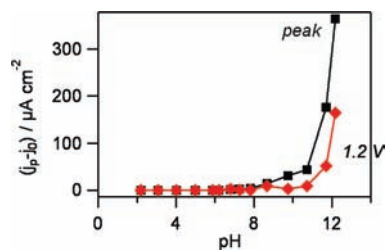# Electrocatalytic Oxidation of Alcohols on Gold in Alkaline Media: Base or Gold Catalysis?

Youngkook Kwon, Stanley C. S. Lai,[†] Paramaconi Rodriguez, and Marc T. M. Koper*

Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
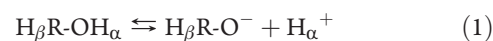
S *Supporting Information*

ABSTRACT: On the basis of a comparison of the oxidation activity of a series of similar alcohols with varying pK_a on gold electrodes in alkaline solution, we find that the first deprotonation is base catalyzed, and the second deprotonation is fast but gold catalyzed. The base catalysis follows a Hammett-type correlation with pK_a, and dominates overall reactivity for a series of similar alcohols. The high oxidation activity on gold compared to platinum for some of the alcohols is related to the high resistance of gold toward the formation of poisoning surface oxides. These results indicate that base catalysis is the main driver behind the high oxidation activity of many organic fuels on fuel cell anodes in alkaline media, and not the catalyst interaction with hydroxide.

In recent years, there has been tremendous interest in using gold as a catalyst for various heterogeneously catalyzed oxidation reactions.[1] In gas phase catalysis, gold becomes active toward oxidation reactions, primarily carbon monoxide oxidation,[2] when dispersed as small nanoparticles on an oxidic support.[2−5] Simultaneously, in the area of electrocatalysis, alkaline electrolyte media are receiving increasing attention as a medium offering higher stability to materials and often also higher catalytic activity.[6] Interestingly, there is growing awareness that the alkaline environment is in fact key to making gold, as well as other electrocatalysts such as platinum and palladium, such active oxidation catalysts, without the need for small particles or an oxidic support.[7−13] This has long been known in electrocatalysis,[12] but there is still a lack of detailed understanding as to why the combination of base and gold makes such an active and selective oxidation catalyst.

In alkaline media, many of the organic molecules whose oxidation properties have been studied in the (electro)catalysis literature, such as ethanol and glycerol, take part in an acid–base equilibrium involving the alcoholic group. In relation to the ethanol oxidation on a gold electrode,[13] we have shown that the activity varies in a highly nonlinear fashion with pH, as illustrated in Figure 1. Similar results have been obtained with methanol (Figure S1) and glycerol oxidation on gold.[14,15] It is well-known that the main products of ethanol oxidation on gold are acetaldehyde and acetic acid,[16] that is, no catalytic bond breaking takes place. On the basis of these results, we argued that, at a pH higher than ca. 11, the ethoxy anion is the reactive species, its concentration steeply increasing with higher pH. This species is then more easily oxidized to acetaldehyde. As a result, at pH = 13, the activity for ethanol oxidation is orders of magnitude higher than in acidic media.

Figure 1. Measured current j_p for 0.5 M ethanol oxidation on a gold electrode at peak potential (black curve) or at 1.2 V vs RHE (red curve) minus the background current j_0 as a function of the electrolyte pH using 0.1 M phosphate buffers. For details, see ref 13.

Therefore, at high pH the alcohol deprotonates:

$$H_\beta R\text{-}OH_\alpha \rightleftarrows H_\beta R\text{-}O^- + H_\alpha^+ \qquad (1)$$

with the pK_a of this reaction depending on the nature of R, and with HRO⁻ being significantly more reactive than HROH. This idea is not new (see e.g., refs 8, 17, and 18), but we are not aware of any explicit proof as would be afforded by establishing a Hammett-type relationship[19] between the reactivity of the alcohol and its pK_a, that is, a lower pK_a leading to a higher reactivity.

Figure 2a,b collects the positive-going voltammetric potential sweeps for a number of alkyl-alcohols (at 10 mM concentration) on a gold electrode in 0.1 M NaOH, and Figure 2c plots the onset potential, defined as the potential at which the oxidation current is twice that of the blank background, versus the pK_a of the corresponding alcohol.[20] Alternatively, differences in activity on the potential scale can be appreciated in the Tafel plots of Figure 2d, focusing on the low onset currents. Even though definitions of overall activity are imperfect and ambiguous, Figure 2 by and large confirms the above expectation: alcohols with a low pK_a, such as the sugar alcohols or glycerol, have a high oxidation activity, whereas alcohols with a high pK_a (such as isopropanol and isobutanol), are significantly less active at pH = 11. To activate such an alcoholic group, a "real" catalyst, such as platinum, is much better suited. Methanol seems to deviate somewhat from the main trend, a possible reason for which will be discussed below.
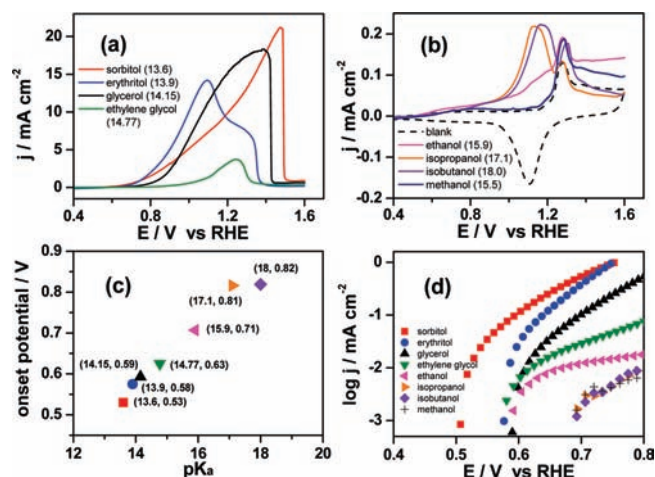
We note that we have confirmed by online HPLC[21] or literature data that the main oxidation products of the alcohols in Figure 2a,b are their corresponding aldehydes. However,

