The Oxidation of Gluconic Acid with Platinum on Carbon as Catalyst

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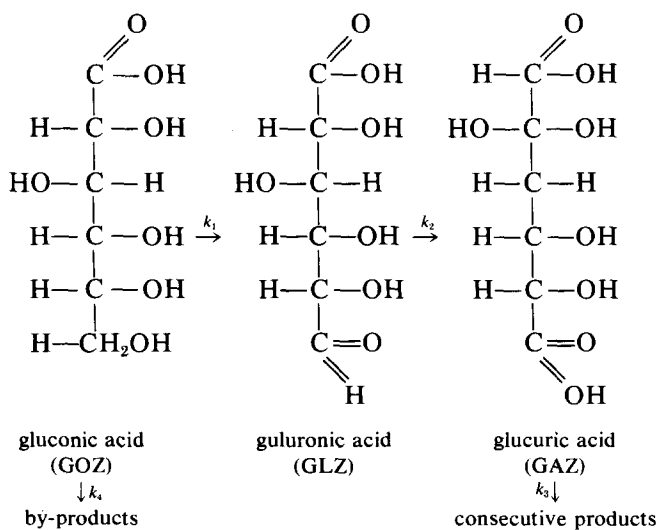*Department of Chemical Engineering, University of Technology, Eindhoven, The Netherlands*

In the oxidation of gluconic acid with platinum on carbon as catalyst, a deactivation of the catalyst takes place due to both chemisorption of oxygen (formation of Pt–O) and oxidation of the platinum surface (formation of PtO_2). Both types of deactivation can be reversed by temporarily replacing the oxygen flow by a nitrogen flow. Chemisorbed oxygen reacts relatively rapidly with the intermediate product guluronic acid and relatively slowly with gluconic acid and glucaric acid. Consequently, the degree of coverage by chemisorbed oxygen changes in batch experiments due to the change of the concentration of gluconic acid and its reaction products. The deactivation due to the formation of PtO_2 and the oxidation reaction are chemically coupled, and are explained in the same way as in the oxidation of glucose.

INTRODUCTION

In the preceding paper (*1*) we described the oxidation of glucose with platinum on carbon (Pt/C) as catalyst. In the course of an experiment, a strong inhibition of the catalyst activity took place, which was thought to be due to the formation of platinum oxide (PtO_2). In the present article, we will discuss the oxidation of gluconic acid

with Pt/C as catalyst. The oxidation of gluconic acid to glucaric acid proceeds via the intermediate product L-guluronic acid: by-products are formed by catalytic side reactions starting from both gluconic acid and glucaric acid (*2*). The situation is somewhat different from that found in the oxidation of glucose, because gluconic acid reacts relatively slowly with chemisorbed oxygen (Pt–O), so that the decrease in the reaction rate is effected both by chemisorbed oxygen and by the formation of PtO_2.

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gluconic acid
(GOZ)
$\downarrow k_4$
by-products

guluronic acid
(GLZ)

glucuric acid
(GAZ)
$k_3\downarrow$
consecutive products

14

EXPERIMENTAL

The experiments were carried out in a stirred-tank batch reactor. The experimental procedure and the preparation of the catalyst were the same as in the oxidation of glucose (*1*). Two different starting procedures were used.

Starting procedure A. The catalyst suspension was brought to the required temperature in the oxidation gas atmosphere (gas flow rate: 1 liter/min), and the experiment was started by introducing the concentrated gluconic acid solution into the reactor.

Starting procedure B. The catalyst suspension was brought to the required temperature in a nitrogen atmosphere. After introducing the concentrated gluconic acid solution into the reactor, the suspension was kept in a nitrogen atmosphere for 10 min. Thereafter, the nitrogen flow was stopped, and the experiment was started by introducing oxygen or the oxygen-containing gas at a flow rate of 1 liter/min.

The following reaction products are formed in the oxidation of gluconic acid: guluronic acid, glucaric acid, and C_1–C_5 mono- and dicarboxylic acids. Gluconic, guluronic, and glucaric acids were analyzed by means of ion-exchange chromatography (*2*), and the C_1–C_5 mono- and dicarboxylic acids could be analyzed by means of isotachophoresis (*3*).

