JOURNAL OF CATALYSIS **161,** 720–729 (1996)
ARTICLE NO. 0234

Platinum Catalysts Modified by Adsorbed Amines: A New Method of Enhancing Rate and Selectivity of L-Sorbose Oxidation

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Received November 6, 1995; revised February 9, 1996; accepted February 29, 1996

The Pt-catalyzed oxidation at C-1 of unprotected L-sorbose to 2-keto-L-gulonic acid, an intermediate in vitamin C synthesis, has been studied using molecular oxygen and neutral aqueous solution. The performance of Pt/alumina and Pt/C catalysts could be improved by addition of small quantities of tetraalkylammonium hydroxides, trialkyl-, triaryl-, and cycloaliphatic amines. The optimum modifier : Pt_s molar ratio is around 0.1, which corresponds to an amine : sorbose molar ratio of 1 : 1700. Rate enhancement (by a factor of up to 4.6) can be obtained when the pK_a is around 10 or higher, and this correlation depends very little on the chemical structure of the amine. Rate acceleration is proposed to be connected with the hydration of the intermediate aldehyde (bifunctional catalysis). The influence of supported N-bases on the selectivity of Pt is a function of their chemical structure. The best results, 95% selectivity at 30% conversion and about 40% selectivity enhancement in the whole investigated conversion range, was obtained with Pt/C and hexamethylenetetramine. Electrochemical model studies revealed that hexamethylenetetramine is adsorbed on Pt and not oxidized during reaction. Molecular modeling suggests that the preferential oxidation at C-1 is due to complex formation by H-bonding between hexamethylenetetramine and sorbose. The adsorption of this complex on Pt results in a tilted position of the reactant in which only C-1 is exposed to oxidative dehydrogenation. © 1996 Academic Press, Inc.

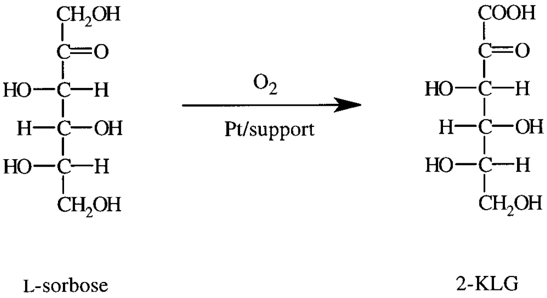
INTRODUCTION

The industrial production of vitamin C is still based on the Reichstein–Gruessner synthesis (1, 2) developed in 1934. In the conventional route the oxidation of the C-1 hydroxyl group of L-sorbose to the corresponding carboxylic acid proceeds in three steps. The method requires the protection (and subsequent hydrolytic deprotection) of the other four reactive hydroxyl groups to achieve good selectivity.

A considerable effort has been expended in the past in order to substitute the conventional stoichiometric oxidation (with NaOCl or $KMnO_4$) by a catalytic method and perform the transformation of L-sorbose to 2-keto-L-gulonic acid (2-KLG) in one step. Heyns (3, 4) reported first the Pt-catalyzed aqueous phase oxidation of unprotected L-sorbose with molecular oxygen according to Scheme I. The reaction is based on the unique properties of Pt metals: they can activate molecular oxygen and alcohols under very mild conditions. Excellent selectivities have been obtained in the partial oxidation of several thermolabile reactants, such as carbohydrates and steroids, under very mild conditions (for reviews see Refs. 4–9). The reactivity of the hydroxyl groups of polyols can be tuned by promoting Pt or Pd with Bi, Pb, or some other metals, metal oxides, or metal phosphates (9–13). A disadvantage of this aerobic oxidation method is the frequently observed catalyst deactivation which necessitates high catalyst loadings, sometimes even after promotion with heavy metals (14–17).

Unfortunately, not only the reaction rate but the selectivity is also moderate in the direct oxidation of L-sorbose to 2-KLG (3, 17–19). After screening a broad range of supported Pt and Pd catalysts, a maximum of 67% selectivity at 58% conversion has been obtained with a 5 wt% Pt/alumina (19). Promotion with Bi or Pb improves the initial rate but has a detrimental effect on the selectivity. It has been shown that the primary reason for poor catalyst performance is the formation of strongly adsorbed by-products (self-poisoning of Pt, (19, 20)). The increasing contamination of active sites results in overoxidation (too high oxygen coverage of Pt). Partial corrosion of Pt and promoter metals in the neutral aqueous solution in the presence of the good chelating agent 2-KLG has also been proved.

It has been shown recently (21) that the pH of the aqueous medium is the most important parameter in the direct



SCHEME I

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oxidation of L-sorbose. At low pH the selectivity is good but catalyst deactivation prevents high conversion. With increasing pH (above 7.5) the rate is enhanced and the selectivity drops, mainly due to the poor stability of 2-KLG even in the absence of catalyst and oxygen. To overcome this limitation we used an analogy with asymmetric catalysis. The most successful technique in heterogeneously catalyzed enantioselective hydrogenations is the modification of the active metal (Ni or Pt) by traces of strongly adsorbing chiral compounds (22, 23). We assumed that the performance of Pt in sorbose oxidation can also be improved by strongly adsorbing molecules, without changing the bulk characteristics of the medium. Promising candidates for modifiers are soft bases, such as tertiary amines, due to the soft acidity of Pt.

In a preliminary report we presented the first success of this technique (21). The aim of the present work is to study the correlation between the chemical structure and basicity of various N-bases and their influence on the rate and selectivity of sorbose oxidation. Electrochemical model experiments and molecular modeling studies were used to elucidate the nature of Pt–reactant–modifier interactions during the oxidation process.

EXPERIMENTAL

Materials

Data and codes of supported Pt catalysts used for the oxidation reaction are collected in Table 1.

A Pt powder catalyst, used for electrochemical model experiments, was prepared by hydrogen reduction of the corresponding hydroxide at 30°C. The hydroxide was precipitated from an aqueous H_2PtCl_6 solution with a dilute $NaHCO_3$ solution at 90°C. The catalyst was filtered off, washed with water to remove residual Cl^- ions, and dried at 105°C. A metal dispersion of 0.052 was determined from the hydrogen region of an electrochemical polarization curve (24).

