JOURNAL OF CATALYSIS 67, 1–13 (1981)

The Oxidation of Glucose with Platinum on Carbon as Catalyst

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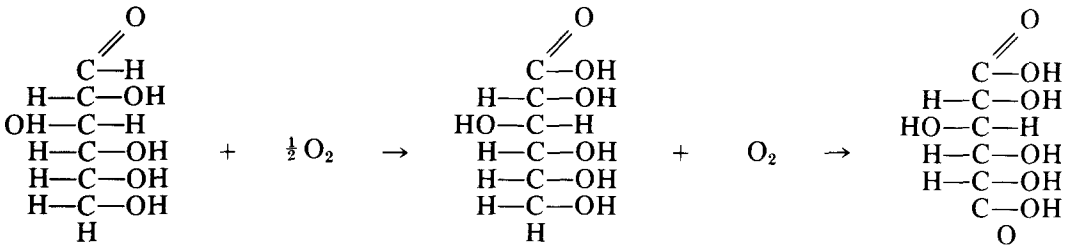
Received April 2, 1979; revised June 25, 1980

This paper deals with the oxidation of glucose in a weakly alkaline medium with platinum on carbon as catalyst. Glucose reacts very fast with chemisorbed oxygen (Pt–O) to yield gluconic acid, while in an oxygen-containing atmosphere a side reaction occurs, resulting in the formation of appreciable amounts of uronic acids. Most probably, this side reaction involves molecular oxygen, resulting in the oxidation of both the primary alcohol group and the aldehyde group of glucose. In the course of an experiment a strong catalyst deactivation takes place, which can be reversed by temporarily replacing the oxygen flow by a nitrogen flow. The deactivation of the catalyst is ascribed to the formation of platinum oxide (PtO_2). The formation of PtO_2 and the oxidation of glucose are chemically coupled. The reactivation of the catalyst in the absence of oxygen is a reduction reaction between PtO_2 and adsorbed glucose.

INTRODUCTION

Carbohydrates are produced in nature in large quantities by photosynthesis and can be used as a feedstock for the chemical industry. Surveys of the industrially interesting reactions of carbohydrates are given in the literature (*1–3*). This paper deals with one of these reactions, the oxidation of carbohydrates, and more specifically the oxidation of glucose with platinum on carbon as catalyst.



These oxidation products, gluconic acid and glucaric acid, have a high sequestering capacity, i.e., the capacity to form soluble complexes with metal ions, and are therefore possible alternatives for the polyphosphates in synthetic detergent compositions.

The oxidation of glucose is carried out in a weakly alkaline aqueous medium with oxygen as oxidizing agent. De Wilt and van der Baan (*4*) studied the kinetics of the oxidation of glucose to gluconic acid with Pt/C (platinum on carbon) as catalyst. The kinetic model developed by De Wilt and based on the dehydrogenation mechanism (*5*), has been generally accepted:

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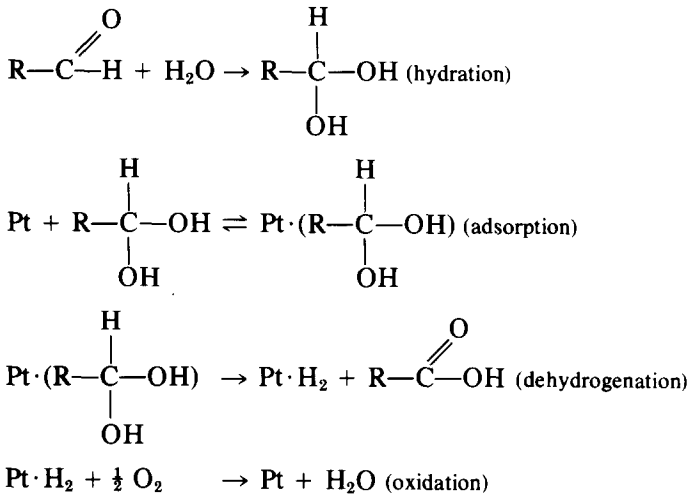


During our study of the oxidation of glucose and gluconic acid, we observed phenomena that could not be explained by the above mechanism. We developed a new model in which the interaction between oxygen and the platinum catalyst is a very important factor. This reaction model is the subject of the present paper.

EXPERIMENTAL

Nomenclature

A	Catalyst activity
[cat]	Catalyst concentration (mmol liter^{-1})
G	Glucose
Δ[G]	Glucose conversion
GDA	Glucose dialdehyde
GOZ	Gluconic acid
K	Adsorption constant (liter^{-1} mmol)
k_r	Reaction rate constant (liter (g cat)$^{-1}$ min^{-1})
r	Reaction rate (mmol liter^{-1} min^{-1})
r_0	Initial reaction rate (mmol liter^{-1} min^{-1})
S	Selectivity
t	Time (min)
θ	Degree of coverage
θ_{Pt-O}	Degree of coverage by chemisorbed oxygen
θ_{PtO_2}	Degree of oxidation of the platinum surface

General Reaction Procedure

The experiments were carried out in a batchwise operated, vigorously stirred tank reactor. A sketch of this reaction system is given in Fig. 1. The pH of the reaction mixture was controlled by automatic titration.

