



Analytical challenges in direct oxidation of L-sorbose

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ABSTRACT

A review of literature concerning direct platinum catalyzed oxidation of L-sorbose reveals great differences in selectivity obtained by different researcher groups. Thus, the question arises whether or not the results reported up to now are comparable at all. In order to clarify this issue, two heterogeneous platinum catalysts known from literature as well as one in-house platinum catalyst were applied in the oxidation of L-sorbose under equal reaction conditions. All samples were analyzed using two different HPLC methods. Selectivity towards 2-keto-L-gulonic acid was determined on the basis of these analytical data. A comparison revealed a great discrepancy between the results, which can be found in relevant publications and the results of this study.

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1. Introduction

L-sorbose and 2-keto-L-gulonic acid (abbreviated to 2-KGA in the following) are the intermediate products for vitamin C production via Reichstein–Grüssner route (Fig. 1) [1]. This multi-stage industrial process using D-glucose as starting material and including different chemical and biotechnological steps was developed in the early 1930s and being constantly improved since then. At the moment, the transformation of L-sorbose into 2-keto-L-gulonic acid requires additional labour-intensive and time-consuming protection and deprotection steps. Direct selective catalytic sorbose oxidation in just one step might simplify the process significantly and reduce manufacturing costs. This issue has therefore been subject of intense research for many years [2–18]. Heterogeneous platinum based catalysts were found to be promising for sorbose oxidation with oxygen in aqueous medium. Results concerning the selectivity towards 2-KGA formation of about 60% at 90–95% sorbose conversion were published in [2]. A selectivity of 63% at 79% conversion was reported some decades later [4]. In more recent studies a selectivity of 67% at 58% sorbose conversion was reported using a commercial platinum catalyst [5] and about 80% selectivity at 50% conversion when a modified catalyst was used [8]. The problem concerning the reliability of the analysis methods used in previous works was already pointed out in [5]. Investigations concerning catalyst development for this reaction were carried out at our institute as well [10,11], in

which selectivities of about 50% could be achieved using different polymer stabilized platinum catalysts. Shortly afterwards another research group reported of significantly higher selectivity (more than 95%) obtained with similar catalytic systems [15,17,18]. In general, direct comparison of catalytic results from literature is difficult because different groups used diverse catalysts, reaction conditions and analytical methods. The scope of this work was a comparison of selected platinum catalysts and reaction conditions with particular emphasis on the selectivity towards 2-keto-L-gulonic acid formation determined with two different analytical methods. For this purpose, one of the in-house platinum catalysts and in-house sorbose oxidation conditions were examined in addition to the catalysts and conditions known from literature [5,16].

2. Experimental

2.1. Catalyst preparation

The commercial catalyst 5% Pt AP RD code 286064, BASF Italy (5% Pt/Al₂O₃, formerly code 7004, or Escat 24, Engelhard), was mainly used by Baiker's group [5–7,9]. In this study, the catalyst was pre-reduced by introducing a hydrogen gas stream into the catalyst suspension in deionised water for 6 min immediately before the addition of sorbose and the beginning of oxidation.

1.72% Pt/HPS (hypercrosslinked polystyrene MN-270, Purolite) catalyst, which was used by Sulman's group, was prepared according to the procedure described in literature [16]. For the preparation of 15 g catalyst 0.645 g dihydrogen hexachloroplatinate(IV) hydrate

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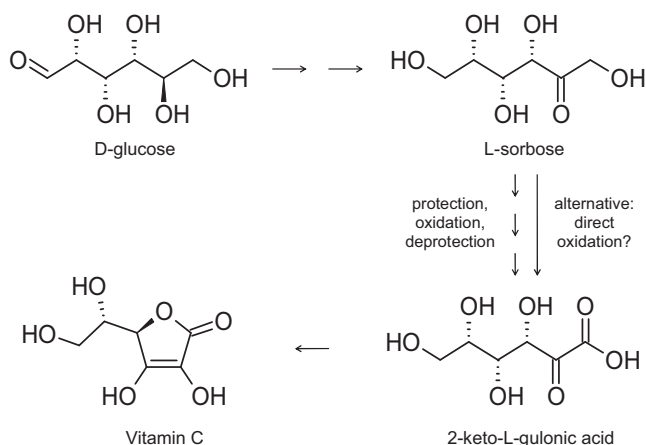


Fig. 1. Scheme of the Reichstein–Grüssner process (and direct oxidation of L-sorbose as an alternative route).

(40.0% Pt, Chempur) were dissolved in 30 ml tetrahydrofuran ($\geq 99.5\%$ p.a., ACS reagent, Carl Roth) and added to 14.74 g of HPS MN-270. The suspension was stirred for 10 min and dried at 70°C for 24 h. The precursor was used for sorbose oxidation without prior reduction [16].

For the preparation of the in-house 1% Pt/ Al_2O_3 (vTI) catalyst (12.5 g) 12.38 g alumina (Puralox KR-90, Sasol) were dispersed in 220 ml deionised water at ambient temperature. 31.25 ml dihydrogen hexachloroplatinate(IV) hydrate stock solution (4 g Pt l^{-1} , H_2PtCl_6 hydrate containing 40.0% Pt, Chempur) were added at once to the vigorously stirred suspension. After 45 min 0.33 g sodium borohydride (96% NaBH_4 , Sigma–Aldrich) were dissolved in 15 ml water and added in one portion to the suspension. When gas formation was completed, the catalyst was filtered, washed with warm ($50\text{--}60^\circ\text{C}$) deionised water and dried overnight at 70°C .