Compounds used are designated as numbers and the corresponding structural formulae are presented in Tables 2 and 3. Tetramethylammonium hydroxide (**1**, 25% in water, Fluka), tetrabutylammonium hydroxide (**2**, 40% in water, Fluka), triethylamine (**3**, >99.5%, Fluka), tributylamine (**4**, >99%, Fluka), triphenylamine (**5**, >98%, Fluka), pyridine (**6**, >99%, J. T. Baker), quinoline (**7**, >95%, Fluka), acridine (**8**, >95%, Fluka), pyrazine (**9**, >98%, Fluka), quinoxaline (**10**, 97%, Fluka), quinuclidine (**11**, >98%, Fluka), diazabicyclooctane (**12**, 97%, Fluka) hexamethylenetetramine (**13**, >99.5%, Fluka), 2-propanol (>99.5%, Riedel–de Haën), and L-sorbose (≥99%, Fluka) were used as delivered. Distilled water (after ion exchange) was used for the experiments.

TABLE 1

Catalysts Used for L-Sorbose Oxidation

Catalysts[a]	Composition	Origin	Dispersion by TEM	Dispersion by H_2-chemisorption
A	Pt/alumina	Engelhard Escat 24	0.30	0.24
B	Pt/alumina	Engelhard No. 4759	—	0.22
C	Pt/C	Engelhard Escat 21	—	0.29
D	Pt/C	Engelhard Escat 23	—	0.31

[a] Pt loading of all catalysts is 5 wt%.

TABLE 2

Influence of the Molar Ratio of Modifier to Surface Pt Atoms on the Average Reaction Rate and Selectivity to 2-KLG; 5 wt% Pt/A1₂O₃ (A), Standard Conditions

Modifier		Modifier/Pt_s (mol/mol)	S^a %	$Rate^b$ mmol (g_{cat} h^{-1})
—	—	—	89	2.64
6		0.1	94	2.54
6		0.4	62	1.55
6		1.0	—	<0.1
11		0.1	92	5.2
11		0.5	76	3.41
11		1.0	43	2.8

[a] Selectivity at 10% conversion.

[b] Average rate between 0 and 30% conversion.

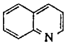
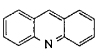
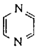
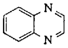
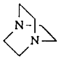
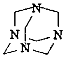
Catalyst Modification

In situ catalyst modification was applied with water-soluble amines and performed in the same glass reactor used for sorbose oxidation (see below). A quantity of 0.6 g catalyst was suspended in 40 ml water at ambient temperature and the system was flushed extensively with nitrogen. After 20 min reduction of the catalyst with hydrogen at atmospheric pressure, hydrogen was substituted by nitrogen, the proper amount of modifier, dissolved in 2 ml water, was added and the slurry was mixed for at least 90 min.

In the case of water-insoluble amines, the modification was performed *ex situ*. The procedure was similar to that described above, but 0.8 g catalyst was suspended in 50 ml isopropyl alcohol and the modifier was dissolved in 2 ml isopropyl alcohol. After 120 min mixing, the solvent was evaporated and the catalyst was dried in vacuum at 50°C for 20 min. A weight of 0.6 g of dried catalyst was used for the oxidation reaction.

TABLE 3

Average Reaction Rate and Selectivity Using 5 wt% Pt/Al_2O_3 (A) Modified with Amines; Standard Conditions, Modifier: $Pt_s = 0.1$

Modifier		pK_a	S[a] (%)	Rate[b] mmol (g_{cat} h^{-1})
—	—	—	71	2.64
1	$Me_4N^+OH^-$	ca. 14	28	12.2
2	$Bu_4N^+OH^-$	ca. 14	42	9.7
3	Et_3N	10.7[c]	58	6.64
4	Bu_3N	9.9[c]	62	5.8
5	Ph_3N	4.8[d]	44	6.81
6		5.3[c]	72	2.54
7		4.9[c]	71	1.69
8		5.6[c]	75	1.49
9		0.65[e]	73	1.53
10		0.56[e]	64	1.64
11		10.9[c]	62	5.2
12		8.7[f]	69	2.27
13		8.87[g]	81	1.23

[a] Selectivity at 30% conversion.

[b] Average rate between 0 and 30% conversion.

[c] See Ref. (33)

[d] See Ref (37).

[e] See Ref. (34).

[f] See Ref. (35).

[g] See Ref. (36).

Oxidation of L*-Sorbose*

The oxidation reactions were performed in a 200-ml flat-bottomed glass batch reactor (diameter 55 mm) equipped with mechanical stirrer (diameter 28 mm), gas distributor, condenser, combined temperature and pH electrode (Metrohm, 6.02181.010), and combined reference and measuring electrode (Metrohm, 6.0415.100). The reproducibility of the potential measurement was ±10 mV. More details of the method can be found elsewhere (25–27). The temperature was controlled with a water bath within ±1°C. The oxygen flow rate (5 ml min^{-1}) was measured by a rotameter.

A weight of 0.6 g of *ex situ* modified catalyst was suspended in 40 ml water under nitrogen and heated to 50°C. In case of *in situ* modification the slurry was heated under nitrogen to 50°C directly after catalyst preparation. Then 2.2 g L-sorbose was added and the pH adjusted to 7.3 by dosing 0.4 *M* aqueous Na_2CO_3. The oxidation reaction was started by substituting nitrogen with oxygen. During reaction the pH was controlled by automatic titration with 0.4 *M* Na_2CO_3. Samples of 1 ml of the reaction mixture were periodically taken, filtered, and stored at 5°C. Standard conditions (pH 7.3, $T = 50°C$, $P(O_2) = 1$ bar, $n = 1100$ rpm; catalyst, L-sorbose weight ratio of 0.27; modifier, $Pt_S = 0.1$ molar ratio) were applied if not otherwise stated. Under these conditions the reactor worked in a transport limited regime.

The samples were analyzed by HPLC using a Waters liquid chromatograph (pump, 600 E; autosampler, 717; UV detector, 486; RI detector, 410; and integrator, 746). The separation was carried out at 30°C on a 250 × 4-mm stainless-steel column slurry-packed with Nucleosil-5 NH_2 resin (Macherey Nagel). The eluent consisted of 4.5 g KH_2PO_4/330 ml water/670 ml acetonitrile with a flow rate of 0.8 ml min^{-1} and a column pressure of 90 bar. Peak detection was performed with a refractive index (RI) detector thermostated at 35°C. Conversion and selectivity were obtained by using the external standard method. Concentrations were corrected for dilution during pH-controlling and for the effect of sampling.