Unless stated otherwise, the following reaction conditions were applied:

[GOZ]$_0$ (mmol/liter)	[cat] (g/liter)	V_0 (liter)	O$_2$ in oxidation gas (%)	T (°C)	pH	Pt/C (%)
200	40	0.500	100	55	10	5

RESULTS

Figure 1 gives the concentration of gluconic acid as a function of the reaction time for both starting procedures A and B, and it is seen that they result in widely different reaction rates. In the case of the oxidation
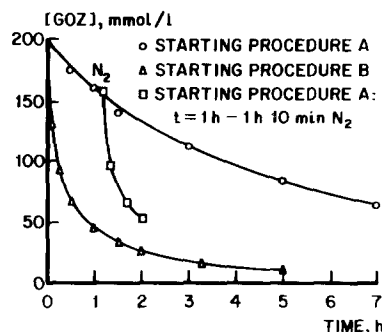

FIG. 1. Influence of the starting procedure on the oxidation rate of gluconic acid.

of gluconic acid, this difference is about a factor 14, whereas with the oxidation of glucose it was only a factor of 1.4. With starting procedure B the initial reaction rate did not change when the catalyst was kept together with gluconic acid in a nitrogen atmosphere for only 1 min instead of the customary 10 min. An initial reaction rate which was between those of the two starting procedures was obtained when the oxygen flow was started immediately after the addition of gluconic acid to the catalyst suspension in a nitrogen atmosphere (contact time between gluconic acid and the catalyst in the nitrogen atmosphere was about 0.5 min).

If starting procedure B is applied, an initially fast reaction takes place immediately after adding the gluconic acid solution to the catalyst suspension in a nitrogen atmosphere. This reaction stops in less than 1 min: guluronic acid and glucaric acid (respectively 7 and 2 mmol/liter) are the main reaction products. The rate of this reaction is much lower in an oxygen atmosphere than in a nitrogen one: in a sample taken after a reaction time of 1 min in an experiment with starting procedure A, the concentrations of guluronic acid and glucaric acid were, 2 and 1 mmol/liter, respectively.

Temporarily replacing the oxygen flow by a nitrogen flow results in an increase in the reaction rate both with starting procedure A and with procedure B. This is

illustrated in Fig. 1 for the case of starting procedure A. Replacing the oxygen flow by a nitrogen flow for a period of 10 min after a reaction time of 1 hr results in a reaction rate which is almost the same as the initial reaction rate obtained with starting procedure B.

Gluconic acid which is formed during the oxidation of glucose (starting procedure A) is oxidized much faster than when under the same conditions gluconic acid itself is used as starting material. This is illustrated in Fig. 2, which gives the course of the oxidation of gluconic acid when the experiment (initial concentration: 200 mmol liter^{-1}, pH = 10, 55°C, 20 g 5% Pt/C, starting procedure A) is started with respectively glucose and gluconic acid. At the conditions applied, glucose is oxidized rapidly to gluconic acid: the reaction is complete within about 15 min.

The influence of the adsorption of oxygen on the reaction rate was investigated as follows. The catalyst (10 g 5% Pt/C) was reduced with gluconic acid in a nitrogen atmosphere. Subsequently, the catalyst was filtered off in a nitrogen atmosphere and washed with oxygen-free water. This reduced catalyst was transferred to the reactor. After having been heated to a temperature of 55°C, the catalyst slurry was contacted with oxygen for various times, before the reaction was started by the addition of a concentrated gluconic acid solution to the reactor contents. In Table 1, the
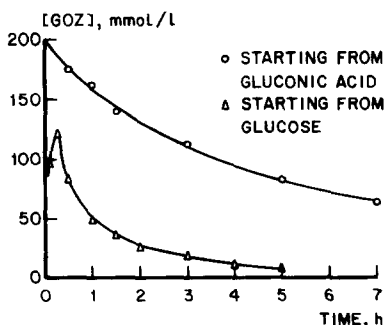
TABLE 1

Initial Reaction Rate as a Function of the Contact Time τ between Catalyst and Oxygen

τ (min)	r_0 (mmol liter^{-1} min^{-1})
0 (starting procedure B)	8.0
5	2.5
30	1.4
60	1.1
150	0.78
∞ (starting procedure A)	0.57

initial reaction rate is given as a function of the contact time τ with oxygen. We see that a considerable contact time between oxygen and an initially reduced catalyst is required to deactivate a catalyst through oxygen adsorption.

The inhibiting effect by chemisorbed oxygen was further studied in experiments with various oxygen concentrations, using starting procedure B. In Fig. 3A, the concentration of gluconic acid is given as a function of the reaction time for different oxygen concentrations (dilution with nitrogen, oxygen flow rate: 1 liter/min in all cases). The reaction rate increases at decreasing oxygen concentration. In the oxidation of glucose, in which case an inhibiting effect by chemisorbed oxygen is very slight or not observed at all, a positive order of 0.2–0.3 in the oxygen concentration was found.