The experimental procedure was as follows. The required amount of catalyst + 450 ml water were heated in the reactor to the required temperature. Then, 50 ml of a concentrated glucose solution, which was at the required temperature and pH, was added. During an experiment a number of samples (about 5 ml) were taken with a syringe. After the catalyst was filtered off, the samples were stored in a refrigerator until analysis. Corrections were applied for the dilution with alkali and sampling. 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 glucose solution into the reactor.

Starting procedure B. The catalyst was brought to the required temperature in a nitrogen atmosphere. After introducing the concentrated glucose solution into the reactor, the suspension was kept in a nitrogen

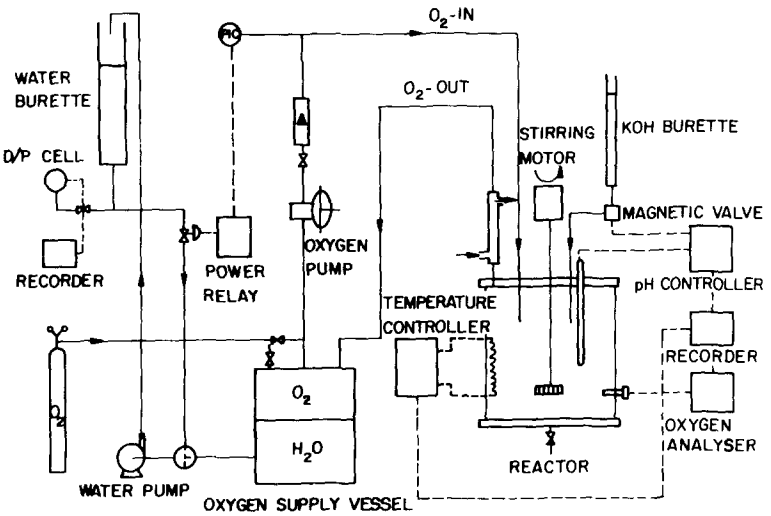


FIG. 1. Batch reaction system.

atmosphere for 10 min. Thereafter, the nitrogen flow was stopped, and the experiment started by introducing oxygen or the oxygen-containing gas at a rate of 1 liter/min.

Unless stated otherwise, the following reaction conditions were applied:

$[G]_0$ (mmol/liter)	[cat] (g/liter)	V_0 (liter)	O_2 in oxidation gas (%)	T (°C)	pH	Pt/C (%)
200	4	0.500	100	55	9	5

The reaction rate was not limited by the mass transfer rate.

Preparation of the Catalyst

A solution of 10 g hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) in 100 ml H_2O was added to 72 g active carbon (Norit PK 10 × 30) at room temperature, while nitrogen was bubbled through the suspension. After a period of 5 hr adsorption equilibrium was reached, and the suspension was cooled to 0°C. After addition of 170 ml 35% formaldehyde solution, the platinum acid was reduced by the slow addition of 90 ml 30% KOH over a period of 1 hr. After standing overnight, the catalyst was filtered off and washed with distilled water until the filtrate was neutral. The catalyst was dried at 50°C and sieved to remove fines. For batchwise experiments the catalyst was ground to a fine powder of about 50 μm.

Analysis

The reaction samples were analyzed by ion-exchange chromatography. Details on the experimental procedure have been given elsewhere (*7*).

The following compounds were determined by this procedure: glucose, gluconic acid, glucaric acid, guluronic acid, and glucuronic acid. Besides these main products a number of other products (C_1 – C_5 mono- and dicarboxylic acids) were formed in low concentrations (representing oxidation of less than 10% of the initial amount of glucose).

Quantitative analysis of these compounds, which was not carried out in a routine way in the present study, could be carried by isotachophoresis (*8*).

RESULTS

Figure 2 gives the concentration of glucose as a function of the reaction time for both starting procedure A and B ($[G]_0$ = 200

mmol/liter, [cat] = 8 g/liter). We see that starting procedure B results in a somewhat higher initial reaction rate than starting procedure A and that the reaction rates decrease during an experiment. However, replacing the oxygen flow by a nitrogen flow for 5 min after a reaction time of 30 min results in a temporary increase in the reaction rate by a factor of 2.4. This increase rate is much higher than the ratio of the initial rates for the two starting procedures (factor 1.4).

The reaction rate can decrease during an experiment due to a decrease of the glucose concentration, reversible adsorption of reaction products on the catalyst, and deactivation of the catalyst. We have carried out a number of experiments to investigate these possibilities more closely. In these experiments, the reaction rate was calculated from the caustic soda consumption, which can be measured much more accurately than the glucose conversion. A linear relation between caustic soda consumption and glucose conversion was generally obtained because consecutive reactions of gluconic acid occurred only to a minor extent.

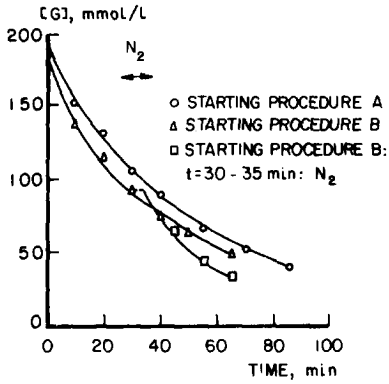
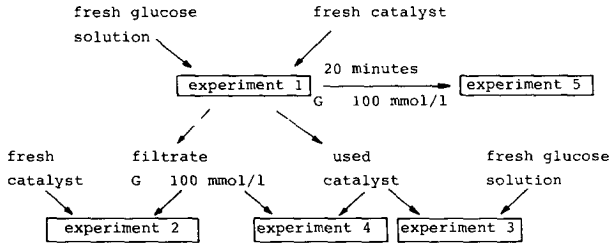


FIG. 2. Influence of the starting procedure on the rate of glucose oxidation.