2.2. L-sorbose oxidation

L-sorbose oxidation was carried out in a thermostated glass reactor (volume 500 ml) equipped with thermometer, pH electrode SL 80–120 pH (Schott), burette, glass frit for oxygen supply, reflux condenser and mechanical stirrer (1000 rpm). The catalyst was suspended in deionised water and heated to the desired temperature. The catalyst 5% Pt/ Al_2O_3 (BASF) suspended in water was pre-reduced with hydrogen. The reaction was started by addition of sorbose (L-(–)-sorbose, $\geq 98.0\%$, Sigma) solution and by introducing oxygen at atmospheric pressure into the suspension. The pH was kept constant at a desired value by addition of a titration reagent (sodium carbonate anhydrous extra pure, Merck; sodium hydrogen carbonate, $\geq 99.7\%$, p.a., ACS reagent, Riedel-de Haën; sodium hydroxide, $\geq 99\%$, Carl Roth) solution using a TitroLine alpha plus titration unit (Schott). Samples of the reaction mixture were filtered and analyzed by HPLC. Sorbose oxidation was carried out using three different sets of reaction conditions, two of them (referred to as A and B) from literature [5,16] and one additional (C) for comparison. Unlike the conditions from [5], in A the oxygen flow rate was held constant at a value of 500 ml min^{-1} . All reaction conditions applied in this work are summarized in Table 1.

2.3. Analysis

The samples were analyzed by HPLC using a Shimadzu system (pump LC-10AT, autosampler SIL-10A, UV detector SPD-6AV, RI detector RID-6A and CLASS-LC10 program). Two HPLC methods were applied to all experiments to separate sorbose and reaction

products and to determine their concentrations using the external standard method. The one method is described by Baiker's group in [7] and the other was developed for comparison. None of the analytical methods Sulman's group applied in their work was used in this comparative study. They used either the iodometric method of Heyns [19] for 2-KGA determination [12,13], which is known to be obsolete and unreliable [5], or the description of the newer HPLC and GC methods did not include sufficient details [13,16] such as HPLC column dimensions [16] so that those methods could not be replicated.

Method I, referred to as "Nucleosil" [7]: The separation was carried out at 30°C on a $250\text{ mm} \times 4.6\text{ mm}$ HPLC column (the $250\text{ mm} \times 4\text{ mm}$ column from [7] is not commercially available at present) filled with Nucleosil-5 NH_2 resin (Macherey–Nagel) using a solution of $4.5\text{ g KH}_2\text{PO}_4$ in 330 ml water and 670 ml acetonitrile at a flow rate of 0.8 ml min^{-1} (70 bar) as eluent. Detection of sorbose was carried out with the RI detector [7]. In addition, the UV detector (210 nm) was used for exacter 2-KGA determination. Samples were diluted 10-fold with water.

Method II, developed for comparison and referred to as "Aminex": The separation was carried out at 40°C on two $300\text{ mm} \times 7.8\text{ mm}$ Aminex HPX-87H HPLC columns (Bio-Rad) connected in series using aqueous sulphuric acid solution (5 mmol l^{-1}) at a flow rate of 0.4 ml min^{-1} (85 bar) as eluent. UV detector (210 nm) was applied for determination of 2-KGA concentration and RI detector for sorbose determination. Samples were diluted 20-fold.

Selected samples were analyzed by HPLC using the method of the standard addition. Certain amounts of sorbose and 2-KGA were added to the original samples and the experimental concentrations after the addition were compared to the calculated concentration values.

3. Results and discussion

3.1. Analysis

The comparison of the concentrations of L-sorbose and 2-KGA and, thus, conversion and selectivity, showed a good correlation between the data obtained by the two different HPLC methods. The difference in selectivity at moderate sorbose conversion degrees was mainly below 5%. Further on, the results of the standard addition (addition of certain amounts of sorbose and 2-KGA to the original sample and comparison of the concentrations before and after the addition) showed good results for sorbose and 2-KGA for both methods as well. The deviation from the calculated concentration after the standard addition was less than 5% value for all samples. This is a sign that rather reliable sorbose and 2-KGA concentration and also conversion and selectivity results could be obtained using these two analysis methods.

In some cases, however, the differences between the results obtained by the Nucleosil and the Aminex method were more pronounced. In particular this concerned the concentration of 2-KGA and the selectivity at higher conversion degrees of sorbose.

Examples of the concentration-time diagrams for the Pt/ Al_2O_3 (BASF) catalyst, which illustrate these, are shown in Fig. 2. In these diagrams it can be clearly seen that the difference between the concentrations of 2-KGA and, thus, the selectivity, determined using the different HPLC methods, is particularly high under Sulman's group reaction conditions B and that this difference increases with an increasing sorbose conversion degree. The reason for this discrepancy probably results from an incomplete separation of the various sample components by HPLC and, thus, difficulties concerning an accurate peak-area determination [20]. An example is shown in Fig. 3 for the Pt/ Al_2O_3 (BASF) catalyst used under conditions A.

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