARKOW, *Chem. Ingr. Tech.*, 35 (1963) 494.
6 F. ULLMANN, ed., *Encyklopädie der technische Chemie*, Band 8, 3. Edition, p.199.
7 INVENTA A. G., Brit. Patent, 840,821 (1960); 834,771 (1959); U. S. Patent, 3,030,429 (1962); Atlas Chem. Ind., Inc., Belg. Patents, 635,207; 635,208; 635,247 (1964).
8 D. KORF, *Dissertation*, University of Delft (1963); C. BOELHOUWER, D. KORF, AND H. I. WATERMAN, *J. Appl. Chem.* (London), 10 (1960) 292.
9 R. W. BAILEY AND J. B. PRIDHAM, *Chromatog. Rev.*, 4 (1962) 114; L. HOUGH AND J. K. N. JONES, *Methods Carbohydrate Chem.*, 1 (1962) 21; W. A. VINCENT, *Nature*, 196 (1962) 771; D. WALDI AND F. MUNTER, *Naturwiss.*, 49 (1962) 393; D. WALDI AND H. R. LANGE, *Naturwiss.*, 50 (1963) 126; H. SIEGEL AND A. B. BULLOCK, *Anal. Chem.*, 36 (1964) 502; H. H. BRGWNELL, *J. Chromatog.*, 19 (1965) 556.
10 A. J. CHARLSON AND N. K. RICHTMYER, *J. Am. Chem. Soc.*, 82 (1960) 3428; see also, *J. Chromatog.*, 7 (1962) Table 53.
11 H. G. BRITTON, *Biochem. J.*, 85 (1962) 402; J. M. VAUGHAN AND E. E. DICKEY, *J. Org. Chem.*, 29 (1964) 715; see also, *J. Chromatog. Data*, 16 (1964) Tables 1 and 3.

12 E. STAHL AND U. KALTENBACH, *J. Chromatog.*, 5 (1961) 351.
13 M. ROGOZINSKY, L. M. SHORR, AND A. WARSHAWSKY, *J. Chromatog.*, 8 (1962) 429.
14 H. BÜHRING. *J. Chromatog.*, 11 (1963) 452; J. BOHEMEN, S. H. LANGER, R. H. PERRETT, AND J. H. PURNELL, *J. Chem. Soc.*, (1960) 2444; R. H. PERRETT AND J. H. PURNELL, *J. Chromatog.*, 7 (1962) 455.
15 S. SANDLER AND R. STROM, *Anal. Chem.*, 32 (1960) 1890; C. LANDAULT AND G. GUIOCHON, *J. Chromatog.*, 9 (1962) 133.
16 J. E. ZAREMBO AND I. LYSYJ, *Anal. Chem.*, 31 (1959) 1833; J. J. KIRKLAND, *ibid.*, 35 (1963) 2003; O. F. BENNETT, *Anal. Chem.*, 36 (1964) 684; W. M. SCHWECKE AND J. H. NELSON, *Anal. Chem.*, 36 (1964) 689; I. LINDGREN, *Acta Chem. Scand.*, 19 (1965) 247; W. F. CASAZZA AND R. J. STELTENKAMP, *J. Gas Chromatog.*, 3 (1965) 253; U. P. SCHLUNEGGER, *J. Chromatog.*, 20 (1965) 23.
17 I. GHANAYEM AND W. B. SWANN, *Anal. Chem.*, 34 (1962) 1847; A. DAVIS, A. ROALDI, AND L. E. TUFTS, *J. Gas Chromatog.*, 2 (1964) 306; V. N. BALAKHONTSEVA AND R. M. POLTININA, *J. Anal. Chem. U.S.S.R.*, 19 (1964) 699.
18 C. T. BISHOP, *Advan. Carbohydrate Chem.*, 19 (1964) 95; J. S. SAWARDEKER, J. H. SLONEKER, AND A. JEANES, *Anal. Chem.*, 37 (1965) 1602; C. C. SWEELEY AND B. WALKER, *Anal. Chem.*, 36 (1964) 1461; R. G. ALEXANDER AND J. T. GARBUTT, *Anal. Chem.*, 37 (1965) 303; J. S. SAWARDEKER AND J. H. SLONEKER, *Anal. Chem.*, 37 (1965) 945; G. WULFF, *J. Chromatog.*, 18 (1965) 285; T. FURUYA, *J. Chromatog.*, 18 (1965) 152; Y. C. LEE AND C. E. BALLOU, *J. Chromatog.*, 18 (1965) 147; J. KAGAN AND T. J. MABRY, *Anal. Chem.*, 37 (1965) 288.
19 S. DAL NOGARE AND R. S. JUVET, JR., *Gas–Liquid Chromatography*, Interscience, New York, (1962) p. 258.