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Electrocatalytic Oxidation of Saturated Oxygenated Compounds on Gold Electrodes[1]

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The electrocatalytic oxidation of several saturated oxygenated organic compounds (ethanol, ethylene glycol, acetaldehyde, glycolaldehyde, glyoxal, acetic acid, glycolic acid, glyoxylic acid, oxalic acid, glycerol, and the four butanol isomers) was investigated on gold electrodes both in acid and alkaline medium using cyclic voltammetry. For all the compounds investigated in this work, gold behaves as a poor electrocatalyst in acid medium, except for the oxidation of glyoxylic acid and oxalic acid. In alkaline medium, conversely, gold is an excellent electrocatalyst (even much better than platinum), particularly for the oxidation of the aldehyde functional group and the alcohol group.

INTRODUCTION

Electrocatalysis can be defined as heterogeneous catalysis by the electrode material of electrochemical reactions, such as those occurring in fuel cells or in organic electrosynthesis. The electrocatalytic activity of a given electrode for a certain reaction may be characterized by the current density at a chosen potential, which is proportional to the specific activity, when referred to the effective active surface, as has been done in this work.

According to several studies undertaken in recent years, gold is generally considered as a poor electrocatalyst. It is true that when looking into its electrocatalytic properties toward a test reaction such as the electrochemical oxidation of formic acid in aqueous solution, a gold electrode appears comparatively inactive with respect to a platinum electrode or even to palladium and rhodium electrodes, either in acid (*1*) or in neutral medium (*2*). Even when increasing the temperature at which the electrooxidation of formic acid is carried out, its activity still remains lower than that of platinum (*3*). Furthermore, gold electrodes are practically inactive for the oxidation of methanol, an important fuel for fuel cell technology. On the other hand, it is clear from the literature that the activity of gold is inhibited by foreign metal adatoms for all the systems so far investigated. This behavior contrasts strongly with that of the other noble metals, Pt, Rh, Ir, and Pd, for which the activity is usually enhanced by underpotential deposition of submonolayers of Pb, Bi, Tl, or Cd (*4, 5*).

However, it must be emphasized that most of these studies were carried out in acid electrolytes. The situation is different if the electrooxidation is carried out in alkaline solutions. It was shown earlier, for example, that the current densities obtained during the electrochemical oxidation of ethylene glycol were about four times higher with gold than with platinum (*6*). This result suggests that gold might be a good catalyst for the electrochemical oxidation of alcohols in alkaline medium and we have therefore undertaken a systematic survey of the oxidation of aliphatic alcohols and related compounds on gold electrodes.

In the present work the behavior of a gold electrode is illustrated with respect to

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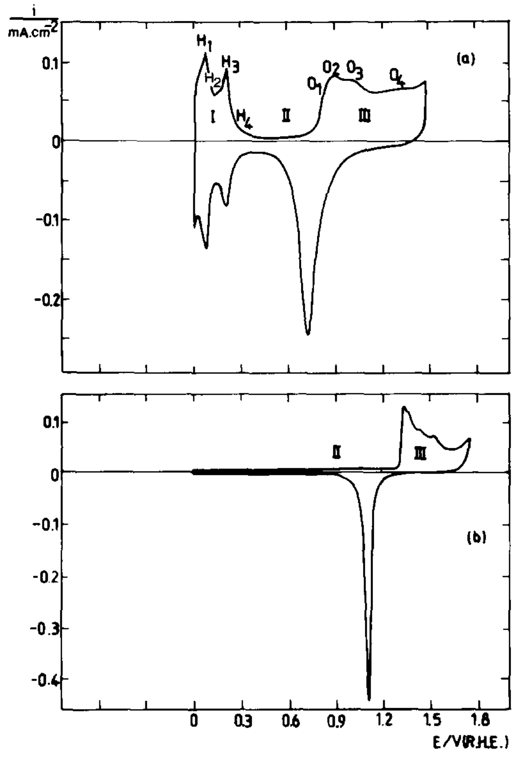

FIG. 1. Cyclic voltammograms of a noble metal electrode in an acid supporting electrolyte (0.5 *M* H_2SO_4, 25°C, 50 mV · s^{-1}): (a) platinum electrode, (b) gold electrode.

several reactions: oxidation of formate, comparative oxidation of C_2 saturated organic compounds, oxidation of glycerol, and oxidation of the butanol isomers.

