CATALYTIC HYDROGENOLYSIS OF SACCHARIDES

II.* FORMATION OF GLYCEROL

By G. van LING and J. C. Vlugter

The selectivity of the formation of glycerol from saccharides and hexitols by catalytic hydrogenolysis is determined by a number of reaction variables. Evaluation of the results of variations in operating conditions was effected by the use of the parameters: cleavage selectivity, hydrogenation selectivity, and cleavage percentage. There were strong indications that the cleavage selectivity was controlled by the molecular structure of the saccharide used, being considerably higher for a fructofuranose structure than for a pyranose one.

The main reactions were cracking, isomerisation, acid formation, hydrogenation, dehydrogenation, and dehydration. Of these, cracking and hydrogenation reactions had the greatest influence on the glycerol yield. The choice of the catalyst is difficult, because of the conflicting demands for maximum hydrogenation selectivity and maximum cleavage percentage.

Introduction

The main products of the high-pressure catalytic hydrogenation and hydrogenolysis of saccharides are glycerol, ethylene glycol, hexitols, and propane-1,2-diol. Since glycerol is the most important product commercially, the reaction must be designed to give maximum glycerol yield. Experimentally, the study of slurry reactions is much less complicated when using a batchwise reactor than a continuous system, and, therefore, only batchwise experiments were studied. The results of the hydrogenolysis of some saccharides are compared with the hydrolysis of glucitol as starting material in order to investigate whether hexoses must be hydrogenated and cracked simultaneously or not. Experiments with glycerol give information about propane-1,2-diol formation.

Experimental

Hydrogenation was carried out with sucrose, glucose, fructose, methyl-α-D-glucopyranoside, inulin, glucitol, and glycerol in a 250 ml autoclave (Type A. Hofer, Germany). The autoclave contained a vertically pulsating, electromagnetic stirrer, operating at 60 strokes/min.

The autoclave was charged with 50 g saccharide (glucitol and glucose: 25 g), 5 g catalyst CuO–CeO–SiO (for glucitol, and glucose: 2.5 g), and 75 g methanol-water (75 : 25 by wt.). The autoclave was then filled with hydrogen and heated to the desired temperature (200°—250°) in about 45 minutes. Where necessary, during the reaction period more hydrogen was added as some reaction takes place in the heating-up period. Sucrose is reactive from about 180° with formation of methyl-α-fructofuranosides, 2,6-anhydro-α-fructofuranose, and hexitols. Glucose and fructose consume hydrogen from about 150° while glucitol and glycerol become reactive above 200°. The analytical methods used are described in Ref. 4.

Results

Experiments were carried out under the following reaction conditions: temperature 200°—250°, pressure 100—300 atm., time 10—120 min., Ca(OH)₂-addition 0—5 % calculated on the weight of the base material.

Previous experiments show that the glycerol yields decrease in the order: sucrose (> 40 wt.-%), fructose and inulin (30—40 wt.-%), glucose (> 30 wt.-%), glucitol (20—30 wt.-%) and methyl-α-D-glucopyranoside (0—1 wt.-%). Three parameters have been introduced to compare the results of the experiments: cleavage selectivity (C.S.), hydrogenation selectivity (H.S.), and cleavage percentage (C.P.).

Cleavage selectivity

This parameter indicates the selectivity of the cleavage of the carbon-carbon chain. It is expressed in terms of the ratio of (glycerol + propane-1,2-diol) to (ethylene glycol + tetritol + glycerol + propane-1,2-diol) content. It was found that any starting material tested was characterised by its own constant C.S. and the following average C.S. values were obtained: sucrose ~ 72 %; glucose, fructose, and glucitol ~ 67 %; inulin ~ 88 %.

Using such catalysts as copper chromite, Ni-SiO₂, and Ru-SiO₂, instead of CuO–CeO–SiO₂, a C.S. for sucrose of ~ 70 % has been found. Experiments with Pd-SiO₂ and Pt–C are difficult to compare, because of strong splitting-off of hydroxyl groups.

When the alkali added was 1 % NaOH instead of 1 % Ca(OH)₂, a C.S. for sucrose of 71 % was found.

A C.S. of ~ 69 % can be calculated from the work of Clark, which deals with catalytic hydrogenolysis of glucitol with a nickel catalyst.

The apparently higher C.S. of sucrose, compared with glucose, is explained by the C.S. of the fructofuranoside part of sucrose, as the C.S. of the polyfructofuranoside inulin shows.

The percentage of (glycerol + propane-1,2-diol), obtained from hydrogenolysis experiments, has been compared with the formation of lactic acid by alkaline degradation of saccharides which was studied by Breen. Except for fructose, there is good agreement in the total percentage of C₂-fragments formed (see Table I).

For these reasons, it is assumed that cleavage selectivities are a property of the saccharides tested, independent of reaction variables, catalysts, and alkaline additions. This hypothesis means an extension of the thermodynamic consideration of Natta et al. concerning the cleavage of saccharides during catalytic hydrogenolysis, emphasising the importance of the molecular structure. Cleavage of the carbon-carbon chain of glucose, fructose, and the glucopyranoside part of the hydrolysed sucrose is assumed to occur mainly via


Formation of C₃-fragments from saccharides—comparison of lactic acid formation by alkaline degradation and formation of propane-1,2-diol and glycerol by catalytic hydrogenolysis

<table>
<thead>
<tr>
<th>Saccharide</th>
<th>Lactic acid, %</th>
<th>Propane-1,2-diol+glycerol, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose</td>
<td>56.8</td>
<td>~ 60</td>
</tr>
<tr>
<td>Glucose</td>
<td>31.5</td>
<td>~ 40</td>
</tr>
<tr>
<td>Fructose</td>
<td>31.6</td>
<td>~ 50</td>
</tr>
<tr>
<td>α-D-Methylglucopyranoside</td>
<td>1.3</td>
<td>~ 1</td>
</tr>
<tr>
<td>Inulin</td>
<td>64.7</td>
<td>~ 63</td>
</tr>
</tbody>
</table>

glucose-1,2-diol. As suggested by Schmidt,⁹ the double bond weakens the C₃-C₄-bond, thus favoring the formation of a triose-enediol molecule and a glycerose molecule. A small degree of cleavage of glucose-1,2-diol occurs at C₃-C₄ and C₅-C₆, forming glycol and the tetrots, erythritol and threitol. Cleavage of glucose-1,2-diol on C₅-C₆ is a minor factor. Formation of arabinohitet results from cracking of glucose and fructose on C₆-C₇.

