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Aerobic Oxidation of Glucose with Gold Catalyst: Hydrogen Peroxide as Intermediate and Reagent

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Abstract: Careful analytical determinations show that the gold-catalysed aerobic oxidation of glucose occurs through a two-electrons mechanism leading to gluconate and hydrogen peroxide. This latter decomposes before reaching the critical concentration for competing with O_2 in glucose oxidation. A mechanism of glucose oxidation on gold nanoparticles is presented.

Keywords: catalytic oxidation; glucose oxidation; gold; hydrogen peroxide; oxygen

Clean syntheses, based on the use of natural renewable reagents, in water solution under mild conditions, are highly desirable processes and often a catalytic step is the key factor for successful applications.[1] Inorganic catalysis, as an alternative to enzymatic catalysis, could represent a powerful tool for many oxidation processes using atmospheric oxygen or hydrogen peroxide. In the case of dioxygen, platinum group metals are the most investigated catalysts.[2,3] In recent years new efficient catalytic systems, based on the peculiar properties of nanometric gold particles, have been developed for the liquid phase oxidation of polyols,[4–9] amino alcohols[10] and glucose[11] to carboxylates.

In particular, it has been shown that glucose, the abundant and cheap starting material for the production of many chemicals,[12] can be efficiently oxidised to gluconate using supported and unsupported gold nanoparticles, gold catalysis being competitive with respect to enzymatic catalysis.[13]

During these studies, however, information was lacking on the oxidation mechanism and even the stoichiometry of the reaction was never fully ascertained.

While the kinetics of the aerobic oxidation of glucose catalysed by colloidal gold has recently been investigated[14] and compared with the enzymatic catalysis,[15] in the present study we report new molecular aspects of reagent activation on gold particles, demonstrating that hydrogen peroxide is formed by two-electrons reduction of dioxygen. The role of H_2O_2 as a possible competitor of O_2 is also discussed.

Several oxidation tests have been carried out at different pH values, by bubbling dioxygen at atmospheric pressure and 303 K into the aqueous solution of glucose in the presence of colloidal gold particles having a mean diameter of 3.6 nm. The experimental procedure, based on the automatic titration of gluconic acid with NaOH at a fixed pH value, has been already reported.[13] As derived from Table 1, the initial TON (mol of reacted glucose per mol of total gold per hour), is strongly dependent upon pH, varying from 2700 h^{-1} at pH 7, through 10,500 h^{-1} at pH 9.5 up to 45,000 h^{-1} at pH 12. In any case, the rate declines with time owing to the instability of colloidal particles in the presence of gluconate.[13]

Analytical determinations allowed us to detect hydrogen peroxide, by the titanium sulphate test[16] and quantify it by permanganate titration[17] in the reaction solution: at pH 7 it was formed approximately in a 1:1 ratio with respect to gluconate and accumulated in the first 900 s. By increasing the alkalinity, we always observed H_2O_2 amounts below the stoichiometric value at pH 9.5 and only trace amounts at pH 12. It is known that hydrogen peroxide decomposition is favoured by alkali.[18] However, in addition to H_2O_2 decomposition, its reaction with glucose should also be taken into ac-

Table 1. Analytical data of the reacting solutions. $[Au] = 2.5 \cdot 10^{-5}$ M; [Glucose] = 0.35 M; $T = 303$ K; $O_2 = 6$ NL·h^{-1}.

Test	pH	t (s)	Conversion %	$M(H_2O_2)_{found}$	$M(H_2O_2)_{calcd.}$
1	7	100	0.45	$1.9 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
2	7	400	0.92	$3.7 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$
3	7	900	1.68	$5.2 \cdot 10^{-3}$	$6.4 \cdot 10^{-3}$
4	9.5	100	2.61	$6.2 \cdot 10^{-3}$	$9.9 \cdot 10^{-3}$
5	9.5	400	8.12	$10.5 \cdot 10^{-3}$	$30.9 \cdot 10^{-3}$
6	9.5	900	14.50	$5.3 \cdot 10^{-3}$	$54.9 \cdot 10^{-3}$
7	9.5	1900	18.34	$< 0.1 \cdot 10^{-3}$	$69.7 \cdot 10^{-3}$
8	12	110	9.06	$0.3 \cdot 10^{-3}$	$34.4 \cdot 10^{-3}$
9	12	170	13.61	$0.1 \cdot 10^{-3}$	$51.7 \cdot 10^{-3}$
10	12	230	14.83	$< 0.1 \cdot 10^{-3}$	$56.3 \cdot 10^{-3}$

Table 2. Oxidation of glucose by continuous addition of H_2O_2 under N_2. [Au] = $2.5 \cdot 10^{-5}$ M; [Glucose] = 0.35 M, T = 303 K, pH = 9.5; N_2 = 6 NL·h^{-1}.