Electrochemical Polarization

All potentials in the paper are referred to the reversible hydrogen electrode emerging in the same supporting electrolyte which was in the main compartment of the cell. Nitrogen (99.995%) was bubbled continuously through the cell to deoxygenate the solution.

The electrochemical cell, the modified carbon paste electrode and the experimental setup used for cyclic voltammetric measurements have been described previously (24, 28). Pt catalyst powder (2 mg) was dispersed on the surface of the flat carbon paste and polarized with a sweep rate of 2 mV s^{-1}. The speed of the rotating carbon paste electrode was 500 min^{-1}. A Pt rod counter electrode and an Ag/AgCl/KCl_{sat} ($E = 197$ mV) reference electrode were used. The latter was separated from the main compartment of the cell by two diaphragms to avoid the pollution of the electrolyte by Cl^- ions.

Polarizations were carried out in a nitrogen atmosphere at 25°C in 40 ml 1 wt% aqueous Na-acetate supporting electrolyte (pH adjusted to 7.3). At first, the catalyst powder was reduced and oxidized electrochemically between 25 and 1025 mV. This first cycle is not shown in the figures. The second cycle provides the reference (unmodified Pt). During the third cathodic polarization 1 ml supporting electrolyte containing the proper amount of amine was injected before hydrogen adsorption started, as illustrated in Fig. 1. (At this point both oxygen and hydrogen coverage on Pt is negligible.) For the sake of simplicity, only the anodic sweeps of the second and third cyclic voltammograms are compared in Figs. 6 and 7. A new portion of catalyst was used for each series of experiments.

The degree of coverage of Pt by amines (θ) has been determined from the hydrogen region of the anodic sweeps

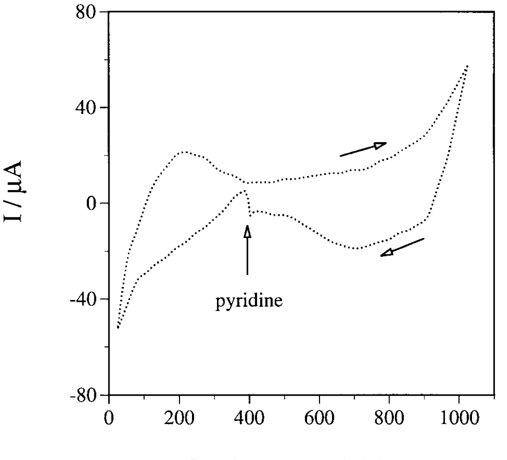


FIG. 1. Third cyclic voltammogram of Pt during which 12 mg pyridine (**6**) is injected into the solution; 1 wt% aqueous Na-acetate (pH adjusted to 7.3); sweep rate, 2 mV s^{-1}.

of the second and third cycles,

$$\theta = (N_{H,0} - N_{H,A})/N_{H,0},$$

where $N_{H,0}$ and $N_{H,A}$ are the amounts of adsorbed hydrogen in the absence and presence of an amine, respectively (29, 30).

For the determination of the rate of electrocatalytic oxidation of L-sorbose, 1 ml supporting electrolyte containing 0.5 wt% sorbose was added at the end of the second polarization cycle. The reaction rate was calculated from the difference between the anodic sweeps of the second and third cycles in the potential range of 450–900 mV.

Hydrogen Chemisorption

Hydrogen chemisorption was measured in an all-glass system equipped with an oil diffusion pump. The hydrogen used was 99.999% purity. About 0.5 g of sample was first evacuated at 150°C for 2 h and then reduced at 200°C with hydrogen for 3 h. Afterward the samples were degassed at 200°C overnight. Adsorption was carried out at 25 ± 1°C starting with an initial pressure of ca. 5×10^3 Pa, and the system was allowed to equilibrate for 2 h. After the first isotherm was measured, the samples were evacuated to 10^{-3} Pa for 2 h and the physisorption isotherm was then measured, also at 25 ± 1°C.

Molecular Modeling

Biosym programs Insight II (version 2.3.5) and Discover (version 2.96) were used in the molecular modeling study. Molecular mechanics minimum energy calculations were performed using the CVFF force field and the default values as supplied by the software. X-ray data from the Cambridge Structural Database (CSD) for the modifiers (**11**, **12**, **13**) and L-sorbose were used as starting coordinates for the minimizations.

RESULTS

Influence of Modifier: Pt_s Ratio

In preliminary experiments the catalytic performance of amine-modified catalysts was studied as a function of the molar ratio of amine to surface Pt atoms (Pt_s). Two examples, the influence of an aromatic (**6**, pyridine) and a cycloaliphatic (**11**, quinuclidine) amine are shown in Table 2. In general, high modifier loadings in the range of 0.1–1.0 result in a catalytic behavior similar to that of a strongly deactivated Pt/alumina catalyst, likely to be due to a too-high coverage of active sites by the modifier. (The adsorption of amines on Pt will be discussed later.) The best selectivities and reaction rates were obtained using rather low amounts of amine. Accordingly, the influence of the chemical structure of various amines on the performance of Pt/alumina was investigated with a molar ratio of modifier to Pt_s of 0.1–0.2.

Rate Enhancement by Modification with Amines

The reaction rate has been determined as the average rate of L-sorbose consumption between 0 and 30% conversion. This value is considered only as a qualitative measure of the activity of the catalyst. The reactor worked in a transport limited regime; i.e., both the rate of the surface oxidation reaction and the rate of oxygen transport from the gas phase to the catalyst surface had an influence on the rate of sorbose consumption. These conditions were necessary to avoid rapid catalyst deactivation due to overoxidation of active sites, in agreement with earlier observations (12, 19, 31, 32).

The influence of various tetraalkylammonium hydroxides and tertiary amines as modifiers on the rate of sorbose consumption and selectivity to 2-KLG is summarized in Table 3. (Primary and secondary amines were not used to avoid any possible interaction between the amine and the carbonyl compound reactant or product.) Unfortunately, there is a considerable deviation among the pK_a values of certain amines reported in the literature (33–37), which weakens any conclusion concerning the correlation of reaction rate with pK_a. In addition, no pK_a values were found for tetraalkylammonium hydroxides and therefore they were estimated as being approximately 14.