Repeated Use of Catalyst and Reaction Mixtures

Experiment 1, under standard conditions, and with starting procedure A, was continued for a period of 20 min. Thereafter, the catalyst was filtered off and washed with 3 liters hot water to remove adsorbed reaction products as much as possible. The filtrate was concentrated in a film evaporator and glucose was added to obtain again 500 ml glucose solution with a concentration of 100 mmol/liter. Thereafter, two new experiments were carried out: the filtrate with fresh catalyst (experiment 2) and the used catalyst with a fresh glucose solution (experiment 3). In addition, an experiment (experiment 4) was carried out in which the filtrate and used catalyst were used together in a new experiment, and an experiment (experiment 5) in which the glucose concentration was raised to 100 mmol/liter after a reaction time of 20 min and thereafter continued for another 20 min. The period of time between the end of experiment 1 and the start of experiment 3 was the same as the time between experiment 1 and 4 (1 hr).

Results are given in Fig. 3. Both experiments 2 and 3 show a lower reaction rate than experiment 1. A part of the decrease of reaction rate during an experiment seems to be caused by adsorption of reaction products on the catalyst surface (compare ex-



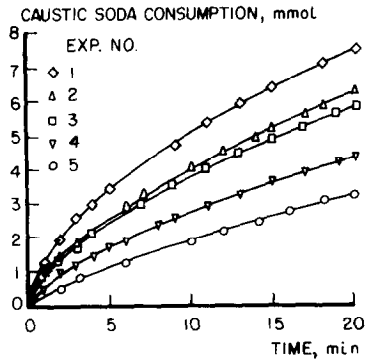


FIG. 3. Reuse of reaction mixture and catalyst. Initial concentration of glucose: 100 mmol liter^{-1} in all experiments. Experiment 1: fresh catalyst + fresh glucose solution. Experiment 2: fresh catalyst + reaction mixture from previous experiment. Experiment 3: used catalyst from previous experiment + fresh glucose solution. Experiment 4: used catalyst from previous experiment + reaction mixture from previous experiment. Experiment 5: glucose concentration was increased to 100 mmol liter^{-1} after a reaction time of 20 min in experiment 1.

periments 1 and 2), while another part of the decrease of reaction rate seems to be caused by a decrease of the number (or the nature) of the active sites on the catalyst surface (compare experiments 1 and 3). From the difference in reaction rate between experiments 4 and 5, it is concluded that some reactivation of the catalyst has taken place between the end of experiment 1 and the start of experiments 3 and 4.

That the reaction rate of experiment 3 can largely be restored to the experiment 1 level is shown for a standard experiment that was continued for 16 hr. Subsequently the catalyst was filtered off and washed with 3 liters water at 90°C and then used in a new experiment.

As is shown in Fig. 4, the activity of the catalyst was very low in the new experiment, but could easily be restored by replacing the oxygen by nitrogen for 6 min. Such a strong deactivation of the catalyst was not observed when the catalyst was contacted overnight with either oxygen or with glucose in a nitrogen atmosphere.

Experiments at Constant Glucose Concentration

In the experiments described so far, a part of the decrease of the reaction rate will be caused by a decrease of the concentration of glucose. Although this effect is not large as shown in Fig. 5 for the initial rate we undertook a number of experiments in which [G] was kept constant (within 5%) by addition of a concentrated glucose solution commensurate with the caustic soda consumption. As the order of the reaction rate

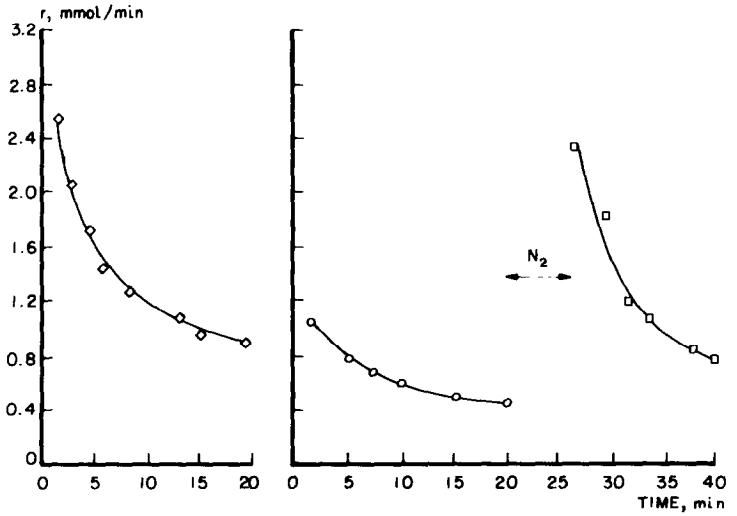


FIG. 4. Reaction rate versus time for fresh catalyst with fresh glucose solution (◇), catalyst used during 16 hr with fresh glucose solution (○), and after N_2 regeneration (□).

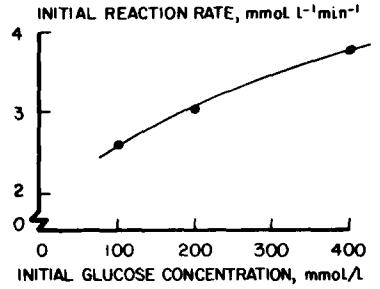


FIG. 5. Initial reaction rate as a function of the initial glucose concentration.

in glucose is small, small variations of [G] will affect the reaction rate only to a negligible extent.