Comparison of the Electrocatalytic Behavior of Gold and Platinum Electrodes

By way of further introduction, it is useful to recall the behavior in cyclic voltammetry of a gold electrode in the supporting electrolyte alone and also to compare it with that of a platinum electrode, which, being widely used by most electrochemists, can be considered as a model electrode for electrocatalysis.

1. Cyclic voltammetry and characteristics of the electrode surface. Cyclic voltammetry is a widely used electrochemical technique which allows one to investigate the transient reactions occurring on the electrode surface when the potential applied to the electrode is varied linearly and repetitively at a constant sweep rate between two given suitable limits. The steady-state current–potential curves (the so-called "voltammograms") recorded provide direct information on the adsorption–desorption processes and allow one to estimate the catalytic properties of the electrode surface (*7, 8*).

The voltammogram of a platinum electrode recorded at 25°C in 0.5 *M* H_2SO_4 at a sweep rate of 50 mV · s^{-1} between a lower limit (E_c = 0.0 V/RHE) and an upper limit (E_a = 1.5 V/RHE), where RHE (reversible hydrogen electrode) is the reference electrode, displays three regions according to the applied potential (Fig. 1a). Region I at lower potentials is associated with the adsorption (reduction peaks)–desorption (oxidation peaks) of hydrogen, whereas region III at higher potentials reveals the adsorption (oxidation peaks)–desorption (reduction peak) of oxygenated species at the electrode surface (*9, 10*). Between them is the double-layer region II, where no net electrochemical reaction occurs, and which is characterized by small currents associated with the charge and discharge of the double-layer capacity.

Considering now a gold electrode, the voltammogram recorded under the same experimental conditions (0.5 *M* H_2SO_4, 50 mV · s^{-1}, 25°C) is relatively much simpler, the hydrogen region having disappeared (Fig. 1b). The double-layer region is remarkably spread out in potential (from 0.0 to 1.3 V/RHE). The oxygen region is again characterized by the occurrence of several adsorption peaks and usually of a single desorption peak at about 1.1 V/RHE.

When the same experiments are performed in alkaline medium, 0.1 *M* NaOH, instead of acid electrolyte, the main features of both voltammograms remain unchanged (Fig. 2a for platinum and Fig. 2b for gold). However, there is an interesting point to note, namely, the existence of greater currents in the double-layer region

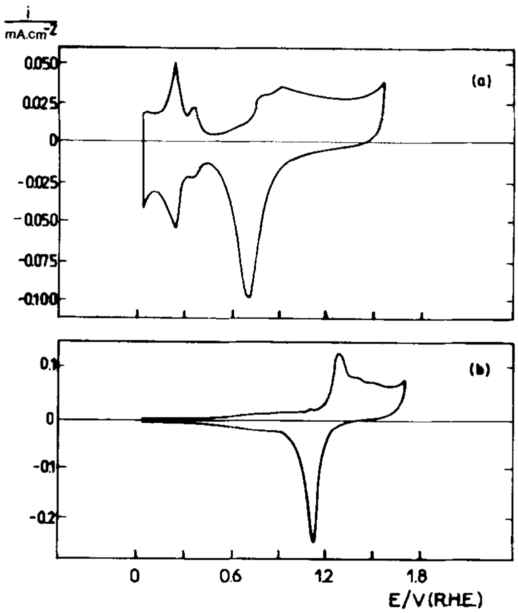

FIG. 2. Cyclic voltammograms of a noble metal electrode in alkaline supporting electrolyte (0.1 *M* NaOH, 25°C, 50 mV · s^{-1}): (a) platinum electrode, (b) gold electrode.

for both electrodes. These currents arise from Faradaic processes associated with the oxygen region, which begin earlier in alkaline medium, particularly for the gold electrode, where the onset of the adsorption of oxygenated species begins at 0.4 V/ RHE (Fig. 2b). Although the voltammetric investigation does not allow one to identify this kind of adsorbed species, it is reasonable to think that this current is related to earlier OH adsorption, as far as this process is supposed to be favored in alkaline medium. Therefore this layer will necessarily affect the catalytic properties of a gold surface in alkaline medium (as compared with its behavior in acid medium), and may explain part of the results which will be given below.

The effective electroactive surface may be determined directly with the voltammogram by evaluating the quantity of electricity involved in the adsorption–desorption of hydrogen (region I) or oxygen (region III). The quantity of electricity is obtained by integration of the current–potential curves, because the potential varies linearly with time. The active surface area is then calculated by assuming the formation of a complete monolayer of adsorbed hydrogen at the reversible potential of a hydrogen electrode (which needs 210 $\mu C \cdot cm^{-2}$ in the case of Pt), or the formation of a known part of a monolayer of adsorbed oxygen at a given potential (case of Pt and Au). The current densities are then obtained by dividing the measured current intensities by the effective surface in order to compare the electrocatalytic activity independently of the geometric surface.