Test	t (s)	$M(H_2O_2)_{added}$	M(gluconate)	$M(H_2O_2)_{found}$	% $H_2O_{2decomp.}$
1[a]	100	$2.0 \cdot 10^{-3}$	0	$1.5 \cdot 10^{-3}$	25
2[a]	200	$4.0 \cdot 10^{-3}$	0	$2.8 \cdot 10^{-3}$	30
3[a]	500	$1.0 \cdot 10^{-2}$	0	$7.0 \cdot 10^{-3}$	30
4[a, b]	950	$1.2 \cdot 10^{-1}$	$1.9 \cdot 10^{-2}$	$6.3 \cdot 10^{-2}$	32
5[b]	1800	$3.4 \cdot 10^{-1}$	$8.2 \cdot 10^{-2}$	$7.0 \cdot 10^{-2}$	55
6[b]	2300	$4.5 \cdot 10^{-1}$	$1.1 \cdot 10^{-1}$	$1.2 \cdot 10 \cdot ^{1}$	40

[a] $[H_2O_2] = 8\ 10^{-7} \cdot mol \cdot s^{-1}$.
[b] $8 \cdot 10^{-6}$ mol·s^{-1}.

count as a possible event. To verify this point, H_2O_2 was tested as a substitute for the O_2 reagent under similar conditions: it was continuously added by an automatic syringe to a 0.35 M glucose solution under nitrogen flow in order to produce, in the first 1000 s, local concentrations ranging from 10^{-3} to 10^{-1} mol·L^{-1}.

Following the rate of gluconate formation, reported in Table 2, we can observe that, for the tests at pH 9.5 no gluconic acid was titrated in the presence of H_2O_2 concentrations up to $7 \cdot 10^{-3}$ M (tests 1–3), whereas a consistent decomposition of the reagent (25–30%) always took place. Glucose oxidation started only when the H_2O_2 concentration was between 10^{-2} and 10^{-1} M (tests 4–6) meaning that the loss of H_2O_2, outlined in Table 1 at pH 9.5 and pH 12 (tests 4–10), is mainly due to decomposition.

More detailed information on the H_2O_2 reactivity has been derived considering the rate of glucose oxidation using different initial concentrations of H_2O_2, in the presence of a constant amount of gold sol, as represented in Figure 1.

From these data, the slope has been calculated in the 20–40 s interval owing to experimental uncertainty in the first 20 s, and the linear correlation between rate and H_2O_2 concentration is represented in Figure 2.

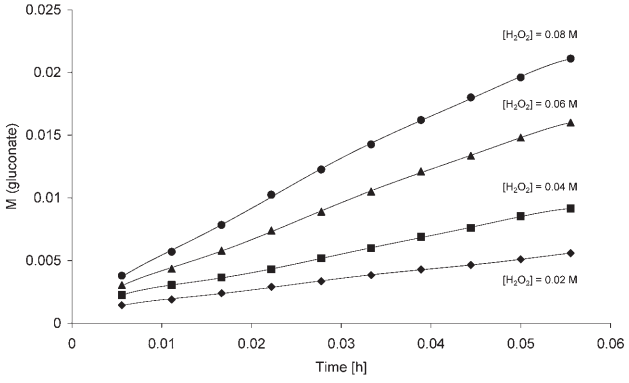


Figure 1. Glucose conversion at different H_2O_2 concentrations. [Au] = $2.5 \cdot 10^{-5}$ M; [Glucose] = 0.35 M, T = 303 K, pH = 9.5; N_2 6 NL·h^{-1}.