The reaction rate is given as a function of the reaction time in Fig. 6. Initially the reaction rate decreases strongly but only a small difference in reaction rate between starting procedure A and B is observed. Consequently, the observed deactivation cannot, or only to a very minor extent, be ascribed to chemisorbed oxygen.

The reaction rate at constant [G] for starting procedure B is replotted as a function of the quantity of glucose converted as the lower line of Fig. 7. When at some conversion the experiment is interrupted by replacing oxygen by nitrogen for 15 min we obtain, after reintroducing oxygen, the reaction rates depicted by the upper curve. The length of the nitrogen period is not critical. The same results are obtained with nitrogen purges of 2 and of 30 min. The deterioration of the reaction rate after oxygen is reintroduced is depicted by the dotted lines. The gain in catalyst activity which can be obtained by this procedure increases as the experiment proceeds. However, a part of the catalyst deactivation during an experiment (i.e., the degree of deactivation represented by the upper curve of Fig. 7) cannot be restored by a nitrogen purge. We suppose that this phenomenon is related to the findings in Fig. 3, that a part of the decrease of the catalyst activity is caused by adsorption of reaction products on the catalyst surface (compare experiments 1 and 2 of Fig. 3).

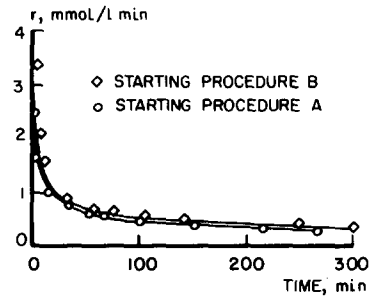


FIG. 6. Reaction rate versus time for both starting procedure A and B. Experiments at constant [G] (200 mmol liter^{-1}).

Product Distribution

We investigated the selectivity of the fast initial reaction shown in Fig. 6 for both starting procedures by using a high catalyst/glucose ratio: 10 mmol glucose was added to a suspension of 10 g 9.7% Pt/C (4.9 mmol Pt) in a nitrogen atmosphere. The rate of this reaction was such that it could not be measured: even at a temperature of 2°C the reaction was complete in less than 1 min.

Besides gluconic acid (4.8 mmol) only a few percent uronic acids (0.3 mmol) were formed as reaction products. As the quantity of gluconic acid that was formed in this

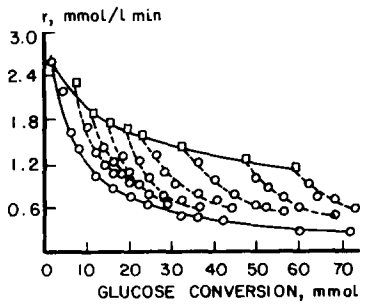
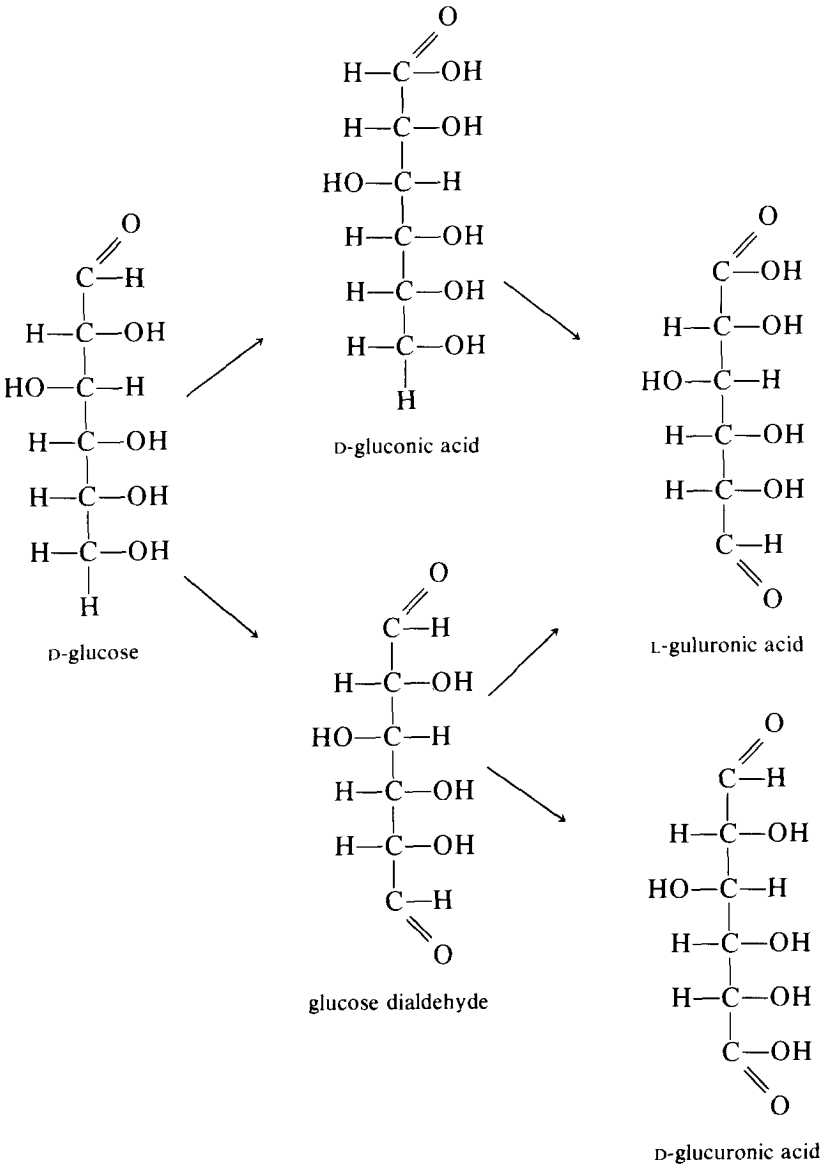


