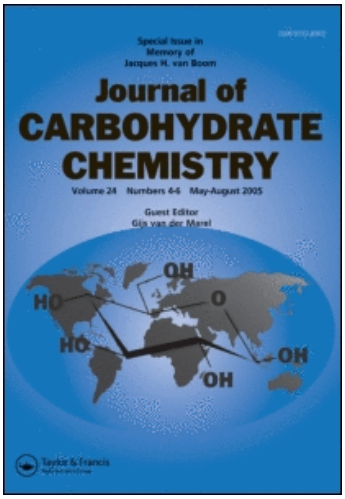

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EFFECT OF pH IN THE Pd-CATALYZED OXIDATION OF D-GLUCOSE TO D-GLUCONIC ACID

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ABSTRACT

The pH effect on the Pd-catalyzed oxidation of glucose to gluconic acid was studied. The oxidation reactions were performed in the pH range 2 to 9 in a batch reactor using Pd/C or Pd black as the catalysts and monitoring the behaviour of the catalyst during the oxidation reaction. The Pd-glucose system was also studied by cyclic voltammetry. It is concluded that gluconic acid in its free form reversibly inhibits the oxidation process in acidic media.

INTRODUCTION

The oxidation of carbohydrates is an important tool to obtain compounds with new chemical and physical properties. For instance, oxidation of the anomeric center and of the hydroxymethyl group of monosaccharides is well-documented, whereas glycolic oxidation of polysaccharides leads to good sequestering agents.[2,3] Carbohydrate oxidation reactions have been performed by enzymes and microorganisms as well as by homogeneous or heterogeneous chemo-catalysis.[4]

The application of noble metal catalysts in the oxidation of carbohydrates introduces several problems. The fragility of the substrates and their polyfunctionality raises selectivity problems.[5,6] Recently, leaching of active platinum sites from the catalyst has been reported.[7,8] Moreover, many parameters have to be controlled such as pH, temperature, surface oxygen coverage, and the nature and stability of the catalyst in order to obtain the desired products.

We have investigated the effect of pH on the noble metal catalyzed oxidation of glucose to gluconic acid in aqueous solution. Previous studies of this reaction have been focussed mainly on the nature of catalysts used.[9-11] Here we report on catalysts based on Pd. Under alkaline conditions, Pd catalysts are known to provide high yield as well as high selectivity, comparable to biocatalytic systems. Selectivity problems encountered during the oxidation of glucose were discussed elsewhere.[12] In the present study the pH range 2-9 was scanned by monitoring the conversion in a batch reactor as well as by cyclic voltammetry of Pd-glucose system.

RESULTS AND DISCUSSION

The effect of pH (region 5-9) on the oxidation of glucose to gluconic acid over Pd/C is presented in **FIG. 1**. Under alkaline conditions, the oxidation reaction is very fast and the total amount of glucose is oxidized selectively (> 99 % according to HPLC) to gluconic acid in 30 min. The fact that this high selectivity is not completely reflected by the pH 9 curve in **FIG. 1** is due to adsorption of some gluconic acid onto the carbon support. However, the oxidation reaction in neutral or acidic media does not reach completion even after a reaction time of 6 h. Nevertheless, the selectivity of the catalyst toward gluconic acid remains unchanged. The initial rate of the oxidation reaction decreases with decreasing pH. Furthermore, we can notice at pH 5 the appearance of a flat steady state line in kinetic curves which reflects an inhibition of the oxidation process. The time before this state is reached is pH dependent.

These observations are more pronounced when the oxidation reaction is carried out without pH control. During this