2. *Example of electrocatalytic oxidation on gold.* The first example which can be chosen to illustrate the catalytic activity of a gold electrode is the oxidation of formic acid. When HCOOH is added to a 0.5 *M* H_2SO_4 solution at room temperature, almost no oxidation current is seen and the voltammogram is practically identical to the one recorded in the supporting electrolyte alone. However, when the temperature is increased, a slight oxidation current becomes noticeable and reaches about 0.3 mA cm^{-2} with 10^{-2} *M* HCOOH at 80°C (Fig. 3a). It is clear from this figure that the adsorbed oxygen atoms act as inhibitors for the organic oxidation and that the electrode surface recovers its catalytic properties during the backward sweep, which becomes superimposed on the forward sweep, as soon as this adsorbed oxygen is reduced. This rather simple behavior is characteristic of a quasi-stationary single oxidation process. A much more complex situation is found when formic acid is oxidized on platinum (Fig. 3b). The various peaks, which do not display any coinciding part during the forward and backward sweeps, can be related to different potential dependent oxidation processes, including the formation of strongly bonded intermediates, which poison the electrode surface.

EXPERIMENTAL

All the voltammograms were recorded under standard conditions (except when

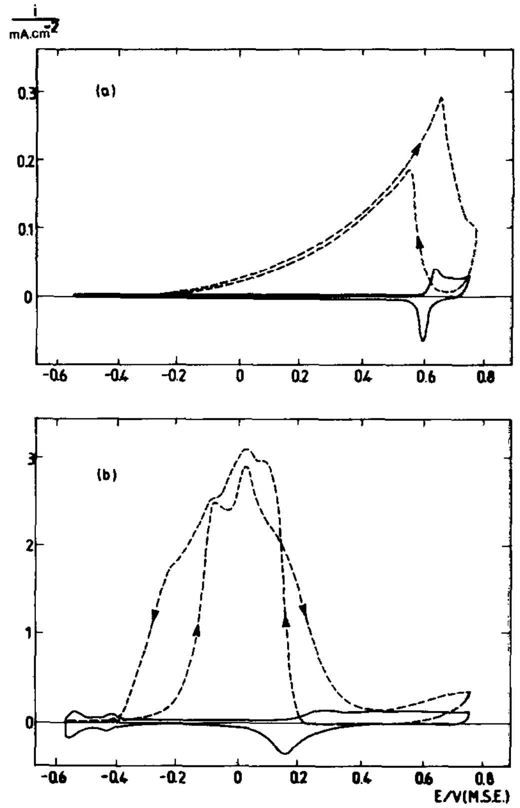

FIG. 3. Cyclic voltammograms for the electrooxidation of formic acid in acid medium (0.5 *M* H_2SO_4, 80°C, 20 mV · s^{-1}); (a) at a gold electrode, (b) at a platinum electrode. (—) Supporting electrolyte alone; (---) supporting electrolyte with 10^{-2} *M* HCOOH.

specified in the text) for a 0.1 *M* concentration in electroactive species, at 25 ± 0.1°C, and at a sweep rate of 50 mV · s^{-1}. This sweep rate was chosen as a compromise between low values where the *i*(*E*) curves can be considered as stationary, and high values where they are transient. This allows us to compare the relative specific electrocatalytic activities of platinum and gold for different oxidation reactions, in a way which is relevant for applied problems (e.g., in fuel cell reactions). Ultrapure metals (99.999%) provided by Johnson-Matthey Corporation were used to prepare the electrodes (geometric area about 0.1 cm^2). The solutions were prepared from Merck Suprapur supporting electrolytes dissolved in pure water which was deionized, and then further one or two times distilled.

The experiments were performed with conventional equipment. A Wenking PGS 77 potentiostat is driven by a PAR 175 waveform generator in order to impose a potential difference *E* between the working electrode WE (gold or platinum) and a reference electrode RE. The potentials, although measured vs a mercurous sulfate electrode (MSE), are often given vs the reversible hydrogen electrode (RHE) in the same solution. Under standard conditions (pH 0), the two scales differ by about 650 mV, the MSE being more positive. The currents flow between WE and a gold (or platinum) counterelectrode CE.