FIG. 7. Reaction rate versus glucose conversion; lower curve (full line, ○): starting procedure B, [G] = 200 mmol liter^{-1}. The experiment presented by the lower curve was carried out a number of times and interrupted by replacing O_2 by N_2 after various times. The upper curve (full line, □) represents the reaction rates just after reintroducing oxygen into the reactor. The dotted lines give reaction rate as function of conversion after reintroducing oxygen.

reaction required a number of oxygen atoms that is almost equal to the number of platinum atoms on the catalyst, it can be concluded that the dispersion of the catalyst is close to 1.



The concentrations of glucose, gluconic acid, guluronic acid, and glucuronic acid are given as a function of the reaction time in Fig. 8 ([cat] = 4 g/liter, $[G]_0$ = 200 mmol/liter). This figure shows that a substantial oxidation of the primary alcohol group takes place under the conditions applied. The formation of uronic acids indicates that the oxidation in the presence of gaseous oxygen occurs, at least partly, according to a mechanism different from the reaction between glucose and chemisorbed oxygen, since the latter yields gluconic acid almost exclusively. A further interesting

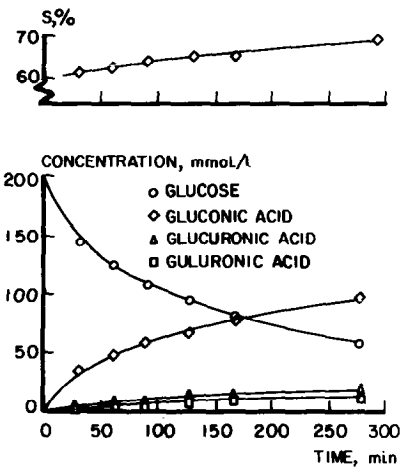


FIG. 8. Distribution of main products and selectivity in the oxidation of glucose.

point in Fig. 8 is the selectivity toward gluconic acid, which slowly increases during an experiment: the initial selectivity is about 60%, while the integral selectivity after a reaction time of 270 min is about 70%; the differential selectivity after this reaction time is about 80%. This is an interesting observation, since one would expect a decreasing selectivity for gluconic acid due to consecutive reactions of gluconic acid, for instance glucaric acid (*8*). The selectivity for gluconic acid does not significantly depend upon $[G]_0$, [cat], and $[O_2]$: in all cases the integral selectivity varies between 60 and 70%. When a high (>80–90%) conversion was obtained, the selectivity to gluconic acid was found to decrease due to consecutive reactions (*8*). The reuse of a deactivated catalyst (Fig. 4) results in an increase in the selectivity by about 10%. The increase in the selectivity as the deactivation proceeds is manifested much more strongly in experiments that were carried out in a trickle-bed reactor: a selectivity of almost 100% has been obtained with a highly deactivated catalyst (*6*).

DISCUSSION

A strong decrease of the catalyst activity takes place in the experiments described above. Part of this catalyst deactivation can be restored by temporarily stopping the oxygen flow (Figs. 2, 4, and 7) (the "oxygen effect"), while another part of the catalyst deactivation cannot be restored by this procedure (Fig. 7) and is ascribed to the reversible adsorption of products. That products are involved follows from the experiments presented in Fig. 3, and that they are reversibly adsorbed follows from the fact that a strongly deactivated catalyst can be reactivated to its initial activity by washing the catalyst with hot water and temporarily replacing the oxygen by nitrogen (Fig. 4). Consequently, the activity decrease depicted by the upper curve of Fig. 7 is ascribed to reversible product adsorption. As for this curve the oxygen effect is ruled out, we may as a first approximation try to describe the reaction rate by a single site Langmuir–Hinshelwood model:

$$r = -\frac{d[G]}{dt} = \frac{k_r[G]}{1 + K_1[G] + K_3\Delta[G]}\,[\text{cat}] \quad (1)$$

in which:

- [cat] = Catalyst concentration, g liter^{-1}
- [G] = Concentration of glucose, mmol liter^{-1}
- Δ[G] = Conversion of glucose, mmol liter^{-1}
- K_1 = Adsorption constant of glucose, liter mmol^{-1}
- K_3 = Weighted average adsorption constant of the various reaction products, liter mmol^{-1}
- k_r = Reaction rate constant, liter min^{-1} g cat^{-1}
- r = Reaction rate, mmol liter^{-1} min^{-1}
- t = Time, min.