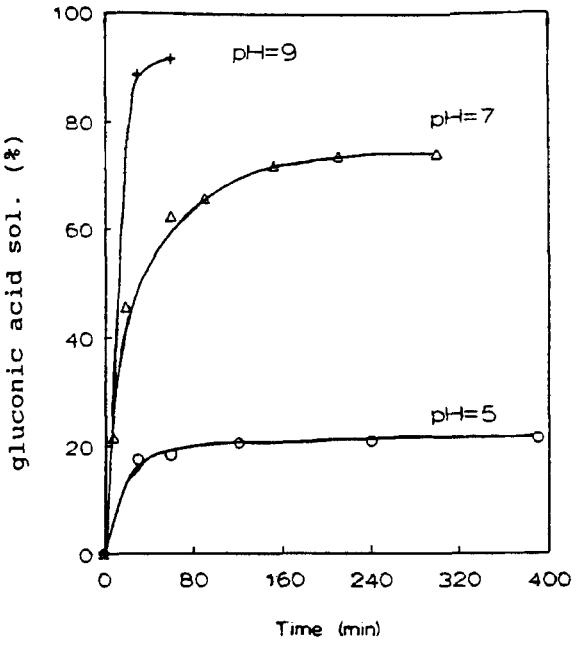


FIG. 1. Effect of pH on the oxidation of glucose to gluconic acid. Glucose = 0.05 M (80 mL), 0.1 g (5% Pd/C) catalyst, T = 50°C, $p(O_2)$ = 0.2 atm, p(total) = 1.0 atm.

experiment the pH is about 5 at the start and decreases quickly to reach pH 3 due to the formation of gluconic acid. The inhibition state was attained rapidly and the oxidation process stopped after 15 min. No further oxidation of gluconic acid in this state is observed. The conversion curves related to the oxidation reaction without pH control and at pH 5 are presented in **FIG. 2.** Note that the amount of catalyst is the fourfold of that in **FIG. 1,** due to its low activity in acidic media.

Two hypotheses could explain the inhibition of the oxidation process in neutral as well as in acidic media:
(i) Poisoning of the catalyst by oxygen leading to the formation of an inactive palladium oxide layer; (ii) interaction of the catalyst with free gluconic acid. Several experiments have been performed to distinguish between (i) and (ii).

a. Reactivation of the catalyst by reduction with H_2. The oxidation reaction was run for 3 h without pH control. After this period no additional oxidation was observed. Reactivation of the catalyst by reduction was attempted as follows: the

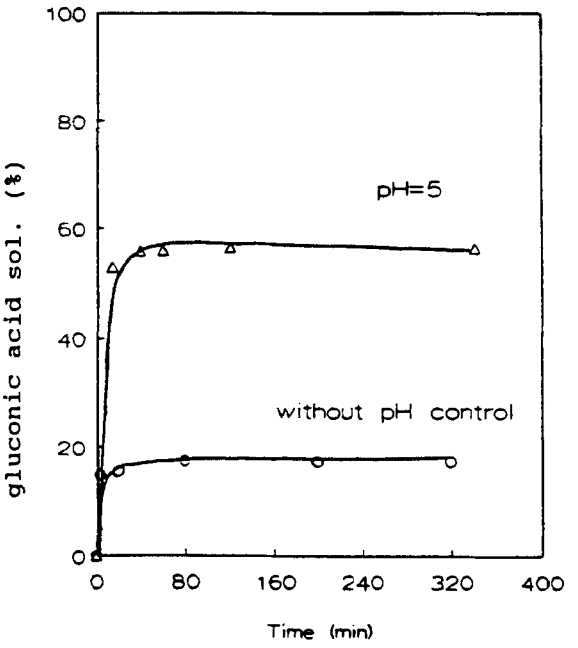


FIG. 2. Oxidation of glucose to gluconic acid without pH control. Glucose = 0.05 M (80 mL), 0.4 g (5% Pd/C) catalyst, T = 65°C, $p(O_2)$ = 0.2 atm, p(total) = 1.0 atm.

reaction system was flushed with nitrogen for 5 min to remove oxygen from the reactor, hydrogen was bubbled through the reactor for 30 min and the system was flushed with nitrogen for 5 min. Upon replacing the gas phase with pure oxygen to restart the reaction, the oxidation does not proceed (see **FIG. 3**). This result is inconsistent with the first hypothesis.

b. Reactivation of the catalyst by raising the pH to 9. The oxidation reaction was run until the inhibition state was reached. After 3 h, the catalyst was reactivated by addition of KOH solution until pH 9 was reached, and to dissociate any gluconic acid complex formed in which the catalyst might be involved. The pH was kept constant in the usual way after reactivation.

