

Oxidation of L-sorbose with molecular oxygen on platinum modified by metals, amines and phosphines

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Abstract

The oxidative dehydrogenation of L-sorbose to 2-keto-L-gulonic acid in aqueous medium is reviewed with special emphasis on the use of promoted platinum catalysts. The activity of alumina- or carbon-supported platinum can be increased by selective deposition of bismuth or lead onto the supported platinum particles, and by preadsorbed strongly basic tertiary and quaternary amines. Both methods have a negative influence on the selectivity, but the effect of supported N-bases is less detrimental. Aromatic and cycloaliphatic amines, some phosphines and aminophosphines improve the selectivity to 2-keto-L-gulonic acid. The amine and phosphine modifiers are used in very small amounts, less than 600 ppm related to sorbose. The best modifier is hexamethylenetetramine, which provides 99–95% selectivity up to 30% conversion. The efficiency of metal, amine and phosphine type promoters is compared.

Keywords: Oxidation; L-Sorbose; Supported platinum; Modification

1. Introduction

The transformation of L-sorbose to 2-keto-L-gulonic acid (2-KLG) is one of the key steps in the industrial production of L-ascorbic acid [1,2]. In order to achieve acceptable oxidation selectivity, L-sorbose is first protected with acetone, and 2,3:4,6-di-O-isopropylidene-L-xylo-2-hexulofuranose (diacetone-L-sorbose) is oxidized to the corresponding acid, followed by hydrolytic deprotection to 2-KLG (Scheme 1). The need to develop a low cost industrial process for vitamin C production initiated a considerable development of all three steps of the

original synthesis. For example, a Pt-metal catalyzed oxidation with air [3–8] was proposed to substitute the second step, the conventional stoichiometric oxidation. The oxidation of diacetone-L-sorbose is almost quantitative over a 0.8 wt.-% Pd/C in aqueous alkaline solution at 130°C and 3.5 bar [8].

The electrolytic oxidation of diacetone-L-sorbose was also thoroughly investigated in the past decades [9–15]. A maximum of 90–96% chemical yield was obtained using various graphite, oxidized Ni or Ni-based bimetallic electrodes in strongly alkaline aqueous solutions. In a pilot plant scale Ni electrodes ('Swiss-Roll') provided 99% conversion and about 70% faradaic yield. A disadvantage is the

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necessary presence of Ni ions in the electrolyte for the stabilization of the Ni electrode.

It was attempted to eliminate the protection–deprotection steps and perform the chemical [16–18] (or biochemical [19]) oxidation of L-sorbose to 2-KLG in one step. The best results were obtained with the Pt-catalyzed aerobic oxidation. Many parameters of the reaction are very attractive: neutral aqueous solutions can be used under very mild conditions with the cheapest oxidant molecular oxygen. However, the yields are moderate, the reaction is slow and the Pt/sorbose weight ratios are uneconomically high: in average 1 g Pt metal can convert only 0.3–8 g sorbose in 1 h [16–18].

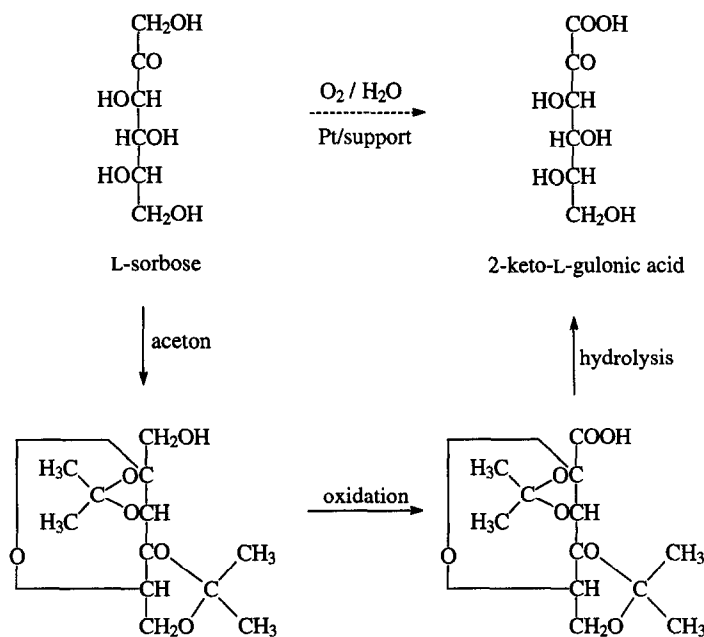
Intrigued by the industrial importance of the reaction, we also studied the Pt-catalyzed direct oxidation of L-sorbose with molecular oxygen [20–23]. It is clear from earlier investigations [16–18,20] that none of the (supported) Pt metals are really efficient catalysts. Here we discuss the possibilities of improving the performance of Pt by modification with heavy metal promoters, and preadsorbed amines and phosphines.

2. General characteristics of the platinum–metal catalyzed oxidation of alcohols and polyols

Platinum metals are among the few solid catalysts which can activate molecular oxygen under ambient conditions. Good selectivities have been obtained in aqueous medium in the oxidation of sensitive, thermolabile alcohols to carbonyl compounds or carboxylic acids (for reviews see Refs. [2,24–31]). The sometimes outstanding selectivity is attributed to two main reasons:

(i) Pt metals *catalyze* the oxidation of alcohols and aldehydes but are inactive in the oxidation of many other functional groups (e.g. C=C double bond, carboxyl group, and carbonyl groups stabilized by two alkyl groups, an aryl group or a C=C double bond in α positions), and

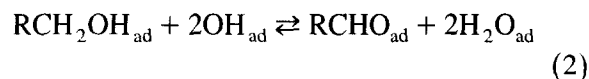
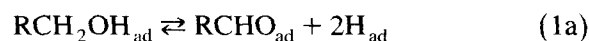
(ii) the rate of oxidation of OH groups in polyols is a function of its surroundings (primary or secondary alcohol, axial or equatorial position, possible steric hindrance, etc.).



Scheme 1.