In the above formula it is supposed that the product distribution is constant during an experiment. This assumption is reasonable because the selectivity toward gluconic acid increases only slightly during an experiment (Fig. 8). From Eq. (1) we obtain:

$$\frac{[\text{cat}]}{r} = \frac{1 + K_1[\text{G}]}{k_r[\text{G}]} + \frac{K_3\Delta[\text{G}]}{k_r[\text{G}]}. \quad (2)$$

If reaction products are absent ($\Delta[\text{G}] = 0$), we can write for the initial reaction rate r_0:

$$\frac{[\text{cat}]}{r_0} = \frac{1 + K_1[\text{G}]_0}{k_r[\text{G}]_0} \quad (3)$$

in which $[\text{G}]_0$ is the initial concentration of glucose. k_r and K_1 can be calculated from a plot of $1/r_0$ versus $1/[\text{G}]_0$ (data from Fig. 5).

We calculate: $k_r = 0.015$ liter g cat^{-1} min^{-1}, $K_1 = 0.013$ liter mmol^{-1} (pH = 9, 55°C). K_3 can be calculated from the upper curve of Fig. 7: in Fig. 9 the data of the upper curve of Fig. 7 are given as $1/r$ as a function of $\Delta[\text{G}]$. Taking into account the simple kinetic model used, the fit is satisfactory. With $K_1 = 0.013$ liter mmol^{-1} we calculate from this figure: $K_3 = 0.021$ liter mmol^{-1}, and decreases later on.

More interesting is the deactivation that can be reversed by temporarily stopping the oxygen flow. We will describe this "oxygen effect" by the activity A of the catalyst. A is the ratio of k_r at time t ($k_{r,t}$) to k_r at time zero ($k_{r,0}$)

$$A = \frac{k_{r,t}}{k_{r,0}}. \quad (4)$$

$A = 1$ in the upper curve of Fig. 7. Thus, we can write for the reaction rate r:

$$r = -\frac{d[\text{G}]}{dt} = \frac{k_{r,0}A[\text{G}]}{1 + K_1[\text{G}] + K_3\Delta[\text{G}]}[\text{cat}]. \quad (5)$$

We can write for the activity A:

$$A = \frac{r}{[\text{cat}]}\frac{1 + K_3'[\text{G}]}{k_{r,0}'[\text{G}]} \quad (6)$$

in which:

$$k_{r,0}' = \frac{k_{r,0}}{1 + K_1[\text{G}]}, \qquad K_3' = \frac{K_3}{1 + K_1[\text{G}]}. \quad (7)$$

With the known values of $k_{r,0}$ (0.015 liter g cat^{-1} min^{-1}), K_1 (0.013 liter mmol^{-1}), and K_3 (0.021 liter mmol^{-1}) (pH = 9, 55°C), the activity A can be calculated. A number of experiments in which the glucose concentration was kept constant and starting procedure B was applied were carried out with various amounts of catalyst, various glucose concentrations, and various amounts of oxygen in the oxidising gas.

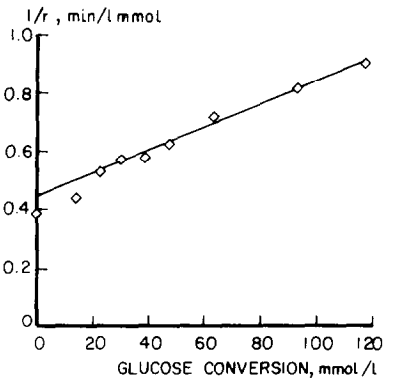


FIG. 9. $1/r$ (after N_2 regeneration) versus glucose conversion.

In Figs. 10 and 11 the activity A is given as a function of the conversion, with respectively [G] and percentage O_2 as parameter. The deactivation pattern depends only to a minor extent on the reaction conditions ([G], percentage O_2): at the same conversion almost the same degree of deactivation is obtained. This is shown more clearly in the experiments at various [cat]: in Fig. 12 the activity A is given as a function of the conversion/g catalyst, with the catalyst concentration as parameter. The degree of deactivation does not depend upon the total conversion, but on the conversion/g catalyst. This means that the deactivation is

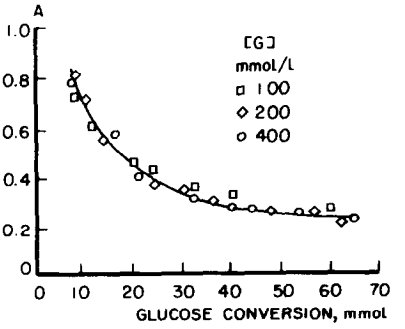


FIG. 10. Catalyst activity versus glucose conversion with [G] as parameter.

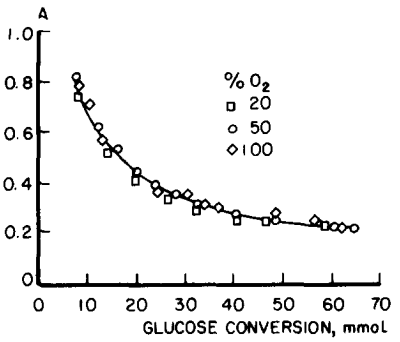


FIG. 11. Catalyst activity versus glucose conversion with percentage O_2 as parameter.

directly coupled to the chemical reaction: a fast reaction results in a fast deactivation and a slow reaction in a slow deactivation. In this respect it should be recalled that contacting the catalyst with either oxygen or glucose does not result in deactivation.