All the glassware was carefully washed before each experiment and the solutions were deaerated by bubbling very pure nitrogen for at least 20 min (more in alkaline medium) in order to remove any dissolved oxygen, until a correct voltammogram for platinum was obtained. This procedure is very important, since the high activity of Pt allows one to detect impurity traces even in very low concentrations (as low as 10^{-8} *M*, for example, in the case of Cl^-). Moreover any metallic surface impurity would be also detected unambiguously by some minor changes in the voltammogram features.

RESULTS

Comparative Oxidation of Various C_2 Satured Organic Compounds on Gold Electrodes (*11*)

The electrochemical oxidation of 10 organic compounds containing two carbon atoms (ethane, ethanol, acetaldehyde, acetic acid, ethylene glycol, glycolaldehyde, glycolic acid, glyoxal, glyoxylic acid, and oxalic acid) was investigated on gold electrodes, both in acid and alkaline media, using cyclic voltammetry under the experimental conditions specified above.

Such a survey is interesting in order to

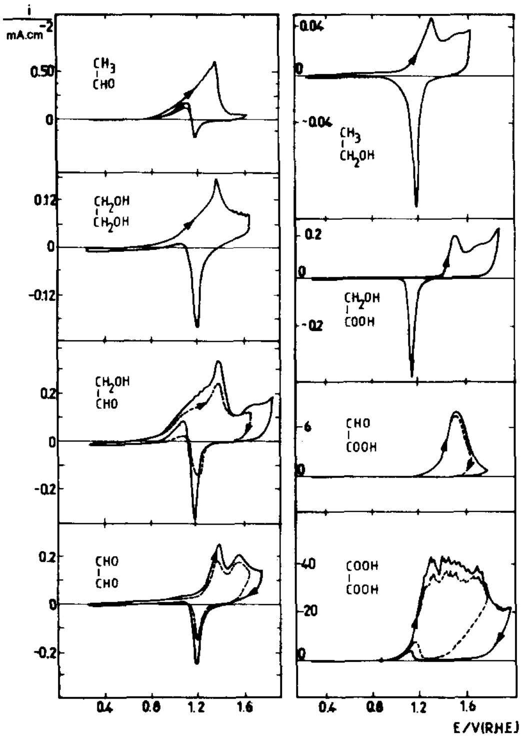

FIG. 4. Oxidation of various C_2 saturated organic compounds on a gold electrode in acid medium (0.1 *M* $HClO_4$, 0.1 *M* organic, 25°C, 50 mV · s^{-1}).

deduce if there are any inductive effects (electronic and/or steric) coming from the functional groups.

The voltammograms recorded in 0.1 *M* $HClO_4$ + 0.1 *M* organic are given in Fig. 4. The peak characteristics, i.e., the maximum current densities i_M and the corresponding peak potential E_M are listed in Table 1. Similarly, the results obtained in alkaline solution (0.1 *M* NaOH) for the oxidation of 0.1 *M* organic are given in Fig. 5 and are also listed in Table 1.

From these experiments it appears that:

(i) in acid medium, only glyoxylic acid and oxalic acid are significantly oxidized, involving the breaking of the C–C bond;

(ii) gold has a much better activity in alkaline medium than in acid medium;

(iii) in alkaline medium gold is strongly active for oxidation of the aldehyde group (with the exception of glyoxal which undergoes a Cannizzaro reaction leading to glycolate) and reasonably active for oxidation of the alcohol group;

(iv) the C–C bond is not easily broken in alkaline medium; as a result oxalate is not oxidized.

The question that arises now is how to compare the activity of gold with that of platinum under similar conditions of concentrations and of other experimental parameters. Thus the same series of organics was also investigated with platinum in the laboratory and the results are discussed in detail elsewhere (*12*). In order to compare better the electrocatalytic activity of gold and platinum electrodes, the voltammograms during the positive sweep are given schematically as rectangular triangles