In the past fifteen years numerous papers have reported the advantages of promoting Pt or Pd with metals, metal oxides or metal phosphates, which promoters are alone inactive in the oxidation of alcohols at close to ambient conditions [32–40]. Despite the extensive investigations, the role of the second (inactive) component is still ambiguous, likely due to the very limited access to direct evidences or in situ measurements [41–45]. A recent impressive example on the crucial role of catalyst composition is the partial oxidation of glycerol with air at close to ambient conditions [46]. Using a Pd/C catalyst in alkaline medium, the product is mainly glyceric acid, as shown in Scheme 2. On the contrary, the secondary OH group is oxidized preferentially in acidic medium over Bi-promoted Pt.

An oxidative dehydrogenation mechanism has been generally accepted for the oxidation of alcohols [47–50]. The oxidizing species (O_{ad} or OH_{ad} , depending on the pH) reacts with the hydrogen formed in the dehydrogenation of alcohol on Pt^0 or Pd^0 active sites, or directly with the adsorbed alcohol. Showing for illustration only the primary alcohol \rightarrow aldehyde transformation in neutral or slightly alkaline aqueous medium, the following steps can be formulated:



It is important that the activity of Pt^0 is much higher than that of the oxygen-covered surface Pt atoms (Pt^{n+}). As a consequence, the rate of the overall reaction depends on the oxygen coverage of the active metal. A too high rate of oxygen supply (related to the rate of oxygen

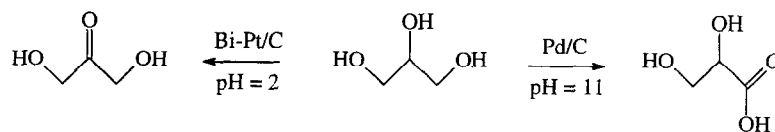
consumption by the reactant alcohol) results in high oxygen coverage of Pt or Pd and a drop in the overall reaction rate. The phenomenon is termed ‘over-oxidation’ or ‘oxygen poisoning’ [47,51,52].

A drawback of this environmentally friendly process is the frequently observed catalyst deactivation. The main reason of the loss of catalytic activity is the strong adsorption of various types of by-products and degradation products, such as dimers and oligomers, carboxylic acids, and CO [53–57]. Metal leaching during alcohol oxidation has also been evidenced when using Pd/ $CaCO_3$ [58], Pb/Pd/C [59] and Pt/C [60] catalysts. Metal dissolution, which may be considered as an irreversible catalyst deactivation [60], is a potential hazard in practical application of the method.

3. One-step oxidation of L-sorbose to 2-keto-L-gulonic acid

3.1. Reaction conditions

The catalytic oxidation experiments were performed in a batch reactor, at a constant mixing rate and constant pH, using oxygen at atmospheric pressure [20–23]. The reactor worked in a mass transport limited regime, which was necessary to avoid the over-oxidation of the catalyst, as discussed above. In general, the rate of the surface chemical reaction changes with conversion. Accordingly, the rate of oxygen supply (rate of mass transport) has to be tuned to the actual rate of alcohol oxidation (surface chemical reaction) in order to avoid a too high oxygen (OH) coverage on Pt. The rate of oxygen supply can be controlled based on the measurement of dissolved oxygen



Scheme 2.

in the liquid phase [61]. A better solution is the continuous measurement of the catalyst potential during the oxidation reaction, which provides direct, on-time information on the oxidation state of metallic sites [62]. The application of the catalyst potential for interpreting the catalytic performance will be shown later.

Reaction rates were determined from the rate of sorbose consumption, followed by the base consumption or HPLC analysis [20]. As a consequence of working in the mass transport limited regime, initial and average reaction rates are considered as only qualitative measures of catalytic activity. An order of activity can be determined when comparing various catalysts under identical reaction conditions, but the real differences in activities can be considerably higher than the measured deviations. (Under extreme mass transport limitations the overall reaction rate is practically independent of the catalyst nature.)

The most important reaction parameters were optimized by the simplex method [20]. The optimum conditions for obtaining maximum yield with limited amount of catalyst are: 50°C, 1 bar O₂, pH = 7.3, in a 0.28 mol l⁻¹ aqueous sorbose solution, at a catalyst/sorbose weight ratio of 0.20. Under these conditions catalyst deactivation prevented the full conversion of sorbose (67% selectivity at 58% conversion). An increase of catalyst loading enhances the final conversion, but this direction cannot provide an economic solution. Note that the best reported 2-KLG yield of 62% [16] was obtained using a 5.5 times higher Pt/sorbose weight ratio, at ambient temperature and a pH of 7.2.

A study of the stability of 2-KLG under

Table 1

Influence of pH, temperature and presence of Pt/alumina catalyst on the decomposition of 2-KLG (*c*⁰ = 50 g l⁻¹ 5 wt.-% Pt/alumina, Pt dispersion: 0.30, catalyst/2-KLG = 27 wt.-%, 1 bar O₂)

<i>T</i> (°C)	pH	Catalyst ^a	Rate of decomposition ^b (% h ⁻¹)
40	9.0	–	1
45	9.0	–	2
55	9.0	–	9.5
55	8.0	–	5
55	7.5	–	2
55	7.3	–	0.5
50	7.3	+	1.5
60	7.3	+	8.5
50	9.0	+	36
60	9.0	+	49

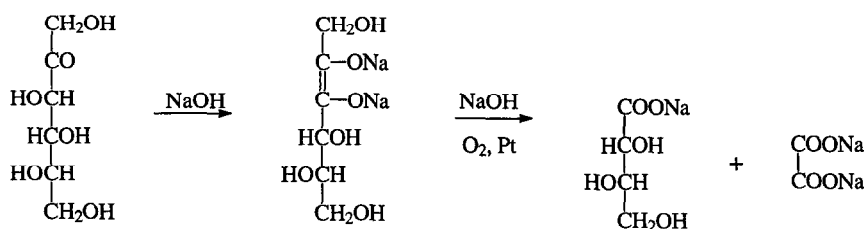
^a + Indicates that catalyst was present.