Modification of alumina-supported Pt with strongly basic tetraalkylammonium hydroxide provides significant rate enhancement. For example, the use of **1** or **2** as modifiers results in a 3.7- to 4.6-fold higher rate of sorbose consumption, compared to the rate obtained with unmodified Pt/alumina under otherwise identical conditions. Similar rate acceleration, but to a less extent, was observed using trialkyl- and triarylamines **3**–**5** (pK_a between 5 and 11). Aromatic

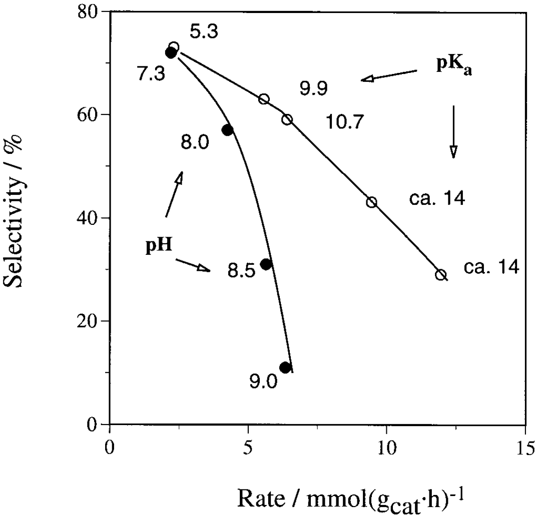


FIG. 2. Influence of (●) bulk pH and (○) basicity of tri- and tetraalkylamine modifiers on the average reaction rate and selectivity to 2-KLG in the oxidation of L-sorbose; 5 wt% Pt/Al_2O_3 (A), modifier to Pt_s molar ratio of 0.2, standard conditions.

amines **7–10** (pK_a between 0.5 and 5.5) have a negative effect on the reaction rate, except when pyridine (**6**) was used as modifier. Interesting results were obtained with cycloaliphatic amines **11–13**. Quinuclidine (**11**) provided a 2-fold rate acceleration, whereas hexamethylenetetramine (**13**; pK_a lower by 2) decreased the average rate by the same degree. As a first approximation we propose that rate enhancement can be expected only when the pK_a value of the amine is around 10 or higher (except for the triarylamine, 5).

Influence of Amines on the Selectivity

Figure 2 demonstrates the advantage of using supported N-bases instead of increasing the pH of the aqueous solution. Here the rate of sorbose oxidation and the selectivity to 2-KLG is shown as a function of (i) the basicity of some tri- and tetraalkylamines (working at a bulk pH of 7.3) and (ii) the pH of the aqueous solution using unmodified Pt/alumina. The rate of sorbose consumption can be increased by increasing the bulk pH, but this results in a drop in selectivity to 2-KLG. Simple tetraalkylammonium hydroxides and trialkylamines provide rather poor selectivities, compared to those measured in the presence of aromatic and cycloaliphatic N-compounds (Table 3). Nevertheless, significantly higher selectivities were obtained at the same reaction rate when using catalytic amounts of trialkylamine or tetraalkylammonium hydroxide modifiers, compared to the case when the bulk pH was increased.

In the following part the discussion will be focused on the use of aromatic and cycloaliphatic amines, as our main purpose was to achieve the highest possible selectivity even at the expense of moderate oxidation rate.

The oxidation of L-sorbose on Pt/alumina (A, Table 1) modified with aromatic amines is characterized by a 5–10% increase in selectivity to 2-KLG up to 25–30% conversion, compared to the unmodified reaction. The change of selectivity with conversion in the presence of pyridine (**6**), quinoline (**7**), and acridine (**8**) as modifiers is illustrated in Fig. 3. The decrease of reaction rate with increasing number of benzene rings of the aromatic amines (**6**–**8** in Table 3) indicates an increasing "geometric blocking" of the Pt surface by the modifier. Unfortunately, this site blocking has only a minor positive effect on the selectivity. A similar but much more significant influence of the decrease of the size of active site ensembles by Bi adatoms has already been reported for alcohol oxidation (25, 38). A likely explanation for the minor blocking effect in the case of aromatic amines is that they can "move" relatively easily on the Pt surface and cannot efficiently decrease the size of active site ensembles.

The heteroaromatic amines studied have a planar two-dimensional structure. The possible influence of a three-dimensional-like structure was investigated using cycloaliphatic amines. Figure 4 shows the catalytic performance of Pt/alumina modified with quinuclidine (**11**), diazabicyclooctane (**12**), and hexamethylenetetramine (**13**). A significant improvement of selectivity over the whole investigated conversion range was achieved only with **13**. High selectivity of 97% at 20% conversion, compared to 81% for the unmodified reaction, was obtained. The decrease of selectivity above 20% conversion is attributed to consecutive side reactions (product degradation) which are not affected by the modifier. Another possible explanation is the partial protonation of **13** by the product 2-KLG or by acidic byproducts, which weakens the adsorption of the amine on

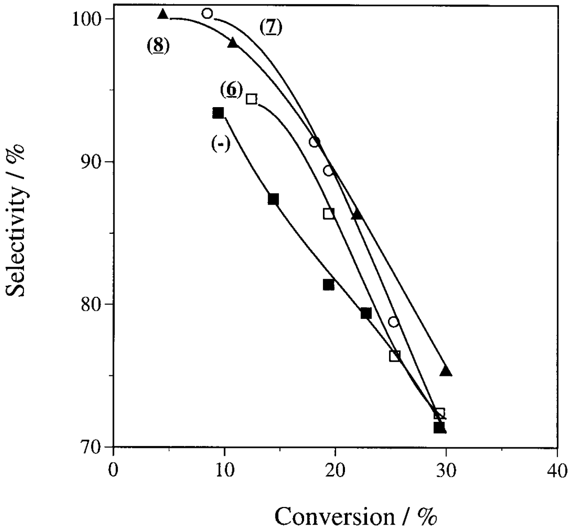


FIG. 3. Selectivity to 2-KLG as a function of sorbose conversion using (■) 5 wt% Pt/Al_2O_3 (A) without modification or modified with (□) pyridine (**6**), (○) quinoline (**7**), and (▲) acridine (**8**); modifier to Pt_s molar ratio of 0.1, standard conditions.