The reaction restarted immediately (**FIG. 4**), and the total amount of glucose was oxidized within 15 min.

c.Pre-adsorption of gluconic acid. Some oxidation experiments were carried out in which the catalyst was pretreated in solution with gluconic acid, trifluoroacetic acid or $HClO_4$ before adding the substrate.

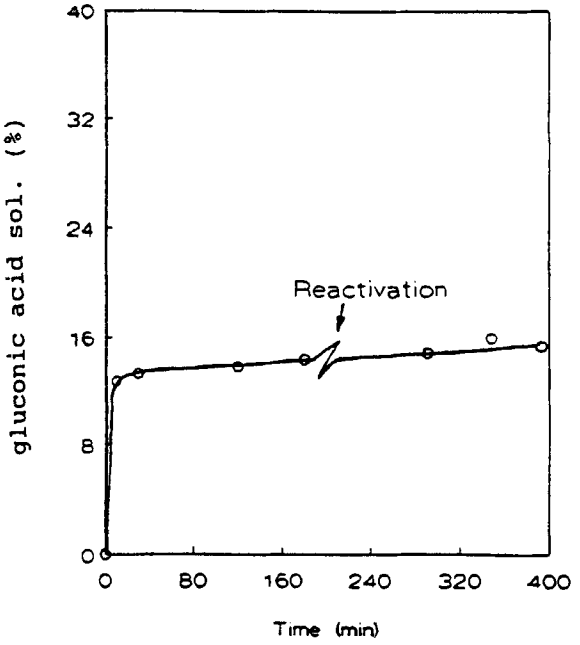


FIG. 3. Attempted reactivation of the catalyst in acidic medium by reduction with H_2. Glucose = 0.05 M (80 mL), 0.4 g (5% Pd/C) catalyst, T = 65°C, $p(O_2)$ = 0.2 atm, p(total) = 1.0 atm, without pH control.

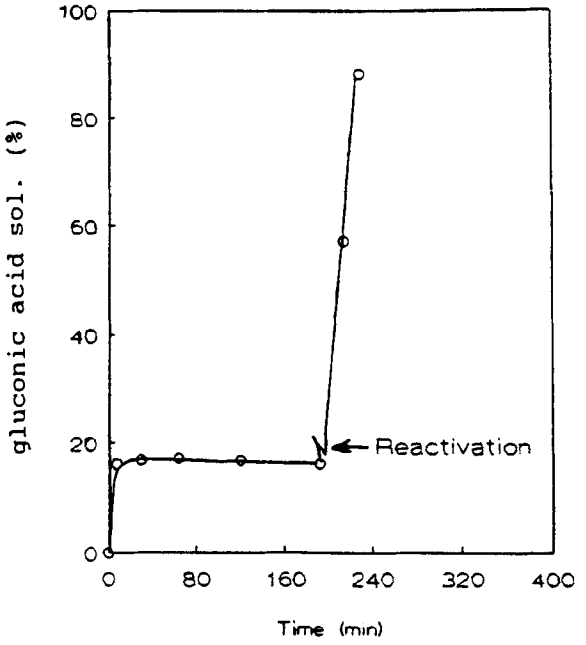


FIG. 4. Oxidation of glucose without pH control; reactivation of the catalyst by raising the pH to 9. Glucose = 0.05 M (80 mL), 0.4 g (5% Pd/C) catalyst, T = 65°C, $p(O_2)$ = 0.2 atm, p(total) = 1.0 atm.