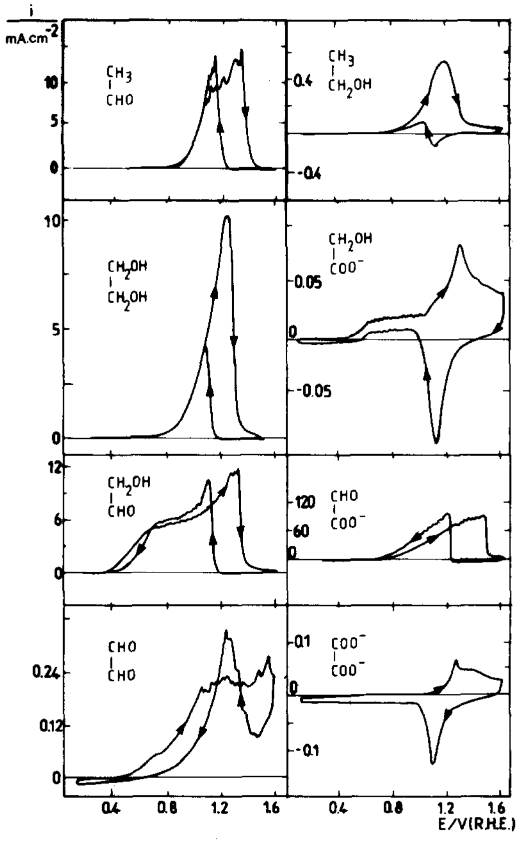

FIG. 5. Oxidation of various C_2 saturated organic compounds on a gold electrode in alkaline medium (0.1 *M* NaOH, 0.1 *M* organic, 25°C, 50 mV · s^{-1}).

TABLE 1

Maximum Current Densities (i_M) and Maximum Peak Potentials (E_M) Observed during the Electrooxidation of Various C_2 Organic Compounds

Compound		In 0.1 *M* $HClO_4$		In 0.1 *M* NaOH	
		i_M (mA · cm^{-2})	E_M (V/RHE)	i_M (mA · cm^{-2})	E_M (V/RHE)
CH_3–CH_3	Ethane	No oxidation		No oxidation	
CH_3–CH_2OH	Ethanol	No oxidation		Nearly no oxidation	
CH_3–CHO	Acetaldehyde	0.7	1.35	16.0	1.30
CH_3–COOH	Acetic Acid	Nearly no oxidation		No oxidation	
CH_2OH–CH_2OH	Ethylene glycol	Nearly no oxidation		10.5	1.25
CHO–CH_2OH	Glycoladehyde	Nearly no oxidation		11.0	1.30
CH_2OH–COOH	Glycolic acid	Nearly no oxidation		Nearly no oxidation	
CHO–CHO	Glyoxal	Nearly no oxidation		Nearly no oxidation	
CHO–COOH	Glyoxylic acid	8.2	1.50	107	1.25
COOH–COOH	Oxalic acid	50.0	1.25	No oxidation	

ABC, where the base AB is drawn on the potential axis between the onset of the organic electrooxidation (A) and the peak potential (B), and the height BC represents the magnitude of the peak current densities (Fig. 6a for acid medium and Fig. 6b for alkaline medium). From the comparison of the behavior of the two electrodes, it is noticeable that platinum shows a higher activity in acid medium (especially because it is active for alcohol oxidation), but, remarkably and conversely, gold is a much better catalyst than platinum in alkaline medium, leading, for example, to nearly 100 mA · cm^{-2} for glyoxylate oxidation, i.e., five times more than platinum.

This comparison is summarized in Table 2, where the absence of reactivity of a given functional group (–COOH, –CHO, –CH_2OH, or –CH_3) is denoted by the minus sign and the presence of reactivity by the plus sign, the number of the latter varying from 1 to 3, representing a low, medium, or high reactivity.

Electrooxidation of Glycerol (13)

This example is to illustrate again the very good catalytic properties of gold toward electrooxidation of alcohols in alkaline medium, as compared to platinum.

Solutions of 0.1 *M* glycerol, CH_2OH–$CHOH$–CH_2OH, were oxidized on gold and platinum electrodes (*14*). The voltammograms obtained on the respective electrodes in alkaline medium are given in Figs. 7a and 7b, respectively, and the electrocatalytic activity is summarized in Table 3 for acid and alkaline media. As can be seen from this table, current densities for glycerol oxidation as large as 15 mA · cm^{-2} can be obtained on gold electrodes in alkaline medium, while a platinum electrode gives much smaller currents. Furthermore, the difference of the glycerol reactivity in acid and basic media is striking, gold electrodes being totally inactive in acid medium.