^b Relative amount of 2-KLG, converted in 1 h.

reaction conditions revealed that the low temperature and pH, necessary for the optimum in 2-KLG yield, is mainly determined by the rate of product decomposition. Table 1 illustrates that 2-KLG rapidly decomposes in aqueous solution at temperatures above 55°C and pH above 7.5, even in the absence of any catalyst. When both oxygen and a 5 wt.-% Pt/alumina catalyst are present at 60°C and a pH of 9, almost half of the product decomposes in 1 h. It has been reported [16] that in strongly alkaline medium (pH > 11) also L-sorbose decomposes rapidly via enolate formation followed by oxidative C–C bond breaking (Scheme 3), and 2-KLG is not formed at all.

3.2. Influence of metal promotion

A preliminary test of some commercial carbon- and alumina-supported Pt and Pd catalysts revealed, that Pd has rather low performance in



Scheme 3.

sorbose oxidation [20]. Pt is more active and selective, but the reaction is still too slow and the catalysts deactivate easily.

The reaction rate can be increased and catalyst deactivation suppressed by Bi or Pb promotion of Pt/alumina, as shown in Fig. 1. Promotion was performed with a special technique, by which the promoter metal could be selectively deposited onto the surface of supported Pt particles [41,45]. The presence of bimetallic particles was proved with scanning electron microscopy combined with energy dispersive X-ray analysis. The influence of promotion is a function of the promoter/Pt ratio. For the comparison of Bi and Pb promoters, two catalysts possessing similar 'theoretical' coverages of platinum have been chosen. When selecting the two promoted catalysts (Bi/Pt = 9 wt.-%, Pb/Pt = 15 wt.-%), the following assumptions were made: (i) each Bi or Pb adatom covers 3 or 2 surface Pt atoms, respectively [63,64], and most of the promoter deposits as adatoms (preferential formation of

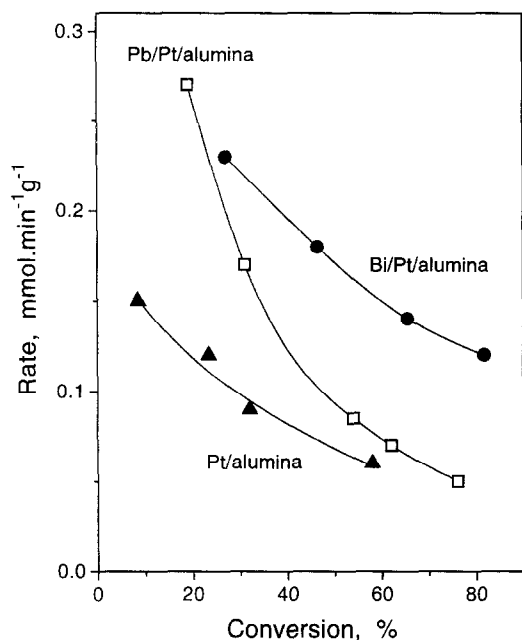


Fig. 1. Rate of sorbose oxidation as a function of conversion over unpromoted, Bi- and Pb-promoted Pt/alumina catalysts (5 wt.-% Pt/alumina; Pt dispersion: 0.30; Bi/Pt = 9 wt.-%; Pb/Pt = 15 wt.-%; catalyst/sorbose = 10 wt.-%; modifier:sorbose molar ratio = 1:1700, 50°C, 1 bar O₂, $c_{\text{sorbose}}^0 = 0.28 \text{ mol l}^{-1}$, pH = 7.3).

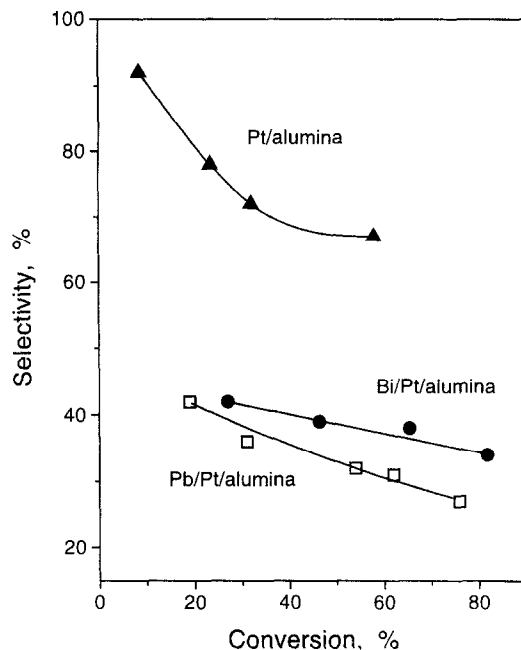


Fig. 2. Selectivity to 2-KLG in the oxidation of sorbose as a function of conversion over unpromoted, Bi- or Pb-promoted Pt/alumina catalysts (for conditions see Fig. 1).

submonolayers instead of multilayer deposition [41,56]).

Unfortunately, the rate enhancement achieved by Bi or Pb promotion is accompanied by a considerable loss of selectivity in the oxidation at the C-1 carbon atom, as illustrated in Fig. 2. Typical side reactions are the oxidation at the C-6 instead of C-1 position, and oxidative degradation by C–C bond breaking [20]. The performance of Bi-promoted Pt/alumina seems to be better than that of the corresponding Pb-promoted catalyst, but concerning the yield of 2-KLG, none of the bimetallic catalysts can compete with the unpromoted Pt/alumina.

3.3. Deactivation of mono- and bimetallic catalysts

The nature of catalyst deactivation during sorbose oxidation is rather complex [20]. The primary reason of catalyst deactivation is the formation and strong adsorption of poisoning species. The continuous measurement of catalyst potential during reaction and electrochemi-

cal model experiments on polycrystalline Pt indicated the initial, destructive adsorption of sorbose on Pt. These strongly adsorbed species could be removed (oxidatively) only on a partially oxygen-covered catalyst, above 0.55–0.6 V (RHE, related to a reference hydrogen electrode immersed in the same solution) [20]. This is the explanation why the reaction rate is very low below 0.6 V and the steady state catalyst potential is 0.7–0.8 V at low conversions. For comparison, similar self-poisoning phenomena of Pt electrodes were observed in aqueous phase during the adsorption of sorbitol or L-glucose [65–67]. Linearly bound CO and $C_xH_yO_z$ type fragments as poisoning species were identified by FTIR.

