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# The oxidation of fructose on Pt/C catalysts. The formation of D-*threo*-hexo-2,5-diulose and the effect of additives

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**Abstract**

This paper describes a study on the oxidation of D-fructose with molecular oxygen on Pt/C catalysts. Two major products are formed: 2-keto-D-gluconic acid and D-*threo*-hexo-2,5-diulose ('5-ketofructose'). Deactivation of the catalyst was observed, caused both by over-oxidation of the active surface and inhibition of the reaction by 2-ketogluconic acid. Although promotion of the catalyst with bismuth did not prevent deactivation, it improved the selectivity to 2-ketogluconic acid, probably due to coordination of fructose to the promoter. Other promoting metals (tin, lead and antimony) and additives like borate and hexamethylenetetramine were less successful. 

*Keywords:* 2-Keto-D-gluconic acid; Bismuth, promoter; Activated carbon; Over-oxidation

## 1. Introduction

The growing demand for application of renewable resources for industrial products has led to an interest in selective and clean procedures to derivatize carbohydrates. An attractive option is oxidation with air over a heterogeneous catalyst, which can be performed in a clean and almost waste-free way. The products are usually biodegradable compounds, which have many potential applications, e.g., as calcium(II) and magnesium(II) sequestering agent in detergent formulations and as metal ion carrier.

The catalytic oxidation of various carbohydrates, particularly of glucose, with molecular oxygen over carbon supported noble metal catalysts has been studied throughout the century and has been reviewed by several authors [1–5]. Platinum and palladium are the most frequently used catalysts. Platinum is generally the more active catalyst, because, due to its higher redox potential, it is less prone to deactivation by oxidation [6]. Palladium is less active for deeper oxidation and is therefore a more selective catalyst.

Although many uncertainties still exist concerning the oxidation of carbohydrates, general agreement exists about the proposed mechanism of oxidative dehydrogenation, as presented by Wieland in 1912 [7]. Hydrogen is abstracted from the carbohydrate and the so formed surface hydrogen is removed by oxygen.

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Recently, much progress has been made in the understanding of the mechanisms of deactivation of the catalyst and the effect of promoters [8–14]. This has led to highly selective and clean procedures for the transformation of glucose into gluconic acid and lactose into lactobionic acid [15], using air and a BiPd/C catalyst. From an economic point of view, this process can compete with the presently used biocatalytic procedure.

Inulin, an oligosaccharide consisting of (2 → 1)-linked β-D-fructofuranosyl units attached to a glucose end group, has become commercially available since the beginning of this decade. It is an important source of fructose and, therefore, procedures are required for the conversion of fructose into materials with useful non-food applications.

Not much work has been done on catalytic oxidation of fructose and other ketoses. In early work of Heyns [16], L-sorbose was oxidized over a 5–10% Pt/C catalyst to 2-keto-L-gulonic acid with a yield of 60%, in a neutral to acidic solution at 30 °C. Apparently, in ketoses, the primary hydroxyl group on C-1 is activated by the adjacent carbonyl group, and this OH-group is attacked preferentially to the other primary hydroxyl group, at C-6 [4]. Studies concerning the oxidation of keto-hexoses were mainly focused to L-sorbose [17,18]. However, Heyns [16] mentioned that D-fructose behaves analogous to sorbose and affords mainly 2-keto-D-gluconic acid upon oxidation.

This paper describes a study on the oxidation of fructose with air over 5 wt.% Pt/C catalysts. The reaction products are identified and the effect of bismuth, tin, antimony and lead deposited on the catalyst is investigated. Furthermore, the effect of additives (borate and hexamethylenetetramine) on the course of the reaction is studied.

## 2. Results and discussion

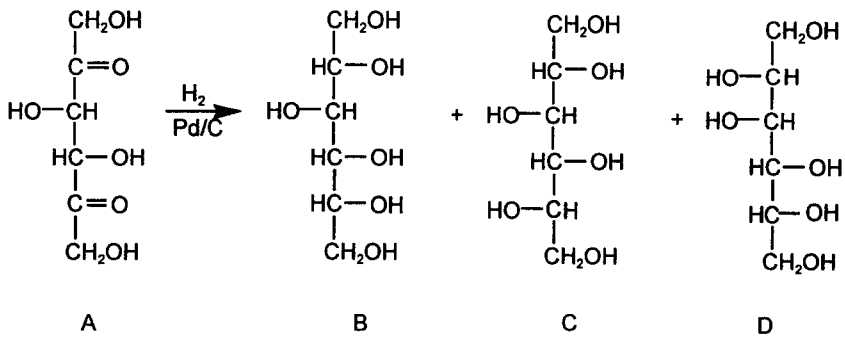
*Catalyst characterization.*—The 5 wt.% Pt/C catalyst consisted of 3–4 nm platinum particles, homogeneously distributed over a chemically activated wood-based carbon support. The nature of the support was identified by its characteristic scanning electron microscopy (SEM) picture, showing the well preserved cell walls, forming large parallel macropores. The main trace element present in the carbon support, as measured by X-ray fluorescence spectroscopy (XRF), was sodium (0.4 wt.%). Other elements, present in concentrations less then 0.05 wt.%, were chlorine, sulfur, silicon, iron and aluminium.