TABLE 2

Comparative Reactivities of Different Functional Groups in the Electrooxidation of C_2 Saturated Organic Compounds

	–COOH or –COO^-	–CHO	–CH_2OH	–CH_3
Acid medium				
Pt	+++	+	+	–
Au	++	–	–	–
Alkaline medium				
Pt	–	+	+	–
Au	–	+++	+	–

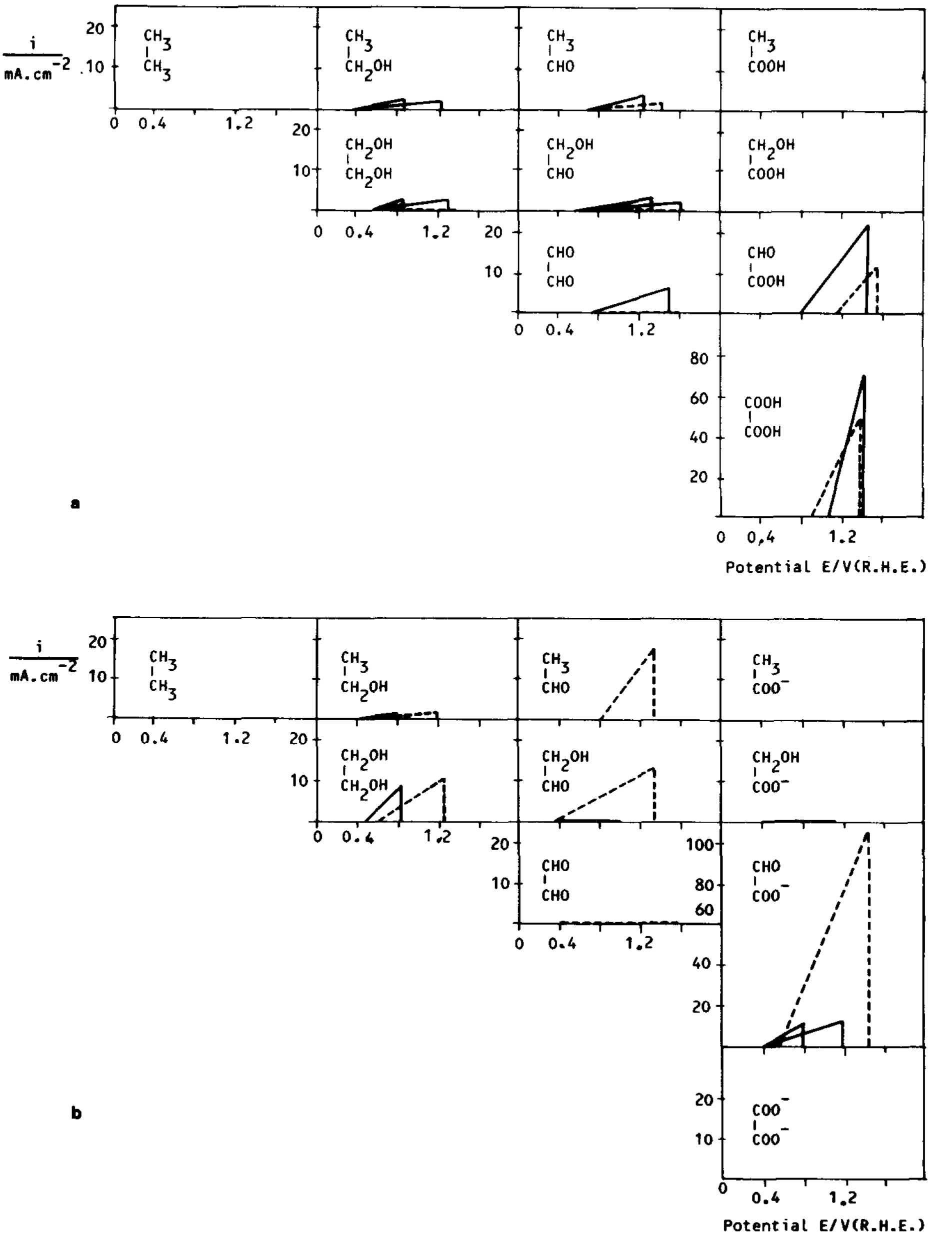

Fig. 6. Schematic comparison of the electrooxidation of various C_2 saturated compounds on a platinum electrode (—) and on a gold electrode (---). Only the positive sweep is given. (a) Acid medium (0.1 *M* $HClO_4$), (b) alkaline medium (0.1 *M* NaOH).

Electrooxidation of the Butanol Isomers on Gold in Alkaline Medium (15)

This last example is chosen to illustrate the fact that the reactivity of an organic molecule may also depend on its molecular structure and that the maximum current densities obtained during electrooxidation at a given electrode are not only related to the surface properties.