The starting procedure not only influences the reaction rate, but also has a considerable effect on the product distribution. Gluconic acid (GOZ) is oxidized to glucaric acid (GAZ) via the intermediate product guluronic acid (GLZ): by-products are formed starting from gluconic acid and glucaric acid:

$$GOZ \xrightarrow{k_1} GLZ \xrightarrow{k_2} GAZ \xrightarrow{k_3} \text{consecutive products}$$
$$\xrightarrow{k_4} \text{by-products.}$$

FIG. 2. Oxidation of gluconic acid starting from glucose and gluconic acid.
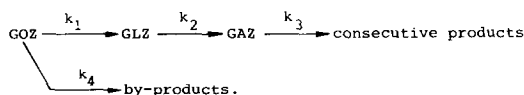
In Figs. 4A and B the concentrations of guluronic acid and glucaric acid are given
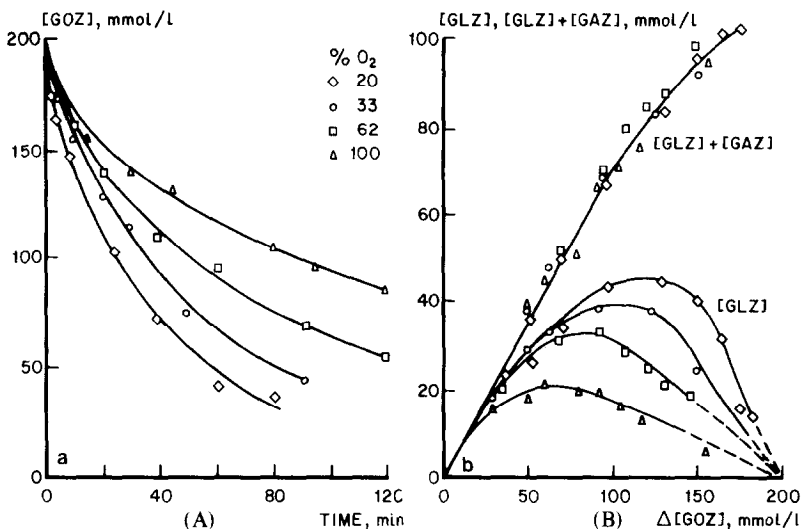
FIG. 3. (A) Reaction rate as a function of the reaction time at various oxygen concentrations. (B) Distribution of main products as a function of the gluconic acid conversion at various oxygen concentrations.

as a function of the concentration of gluconic acid for starting procedures A and B, respectively. If starting procedure B is applied, a relatively high concentration of the intermediate product is obtained.

DISCUSSION

If the catalyst is reduced with gluconic acid before the start of the experiment, a much higher initial reaction rate is obtained than in the case that the catalyst is initially covered by chemisorbed oxygen (Fig. 1). Further, the initial activity of a reduced catalyst decreases when this catalyst is contacted with oxygen before gluconic acid is added to the reactor contents. From these observations we conclude that in the presence of gaseous oxygen and starting
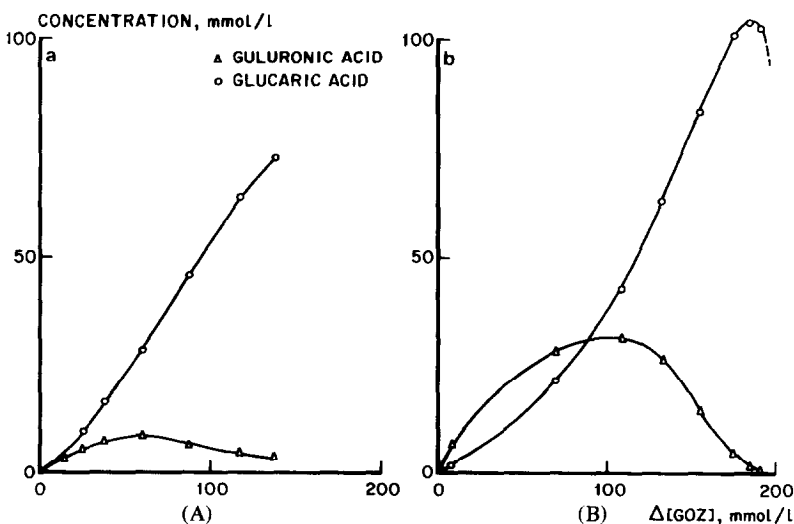
FIG. 4. (A) Distribution of main products as a function of the gluconic acid conversion (starting procedure A). (B) Distribution of main products as a function of the gluconic acid conversion (starting procedure B).