*Course of the reaction.*—During the oxidation of D-fructose, a number of species were formed, of which two in major quantities. Both $^{13}C$ NMR and LC–MS showed that the main product, as already mentioned by Heyns [16], is 2-keto-D-gluconic acid. The identification of the second product, however, was not that straightforward.

After separation of the acidic from the neutral reaction products by anion-exchange chromatography, the second major compound was obtained in the fraction with the neutral products. It had about the same retention time as fructose. This, combined with the fact that the LC–MS spectrum shows a parent peak at *m/z* 161, suggests that the molecular mass is 178 (161 + water–H) and, consequently, that one of the hydroxyl groups of fructose is oxidized to a carbonyl function.

Hydrogenation of this oxidation product on a Pd/C catalyst resulted in only D-mannitol, D-glucitol and L-iditol. The only ketofructose that can give exclusively these products is D-*threo*-hexo-2,5-diulose (see Scheme 1).

The $^{1}H$ and the $^{13}C$ NMR spectra were assigned




Scheme 1. Hydrogenation products of D-*threo*-hexo-2,5-diulose (A), glucitol (B), iditol (C) and mannitol (D).

with a COSY and an attached proton test (APT) experiment [19], respectively. $^{13}C$ NMR showed no signals between 170 and 230 ppm, suggesting that no carbonyl groups were present in this compound. This indicated that the ketone group was hydrated to a *gem*-diol (**3**, Scheme 2), which was confirmed by a resonance at 94.4 ppm. The $^{13}C$ NMR spectrum of this compound is identical to that of D-*threo*-hexo-2,5-diulose, described by Crawford et al. [20], formed by the action of various *Acetobacter* cultures on fructose [21–24]. Moreover, $^{1}H$ NMR showed three AB-systems, as expected from structure **3** (Scheme 2). Therefore, it can be concluded that, besides 2-ketogluconic acid, D-*threo*-hexo-2,5-diulose, or '5-ketofructose', is formed during the oxidation of fructose with molecular oxygen over Pt/C catalysts. The latter compound is somewhat unexpected, since L-sorbose is oxidized first at C-1 and subsequently at C-6 [16]. Furthermore, oxidation of methyl α-D-fructofuranoside gives, under similar conditions, exclusively oxidation at the C-6 position [25], which is sterically the most favored primary hydroxyl function in that case.

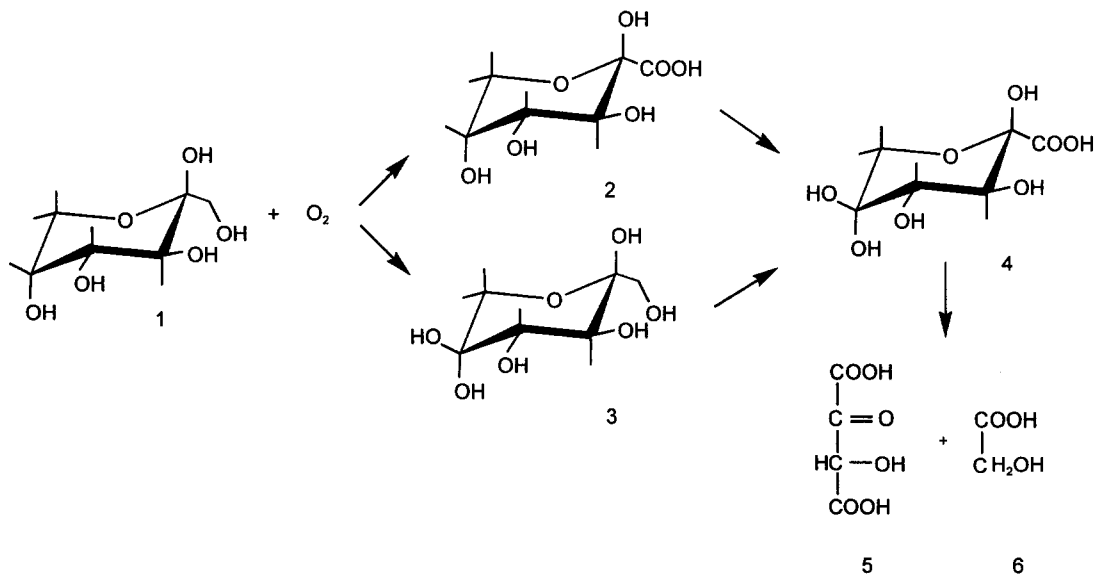
According to Heyns et al. [26], axial OH-groups in pyranose systems are oxidized preferentially compared to equatorial ones. In solutions at 30 °C, 70% of D-fructose is present in the β-pyranose form [27], with an axial OH-group at C-5. The sorbopyranose forms, however, have no axial OH-groups. This may explain why fructose is oxidized both at C-1 and C-5, whereas sorbose is oxidized exclusively at C-1.