Beside the destructive adsorption of sorbose on Pt, a great variety of impurities are produced by side reactions (small chain aldehydes, carboxylic and dicarboxylic acids). These species (partly detected by HPLC analysis) cover an increasing fraction of active sites and decrease the rate of the main reaction. The catalyst has reasonable activity only in an unusually narrow potential range of 0.7–0.85 V. For comparison, in the oxidation of some secondary alcohols to ketones the self-poisoning of Pt is negligible [68,69], and the reactions run smoothly in a broad potential range starting at ca. 0.1 V [31].

Beside the formation of poisoning species, a crucial problem is the irreversible deactivation of the mono- and bimetallic catalysts. Fig. 3 indicates how the surface Bi/Pt ratio of a 0.75 wt.-% Bi/5 wt.-% Pt/alumina catalyst changes during catalyst pretreatment and sorbose oxidation. It was found by XPS analysis [20] that when mixing the catalyst in a neutral aqueous sorbose solution, the surface Bi/Pt ratio decreased even in a nitrogen atmosphere. Almost 30% of the promoter dissolved in 10 min. (In the catalytic experiments this treatment is applied to pre-reduce the catalyst before the oxidation reaction in order to obtain Pt^0 active sites.) On the basis of electrocatalytic model studies [70], this fraction of promoter corresponds to bulk Bi (multilayer deposition, Fig. 3b).

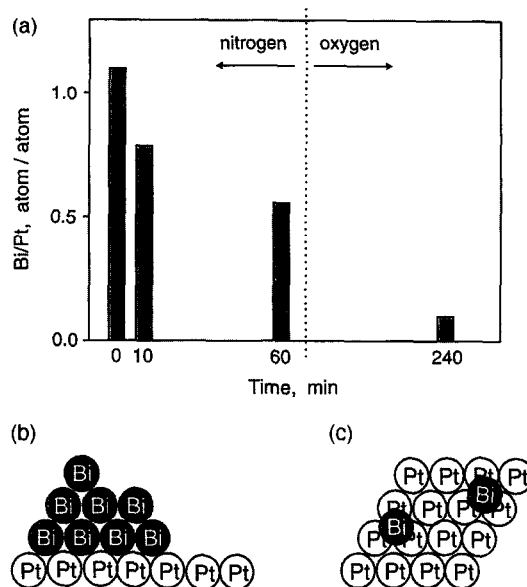


Fig. 3. (a) Surface Bi/Pt atomic ratio of a 0.75 wt.-% Bi/5 wt.-% Pt/alumina catalyst before use and stored in air (0 min), after 10 and 60 min mixing in aqueous sorbose solution under nitrogen, and after the oxidation reaction in atmospheric oxygen (240 min), determined by X-ray photoelectron spectroscopy; $c_{\text{sorbose}}^0 = 0.28 \text{ mol l}^{-1}$, pH = 7.3. (b) Schematic representation of Bi deposition onto Pt. (c) Schematic representation of Bi adatoms on a Pt(111) surface.

The stability of Bi adatoms, i.e., the first mono- or submonolayer, is higher. Still, less than 10% of the original amount of Bi remained on the Pt surface at the end of the oxidation reaction. It is proposed that this small remaining fraction corresponds to the so-called 'irreversibly adsorbed' Bi [71–73], as shown schematically on an ideal Pt(111) surface in Fig. 3c.

Unfortunately, not only Bi, but also Pt dissolves during reaction. An atomic emission spectroscopic analysis [20] indicated about 8% loss of Pt during reaction, which hardly exceeds the experimental error. However, detailed electrochemical model studies and in situ measurements in the liquid cell of a scanning tunnelling microscope provided unambiguous evidence on the corrosion of Pt [74]. When storing a Pt/graphite model catalyst in air in the same aqueous sorbose solution which was used for the oxidation reaction, the total amount of Pt dissolved in 5 days. It seems that 2-KLG is an excellent

chelating agent of Pt. Note that thermodynamically none of the Pt metals are stable in the presence of both oxygen and acid, but the rate of corrosion is usually negligible [75].

3.4. Rate acceleration with strongly basic amines

Metal leaching and irreversible catalyst deactivation could be minimized by working in slightly basic solutions (pH of 8–10, [75]). An increase of pH is also advantageous for the reaction rate but detrimental to the selectivity, as discussed in Section 3.1. To overcome this limitation, an analogy to asymmetric catalysis was used. Good enantioselectivities can be achieved in the heterogeneously catalyzed hydrogenation of activated carbonyl compounds when Ni or Pt, which metals provide the hydrogenation activity, are modified by traces of strongly adsorbing chiral compounds, which are responsible for the enantioselection [76–79]. We assumed that the performance of Pt in sorbose oxidation can also be improved by preadsorbed organic compounds. Promising candidates for modifiers are soft bases, such as amines, due to the soft acidity of Pt.

Accordingly, instead of increasing the pH of water, a neutral solution was applied and the Pt catalyst was modified with basic amines. The rate acceleration obtained with some tertiary and quaternary amines is shown in Fig. 4. The reaction rate in the absence of modifier is marked by a dashed line. Above a limit of about 10, the rate of sorbose oxidation increases rapidly with increasing pK_a of the amine. Interestingly, the rate acceleration is practically independent of the chemical nature of the amine. This is a clear indication of base-catalyzed reaction and bifunctional catalysis.

The amines are used in very low concentration. The molar ratio of each amine modifier to surface Pt atoms is 1 to 10, and the amount of amine is less than 600 ppm related to the amount of L-sorbose.