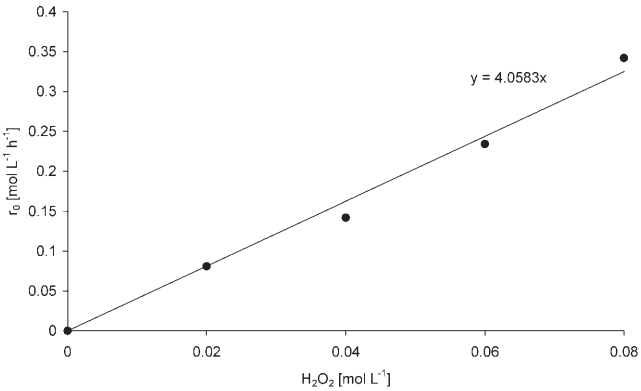


Figure 2. Initial rate of glucose oxidation at different H_2O_2 concentrations.

In ref.[14] an analogous linear plot, related to the glucose oxidation by O_2 at different concentrations, was already determined with a similar experimental procedure using identical values of gold concentration, glucose concentration and temperature. Although the angular coefficient calculated from the plot of Figure 2 (4 h^{-1}) cannot represent the true apparent rate constant, owing to the unknown amount of decomposed H_2O_2, (evaluated as 25–40% of the total in the experiments of Table 1), it can be roughly compared with the apparent rate constant (165 h^{-1}) calculated when O_2 was used as a reagent.[14] According to these data, dioxygen results as being at least one order of magnitude more efficient than hydrogen peroxide at the same concentration. From a practical point of view, however, H_2O_2 can be more easily used at higher concentrations, allowing higher initial TOF as shown in Figure 3.

Considering that the experiment with H_2O_2, carried out in an open reactor under nitrogen flow at atmospheric pressure, allows us to exceed by two times the rate of glucose oxidation observed using O_2 at atmospheric pressure, we can exclude that O_2, formed by H_2O_2 decomposition, is the effective oxidant during the oxidation with hydrogen peroxide.

In conclusion, it has been demonstrated the tendency of gold to catalyse the two- electrons reduction of dioxy-

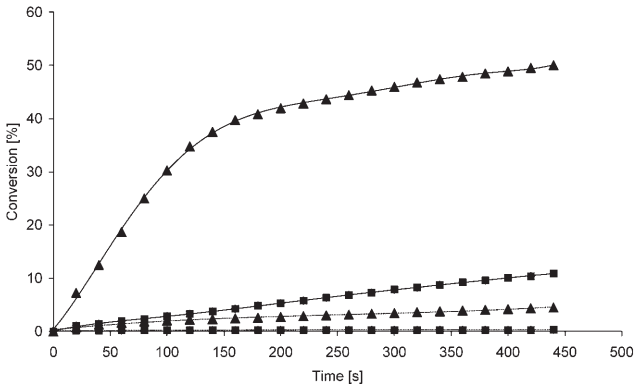
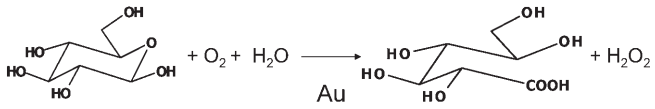


Figure 3. The reactivity of H_2O_2 and O_2 in glucose oxidation. [Au] = $1.4 \cdot 10^{-5}$ M, [Glucose] = 0.35 M, T = 303 K, pH = 9.5; ▲ [H_2O_2] = 0.35 M, N_2 = 6 NL·h^{-1}; ■ O_2 = 6 NL·h^{-1} at 0.1 MPa (10^{-3} M); blanks, without catalyst: lower two lines.

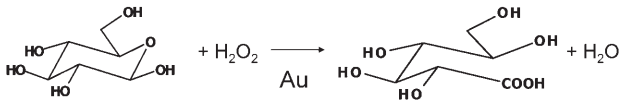
gen forming hydrogen peroxide: this occurs not only in the case of molecular hydrogen as a reducing agent,[19,20] reaction 1, but also using more complex organic molecules, as glucose, according to reaction 2:

$$O_2 + H_2 = H_2O_2 \quad (1)$$



(2)