Besides the two main products, 2-ketogluconic acid (compound **2**, Scheme 2) and '5-ketofructose' (**3**), 2,5-diketogluconic acid (**4**) and products of oxidative cleavage (**5** and **6**) were formed.

*Catalytic performance.*—Fig. 1A presents the concentrations of fructose (**1**), 2-ketogluconic acid (**2**) and '5-ketofructose' (**3**) versus the reaction time, using a 5 wt.% Pt/C catalyst at 30 °C, pH 7.3 and $pO_2$ 0.2 atm. At 300 min, 83% of fructose was converted with a selectivity of 45% to 2-ketogluconic acid and 27% to 5-ketofructose. Higher pH and temperature lead to lower selectivities, because of degradation of the carbon chain; lower pH gives lower initial rates. The amount of NaOH added (Fig. 1A) is much higher than the 2-ketogluconate concentration, indicating that oxidation to diacids and fragments already takes place just after the start of the experiment.

The reactions were conducted at fructose and catalyst concentrations of 12.5 g/L and 6.3 g/L, respectively. Fig. 1B shows that under these conditions the initial reaction rate is not controlled by mass transport, because the initial rate increases linearly with the catalyst concentration.

A major problem concerning activated carbon supported catalysts is the inhomogeneity of this natural material. Different batches can give different performances. The cause of these differences is not clear. This phenomenon is also observed in this study, where different batches from one and the same supplier give different activities, as shown in Fig. 1C.




Scheme 2. Oxidation products of fructose (1), 2-ketogluconic acid (2), D-*threo*-hexo-2,5-diulose (3), 2,5-diketogluconic acid (4), 2-hydroxy-3-butanedioic acid (5) and glycolic acid (6).

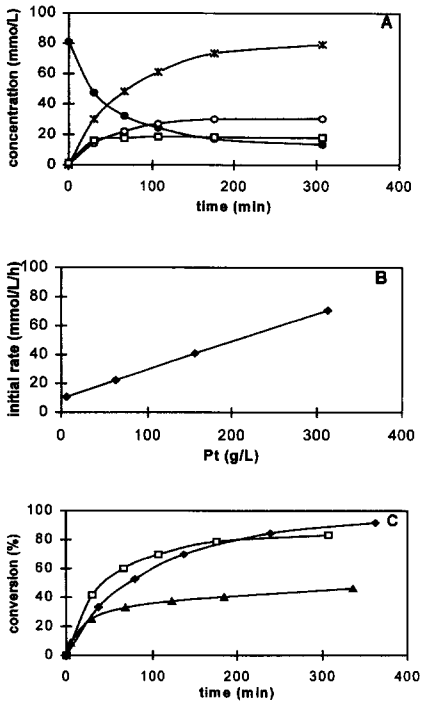



Fig. 1. Oxidation of fructose. $T$ 30 °C, pH 7.3, $pO_2$ 0.2 atm, [fructose] = 12.5 g/L, [5 wt.% Pt/C] = 6.3 g/L. (A) Concentrations of fructose (●), 2-ketogluconic acid (○), '5-ketofructose' (□) and the amount NaOH added (*) versus reaction time (catalyst: Pt/C batch 2). (B) Initial rate versus catalyst concentration. (C) Conversion of fructose on different batches 5 wt.% Pt/C; ♦, batch 1; □, batch 2; ▲, batch 3.

The reason for this is not clear; it is not due to the platinum content and dispersion or to impurities in the support. The selectivity in the fructose oxidation of these batches, however, did not differ much (about 45 and 30% to **2** and **3**, respectively).

Conversions of 100% were never reached, due to deactivation of the catalyst. This phenomenon was also observed in the oxidation of D-glucose on this catalyst, but with that substrate the extent of deactivation was less. The initial rates of both reactions were about 70 mmol/L $h^{-1}$.