Cyclic voltammetric studies [22] indicated

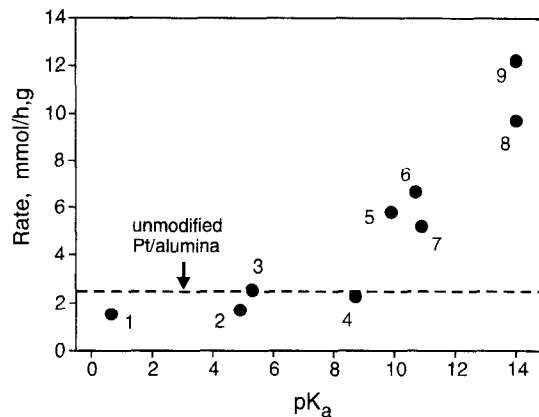
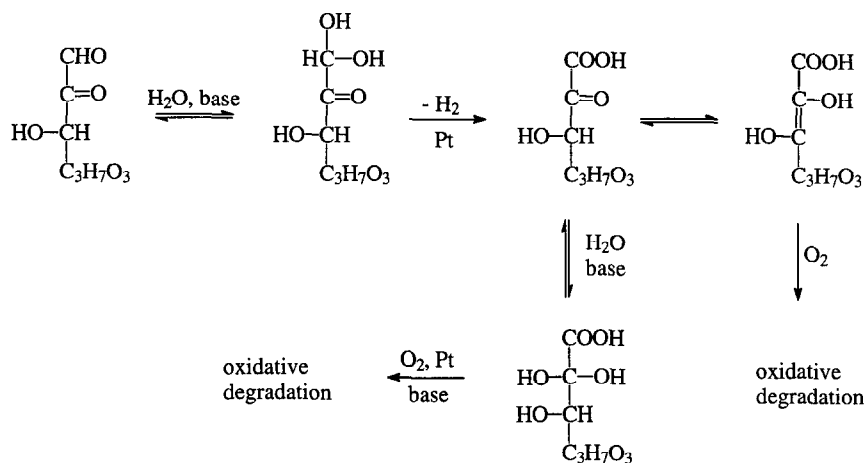


Fig. 4. Influence of various amines on the rate of sorbose oxidation over 5 wt.-% Pt/alumina; modifiers: 1, pyrazine; 2, quinoline; 3, pyridine; 4, diazabicyclooctane; 5, tributylamine; 6, triethylamine; 7, quinuclidine; 8, tetrabutylammonium hydroxide; 9, tetramethylammonium hydroxide (Pt dispersion: 0.30, 50°C, 1 bar O_2 , $c_{\text{sorbose}}^0 = 0.28 \text{ mol l}^{-1}$, pH = 7.3, catalyst/sorbose = 27 wt.-%, modifier/Pt_s = 0.1 molar ratio, modifier:sorbose molar ratio = 1:1700, average rate between 0 and 30% conversion).

that the trialkyl and aromatic amines suppress hydrogen sorption on Pt. The model studies corroborated that the amines are partially adsorbed on Pt under reaction conditions and really act as supported bases. Besides, most of the amines (except triethylamine) are stable in the potential range of sorbose oxidation and are not oxidized on the Pt surface (see Fig. 8).

Concerning the mechanism of the rate acceleration in the presence of basic amines, it is proposed that the rate of hydration of the aldehyde intermediate to a geminal diol intermediate is increased, according to Scheme 4. The oxidative dehydrogenation of the diol on Pt is considerably faster than the oxygen-insertion into the aldehyde, which results in an enhancement of the overall reaction rate. An evidence for this mechanism is that only nonhydrating aldehydes, stabilized by an aromatic ring (e.g. benzaldehyde) or a C=C double bond in α -position (e.g. cinnamaldehyde), can be prepared selectively in aqueous medium [37,62]. In apolar medium several simple aliphatic aldehydes can be prepared with good yields (up to 95%, [80]).

Table 2 provides further support for this interpretation. There was no observable rate acceleration when using Ph_3N or Bu_3N modifiers



Scheme 4.

in the partial oxidation of 1-phenylethanol to acetophenone or cinnamyl alcohol to cinnamaldehyde. In both cases the selectivities are high (> 95%), as the product carbonyl compounds are relatively stable against hydration and further oxidation [45,56]. On the contrary, considerable rate accelerations were observed in the oxidation of D-glucose to D-gluconic acid, and L-sorbose to 2-KLG. In both cases the carbonyl compound reactant or intermediate are hydrated and smoothly oxidized to the corresponding carboxylic acids.

On the basis of this consideration it is easy to understand why the stability of 2-KLG is low and the selectivities in the sorbose → 2-KLG

transformation are considerably lower than those reported for the D-glucose → D-gluconic acid reaction (up to 96% [81–83]). The carbonyl group of 2-KLG is activated by the electron-withdrawing carboxyl group in α position, resulting in its rapid hydration and (oxidative) decomposition (Scheme 4). Beside the hydration, bases accelerate the autoxidation of the product via deprotonation of the enediol intermediate to form the more reactive enedionate anion (see also Scheme 3 [84]). In contrast, the polyhydroxy acid type compound D-gluconic acid is relatively stable against further oxidation (the OH group at C-6 is the most reactive [85–87]).

Table 2

Influence of N-bases on the alcohol → carbonyl compound → carboxylic acid type transformations; (a) 1-phenylethanol: 2 g in 20 ml water, 100 mg catalyst, 40 mg dodecylbenzenesulfonic acid Na salt detergent, 20 mg Li_2CO_3 , 60°C, 1 bar air; (b) cinnamyl alcohol: 1 g in 10 ml water, 50 mg dodecylbenzenesulfonic acid Na salt detergent, 40 mg Li_2CO_3 , 60°C, 1 bar air; (c) D-glucose and L-sorbose: 2.2 g in 40 ml water, 0.6 g catalyst, pH = 7.3, 50°C, 1 bar O_2

Reactant	Type of transformation	Amine ([amine]/[Pt _s])	Catalyst ^a	Relative rate ^b
1-Phenylethanol	>CHOH → >C=O	Ph ₃ N (0.8)	Pt/Al ₂ O ₃	≈ 1
Cinnamyl alcohol	–CH ₂ OH → –CHO	Ph ₃ N (0.8)	Pt/Al ₂ O ₃	0.77
D-Glucose	–CHO → –COOH	Bu ₃ N (0.15)	Pt/C	1.9
L-Sorbose	–CH ₂ OH → –COOH	Ph ₃ N (0.1)	Pt/Al ₂ O ₃	2.6
		Bu ₃ N (0.1)	Pt/Al ₂ O ₃	2.2

^a 5 wt.-% Pt content.