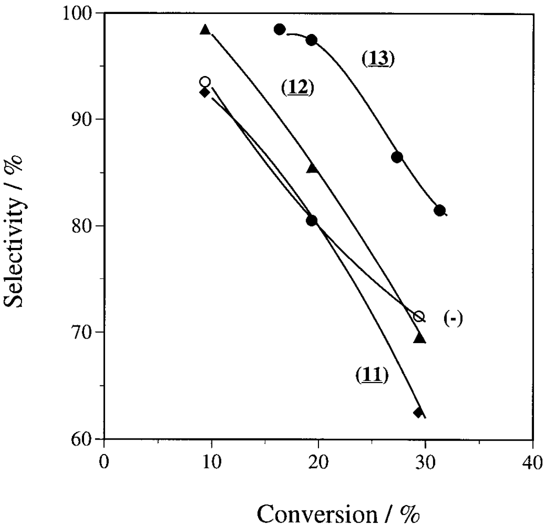


FIG. 4. Selectivity to 2-KLG as a function of sorbose conversion using (○) 5 wt% Pt/Al_2O_3 without modification (A) or modified with (●) hexamethylenetetramine (**13**), (◆) quinuclidine (**11**), and (▲) diazabicyclooctane (**12**); modifier to Pt_s molar ratio of 0.1, standard conditions.

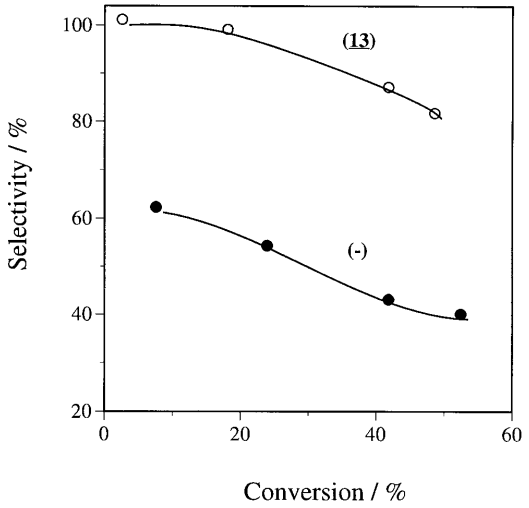


FIG. 5. Selectivity to 2-KLG as a function of sorbose conversion using (●) unmodified and (○) hexamethylenetetramine (**13**)-modified 5 wt% Pt/C (C); modifier to Pt_s molar ratio of 0.1, standard conditions.

Pt. At conversions higher than 30% the reaction became rather slow due to catalyst deactivation.

Comparison of Alumina- and Carbon-Supported Pt Catalysts

An attempt was made to improve selectivity and avoid catalyst deactivation by using other types of Pt catalysts. Typical results obtained with some alumina- and carbon-supported catalysts modified with hexamethylenetetramine (**13**) are shown in Table 4. The molar ratio of **13** to L-sorbose is 1 : 1700. In general, carbon-supported catalysts possess significantly higher activity than alumina-supported Pt. Pt/alumina (A) was used in previous studies as this catalyst afforded the highest selectivity with acceptable rate of sorbose oxidation (19). Unexpectedly, after modification with **13** the order of the catalysts with respect to their selectivity changed significantly. The best result, almost quantitative conversion of L-sorbose to 2-KLG at low conversion, was obtained with a Pt/C catalyst (C, Table 1). This catalyst provided rather poor selectivity without modifier, as illustrated in Fig. 5. Modification with **13** resulted in an average selectivity enhancement by 40% in the whole investigated conversion range. Interestingly, the outstanding performance of the 5 wt% Pt/C catalyst C is limited to modification with hexamethylenetetramine (**13**). When using modifiers **7**, **8**, **9**, **11**, or **12**, the selectivities at 30% conversion were significantly below those values obtained with the similarly modified 5 wt% Pt/alumina catalyst A.

TABLE 4

Oxidation of L-Sorbose to 2-KLG over Various Supported Pt Catalysts Modified with Hexamethylenetetramine (13); Standard Conditions

Catalyst	Composition[a]	S^b (%)	Rate[c] mmol (g_{cat} h^{-1})
A	Pt/alumina	81	1.23
B	Pt/alumina	29	0.82
C	Pt/C	95	4.56
D	Pt/C	47	5.95

[a] Pt loading of all catalysts 5 wt%.

[b] Selectivity at 30% conversion.

[c] Rate of L-sorbose consumption between 0 and 30% conversion.

Electrochemical Model Experiments

The real nature of the Pt–amine–sorbose interaction is not clear from the above results. Is the action of amines limited to base catalysis or do they also take part in the surface oxidation process? Electrochemical model experiments using polycrystalline Pt were performed to reveal some details of the role of amines. The use of unsupported Pt was necessary due to the conductivity requirements of the method. An aqueous solution with a pH of 7.3 was used, similarly to the catalytic measurements. Sodium acetate was applied as conductive salt to mimic the salts of 2-KLG (and other carboxylic acid by-products formed by chain-breaking (19) which are present during the oxidation reaction).

Four amines, tetramethylammonium hydroxide (**1**), triethylamine (**3**), pyridine (**6**), and hexamethylenetetramine (**13**) were chosen to represent the structurally different types of amines used for catalyst modification (Table 3). Figure 6 illustrates the influence of **6** on the hydrogen and oxygen sorption (as OH_{ad} in the neutral solution) characteristics of Pt. The shoulder and maximum on the

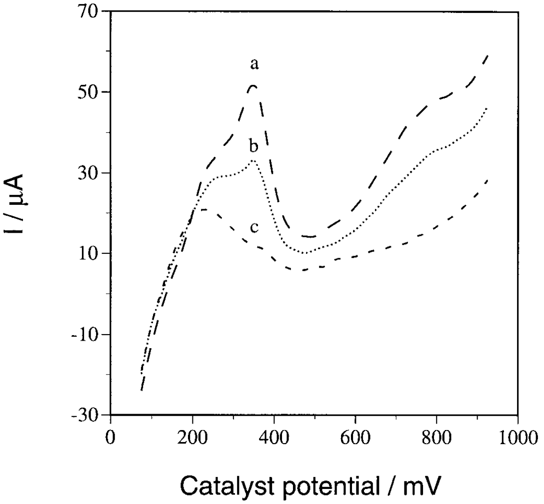


FIG. 6. Positive sweeps of the cyclic voltammograms of Pt in the absence (a) and in the presence of (b) 0.12 mg or (c) 1.2 mg pyridine (**6**); 1 wt% aqueous Na-acetate (pH adjusted to 7.3), 2 mg Pt, 2 mV s^{-1} sweep rate.