Different mechanisms can play a role: metal leaching, particle growth, over-oxidation of the active surface by molecular oxygen, and active site covering by deposition of carbonaceous species or adsorption of reaction products [3,14].

A frequently encountered problem in oxidation of carbohydrates over noble metal catalysts is metal leaching, probably due to complexation of the metal by sugar acids [28,29]. However, after one oxidation experiment, the concentration of platinum in the reaction mixture, as measured with inductively coupled plasma optical emission spectroscopy (ICP–OES) was only 0.1% of the total platinum content. Such a marginal loss of platinum cannot be the cause of the deactivation. It is, however, important to check whether the catalytic effect of platinum is due to heterogeneous and not to homogeneous catalysis. Therefore, after an oxidation experiment, the catalyst was filtered off and the reaction was carried out again with the filtrate and an additional amount of fructose, but without the Pt/C catalyst. No conversion of fructose was detected, which proves the heterogeneity of the reaction.

Another possible cause of deactivation is platinum particle growth during the reaction. According to transmission electron microscopy (TEM) images, the catalyst under study consisted of platinum particles of 3–4 nm on a chemically activated charcoal. During an oxidation experiment, the particle size did not change.

A frequently observed deactivation cause is over-oxidation of the noble metal. De Bruijn [30] studied the oxidation of methyl α-D-glucopyranoside and reported a partial regeneration of the initial activity by temporary changing the oxygen by a nitrogen atmosphere. In the same way, we checked the presence of over-oxidation after 330 min, by bubbling through nitrogen for 20 min and restarting the reaction by applying oxygen again. The result (Fig. 2) demonstrates that the activity increases after nitrogen treatment, although it is not fully recovered. Over-oxidation, therefore, is a cause of deactivation.

Competitive adsorption of reaction products has also been suggested as a cause of deactivation during oxidation [31]. The activity of a used catalyst (obtained after filtration, washing with water and reduction with hydrogen) is practically the same as that of a fresh catalyst (Fig. 2), which demonstrates that the

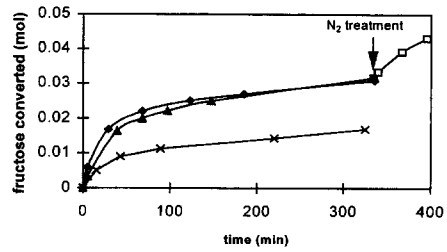



Fig. 2. Oxidation of fructose on Pt/C (batch 3). $T$ 30 °C, pH 7.3, $pO_2$ 0.2 atm, [fructose] = 12.5 g/L, [5 wt.% Pt/C] = 6.3 g/L. Fructose converted on fresh (♦) and used catalyst before (▲) and after nitrogen treatment (□) and with 3.1 g/L 2-ketogluconic acid in the initial reaction mixture (x).

decrease in activity is not due to irreversible poisoning of the catalytic surface. To study possible poisoning by 2-ketogluconic acid, 3.1 g/L of this compound was added to the reaction mixture before the start. This led to a strong decrease in activity of fructose oxidation, as shown in Fig. 2. The initial reaction rate decreased from 66 to 20 mmol/L $h^{-1}$. According to the linear relationship of the initial activity and the platinum surface (Fig. 1B), this means that 2-ketogluconic acid covered 70% of the platinum surface and adsorbs about twice as strong as fructose. Oxidation of 2-ketogluconic acid in the absence of fructose gave 2,5-diketogluconic acid (**4**) as the main reaction product. Both the absence of the latter compound in the competition experiment and the constant selectivity to 2-ketogluconic acid during the course of fructose oxidations indicates that 2-ketogluconic acid is not oxidized in the presence of fructose. A similar phenomenon was also observed by Kunz et al. [32] in the oxidation of isomaltulose. They also found inhibition of the dioxidation by the starting material and developed a process for continuous removal of the products [32,33].

The stronger adsorption of 2-ketogluconic acid can be explained by the presence of an $\alpha$-hydroxycarboxylate unit in the cyclic forms of this compound, which is known to be a chelating function.

*Effect of hexamethylenetetramine.*—In order to improve the selectivity of this catalyst, 1 or 2 mg hexamethylenetetramine (HMTA) was added to the reaction mixture. Brönnimann et al. [34,35] reported on the positive effect of this compound on the selectivity to 2-ketogulonic acid in the oxidation of L-sorbose. This was explained by the adsorption of HMTA on platinum by one of its nitrogen atoms and complexation of sorbose, in which at least one of the other nitrogen atoms interacts with one of the OH functionalities of the carbohydrate. In this way, only the hydroxyl group at C-1 is close to the platinum surface and oxidation at C-1 will be favored.