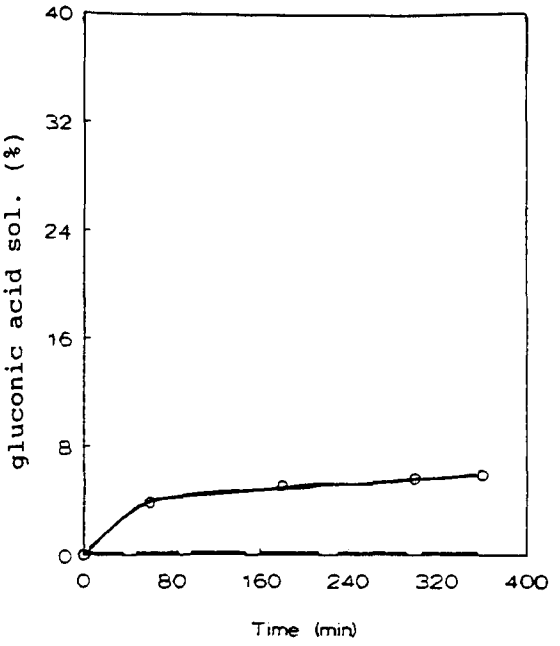


FIG. 5. Oxidation of glucose without pH control; Pre-added gluconic acid (---) or $HClO_4$ (—o—o) to pH 2. Glucose = 0.05 M (80 mL), 0.4 g (5% Pd/C) catalyst, T = 65°C, pH = 2, $p(O_2)$ = 0.2 atm, p(total) = 1.0 atm.

The desired acid was added to the suspension containing the catalyst to pH 2 and the suspension was then stirred for 10 min under nitrogen. Glucose was added and the gas phase was replaced by pure oxygen to start the reaction.

The oxidation of glucose in the presence of $HClO_4$ was found to proceed whereas pretreatment of the catalyst with gluconic acid or trifluoroacetic acid led to an inactive catalyst (see **FIG. 5**).

These results indicate that the inhibition seems to be due to the presence of gluconic acid in its free form since no other product is formed during the oxidation reaction. The addition of base will lead to dissociation of gluconic acid from the catalyst.

d. Effect of the catalyst carrier. When using palladium black as the catalyst, the reaction was found to proceed in the same way as with the palladium on carbon catalyst applying the same Pd surface areas (see **FIG. 6**). The small differences in yield are

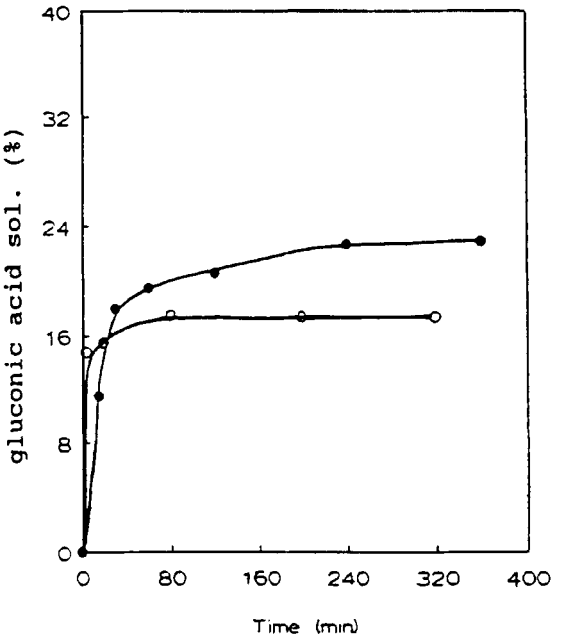
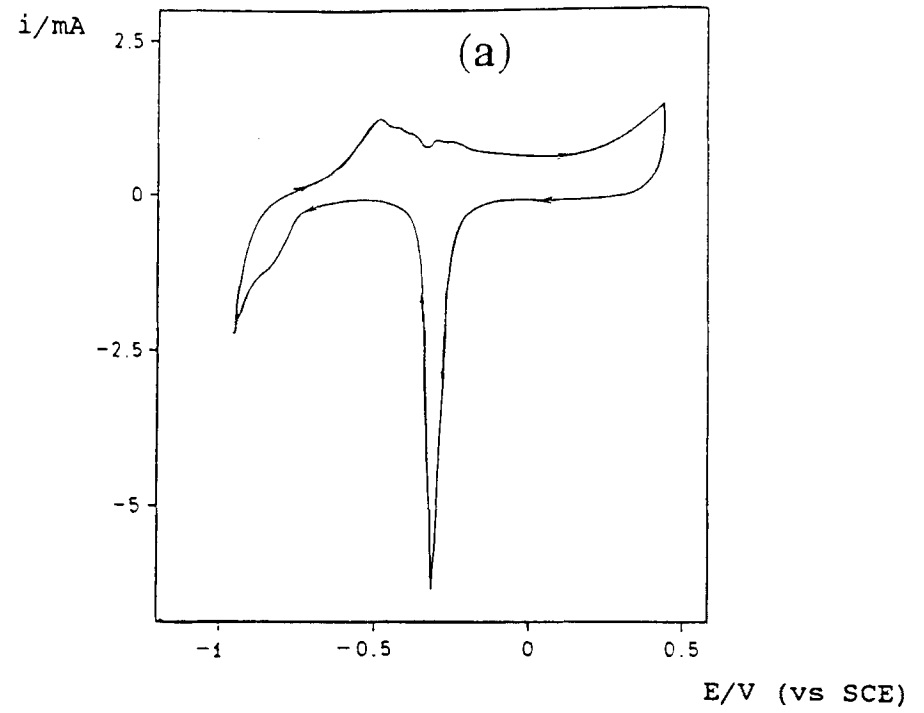