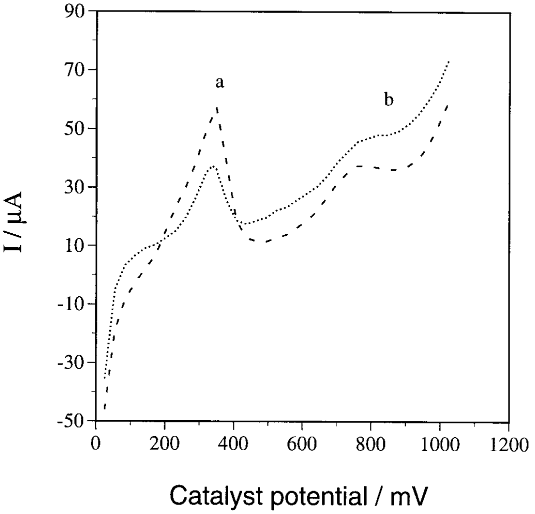


FIG. 7. Positive sweeps of the cyclic voltammograms of Pt (a) in the absence and (b) in the presence of triethylamine (**3**); 1 wt% aqueous Na-acetate (pH adjusted to 7.3), 2 mg Pt, 2 mV s^{-1} sweep rate.

curve of unmodified Pt at 250–350 mV corresponds to the oxidation of adsorbed hydrogen. The presence of **6**, a strongly adsorbing aromatic amine, suppresses both hydrogen and oxygen sorption (below and above ca. 450–500 mV, respectively) on Pt. The higher the amount of **6** injected into the cell during cathodic polarization, the lower is the amount of oxidized (preadsorbed) hydrogen and chemisorbed oxygen (the areas under the anodic sweeps of the voltammograms).

The oxidation of amine modifier itself on the Pt surface could be proved only in the case of triethylamine (**3**). In the presence of **3** a considerable increase in current density was observed in the oxygen region, compared to the reference curve of unmodified Pt (Fig. 7). The oxidation current between 0.45 and 1.0 V increased with increasing amount of **3** in the investigated low concentration range. For comparison, the reaction in the catalytic reactor runs mainly at a catalyst potential of around 0.7 V, as will be discussed below. It is not yet clear what is the extent of oxidation of **3** in the presence of sorbose.

All four types of amine decreased the amount of hydrogen adsorbed on Pt. The correlation between the amine concentration in solution and the coverage of Pt by amine has also been determined, based on the change in the hydrogen sorption characteristics of Pt (29, 30). Figure 8 shows that pyridine (**6**) adsorbs most strongly, as expected, but the other three types of amines also occupy a considerable fraction of active sites. The direct application of this quantitative correlation to Pt/C in the catalytic reactor is not possible as the amine : Pt$_S$: sorbose molar ratios are substantially different in the catalytic and electrocatalytic systems. Nevertheless, the electrochemical model experiments have provided unambiguous evidence that (i) a fraction of the amine modifier is adsorbed on the Pt surface and changes the adsorption characteristics of the active metal, and (ii) triethylamine is oxidized under reaction conditions but the other three types of amines can act only as bases during sorbose oxidation.

Figure 9 demonstrates that the unsupported Pt powder catalyst, dispersed on the rotating carbon paste electrode in the electrochemical cell, is really a good model for the behavior of Pt/C in the catalytic reactor. In the reactor the catalyst potential was measured with a combined electrode (Pt sheet + Ag/AgCl/KCl) during reaction. The catalyst potential is an *in situ* measure of the oxidation state of Pt: the

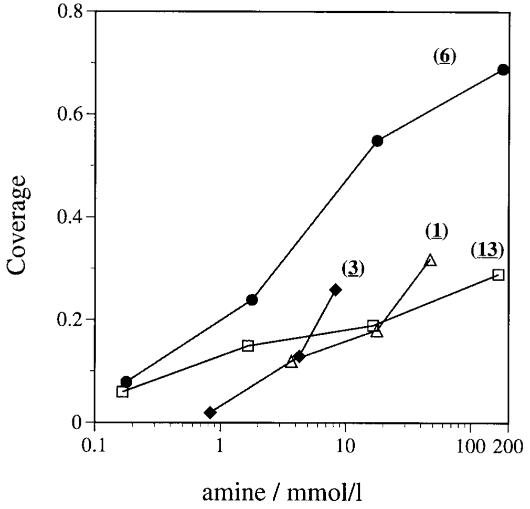


FIG. 8. Coverage of Pt by tetramethylammonium hydroxide (**1**), triethylamine (**3**), pyridine (**6**), and hexamethylenetetramine (**13**) as a function of amine concentration; 1 wt% aqueous Na-acetate (pH adjusted to 7.3), 2 mg Pt.

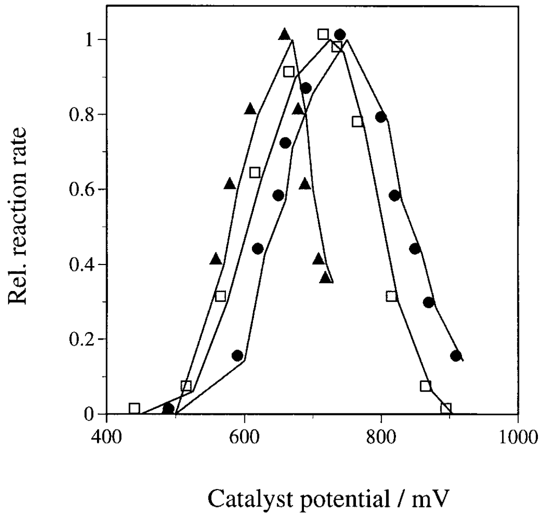


FIG. 9. Relative rate of sorbose oxidation as a function of the potential of (□) unsupported Pt, (●) Pt/C, and (▲) Pt/C modified with hexamethylenetetramine (**13**); modifier to Pt_s molar ratio of 0.1, standard conditions.

higher the potential above 0.45–0.5 V (in this solution), the higher is the oxygen-coverage of Pt (19). The correlation between the relative reaction rate and catalyst potential is very similar in the electrochemical cell and in the reactor, as shown in Fig. 9. The reaction rate is negligible at 0.5 V or below due to the self-poisoning of Pt by L-sorbose (19, 20). After the oxidative removal of by-products, the rate rapidly increases to its maximum at 0.7–0.75 V. A further increase of oxygen coverage (catalyst potential) suppresses the rate of sorbose oxidation due to the decrease of the proportion of active sites (Pt^0). The potential shift of ca. 30–50 mV between the curves of Pt and Pt/C is negligible compared to the different structures (dispersion, support effect, etc.) of the two catalysts.