$$H_2O_2 \xrightarrow[OH^-]{} H_2O + 0.5\ O_2 \quad (3)$$

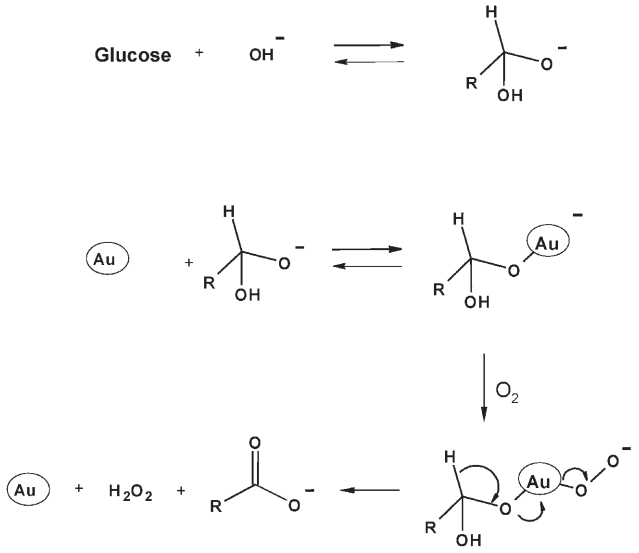


(4)

In the presence of alkali, hydrogen peroxide is mainly decomposed, Equation (3), before reaching a sufficient concentration for oxidising glucose. It is worth noting that Equations (2) and (3) are also the basis of the enzymatic oxidation catalysed by oxidase and catalase, respectively.[15]

Concerning the mechanism of molecular activation, Scheme 1 can be proposed for gold catalysis on the basis of the promoting effect of alkali and the formation of hydrogen peroxide as a reaction product.

The key point is represented by the electron-rich gold species, formed by the hydrated glucose anion with gold surface atoms, which is supposed to activate molecular oxygen by nucleophilic attack. According to previous experiments correlating catalytic activity with particle dimensions,[13] we suppose that an efficient nucleophilic



Scheme 1.

behaviour is determined by the electronic properties of the nanometric gold particles (d < 10 nm).

In the dioxogold intermediate either Au^{+}–O_2^{-} or Au^{2+}–O_2^{2-} couples can be formally considered as a bridge for the two electron-transfer from glucose to dioxygen. Peroxidic-like species have already been supposed as a reaction intermediate during dihydrogen oxidation to water on a gold catalyst.[20]

Experimental Section

A colloidal dispersion of gold, **I**, was prepared by treating a $1.25 \cdot 10^{-4}$ M aqueous solution of Au (as $HAuCl_4$) with $NaBH_4$ ($NaBH_4$: Au = 5) under an N_2 atmosphere, in the presence of a large excess of glucose (0.35 M). The resultant brown sol contained metal particles, stable for several hours in the absence of dioxygen, having a mean diameter of 3.6 nm, determined by TEM performed on a drop of the dispersion evaporated on a copper grid.

The oxidation of glucose with O_2 was carried out in a thermostatted, magnetically stirred reactor (80 mL) with bubbling dioxygen at atmospheric pressure. The reaction was started by adding the gold sol to the O_2 saturated solution. Gluconic acid was continuously titrated at fixed pH value (7.0, 9.5 and 12) with NaOH, using a GPD 751 Titrino apparatus (Metrohm). In the reaction product, only gluconate was detected by HPLC at pH 7 and 9.5 whereas at pH 12 fructose plus other unidentified products (*ca.* 10–15%) were formed.

The oxidation of glucose with H_2O_2, related to the data of Tables 1 and 2, was carried out in a similar apparatus where H_2O_2 (10% w/w) was continuously added by means of an automatic syringe to the glucose solution containing the gold sol, and the kinetics followed by titrating the formed gluconic acid at the given pH. The data referring to Figure 3 were obtained after one-pot addition of H_2O_2 (30%) to obtain a 1:1 ratio to glucose.

For the analytical determinations, the following procedure has been set up: a sample (4–10 mL) of the reacting solution was withdrawn at the indicated times and titrated with a 10^{-2} M $KMnO_4$, 10^{-3} M $MnSO_4$ and 0.08 M H_2SO_4 solution at constant pH of 1.8 ± 0.1 in order to selectively oxidise H_2O_2 in the presence of a large amount of glucose. Blank experiments on glucose-H_2O_2 solutions of similar concentrations showed an acceptable reproducibility (2%).

Acknowledgements

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