FIG. 6. Comparison of Pd black (—●—●—) and 5% Pd/C (—o—o—) in the oxidation of glucose without pH control. Glucose = 0.05 M (80 mL), T = 65°C, $p(O_2)$ = 0.2 atm, p(total) = 1.0 atm, Pd black = 0.09 g, 5% Pd/C = 0.4 g.

assumed to be due to adsorption of gluconic acid on the carbon.

e. Electrochemical oxidation of glucose (Cyclic voltammetry). Cyclic voltammetry is a controlled potential technique. The electrode potential between reference electrode and working electrode is linearly varied from an initial to a final potential and immediately swept back at the same sweep rate to the initial value. The resulting current flow is measured between working electrode and counter electrode. This method is very useful to characterize the behaviour of the surface of the electrode as well as the nature and reactivity of products formed in an electrochemical reaction. The potential sweep in cyclic voltammetry need not to be confined to one sweep. In fact, a great deal of qualitative information on the products formed following the electrode reactions can be obtained by employing multiple sweeps.

Multiple sweeps cyclic voltammetric experiments were performed in alkaline and acidic media under nitrogen to get some



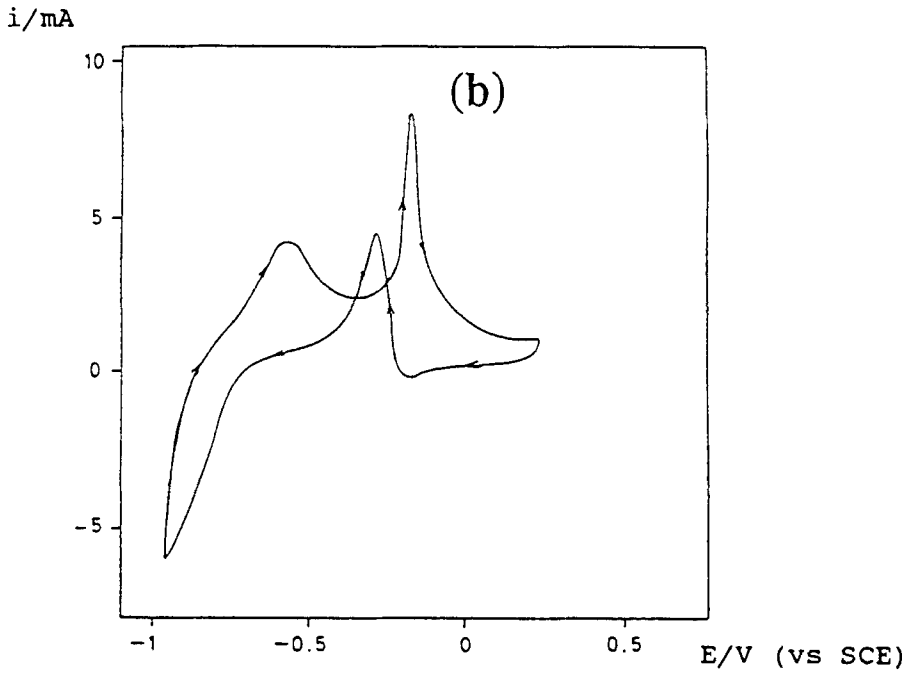


FIG. 7. Cyclic voltammogram of palladium in 0.1 M aqueous KOH (a) and in the presence of glucose = 0.05 M (b), T = 25 °C, sweep rate = 0.05 V/s.