There is a negative potential shift by 60–120 mV measured on Pt/C in the presence of hexamethylenetetramine (**13**) and related to the unmodified Pt/C (Fig. 9). Similar potential shifts by 50–100 mV in the negative direction were observed when using other types of tertiary amine or quaternary ammonium hydroxide modifiers. This shift may be due, at least in part, to the change of pH on the Pt surface compared to the bulk pH of the solution (see also the disturbance in Fig. 1 after the addition of pyridine).

DISCUSSION

Rate Acceleration by Modification with Amines

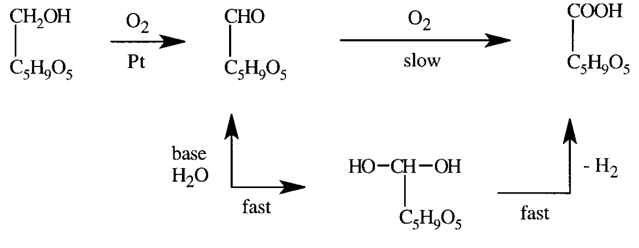
It has been shown that small amounts of supported tetraalkylammonium hydroxides and tertiary amines can significantly enhance the rate of Pt-catalyzed oxidation of L-sorbose to 2-keto-L-gulonic acid. Rate acceleration can be obtained with amines of rather different chemical structure, on condition that the pK_a value is around 10 or higher. This is a clear indication of a base-catalyzed reaction (bifunctional catalysis).

There is further evidence concerning the nature of Pt–amine–sorbose interaction during the oxidation reaction. Electrochemical model experiments proved that all four types of amines (tetraalkylammonium hydroxides, trialkyl-, triaryl, and cycloaliphatic amines) are partially adsorbed on Pt under reaction conditions. The cyclic voltammetric study also showed that triethylamine (**3**) can be oxidized on Pt, but the other types of amines can influence the sorbose oxidation only as bases. It is not yet clear whether there is any interaction between the oxidation of sorbose and **3**.

The effect of supported N-bases is more advantageous than increasing the pH of the aqueous medium. In the latter case even a moderate gain in reaction rate is accompanied by a striking loss of selectivity. Using a tertiary amine or quaternary ammonium hydroxide modifier in catalytic amounts, the selectivity is always higher (at the same rate) than that obtained with unmodified catalyst at higher bulk pH (Fig. 2).

It is known (8, 9) that bases can accelerate the hydration of the aldehyde intermediate of the alcohol → carboxylic acid transformation, as shown schematically in Scheme II. The oxygen insertion to an aldehyde requires higher oxygen coverage of Pt than the oxidative dehydrogenation of an alcohol or geminal diol ("hydrate"), which explains why the former route is considerably slower and why nonhydrating aldehydes can be prepared in good yield (38, 39). A strong support to this conception is the frequently reported absence of pH dependence of the alcohol → carbonyl compound type transformations (39–42). Note that there are other possible interpretations of the effect of bases on the reaction rate, such as the base-catalyzed deprotonation of the hydroxyl group as the first step of the oxidation reaction (31), or the change with pH of surface coverage of Pt by oxygen and reactant (16).

In order to use the rate accelerating effect of amines, they have to be applied in a rather low concentration, typically in a molar ratio of modifier to Pt_s of 0.1–0.2. The amines cover a fraction of active sites (Pt^0) and this effect can surpass the positive influence of base catalysis. The geometric blocking of active sites is clearly indicated by the decreasing