from a high degree of coverage by chemisorbed oxygen, gluconic acid reacts rather slowly with chemisorbed oxygen. If we suppose that adsorption of gluconic acid on the catalyst surface can be described with a single-site Langmuir–Hinshelwood model, we can write for the degree of coverage of gluconic acid, θ_{GOZ}:

$$\theta_{GOZ} = \frac{K_2[GOZ]}{1 + K_2[GOZ]} (1 - \theta_{Pt-O}) \quad (1)$$

where:

K_2 = adsorption constant of gluconic acid, liter mmol^{-1}

θ_{Pt-O} = degree of coverage by chemisorbed oxygen.

If the reduction of the catalyst can be described by reaction between an adsorbed gluconic acid molecule and a chemisorbed oxygen atom, we can write for the reduction rate r (mmol liter^{-1} min^{-1}):

$$r = k_r' \cdot \theta_{Pt-O} \, \theta_{GOZ} \, [cat] \quad (2)$$

where:

k_r' = reaction rate constant, mmol g^{-1} min^{-1}

[cat] = catalyst concentration g liter^{-1}.

Thus, we can write for the reaction rate r between adsorbed gluconic acid and chemisorbed oxygen:

$$r = -\frac{d[GOZ]}{dt} = \frac{k_r[GOZ]}{1 + K_2[GOZ]}$$
$$(1 - \theta_{Pt-O}) \, \theta_{Pt-O}[cat] \quad (3)$$

where $k_r = k_r'K_1$ = reaction rate constant, liter g^{-1} min^{-1}.

If gluconic acid is added to a catalyst which is covered with chemisorbed oxygen, the reduction rate of the catalyst can initially increase [$(1 - \theta_{Pt-O}) \, \theta_{Pt-O}$ will initially increase] if gaseous oxygen is absent (starting procedure B) and can lead to reduction of the catalyst. In the presence of gaseous oxygen (starting procedure A), adsorption of oxygen can take place on reduced platinum sites, so that the degree of coverage by chemisorbed oxygen can remain high.

If glucose instead of gluconic acid (Fig. 2) is oxidized an almost complete reduction of the catalyst takes place, because glucose reacts very rapidly with chemisorbed oxygen. This explains the much higher oxidation rate of gluconic acid if the experiment (starting procedure A) is started with glucose instead of gluconic acid. It is known that oxygen adsorbs very fast on platinum as Pt–O. From Table 1, however, it is concluded that a considerable period of time is required to deactivate a reduced catalyst through oxygen adsorption. This is explained by formula (3). At a high θ_{Pt-O} we write:

$$r = -\frac{d[GOZ]}{dt} \sim (1 - \theta_{Pt-O}). \quad (4)$$

Thus, with the above assumption the reduction rate is proportional to $(1 - \theta_{Pt-O})$. This explains the large difference in reaction rate between starting procedure A and B during a considerable part of the experiments, and the rather long period of time required to deactivate a catalyst through oxygen adsorption.

The above conclusions remain the same if it is supposed that more than one platinum site is involved in the adsorption of gluconic acid.

From Figs. 4A and B it was concluded that the product distribution depends upon the starting procedures applied. The following equations can be derived if the adsorption of gluconic acid and reaction products on the catalyst surface is described by a single-site Langmuir–Hinshelwood model.

$$-\frac{d[GOZ]}{dt} = \frac{(k_1 + k_4)[GOZ]}{1 + \sum_i K_i[i]} [cat] \quad (5)$$

$$+\frac{d[GLZ]}{dt} = \frac{k_1[GOZ] - k_2[GLZ]}{1 + \sum_i K_i[i]} [cat] \quad (6)$$

in which K_i = adsorption constant of product i. The rate constants k_1–k_4 depend upon θ_{Pt-O}, and thus they change during an experiment. The denominators of Eqs. (5)

and (6) represent the reversible adsorption of the various reactants on the catalyst surface, and [cat] represents the *active* catalyst surface. Equation (7) is obtained by dividing Eq. (6) by Eq. (5):

$$-\frac{d[GLZ]}{d[GOZ]} = K_1 - K_2 \frac{[GLZ]}{[GOZ]} \qquad (7)$$

where $K_1 = k_1/(k_1 + k_4)$ and $K_2 = k_2/(k_1 + k_4)$. If the selectivity S is defined here by Eq. (8):

$$S = \frac{[GLZ] + [GAZ]}{[GOZ] - [GOZ]} \qquad (8)$$

then K_1 represents the initial selectivity.