Thus, we conclude that the decrease of A in the oxidation of glucose is coupled to the conversion, and can be expressed by an equation like

$$A = f(\Delta[\mathrm{G}]/\mathrm{g\ catalyst}). \qquad (8)$$

The reactivation of the catalyst is already effected by stopping the oxygen flow for 2 min. Glucose and/or a reaction product must be involved, because no reactivation is obtained if a deactivated catalyst is kept in a nitrogen atmosphere for 2 min in the absence of glucose or reaction products.

The "oxygen effect" deactivation of the catalyst is explained by the assumption that

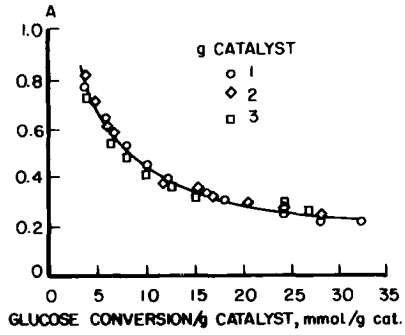


FIG. 12. Catalyst activity versus glucose conversion/g catalyst with the amount of catalyst as parameter.

due to the chemical reaction some compound is formed or adsorbed on the catalyst surface. This compound reacts fast to innocuous products in the absence of oxygen, and is rather stable in an oxygen atmosphere. However, neither the reaction products of the homogeneous oxidation of glucose nor the known reaction products of the catalytic oxidation of glucose show such adsorption behavior.

Analogous phenomena were found by Ostermaier *et al.* (*9*) in the low-temperature oxidation of ammonia with oxygen over Pt/Al_2O_3 as catalyst: contacting the catalyst with either oxygen or ammonia did not result in deactivation of the catalyst, whereas strong deactivation was observed in continuous-flow experiments. Also in their case the activity of the catalyst could be restored by temporarily stopping the oxygen flow. The deactivation was ascribed to the formation of platinum oxide (PtO_2) due to the chemical reaction. The formation of PtO_2, which was supported by hydrogen titration experiments, was explained by the assumption that the chemical reaction produces a sufficiently excited oxygen atom or sufficient local heating to induce the platinum–oxygen reaction. A strong decrease in the catalyst activity due to the formation of PtO_2 was also observed by Amirnazmi and Boudart (*10*) in the decomposition of nitrogen oxide over Pt/Al_2O_3.

The formation of PtO_2 during the reaction can explain our results as well. The reactivity of PtO_2 is relatively low, so that its formation results in a deactivation. The relation between degree of deactivation (degree of oxidation to PtO_2) and conversion (Eq. (8)) agrees with the formation of PtO_2 according to one of the mechanisms proposed by Ostermaier *et al.* (*9*).

Temporarily stopping the oxygen flow results in a reactivation of the catalyst. Thus, in the absence of gaseous oxygen and in the presence of glucose, PtO_2 is decomposed rapidly. This can be explained by the following mechanism:

$$\begin{aligned} Pt + G &\rightleftharpoons Pt \cdot G \\ 2Pt + O_2 &\rightarrow 2Pt\text{–}O \\ O_2 + Pt\text{–}O + Pt \cdot G &\rightarrow Pt \cdot GOZ + PtO_2 \\ PtO_2 + Pt \cdot G &\rightarrow P \cdot GOZ + Pt\text{–}O \\ &\quad (\text{or } H_2O_2) \end{aligned}$$

from which we obtain:

$$-\frac{d\theta_{PtO_2}}{dt} = \frac{k_r[G]}{1 + K_1 G} \cdot \theta_{PtO_2}(1 - \theta_{Pt-O} - \theta_{PtO_2}). \quad (9)$$

θ_{PtO_2} and θ_{Pt-O} represent, respectively, the fraction of the active sites oxidized to PtO_2 and the fraction covered with chemisorbed oxygen. During the reduction of the catalyst in a nitrogen atmosphere, no further formation of PtO_2 will occur, and the reduction rate will initially increase, because the relative increase in the factor $(1 - \theta_{Pt-O} - \theta_{PtO_2})$ will be much higher than the relative decrease in the factor θ_{PtO_2}. The reactivation of the catalyst in the oxidation of ammonia was explained by Ostermaier *et al.* by an analogous mechanism.

We carried out an experiment in which glucose was put into a suspension of a strongly deactivated catalyst in a nitrogen atmosphere (pH = 9, T = 55°C). The reaction was complete within about 1 min, and the selectivity to gluconic acid was above 95%. The amount of glucose converted was almost the same as if a catalyst saturated with chemisorbed oxygen had been used. From the stoichiometry of the reaction between PtO_2 and glucose one would expect a double amount of gluconic acid in this reaction. Therefore, it is possible that H_2O_2 is formed in the decomposition of PtO_2 with glucose, and is decomposed into H_2O and O_2. The use of H_2O_2 (30 mmol) instead of O_2 as oxidant gave a conversion of only 3 mmol glucose into 2.8 mmol gluconic acid; the amount of uronic acids was <0.1 mmol. The rest of the H_2O_2 was decomposed into H_2O and O_2, and thus only a small part of the H_2O_2 was used in the oxidation reaction.