SCHEME II

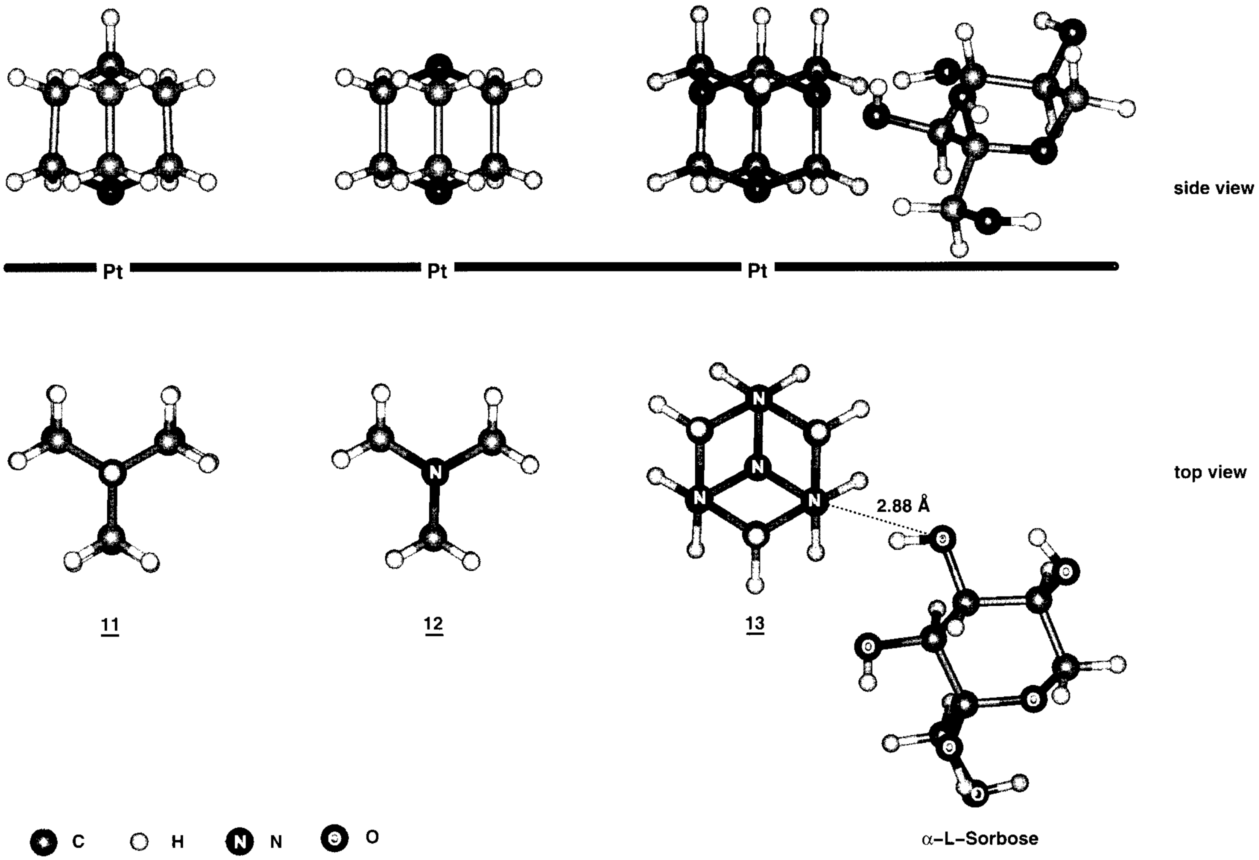


FIG. 10. Side and top views of the models for adsorption on a flat Pt surface of quinuclidine (**11**), diazabicyclooctane (**12**), and an optimized hexamethylenetetramine (**13**)–L-sorbose (α-L-sorbopyranose) complex.

rate of sorbose consumption with increasing number of benzene rings of aromatic amine modifiers **6**–**8**, under otherwise identical conditions.

Trialkyl- and triarylamines are assumed to adsorb on Pt with the electron-rich N atoms lying on the surface ("anchoring" atom) and being surrounded by alkyl or aryl moieties. Their interaction with the *adsorbed* aldehyde intermediate resulting in base-catalyzed hydration is unlikely, as (i) the basicity of the adsorbed N atom should be significantly smaller after interaction with Pt, and (ii) the N atom is sterically not accessible to the carbonyl group of the adsorbed intermediate. It is assumed that the adsorbed amine is only a "reservoir"; the hydration of the reaction intermediate is catalyzed by an unadsorbed amine molecule close to the Pt surface.

*High Selectivity with Hexamethylenetetramine (**13**)*

An intriguing question is to enquire "What is the nature of interaction between Pt, L-sorbose, and hexamethylenetetramine (**13**) which provides the outstanding selectivity to 2-keto-L-gulonic acid?" Although a definite answer cannot be given based on the presented results, we think that a comparison of the structure and influence of the cycloaliphatic amines quinuclidine (**11**), diazabicyclooctane (**12**), and hexamethylenetetramine (**13**) provides some insight. The minimum energy conformations of these modifiers are shown in Fig. 10. The monoamine **11** is likely to be adsorbed on a flat Pt surface as illustrated: the molecule is anchored to the Pt surface (soft acid) by the N-atom (soft base). In this most stable form the N atom is not accessible to any interaction with L-sorbose due to the shielding effect of the alkyl chains, which conclusion is in agreement with the observed negligible effect on selectivity (Fig. 4). Nevertheless, the unadsorbed amine can act as a strong base ($pK_a = 10.9$) which explains the rate acceleration by a factor of 2 (Table 3), as discussed above.

The optimized structure of diamine **12**, adsorbed on a flat Pt surface, is rather similar to that of **11**, except for the second N atom at the "top" of the molecule. This basic N atom is accessible to interaction with L-sorbose but the complex cannot easily adsorb on a flat Pt surface. This amine provides some moderate (5–6%) increase in selectivity to 2-KLG at low conversion, but this positive effect is eliminated by side reactions above 25% conversion (Fig. 4).

The tetramine **13** is proposed to be adsorbed by one N atom facing to a Pt atom. An "upside-down" adsorption mode in which three N atoms could interact with the Pt surface (modeled on an ideal Pt (111) structure) is sterically hindered by the surrounding three methylene groups. When using this amine as modifier, the accessibility of one of the N atoms to an interaction with one of the OH functional groups of L-sorbose is the highest. Several possible complexes between L-sorbose and modifier **13** were optimized. A common feature of these complexes is that after adsorption on a flat Pt surface, the pyranose ring of sorbose is in a tilted, "partially adsorbed" position. Note that the α-L-sorbopyranose structure was considered in the calculations as L-sorbose is present mainly in this form (95%) in aqueous solutions and at ambient temperature (43). Figure 10 shows one example of a H-bond stabilized (by 29 kJ mol^{-1}) assembly of L-sorbose and hexamethylenetetramine **13**. (It is very likely that the other two unadsorbed N atoms also interact with sorbose or water molecules by H-bonding, which is not shown here.) The steric arrangement of the presented **13**–sorbose complex can explain the outstanding preference to C-1 oxidation: only the C-1–O–H fragment of the tilted sorbose molecule is close to the Pt surface, liable to oxidative dehydrogenation.

CONCLUSIONS

It has been demonstrated that the modification of supported Pt by traces of tertiary amines and quaternary ammonium hydroxides can significantly enhance the rate and/or selectivity of sorbose oxidation. The efficiency of this new method is far better than that of tuning the bulk pH of the solution or modifying Pt by heavy metal adatoms. It is likely that the method can be applied in other Pt- or Pd-catalyzed oxidations of sensitive compounds, such as polyols.

A model for the Pt–amine–sorbose interaction which provides a possible explanation for the rate acceleration and selectivity enhancement observed has been proposed. The future refinement of this model requires further evidence concerning the catalytic influence of amines on each of the consecutive reaction steps of the alcohol → acid transformation and the effect of oxidation products on the Pt–amine–sorbose interaction.

ACKNOWLEDGMENTS

Financial support of this work by Hoffmann-La Roche AG, Switzerland, and the "Kommission zur Förderung der wissenschaftlichen Forschung" is gratefully acknowledged.

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