For both starting procedures A and B we find $K_1 = 0.70 \pm 0.05$. K_2 represents the oxidation rate of guluronic acid relative to the oxidation rate of gluconic acid, and this is the term which is of interest here. K_2 was calculated from the slopes of the GLZ curves in Figs. 4A and B, and is given in Fig. 5 as a function of the reaction time for both starting procedures A and B. As was clear from Figs. 4A and B, K_2 is much higher in starting procedure B. In the oxidation of glucose, it was found that the aldehyde group reacts much faster with chemisorbed oxygen than does the alcohol group. This observation can explain the difference in K_2 between starting procedures A and B. If starting procedure A is applied, the degree of coverage by chemisorbed oxygen is high from the beginning of the experiment,

so that guluronic acid is oxidized relatively fast to glucaric acid. In experiments with the commercially available isomer D-glucuronic acid, only a small difference in reaction rate between starting procedures A and B was found and the rates were comparable to those found for the oxidation of glucose.

K_2 increases as a function of the reaction time if starting procedure B is applied, which is explained by a higher θ_{Pt-O} at longer reaction times. In starting procedure A, K_2 decreases especially in the beginning of the experiment. This suggests that initially some decrease of θ_{Pt-O} takes place due to the competition of the oxygen adsorption and the chemical reaction.

The experiments at various oxygen concentrations also illustrate the influence of the degree of coverage by chemisorbed oxygen on the distribution of the main products. In Fig. 3B [GLZ] and [GLZ] + [GAZ] are given as a function of the gluconic acid conversion (Δ[GOZ]) of the experiments of Fig. 3A. [GLZ] + [GAZ] hardly depends upon the oxygen concentration, i.e., the selectivity (Eq. (8)) remains constant, but [GLZ] strongly increases with decreasing oxygen concentrations, and thus with decreasing θ_{Pt-O}.

Until now, the various phenomena in the oxidation of gluconic acid have been explained qualitatively by the degree of coverage of the catalyst by the degree of coverage of the catalyst by chemisorbed oxygen. However, the deactivation due to the formation of PtO_2, which was found to play an important role in the oxidation of glucose (*1*), is also an important factor in the oxidation of gluconic acid. This was established as follows. Gluconic acid was oxidized over a period of 16 hr, and thereafter glucose was added to the reactor contents. The oxidation rate of glucose was much lower than the rate which is obtained if gluconic acid is not oxidized before the start of the oxidation of glucose. The decrease of the reaction rate could be ascribed only to a minor extent to the adsorption of gluconic
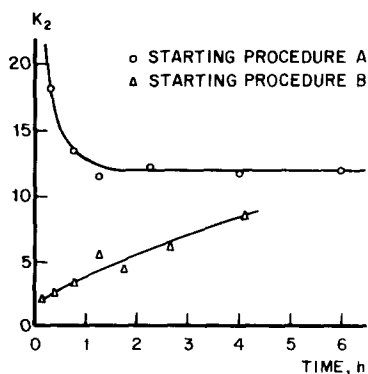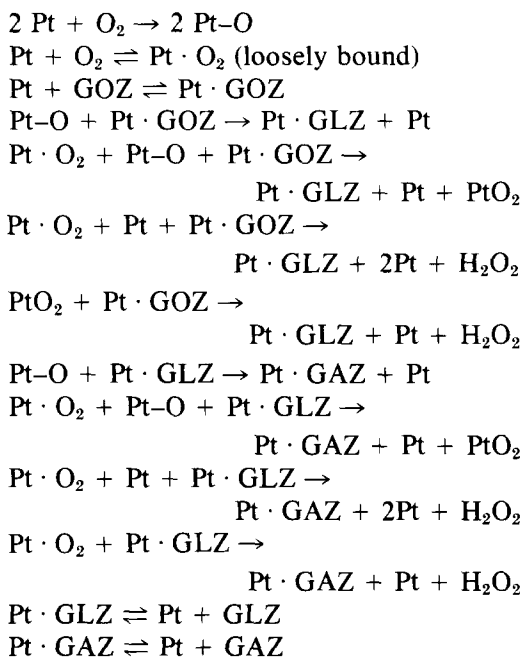

FIG. 5. K_2 as a function of the reaction time for starting procedures A and B.

acid or its reaction products on the catalyst surface, as a strong increase in the reaction rate was obtained by temporarily stopping the oxygen flow. Thus, on the basis of this experiment and the experiments on the oxidation of glucose (1), we assume that deactivation in the oxidation of gluconic acid is due to the formation of both Pt–O and PtO_2.