Four isomeric forms of butanol, namely, *n*-butanol, isobutanol (2-methyl-1-pro-

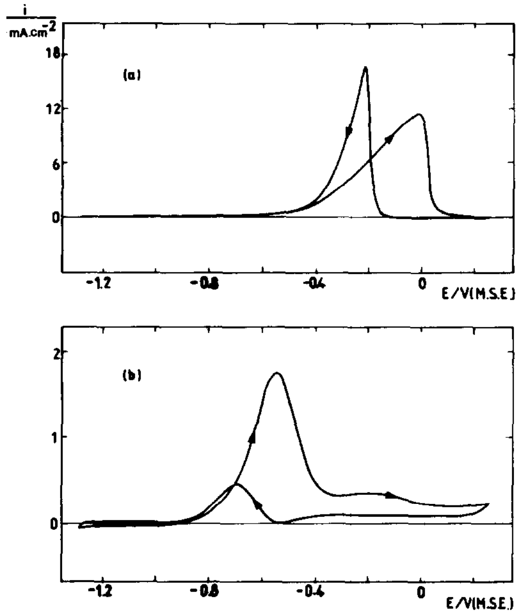

FIG. 7. Oxidation of 0.1 *M* glycerol in 0.1 *M* NaOH at 25°C and 50 mV · s^{-1}: (a) on a gold electrode, (b) on a platinum electrode.

panol), sec-butanol, and t-butanol (2-methyl-2-propanol) were oxidized on gold in 0.1 *M* NaOH solutions, under the same experimental conditions as mentioned above (*16*). Typical voltammograms are given in Fig. 8.

It is concluded that t-butanol is absolutely unreactive at room temperature, *n*-butanol and isobutanol are oxidized with approximately the same magnitude of current densities (3 to 4 mA · cm^{-2}), while sec-butanol is more strongly oxidized and gives current densities twice as great as the two preceding isomers. This is a clear indication of molecular structural effects. However, in the present state of our investigations, it is too early to state definitively if this comes from steric effects, electronic effects, or a contribution of both.

DISCUSSION

The results survey the general catalytic properties of gold for the electrochemical oxidation of small organic molecules.

It is confirmed that the activity of gold in acid medium is less interesting than that of platinum. However, conversely, to a general idea shared by most catalytic chemists and electrochemists, it is demonstrated that gold is a very good catalyst for the electrochemical oxidation of aldehydes and alcohols in alkaline solutions. In the particular cases of acetaldehyde, glycolaldehyde, glyoxylate, ethylene glycol, glycerol, and sec-butanol, it is even much better than platinum and high current densities can be obtained, which in principle is interesting for a possible use in fuel cells. However, the potentials at which the maximum current densities occur are too positive for practical applications in this field. These difficulties may be overcome using gold–platinum alloys, on which the oxidation takes place at much lower potentials with higher rates due to synergistic effects (*17*). On the other hand, if one considers the differences in behavior between gold and platinum, these electrodes could be used for selective oxidation in organic electrosynthesis.

It is not the purpose of this paper to detail the various oxidation mechanisms which are involved in the examples given above. However, such a striking change in behavior between acid and alkaline media is most certainly related to the existence of a submonolayer of adsorbed hydroxyl groups, the formation of which is favored on gold in alkaline medium at rather lower potentials.

TABLE 3

Maximum Current Densities (i_M) in Glycerol Electrooxidation

		i_M (mA · cm^{-2})
In acid medium		
On gold	No activity	0
On platinum	Low activity	0.2
In alkaline		
On gold	Large activity	15.0
On platinum	Medium activity	2.2