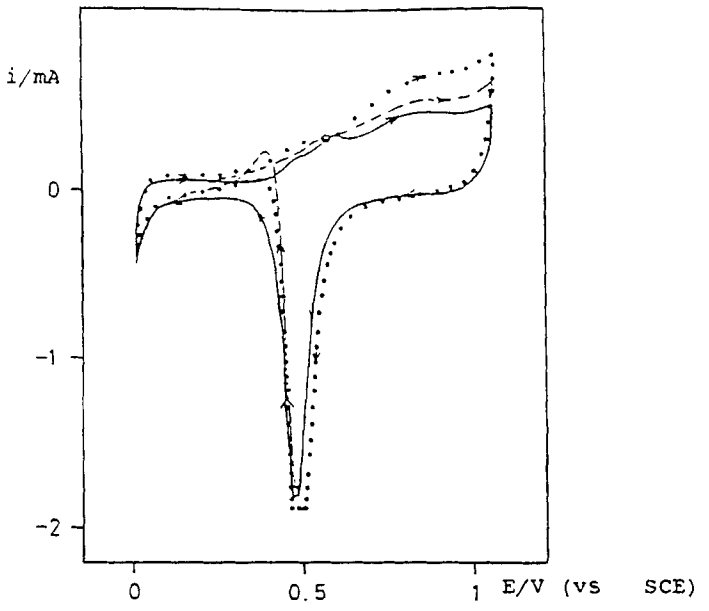


FIG. 8. Cyclic voltammogram of palladium in 0.2 M aqueous $HClO_4$ (———), and in the presence of glucose (- - - - - - -) : first scan, (·····) : scan after a cycling time of 90 min. Glucose = 0.05 M, T = 25 °C, sweep rate = 0.05 V/s.

information on the behaviour of palladium during the oxidation of glucose. Palladium foil was used as working electrode for this purpose which seems permitted since no difference in catalytic activity between palladium black and palladium on carbon was observed in batch reactions.

FIG. 7 represents cyclic voltammograms of palladium in 0.1 M KOH (a) and in the presence of 0.05 M glucose (b). The sweeps are started at -0.95 V. The oxidation of palladium is shown by the anodic curve of **FIG. 7a**. A maximum activity of palladium is reached at 0.45 V. Above this value, the metal is deactivated. During the reverse sweep the oxygen film is reduced as indicated by the peak at -0.32 V. In the presence of glucose (**FIG. 7b**) we notice in the anodic sweep a second peak at -0.17 V due to the oxidation of glucose, but at higher potentials this oxidation is inhibited. In the reverse sweep, glucose is oxidized again at -0.28 V because the oxidized surface species has been reduced. The oxidation peak of glucose in acidic media (0.2 M $HClO_4$, **FIG. 8**) is considerably smaller than

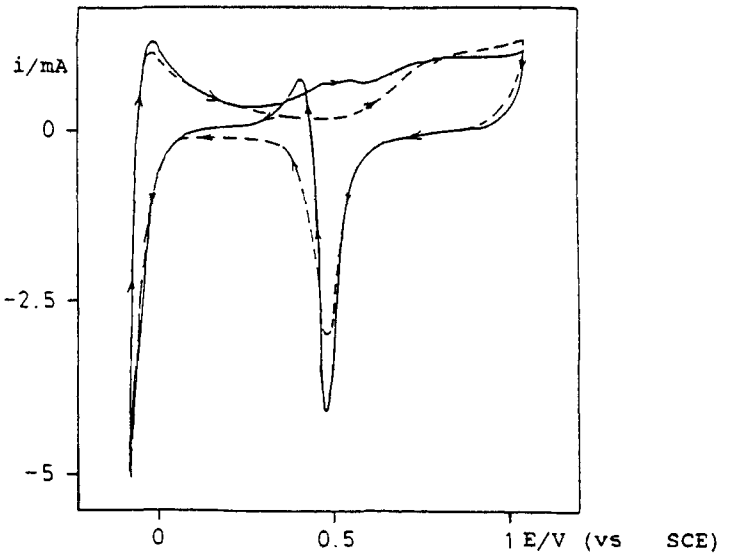


FIG. 9. Cyclic voltammogram of palladium in 0.2 M aqueous $HClO_4$ in the presence of glucose (————) and after adding gluconic acid (— — — —). Glucose = 0.05 M, gluconic acid = 0.05 M, T = 25 °C, sweep rate = 0.05 V/s.