^b Initial rate of reaction over amine-modified catalyst, related to that measured with unpromoted catalyst.

3.5. Selectivity enhancement with cyclic aliphatic and aromatic amines

All the strongly basic tertiary and quaternary amines, which enhance the reaction rate, decrease the selectivity [21,22]. The higher the pK_a of the amine, the lower is the selectivity to 2-KLG. But these amines act as supported bases on the Pt surface and do not increase the pH of the medium. Accordingly, their effect is not so detrimental as that of the increase of bulk pH. As an example, using Et_3N with a pK_a of 10.7 at a bulk pH of 7.3, the average reaction rate increases by a factor of 2.5 and the selectivity (at 30% conversion) drops from 71 to 58%, compared to the reaction performed with unmodified Pt/alumina. The rate enhancement is the same as that obtained by increasing the bulk pH to 9, but at this high pH the selectivity is only 11%.

Testing various tertiary aliphatic, cycloaliphatic and aromatic amines revealed that not only the reaction rate but also the selectivity can be increased, compared to that of the optimized reaction in a neutral aqueous medium. In this respect the chemical structure of modifier is very important, which indicates that special interactions between amine and sorbose are responsible for this effect.

Only weakly basic cycloaliphatic and aromatic amines have a positive effect on the selectivity. Some typical examples are shown in Fig. 5. The most efficient is hexamethylenetetramine, which has a three-dimensional-like structure and several basic N-atoms accessible to interaction with L-sorbose. This modifier provides almost quantitative transformation of sorbose to 2-KLG at low conversion, and the selectivity is above 80% even at 50% conversion. Aromatic amines, such as pyrazine and acridine which possess a planar two-dimensional structure, are less efficient.

A molecular modelling study has been made for the interpretation of the outstanding selectivity in the presence of hexamethylenetetramine [22]. Molecular mechanics calculations were

used to determine the minimum energy conformations of some hexamethylenetetramine–sorbose complexes. Hexamethylenetetramine is assumed to be adsorbed by one N atoms facing to a Pt atom, and the three other N atoms are easily accessible to interaction with one of the OH groups of sorbose. After adsorption of this complex on a flat Pt surface, stabilized by a H-bond, the pyranose ring of sorbose is in a tilted position, as illustrated in Scheme 5. Only the (C-1)–O–H fragment is close to the Pt surface and liable to oxidative dehydrogenation, in agreement with the outstanding selectivity to 2-KLG. Note that several other complexes, stabilized by a H-bond between one of the N-atoms of hexamethylenetetramine and one of the OH groups of sorbose, are possible and have been calculated. Although the proposed model provides a feasible explanation for the enhanced selectivity, the nature of interaction between reactant and modifier requires experimental substantiation.

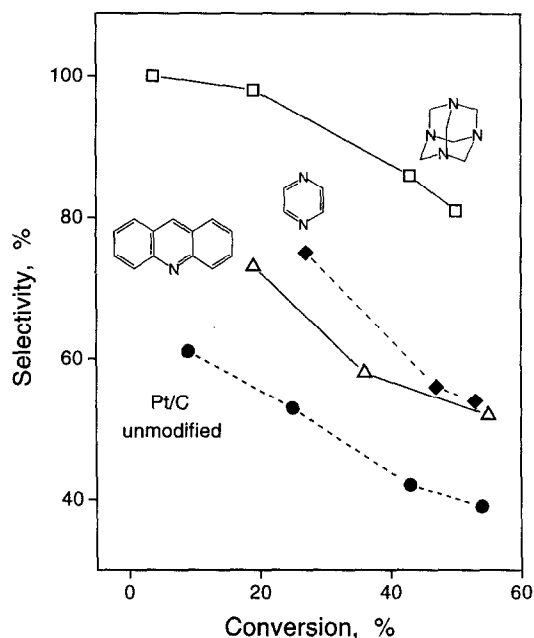
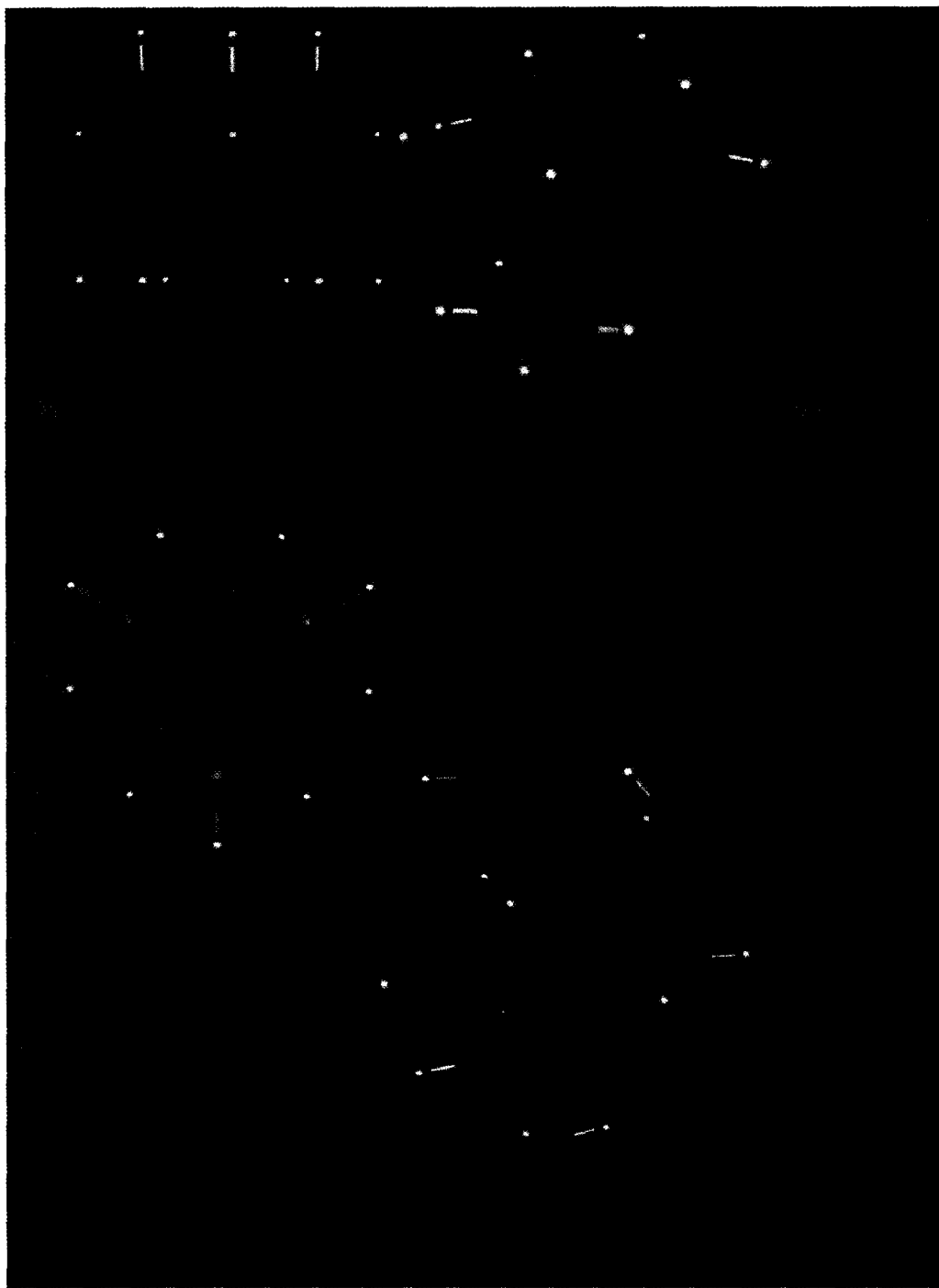