The influence of HMTA on the conversion and selectivity of fructose oxidation is presented in Table 1. This table indeed shows an increase in selectivity, especially at very small concentrations of HMTA. However, the conversion decreased substantially, probably due to poisoning of the catalyst by HMTA. According to a platinum-density of $21.45 \cdot 10^3$ $kg/m^3$ [36] and an average particle size of 4 nm, the platinum surface of 0.5 g of 5 wt.% Pt/C amounts to 1.75 $m^2$. One molecule of HMTA, in the way Brönnimann et al. proposed the coordination to the platinum surface, will occupy about 18 $Å^2$; 2 mg HMTA can therefore cover about half of the total platinum surface present. This is in line with the 50% reduction in activity in the presence of amine.

Table 1
Effect of hexamethylenetetramine (HMTA) on the conversion of fructose and selectivity to 2-ketogluconic acid over 5 wt.% Pt/C (batch 1)[a]

| HMTA (mg) | Conversion (%) | Selectivity (%) | |
|---|---|---|---|
| | After 300 min | After 300 min | At 20% conversion |
| 0 | 87 | 44 | 41 |
| 1 | 55 | 60 | 56 |
| 2 | 41 | 50 | 47 |

[a]See Fig. 1C.
*T* 30 °C, pH 7.3, $pO_2$ 0.2 atm, [fructose] = 12.5 g/L, [Pt/C] = 6.3 g/L.

*Effect of borate.*—Borate can form esters with fructose. At neutral pH and room temperature, negatively charged 1:2 borate–fructose esters are favored, in which the fructose moieties are in the $\beta$-furanose form [37]. This means that the concerning borate ester would not be able to react to 5-ketofructose. Borate might also, via interaction with oxidation products, function as a protective agent against consecutive oxidation reactions [38].

However, addition of boric acid, in fructose–borate molar ratios of 1:5, 1:2 and 5:1 and at pH 7.3 and 11, had no effect on the selectivity to 2-ketogluconic acid. The conversion decreased from 90 to 60% (after 330 min) at pH 7.3 and a fructose–borate ratio of 1:5. At pH 11, the conversions at different fructose–borate ratios amounted to approximately 40%. Apparently, the oxidation of free fructose is much faster than that of its borate esters. Possible explanations are repulsion of the negatively charged complex by the negative charge on the catalyst support or steric hindrance of the platinum–fructose interaction by borate.

*Effect of bismuth.*—A frequently used promoter of catalysts in carbohydrate oxidation is bismuth, which can prevent deactivation of palladium catalysts in the oxidation of glucose. Besson et al. [13] ascribe this effect to a mechanism, whereby the hydrogen atoms on the noble metal, abstracted from the carbohydrate, are not removed by molecular oxygen, but are oxidized by parallel reduction of bismuth(III) oxide to $Bi^0$.

In the present work, bismuth was deposited in three ways, aiming at an atomic ratio Pt:Bi = 5: (i) homogeneous deposition precipitation, in which precipitation of bismuth hydroxide will take place; (ii) precipitation of bismuth by reduction of $Bi^{3+}$ by

Table 2
X-ray photoelectron spectroscopy results of BiPt/C (batch 2[a]), before and after use

| Binding energy (eV) | | Assignment | Literature |
|---|---|---|---|
| Fresh catalyst | Used catalyst | | |
| 71.43 | 71.40 | $Pt^0$ $4f^{7/2}$ | 70.7 [42], 71.1 [43], 71.3–71.5 [44], 72.0 [45] |
| 74.63 | 74.60 | $Pt^0$ $4f^{5/2}$ | 74.0 [42], 74.4–74.8 [44] |
| 158.65 | 158.64 | $Bi_2O_3$ $4f^{7/2}$ | 158.8 [46], 159.8 [47], 159–160.1 [50] |
| 164.95 | 163.84 | $Bi_2O_3$ $4f^{5/2}$ | 164.15 [46], 164.9 [47] |
| | 157.49 | $Bi^0$ $4f^{7/2}$ | 157.4 [49] |
| | 162.64 | $Bi^0$ $4f^{5/2}$ | |

[a]See Fig. 1C.

hydrogen; and (iii) underpotential deposition [13,39,40], in which glucose will cover the platinum surface with hydrogen and the bismuth ions are reduced and deposited on platinum by oxidation of the preadsorbed hydrogen.