in alkaline solution. Moreover, after a cycling period of 90 min, the oxidation peak of glucose decreases. In alkaline medium no degradation was observed. Addition of gluconic acid to glucose in $HClO_4$ (**FIG. 9**) results in complete deactivation of the electrode for the glucose oxidation. The same result is observed when adding trifluoroacetic acid to the electrolysis cell.

When the electrochemical oxidation is performed at 60 °C, the reaction rate is higher but the inhibition effect is also more apparent (see **FIG. 10**).

We conclude that the main inhibiting agent of the oxidation process in neutral as well as in acidic aqueous media is gluconic acid in its free form. The carboxyl function of gluconic acid is the main group involved in the inhibition of the oxidation process since trifluoroacetic acid produces the same effect on the oxidation reaction. The inhibition of the electrochemical oxidation of glucose on a platinum electrode in phosphate buffer at pH 7.4[13] and on a gold electrode in acidic media[14] was reported earlier. Recent study[15] on the oxidation of glucose on platinum electrode in acidic media using Infrared Reflectance

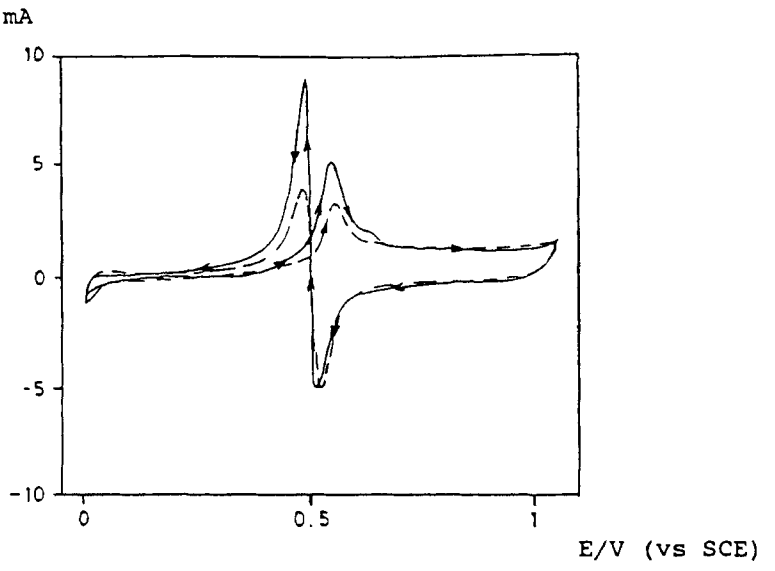


FIG. 10. Cyclic voltammogram of palladium in 0.2 M aqueous $HClO_4$ in the presence of glucose. (————) : first scan, (— — — —) : scan after a cycling time of 30 min. Glucose = 0.05 M, T = 60 °C, sweep rate = 0.05 V/s.

Spectroscopy showed that the main inhibition agent is adsorbed CO of which the gluconic acid is considered to the precursor. However, when using palladium instead of platinum as in our case, the molecular basis for the inhibition of the oxidation reaction seemed to be different. In batch reactor oxidation no arabonic acid and/or arabinose are detected by HPLC analysis. These products are formed when gluconic acid is further oxidized to produce CO. The rapid reactivation upon increase in pH is also in favour of gluconic acid inhibition. Furthermore, pretreatment of palladium catalyst with trifluoroacetic acid leads to inactive catalyst.