Fig. 5. Enhanced selectivity of Pt/C in the presence of hexamethylenetetramine, pyrazine and acridine (5 wt.-% Pt/C, Pt dispersion: 0.29, modifier:Pt_s molar ratio = 0.1, modifier:sorbose molar ratio = 1:1700, catalyst/sorbose = 27 wt.-%, 50°C, 1 bar O₂, $c_{\text{sorbose}}^0 = 0.28 \text{ mol l}^{-1}$, pH = 7.3).

It is not easy to provide an unambiguous explanation for the decrease in selectivity above 20–30% conversion, as shown in Fig. 5. The

most likely interpretation is that hexamethylenetetramine present on Pt favors the oxidation of sorbose at the C-1 position and sup-



Scheme 5.

presses attacks on other parts of the molecule (mainly at C-6). However, it does not influence the consecutive side reactions (degradation), which become dominant with increasing product concentration.

Two other possible interpretations were also considered. At first, working at a controlled pH below the equilibrium pH of the Na-salt of 2-KLG, the amount of free acid increases during reaction. Fig. 6 shows the amount of free 2-KLG as a function of conversion, calculated from the base consumption and the titration curve of 2-KLG with Na_2CO_3 (which base was used during reactions). For comparison, the initial amount of sorbose is 12.2 mmol. The total amount of free acids may be higher than the calculated values due to the formation of acidic by-products (1,6-dicarboxylic acid, oxalic acid, etc.).

In order to elucidate the role of free acids, L-sorbose was oxidized with Pt/C with and without modification by hexamethylenetetramine, in the presence of 2-KLG (Fig. 7). These experiments mimic a 40% conversion of sorbose to 2-KLG. The selectivity is significantly lower when the product is added at the beginning of the reaction. This behaviour indicates the decomposition of 2-KLG on the catalyst and in the liquid phase. Nevertheless, a definite modifying effect of hexamethylenetetramine by ca. 25% can still be observed in the

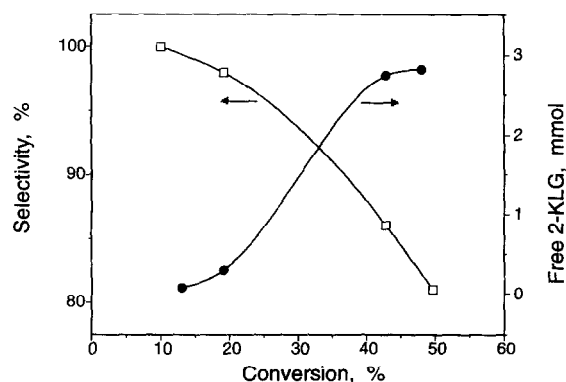


Fig. 6. Selectivity to 2-KLG and the amount of free 2-KLG as a function of sorbose conversion at a controlled pH of 7.3 (for conditions see Fig. 5).

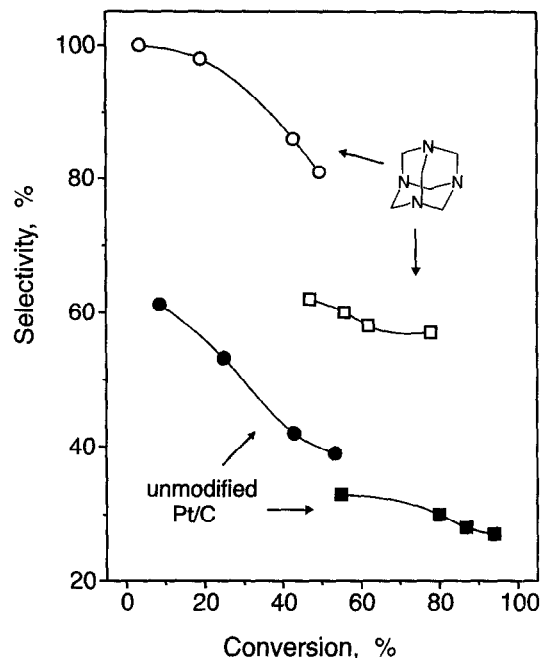


Fig. 7. Selectivity to 2-KLG as a function of conversion on unmodified Pt/C (filled circle) and modified with hexamethylenetetramine (open circle), and the same experiments started with an L-sorbose:2-KLG = 60:40 molar ratio on unmodified Pt/C (filled square) and modified with hexamethylenetetramine (open square); (for conditions see Fig. 5).

whole conversion range investigated. Considering the large excess of free acid to modifier (more than two orders of magnitude at 50% conversion), the loss of selectivity at high conversion due to the protonation of amine can be excluded.