TEM, combined with energy dispersive analysis of X-rays (EDX) revealed that all over these three catalysts, both before and after reaction, the Pt:Bi ratio is almost constant at about 5, indicating that all particles are bimetallic. The formation of bimetallic particles was also reported by Besson et al. [11,13]. No 'bulk' bismuth was detected on the carbon support, although it could be expected that, because of the good conductivity of carbon, underpotential deposition would cause bismuth-deposition on the carbon support [39,41].

Table 2 shows the results of X-ray photoelectron spectroscopy (XPS) analysis of the bismuth-promoted catalyst, prepared by precipitation by means of pH-increase. The peaks at 71.4 and 74.6 eV, present both before and after reaction, can be assigned to the $4f^{7/2}$ and $4f^{5/2}$ levels of $Pt^0$ [42–45]. However, comparison with the data obtained by Kim et al. [42] on physically adsorbed oxygen, $PtO_{ads}$ (binding energies of 71.8 and 75.1 eV), reveals that it cannot be ruled out that this type of oxygen species is present on the platinum surface. At least, no strong bonding between platinum and oxygen was observed. Furthermore, the fresh catalyst showed two peaks, at 158.65 and 163.95 eV, which indicates that bismuth is in the form of bismuth(III) oxide [46,47]. The formation of both bismuth(III) oxide and $Bi_2O_2CO_3$ has been reported earlier [47,48]. However, no data on the binding energy of the latter compound have been reported in the literature.

Curve fitting of the peaks around 160 eV of the used catalyst showed two additional peaks at 157.49 and 162.74 eV, which indicate the presence of $Bi^0$. This oxidation state was also observed by Ismagalov et al. [49] in BiPt/aluminium oxide and BiPd/C catalysts, respectively. Probably, $Bi^0$ is formed during the prereduction of the catalyst.

Fig. 3A shows the conversion as a function of time for the unpromoted and three promoted catalysts. The deactivation of the promoted catalysts is even larger than of the unpromoted one. However, promotion with bismuth has a positive effect on the selectivity to 2-ketogluconic acid, as shown in Fig. 3B, where the selectivity of a promoted and unpromoted catalyst are compared at the same degree of conversion. The selectivity to 2-ketogluconic acid increases at the expense of the formation of 5-ketofructose. This leads to the conclusion that bismuth binds fructose in such

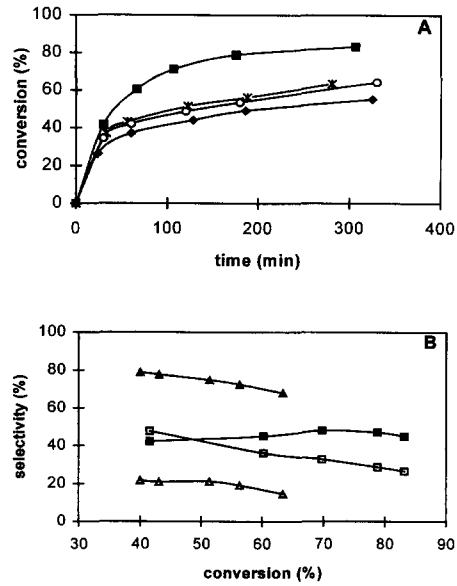



Fig. 3. Oxidation of fructose on different BiPt/C catalysts. $T$ 30 °C, pH 7.3, $pO_2$ 0.2 atm, [fructose] = 12.5 g/L, [5 wt.% Pt/C] = 6.3 g/L. (A) Conversion of fructose versus reaction time on ■, Pt/C; *, BiPt/C (precipitation); ○, BiPt/C (glucose); ◆, BiPt/C (hydrogen). (B) Selectivity to 2-ketogluconic acid (closed figures) and '5-ketofructose' (open figures) versus fructose conversion: △/▲, BiPt/C (precipitation); □/■, Pt/C.

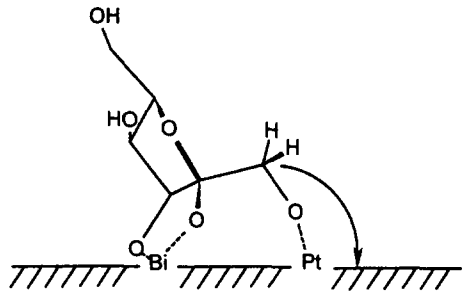



Fig. 4. Coordination of D-fructose to BiPt/C.

a way, that formation of 2-ketogluconic acid is more favorable than formation of 5-ketofructose.

Most likely, bismuth interacts preferentially with the β-D-fructofuranose structure (via the *cis*-diol function), which cannot form 5-ketofructose. Moreover, the coordination may result in an activation of C-1 for oxidation, as illustrated in Fig. 4. Because of a strong interaction with this anomer, bismuth(III) oxide is probably not available for its suggested role as a co-catalyst. Consequently, coverage of the catalyst surface, and thus oxygen poisoning, cannot be reduced in this case.