By analogy with the oxidation of glucose, we propose the following reaction scheme for the oxidation of gluconic acid:

$2 Pt + O_2 \rightarrow 2 Pt–O$
$Pt + O_2 \rightleftharpoons Pt \cdot O_2$ (loosely bound)
$Pt + GOZ \rightleftharpoons Pt \cdot GOZ$
$Pt–O + Pt \cdot GOZ \rightarrow Pt \cdot GLZ + Pt$
$Pt \cdot O_2 + Pt–O + Pt \cdot GOZ \rightarrow$
$\qquad\qquad\qquad Pt \cdot GLZ + Pt + PtO_2$
$Pt \cdot O_2 + Pt + Pt \cdot GOZ \rightarrow$
$\qquad\qquad\qquad Pt \cdot GLZ + 2Pt + H_2O_2$
$PtO_2 + Pt \cdot GOZ \rightarrow$
$\qquad\qquad\qquad Pt \cdot GLZ + Pt + H_2O_2$
$Pt–O + Pt \cdot GLZ \rightarrow Pt \cdot GAZ + Pt$
$Pt \cdot O_2 + Pt–O + Pt \cdot GLZ \rightarrow$
$\qquad\qquad\qquad Pt \cdot GAZ + Pt + PtO_2$
$Pt \cdot O_2 + Pt + Pt \cdot GLZ \rightarrow$
$\qquad\qquad\qquad Pt \cdot GAZ + 2Pt + H_2O_2$
$Pt \cdot O_2 + Pt \cdot GLZ \rightarrow$
$\qquad\qquad\qquad Pt \cdot GAZ + Pt + H_2O_2$
$Pt \cdot GLZ \rightleftharpoons Pt + GLZ$
$Pt \cdot GAZ \rightleftharpoons Pt + GAZ$

In this reaction scheme only the oxidation of gluconic acid to guluronic acid and the consecutive reaction to glucaric acid are taken into account.

Oxygen can be adsorbed either strongly and dissociatively as Pt–O or weakly as molecular adsorbed oxygen ($Pt \cdot O_2$). This latter form of adsorption was postulated for the oxidation of glucose (1).

The rate of the reaction between chemisorbed oxygen and adsorbed gluconic acid is much lower than the reaction rate between chemisorbed oxygen and adsorbed glucose. Consequently, a strong difference in reaction rate between glucose and gluconic acid is found if the reaction is started with a catalyst saturated with chemisorbed oxygen. This agrees with the high selectivity for gluconic acid in the glucose case (1) for reduction of a catalyst which is saturated with chemisorbed oxygen.

In the oxidation of glucose it was found that the alcohol group of glucose can react with weakly adsorbed molecular oxygen, and the same reactions are postulated here for the oxidation of gluconic acid. Just as in the oxidation of glucose, a deactivation due to the formation of PtO_2 takes place.

The aldehyde group of the intermediate product guluronic acid is believed to react in the same way as the aldehyde group of glucose, on the basis of the observation that the reaction rates of glucose and glucuronic acid are about the same, and that in the case of the oxidation of glucuronic acid a strong deactivation takes place due to the formation of PtO_2.

According to the above reaction scheme, the reduction of PtO_2, which is formed during the reaction, can take place by reaction with either adsorbed glucose or adsorbed guluronic acid. Since in the reduction of a deactivated catalyst (due to PtO_2) with glucose a high selectivity toward gluconic acid was found, it was concluded that the aldehyde group of glucose reacts much faster with PtO_2 than does the alcohol group. Therefore, it is reasonable to state that guluronic acid reacts with PtO_2 much faster than gluconic acid.

REFERENCES

1. Dirkx, J. M. H., and van der Baan, H. S., *J. Catal.* **66**, 1–13.
2. Dirkx, J. M. H., and Verhaar, L. A. Th., *Carbohydr. Res.* **73**, 287 (1979).
3. Dirkx, J. M. H., van der Baan, H. S., and van den Broek, J. M. A. J. J., *Carbohydr. Res.* **59**, 63 (1977).
4. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).
5. Spenadel, L., and Boudart, M., *J. Phys. Chem.* **64**, 204 (1960).