Ostermaier *et al.* (*9*) report that the catalyst was also reactivated by treatment of the catalyst with only helium instead of treatment with ammonia in the absence of oxygen, treatment of the catalyst with oxygen only resulting in but a minor reactivation of the catalyst. Our results in the reactivation of the catalyst are not completely the same. A catalyst which has been used in an experiment has a low activity if it is immediately reused in a new experiment without reduction of the catalyst (Fig. 4). However, if a strongly deactivated catalyst is dried at 50°C in air overnight after washing with distilled water, it is almost completely reactivated. A similar result was obtained in the trickle-bed reactor experiments (*6*): washing a deactivated catalyst with H_2O in an oxygen atmosphere resulted in a slow reactivation of the catalyst. Therefore, the following reactivation mechanism should not be excluded:

$$PtO_2 + Pt \rightarrow 2Pt\text{–}O$$

Besides, it is possible that the carbon carrier plays a role in the slow reactivation of the catalyst in an O_2 atmosphere. This would explain the different behavior in reactivation of respectively a deactivated Pt/C catalyst and Pt/Al_2O_3 as reported by Ostermaier *et al.* (*9*).

The selectivity to gluconic acid depends upon the oxidation state of the catalyst. Both Pt–O and PtO_2 react with glucose with a high selectivity to gluconic acid. During the reaction with gaseous oxygen, however, a catalytic side reaction takes place (oxidation of the primary alcohol group of glucose). Therefore, it is reasonable to suppose that molecular oxygen is involved in this side reaction. This reaction possibly occurs according to the mechanism which was postulated by Rottenberg and Thürkauf (*11*) for the oxidation of ethanol with Pt as catalyst, in which oxygen is supposed to abstract hydrogen from the alcohol group to form hydrogen peroxide.

Thus, we can distinguish at least three different reactions in the oxidation of glucose, and we will use the following nomen-

clature:

Reaction I: the reaction in which Pt–O is involved. Selectivity >95%.
Reaction II: the reaction in which molecular oxygen is involved. Selectivity <60%.
Reaction III: the reaction in which PtO_2 is involved. Selectivity >95%.

The selectivity to gluconic acid increases during an experiment (Fig. 8) and can exceed 95% if the catalyst is strongly deactivated. Two explanations for the increase of the selectivity can be given:

(1) The contribution of reaction III to the total reaction rate increases as the deactivation proceeds while the ratio between the rates of reaction I and reaction II remains constant.

(2) The ratio $\text{rate}_{\text{reaction I}}/\text{rate}_{\text{reaction II}}$ increases as the deactivation proceeds.

If the ratio $\text{rate}_{\text{reaction I}}/\text{rate}_{\text{reaction II}}$ is assumed to be independent of the fraction of the catalyst surface oxidized to PtO_2, explanation (1) alone cannot explain the selectivity pattern: the sum of reactions I and II can then be represented by an overall reaction r^1, with selectivity S_1. The integral selectivity in batch experiments during the first 30 min is about 60%, and thus $S_1 < 0.60$. The selectivity of reaction III is close to 1. The differential selectivity during an experiment is then given by:

$$S < \frac{0.60\, r^1 + r_{III}}{r^1 + r_{III}}.$$

In the batch experiments a differential selectivity S of $> 80\%$ can be obtained, and in experiments in a trickle-bed reactor S can exceed 95%.

$$S = 80\%: \quad r_{III}/r^1 = 1$$
$$S = 95\%: \quad r_{III}/r^1 = 7.$$

$r_{III}/r^1 > 1$ means that the reduction rate of the catalyst is higher than the deactivation rate, which would involve a regeneration of the catalyst. Therefore, we conclude that the increasing selectivity during an experiment cannot be ascribed only to reaction III.

In explanation (2) it is assumed that the formation of PtO_2 affects reaction II to a larger extent than reaction I. This is not unexpected because reaction I, which is an oxygen insertion reaction, only requires an adsorbed glucose species and an adsorbed oxygen species, whereas the side reaction, the first step of which is the abstraction of two hydrogen atoms, requires at least three active sites. Moreover, it should be noted that this reaction takes place at the primary hydroxyl group. As it can be expected that the normal adsorption of glucose will be at the aldehyde function, a second site will be required for the interaction of the primary alcohol group with the catalyst. Finally, it should be noted that this reaction takes place only in the presence of oxygen in the gas phase. This means that a loosely bound oxygen species, different from the Pt–O and PtO_2 species discussed before, plays a role in this reaction. The other reaction that takes place only in the presence of oxygen in the gas phase, viz. the deactivation reaction, may take place via the same loosely bound oxygen species.

In conclusion, the reaction scheme for the oxidation of glucose with Pt/C as catalyst can be presented as follows:

$$2Pt + O_2 \rightarrow 2Pt\text{–}O$$
$$Pt + O_2 \rightleftharpoons Pt \cdot O_2 \text{ (loosely bound)}$$
$$Pt + G \rightleftharpoons Pt \cdot G$$
$$Pt\text{–}O + Pt \cdot G \rightarrow Pt \cdot GOZ + Pt$$
$$Pt \cdot O_2 + Pt\text{–}O + Pt \cdot G \rightarrow Pt \cdot GOZ + Pt + PtO_2$$
$$Pt \cdot O_2 + Pt + Pt \cdot G \rightarrow Pt \cdot GDA + 2Pt + H_2O_2$$
$$PtO_2 + Pt \cdot G \rightarrow Pt \cdot GOZ + Pt + H_2O_2$$
$$Pt \cdot GOZ \rightleftharpoons Pt + GOZ$$
$$Pt \cdot GDA \rightleftharpoons Pt + GDA$$

ACKNOWLEDGMENT

We are grateful to Mr. W. J. A. C. van Niftrik for having carried out part of the experiments.

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