These results are comparable with those of Besson et al. [11] and Abbadi et al. [51] in the oxidation of gluconic acid on BiPt/C and by Smits et al. [52] on PbPt/C catalysts, where a large increase in the selectivity to 2-ketogluconic acid was observed. Gluconate has an α-hydroxy carboxylate function, which also can strongly coordinate with $Bi^{3+}$, resulting in an activation of C-2 for oxidation. Glucose, however, occurs for more than 99% in the α- and β-pyranose forms. The configuration of the hydroxyl groups in these anomers is relatively unfavorable for coordination and, therefore, bismuth remains available for the oxidation of the hydrogen at the catalyst surface. As a result, the over-oxidation of the catalyst is suppressed.

The concentration of bismuth in the reaction mixture after 330 min reaction time, as measured by ICP–OES, amounted to 2.3% of the total bismuth content. To verify the heterogeneity of the bismuth promotion, the reaction was carried out in the presence of (i) the unpromoted catalyst and (ii) dissolved $Bi^{3+}$ ions, in the same concentration as present in solution after reaction with a promoted catalyst. The selectivity of the Pt/C catalyst remained the same as the unpromoted catalyst. XRF, carried out after reaction, revealed that no bismuth was deposited on the catalyst.

*Effect of tin, antimony and lead.*—From the data in Table 3, it can be concluded that promotion of the Pt/C catalyst with tin and antimony is less successful than promotion with bismuth. Lead improves the selectivity to 2-ketogluconic acid to the same extent as bismuth. A similar effect of lead was found in the oxidation of gluconate [52].

## 3. Experimental

*Materials.*—The oxidation experiments were carried out with the use of a 5-wt.% Pt/C catalyst, purchased from Acros Chimica (Geel, Belgium). Hexamethylenetetramine, boric acid, antimony(III) chloride, D-glucose (anhydrous) and D-fructose (extra pure) were obtained from Merck KGaA (Darmstadt, Germany). Tin(IV) chloride pentahydrate was obtained from J.T. Baker Chemicals (Deventer, The Netherlands), lead(II) nitrate and bismuth(III) subnitrate monohydrate from Aldrich Chemical Comp., (Milwaukee, USA).

*Catalyst preparation.*—Bismuth promoted catalysts were prepared by deposition of 1% bismuth on the above-mentioned Pt/C catalyst. The introduction of bismuth was performed in three different ways.

Table 3
Effect of various promoters on the conversion of fructose and the selectivity to 2-ketogluconic acid on 5 wt.% Pt/C (batch 3)[a]

| Promoter | Content (wt.%) | Conversion (%) | Selectivity (%) | |
|---|---|---|---|---|
| | | After 330 min | After 300 min | At 20% conversion |
| – | – | 52 | 33 | 27 |
| Bi | 1.7 | 43 | 61 | 65 |
| Pb | 1.0 | 33 | 61 | 64 |
| Sb | 1.1 | 44 | 38 | 37 |
| Sn | 1.9 | 41 | 52 | 47 |

[a]See Fig. 1C.
*T* 30 °C, pH 7.3, $pO_2$ 0.2 atm, [fructose] = 12.5 g/L, [Pt/C] = 6.3 g/L.

A. A 30-mL acidic solution of 28 mg $BiONO_3$ was slowly added (0.8 mL/min) to 50 mL of an aqueous suspension of the catalyst (2 g) and glucose (9 g), under nitrogen and at 40 °C.

B. The bismuth containing solution was added to the catalyst suspension under hydrogen at 40 °C.

C. The pH of the bismuth and Pt/C containing suspension, thermostated at 40 °C, was increased to 8.5, using 1 M NaOH.

After depositing bismuth, the suspension was filtered, the catalyst was washed till neutral and dried in air, first one night at room temperature and then 3 h at 120 °C.

Lead, tin and antimony promoted catalysts were prepared according to method C, using lead(II) nitrate, tin(IV) chloride pentahydrate and antimony(III) chloride as precursors.

*Catalyst characterization.*—Both the metal loadings and impurities in and on the support were measured using X-ray fluorescence spectroscopy, XRF (Philips PW1480). The oxidation states of platinum and bismuth were studied with X-ray photoelectron spectrometry (XPS). The particle diameter and the dispersion of bismuth and platinum were studied with transmission electron spectroscopy (TEM) using a Philips CM 30 T electron microscope, combined with energy dispersive analysis of X-rays (EDX). The structure of the carbon support was studied by scanning electron microscopy (SEM) using a Philips XL 20 apparatus.