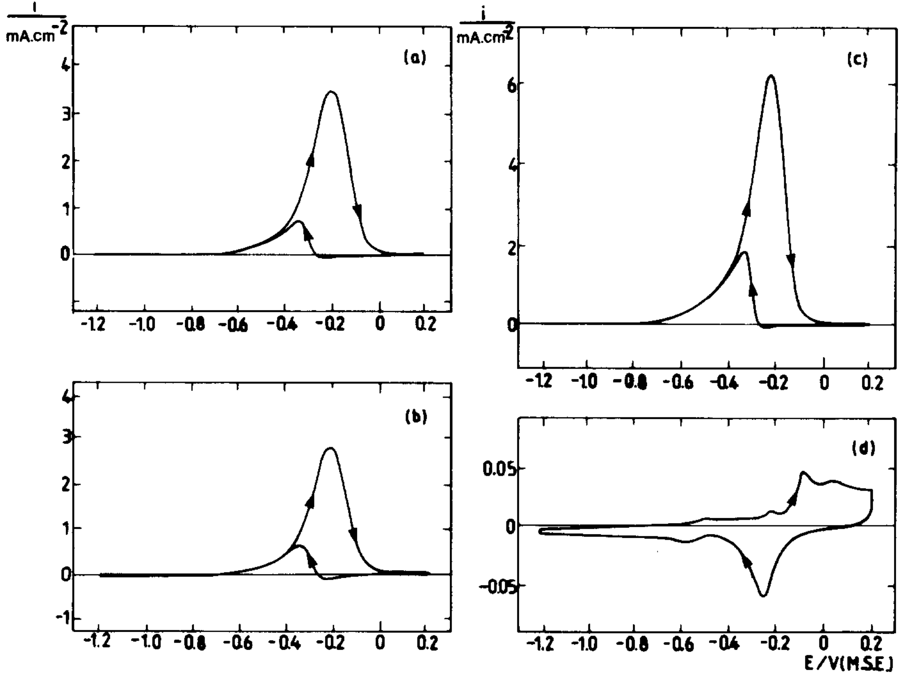

FIG. 8. Comparative oxidation of the butanol isomers on a gold electrode in alkaline medium (0.1 *M* NaOH, 0.1 *M* butanol, 25°C, 50 mV · s^{-1}): (a) *n*-butanol, (b) isobutanol, (c) sec-butanol, (d) t-butanol.

A systematic study is needed to investigate totally the electrocatalytic properties of gold and one of the most important points in electrocatalysis remains the *in situ* identification of adsorbed species and intermediate products of the reactions. This might be done by the use of spectroscopic techniques, such as electromodulated infrared reflectance spectroscopy (EMIRS) (*18*, *19*), which looks very promising in the investigation of electrocatalytic reactions (*20*, *21*).

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REFERENCES

1. Capon, A., and Parsons, R., *J. Electroanal. Chem.* **44,** 239 (1973).
2. Beden, B., Lamy, C. and Léger, J. M., *J. Electroanal. Chem.* **101,** 127 (1979).
3. Crépy, G., Lamy, C., and Maximovitch, S., *J. Electroanal. Chem.* **54,** 161 (1974).
4. Adžić, R. R., *Isr. J. Chem.* **18,** 166 (1979).
5. Beden, B., Kadirgan, F., and Lamy, C., *in* "Proceedings, 33rd I.S.E. Meeting, Lyon, France," September, 1982, Extended Abstracts IV B07, Vol. 2, p. 729.
6. Hauffe, W., Heitbaum, J., and Vielstich, W., *in* "Electrode Materials and Processes for Energy Conversion and Storage" (J. D. E. McIntyre, S. Srinivasan, and F. G. Will, Eds.), PV-77-6, p. 308. The Electrochemical Society, Princeton, N.J., 1977.
7. Gileadi, E., Kirowa-Eisner, E., and Penciner, J., "Interfacial Electrochemistry: An Experimental Approach." Addison-Wesley, Reading, Mass., 1975.
8. Angerstein-Kozlowska, H., Conway, B. E., Barnett, B., and Mozota, J., *J. Electroanal. Chem.* **100,** 417 (1979).
9. Angertein-Kozlowska, H., Sharp, W. B. A., and Conway, B. E., *in* "Proc., Symp. in Electrocatalysis" (M. W. Breiter, Ed.), p. 94. The Electrochemical Society, Princeton, N.J., 1974.
10. Woodard, F. E., Scortichini, C. L., and Reilley, C. N., *J. Electroanal. Chem.* **151,** 109 (1983).
11. Çetin, I., Diplôme d'Etudes Supérieures, University of Istanbul, 1983.
12. Çetin, I., Beden, B., and Lamy, C., to be submitted for publication.
13. Kahyaoglu, A., Thèse de 3ème Cycle, Université de Poitiers, 1981.

14. Kahyaoglu, A., Beden, B., and Lamy, C., *Electrochim. Acta* **29,** 1489 (1984).

15. Takky, D., Thèse de 3ème Cycle, Université de Poitiers, 1983.

16. Takky, D., Beden, B., Léger, J. M., and Lamy, C., *J. Electroanal. Chem.* **145,** 461 (1983).

17. Beden, B., Kadirgan, F., Kahyaoglu, A., and Lamy, C., *J. Electroanal. Chem.* **135,** 329 (1982).

18. Bewick, A., *J. Electroanal. Chem.* **150,** 481 (1983).

19. Bewick, A., Kunimatsu, K., Pons, B. S., and Russell, J. W., *J. Electroanal. Chem.* **160,** 47 (1984).

20. Beden, B., Bewick, A., Kunimatsu, K., and Lamy, C., *J. Electroanal. Chem.* **142,** 345 (1982).

21. Hahn, F., Beden, B., and Lamy, C., *J. Electroanal. Chem.*, **204,** 315 (1986).