Another explanation for the decreasing selectivity could be the oxidative degradation of hexamethylenetetramine during reaction. The adsorption of hexamethylenetetramine on Pt and its stability during the oxidation reaction was studied with electrocatalytic experiments [22]. Unsupported Pt powder catalyst (used due to the conductivity requirement of the method) and an aqueous sodium-acetate solution, with a pH of 7.3, were applied to mimic the catalytic reaction. Fig. 8 shows the anodic branches of cyclic voltammograms of Pt in the absence and presence of hexamethylenetetramine. The comparison of the two curves shows the suppressed

H-sorption on Pt in the presence of amine. The area between the two curves in the hydrogen region (below 0.5 V, RHE) is proportional to the amount of amine adsorbed on Pt. Between 0.5 and 1 V the two curves are almost identical, indicating that hexamethylenetetramine is not oxidized in detectable extent under reaction conditions (0.7–0.9 V).

3.6. Modification with phosphines and sulphur compounds

This new technique can be extended to other types of organic compounds, on two conditions. At first, the modifier should contain an 'anchoring' moiety, such as an aromatic ring or a N or P heteroatom, to achieve a relatively strong adsorption of the modifier on Pt. By this way very small amounts of modifier can efficiently change the performance of Pt. Another requirement is the stability of the molecule against self-oxidation.

Fig. 9 shows some phosphines and aminophosphines, which have positive effect on the selectivity to 2-KLG [23]. The best among them is Bu_3P . The plotted values are not yet optimized; e.g., the selectivity could be in-

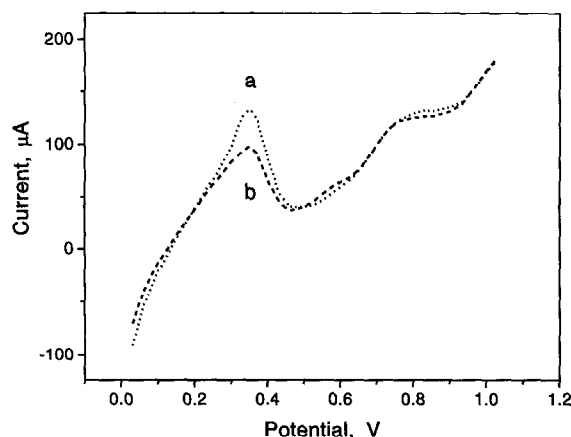


Fig. 8. Positive sweeps of the cyclic voltammograms of Pt in the absence (a) and in the presence of hexamethylenetetramine (b); 2 mg Pt powder, 0.2 mg hexamethylenetetramine, 1 wt.-% aqueous Na-acetate adjusted to pH = 7.3, ambient temperature, 2 mV s^{-1} sweep rate (for more details of the electrochemical method see Ref. [22]).

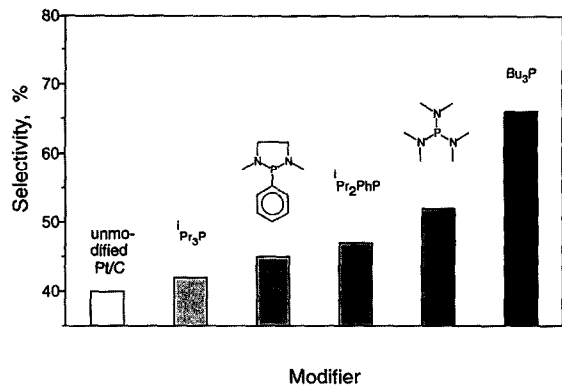


Fig. 9. The influence of some phosphines and aminophosphines on the selectivity to 2-KLG (5 wt.-% Pt/C, Pt dispersion: 0.26; catalyst/sorbose = 27 wt.-%, modifier:sorbose molar ratio = 1:1700, 50°C , 1 bar O_2 , $c_{\text{sorbose}}^0 = 0.28 \text{ mol l}^{-1}$, pH = 7.3).

creased from 47 to 75% by using diisopropylphenylphosphine in 10 times higher concentration.

Some sulphur and amino-sulphur compounds were also tested in sorbose oxidation [88]. Unfortunately, these compounds have a negative effect on the performance of Pt/alumina. For example, benzothiazole and mercaptopyridine decreased the selectivity by 10 to 20% in the whole conversion range, compared to the effect of the corresponding N-base modifiers benzimidazole and pyridine. Beside the poor selectivities to 2-KLG, more rapid catalyst deactivation was also observed.

4. Conclusions

It has been shown that supported Pt catalysts possess moderate selectivity and low activity in the selective oxidation of sorbose to 2-keto-L-gulonic acid. Selective deposition of Bi or Pb onto the supported Pt particles increases the rate but decreases the selectivity. A crucial difficulty of this oxidative dehydrogenation reaction is that the Pt-based bimetallic catalysts corrode in the presence of the product in neutral or acidic medium, while the product ketoacid is not stable even in slightly alkaline medium. This complication can be circumvented and the reaction

rate enhanced by applying strongly adsorbing amines, so-called supported bases, instead of increasing the bulk pH of the medium.

The selectivity to ketogulonic acid can also be improved by traces of cycloaliphatic and aromatic amines, phosphines and aminophosphines. Outstanding selectivities were achieved with hexamethylenetetramine as modifier. The sorbose–modifier interaction can be rationalized by molecular mechanics calculations. The new method for improving the performance of Pt can be extended to the oxidation of other types of primary alcohols and aldehydes. Unfortunately, simultaneous enhancement of reaction rate and selectivity, a requirement of any economic process for sorbose oxidation, could not be achieved yet with the new modifiers and remains an important task of future research.

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