*Oxidation experiments.*—The oxidation experiments were performed in a glass batch reactor of 200 mL, equipped with a gastight stirrer (1500 rpm) and a thermostatic bath. During the reactions, the partial oxygen pressure was kept constant using a differential pressure sensor which operated a large motor burette filled with oxygen. This oxygen burette was held at a constant temperature of 30 °C. The pH was kept constant using a pH meter (Metrohm 654), a pH controller (Metrohm 614) and a motor burette (Metrohm 655), containing 1 M NaOH.

Prior to each experiment, the system, including a 50-mL aqueous suspension of the catalyst, was flushed with nitrogen. After that, the catalyst was prereduced by flushing the system with hydrogen for 30 min. D-Fructose was added under nitrogen and the reaction was started by introducing the required amount of oxygen in the system and activating the pH control system. Unless otherwise stated, the experiments were performed at 30 °C, pH 7.3 and an oxygen partial pressure of 0.2 bar.

*Hydrogenation experiments.*—Hydrogenation experiments were performed using a 5 wt.% Pd/C catalyst and a Parr 4842 autoclave, made of Hastelloy C276 and with a volume of 100 mL, at 100 °C and a hydrogen pressure of 100 bar.

*Analysis of the products.*—Samples taken during the oxidation experiment were centrifuged, after which the supernatant was analyzed and quantified by HPLC, using a Millipore-Waters 590 pump, a 300 × 7.8 mm Rezex organic acid column from Phenomenex, connected to a refractive index detector (Shodex RI SE-51). The samples were eluted with 0.01 M $CF_3CO_2H$ at a flow rate of 0.6 mL/min and a column temperature of 60 °C. The concentrations measured were corrected for the amount of liquid taken from and introduced into the reaction mixture.

The neutral compounds in the reaction mixture were separated from the acidic compounds by anion-exchange chromatography, using Bio-Rad AG2-X8 ($Cl^-$ form). Fructose was removed with yeast (Sigma bakers yeast type II). After standing overnight, the yeast was filtered off with activated carbon (Norit SX2) over Hyflo.

In order to determine the identity of the products, $^1H$ and $^{13}C$ NMR analyses were performed on a Varian Unity-Inova 300 spectrometer, using deuterium oxide as solvent and *tert*-butanol as internal reference ($CH_3$ resonances 1.2 and 31.1 ppm, respectively). $^{13}C$ NMR ($D_2O$, pH 8): β-D-fructofuranoside: δ 64.3 (C-1), 103.1 (C-2), 77.0 (C-3), 76.0 (C-4), 82.3 (C-5), 63.9 (C-6); α-D-fructopyranoside: δ 65.5 (C-1), 99.6 (C-2), 69.2 (C-3), 71.3 (C-4), 70.8 (C-5), 64.9 (C-6); 2-keto-D-gluconic acid: δ 176.1 (C-1), 98.8 (C-2), 70.9 (C-3), 71.6 (C-4), 70.9 (C-5), 65.8 (C-6); D-*threo*-hexo-2,5-diulose: δ 66.5 (C-1 or C-6), 94.3 (C-2), 71.2 (C-3), 74.9 (C-4), 99.5 (C-5), 65.3 (C-6 or C-1).

LC–MS spectra were recorded by coupling the HPLC set-up to a VG 70-SE mass spectrometer operating in the plasma mode. Identification of the products with this method showed D-fructose (**1**): *m/z* 163 ($M^+ - H_2O + H$), 145 ($M^+ - 2H_2O + H$), 127 (100, $M^+ - 3H_2O + H$); 2-keto-D-gluconic acid (**2**): *m/z* 177 ($M^+ - H_2O + H$), 159 ($M^+ - 2H_2O + H$), 141 ($M^+ - 3H_2O + H$), 133 ($M^+ - H_2O - CO_2 + H$), 115 (100, $M^+ - 2H_2O - CO_2 + H$), 97 ($M^+ - 3H_2O - CO_2 + H$); D-*threo*-hexo-2,5-diulose (**3**): *m/z* 161 ($M^+ - H_2O + H$), 143 (100, $M^+ - 2H_2O + H$); 2,5-diketo-D-gluconic acid (**4**): *m/z* 157 ($M^+ - 2H_2O + H$), 131 (100, $M^+ - H_2O - CO_2 + H$), 113 ($M^+ - 2H_2O - CO_2 + H$); 2-hydroxy-3-oxobutanedioic acid (**5**): *m/z* 131 (100, $M^+ - H_2O + H$); glycolic acid (**6**): *m/z* 95 (100, $M^+ + H_2O + H$), 77 ($M^+ + H$).

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