CONCLUSION

The oxidation of glucose to gluconic acid using Pd-based catalysts can be performed in aqueous alkaline solution with high yield but in aqueous acidic media, the oxidation process is inhibited by gluconic acid, the reaction product, in its free

form. The time before inhibition occurs depends on the concentration of free acid which increases with decreasing pH. Therefore, the inhibition occurs rapidly at pH 5 than at pH 7. The precise nature of the gluconic acid-Pd surface adduct has still to be elucidated.

EXPERIMENTAL

Materials. D-Glucose and potassium D-gluconate were purchased from Merck and used without further purification. The 5% palladium on carbon catalyst (palladium dispersion 0.27, as determined by CO adsorption) was obtained from Degussa and palladium black catalyst (palladium dispersion 0.003) was obtained from Strem Chemicals Inc.. The palladium foil was purchased from Janssen Chimica.

Oxidation equipment. Experiments were performed in a thermostatted glass batch reactor of 300 mL, equipped with a glass gas tight stirrer (1500 rpm). The pH was kept constant by using a pH meter (Metrohm 654) coupled to a pH control unit (Metrohm 614) and an automatic burette (Metrohm 655 , 10 mL piston) containing 1.78 M KOH. The oxygen partial pressure of the gas phase could be adjusted to any desired value between 0.05 and 1 atm, and was kept constant during the reaction using an automatic oxygen supply system. This system consisted of a motor burette filled with water as displacing liquid, a thermostatted (30 °C) gas burette filled with oxygen, and a differential pressure sensor, which operated the motor burette. Oxygen and hydroxide uptakes were recorded during the reactions.

Oxidation procedure. Reduction of the catalyst: a desired amount of powdered catalyst was first introduced into the reactor, 50 mL of water was added and the system was flushed with nitrogen for 5 min to remove oxygen from the reactor. Then hydrogen was bubbled through the reactor for 5 min at a high flow rate and low stirring speed, and then for an additional 25 min at a low flow rate and high stirring speed. Finally, the hydrogen was removed from the gas phase by flushing with nitrogen for 5 min.

Starting up of the reaction: a defined amount of glucose was dissolved in 30 mL of water and the solution was added to the

Table 1. Gradient used for HPLC analysis

Time (min)	A%	B%	curve
0	100	0	-
10	100	0	linear
25	60	40	-
30	60	40	linear
35	100	0	-
37 next injection			

reduced catalyst under low nitrogen flow. The system was equilibrated at the preset temperature, and the desired oxygen partial pressure was set by sucking a calculated amount of gas out of the reactor, the gas being automatically replaced by pure oxygen. The reaction started immediately.

Electrochemical oxidation equipment. A three-compartment cell was used to carry out cyclic voltammetry measurements. The working electrode (palladium foil 2 cm^2) and the counter electrode (platinum foil 2 cm^2) were immersed in two compartments which were separated by mass transfer resistant materials (glass frits). The third compartment was occupied by the reference electrode (saturated calomel electrode SCE) and was connected to the compartment of the working electrode via a lugging capillary. Solutions of 0.2 M $HClO_4$ and 0.1 M KOH were used for the oxidation in acidic and alkaline media, respectively. The cyclic voltammetry measurements were carried out at room temperature and at 60 °C, using Wenking potentioscan POS73. The voltammograms were recorded on a Philips XY recorder PM8043. The sweep rate used was 0.05 V/s.

HPLC analysis. The samples were analyzed using a Dionex CarboPac PA1 column, with a Dionex PED 1 pulsed electrochemical detector containing a gold electrode to which potentials of E_1 0.1, E_2 0.6, and E_3 -0.8 V were applied for duration times T_1 0.5, T_2 0.09, and T_3 0.07 s. Two Waters M6000-A HPLC pumps, coupled to a Waters M680 gradient controller were used to adjust the required solvent gradient. NaOH and anhydrous NaOAc were used to prepare eluents in water, which was filtered and degassed with helium prior to the addition of these compounds. All solvents were stored in closed, pressurized vessels with helium splashing. Composition of solvent A and B were as

follows: solvent A = 0.1 M NaOH, solvent B = 0.1 M NaOH and 0.5 M NaOAc. The flow-rate was set at 1 mL/min, and the gradient used is given in Table 1. The chromatographic data were processed using a Spectra Physics SP4270 integrator.

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