The observed Lobry de Bruyn-Alberda van Ekenstein transformation of saccharides explains the occurrence of isomeric polyhydric alcohols such as erythritol-threitol, ribitol-arabinitol-xylitol, and mannitol-glucitol-iditol, found in the reaction products of sucrose, glucose, fructose and isomeric polyhydric alcohols such as erythritol-threitol.

The cleavage percentage and hydrogenation selectivity are important factors in the catalytic hydrogenolysis of saccharides. Hydrogenation selectivity refers to the selectivity of the reaction for high glycerol yields. Hydrogenation selectivity is expressed in terms of the ratio of (glycerol) to (glycerol + propane-1,2-diol) content.

Catalyst hydrogenolysis of sucrose with 1% NaOH gives a lower H.S. than with 1% Ca(OH)₂. This observation, together with earlier work of Korf,¹³ indicates that Ca(OH)₂ is the most selective alkaline addition for maximum glycerol yields.

H.S. decreases strongly at lower hydrogen pressures (< 200 atm.), probably due to insufficient hydrogenation of the triose-intermediates, which, if the hydrogenation is not rapid enough, can be converted ultimately to methylglyoxal, acetal and propane-1,2-diol, as reported by Weidenhagen & Wegner.¹⁴

Hydrogenolysis of glucose involves the conversion of glycerol into propane-1,2-diol. The formation of lactic acid from the triose-intermediates can be explained by the ionic mechanism of Isbell.¹² As H.S. of inulin and sucrose is lower than that of glucose and fructose, it is concluded that H.S. for a fructofuranose structure is lower than for a pyranose one. An explanation is given by Breen,⁷ who describes selective cracking on C₃-C₄ of fructofuranose, resulting in two triose-enediol molecules. It is possible that triose-enediol forms methylglyoxal and lactic acid easily, as also suggested by the Isbell mechanism. An alternative explanation may be that a C=C bond is more difficult to hydrogenate than a C=O bond, using CuO-CeO₂-SiO₂ as catalyst.

H.S. of glucitol is low, which adversely affects high glycerol yields and implies a different reaction mechanism for saccharides and hexitols.

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Thus, for a maximum H.S., high hydrogen pressures and a powerful hydrogenation catalyst, which does not attack the hydroxyl groups, are needed. However, in this case, more hexitols can be formed. In fact, Pd-SiO₂ and Pt-C are less selective for high glycerol yields.

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H.S. decreases with increasing Ca(OH)₂ percentage, due to increasing formation of lactic acid. Furthermore, the reaction glycerol-propane-1,2-diol is accelerated by increasing Ca(OH)₂ percentage.

The decrease of H.S. at higher reaction temperatures and longer reaction times is almost proportional to glycerol conversion.

Cleavage percentage

This parameter is expressed in terms of the ratio of (glycerol+propane-1,2-diol+ethylene glycol+tetritol) to (hexitol+glycerol+propane-1,2-diol+ethylene glycol+tetritol) content.

Fig. 2 represents C.P. as a function of the reaction temperature. It appears that the catalytic hydrogenolysis of saccharides differs from that of hexitols. C.P. of glucose and fructose may be lowered by hydrogenation during the heating-up period. The low C.P. of hexitols conflicts with the requirement of high glycerol yields.

C.P. increases with decreasing hydrogen pressures. However, at low hydrogen pressures dehydrogenation phenomena occur, resulting in undesired products, such as acetal and methylglyoxal (low H.S.).

Fig. 3 represents the influence of Ca(OH)₂ on C.P. showing that, for saccharides, a small addition of Ca(OH)₂ increases C.P.

C.P. increases with longer reaction times, due to further conversion of the hexitols.

Discussion

For maximum glycerol yields all three parameters must be as high as possible. As C.S. is characteristic for any saccharide...
cause they form a favourable complex with the saccharides.\textsuperscript{15,16}

CuO-type catalysts are the most preferable for hydrogenation, as they hydrogenate the triose-intermediates without strong splitting-off of hydroxyl groups. However, the choice of the catalyst is difficult, because of the conflicting reaction demands. Balandin’s ‘Multiplet’ theory\textsuperscript{17,18} predicts the following order for the reactions which occur during the hydrogenation of glucose with nickel catalysts: (i) hydrogenation to glucitol; (ii) splitting-off of primary hydroxyl groups; (iii) formation of acids; (iv) hydrogenolysis of the C–C bond.

The present experiments are in agreement with this theory. The undesired side reaction of primary hydroxyl groups splitting off, results in the formation of methylpentitols, (di-) methylglycerols, butane-2,3-diol, propane-1,2-diol, ethanol, and isopropyl alcohol. Another undesired side reaction is the dehydration of hexitols.\textsuperscript{19}

Large scale operations should probably be based on sucrose, since polyfructofuranosides, like the Jerusalem artichoke and inulin, both of which offer the advantage of high C.S., are not always available in sufficient quantities.

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