Figure 2. Linear sweep voltammograms of (a) alcohols with high j, (b) alcohols with low j on Au electrode in 0.1 M NaOH with a scan rate of 50 mV s^{-1}, (c) plots of the onset potential versus the pK_a, and (d) Tafel plots of the corresponding alcohols.

Figure 3. Decomposition of (a) glyceraldehyde and (b) glycolaldehyde, the primary oxidation products of glycerol and ethylene glycol, respectively, in a nondeaerated O$_2$-containing 0.1 M NaOH solution in the absence of gold, as determined by HPLC.

aldehydes are unstable in alkaline media[20] and, especially in the presence of oxygen, decompose into a variety of products even without a catalyst.

Figure 3 illustrates the temporal evolution of the products of the decomposition of glyceraldehyde and glycolaldehyde, the primary oxidation products of glycerol and ethylene glycol, respectively, in a nondeaerated 0.1 M NaOH solution *in the absence of gold*. Note that this Figure includes products that have been observed as the gold-catalyzed oxidation products of the corresponding alcohols.[8] Figure 3 justifies the conclusion that the role of gold in the oxidation of the aldehydes must be very limited (similar plots for glycerol oxidation on gold are available in ref 14). For the oxidation of the alcohols, the catalytic role of gold is weak but not absent: in the presence of strongly adsorbing anions, it is well-known that under electrochemical conditions gold is much less active,[13,15] suggesting that some interaction with the gold surface is still necessary.

Figure 2 collects our results obtained with alkyl-alcohols. We have also considered and studied the oxidation of alcohols whose pK_a is lowered by functionalization with fluoride, amines, or unsaturated carbon−carbon bonds. Such alcohols typically do not follow the trend illustrated in Figure 2. Fluoroethanols show hardly any oxidation activity on gold in alkaline media (Figure S2 in the Supporting Information), even though fluoroalcohols are textbook examples[20] of alcohols with a low(er) pK_a. Gellman et al.[22] have also observed that the tendency of fluoroethanol to form an adsorbed alkoxide on copper surfaces is increased compared to ethanol, but conversely, the abstraction of the beta hydrogen to form the corresponding aldehyde through

$$H_\beta R\text{-}O_{ads} \rightarrow R\text{=}O_{ads} + H_{\beta,\,ads} \tag{2}$$

was slowed down significantly (the labeling of α and β hydrogen was borrowed from refs 22 and 23). Cong and Masel[23] have confirmed this observation for platinum surfaces, but also observed an enhanced beta-hydrogen elimination on oxidized platinum. Under electrochemical conditions, (gold)oxides appear to show only a small though noticeable activity, in particular for methanol and ethanol. A reaction similar to reaction 2 may explain the electrocatalytic oxidation activity of unsaturated
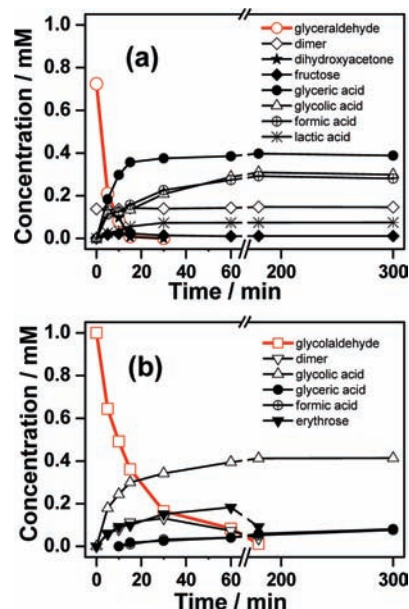
alcohols, that is, allylalcohol (1-propenol) and propargylalcohol (1-propynol), on gold in alkaline media as observed by Holze et al.[24] Compared to propanol, 1-propenol is more reactive, but 1-propynol is less reactive.[24] This trend would agree with the higher reactivity of an allylic H$_\beta$ compared to an propargylic H$_\beta$.[25] We note, however, that these compounds also show oxidation activity on gold in acidic media, so the real story may well be more complicated.[26] Finally, in agreement with a previous report by Luczak,[27] we found that amino-alcohols have a very high oxidation activity in alkaline media, with an oxidation potential as low as 0.4 V (Figure S3). However, in situ FTIR spectroscopy suggests that both the alcohol and the amino groups are involved in the first stages of the oxidation (Figure S4), and therefore, it is unlikely that amino-alcohols are oxidized easily only because of their increased alcoholic acidity.

From the results illustrated in Figures 1−3, the following picture emerges for the catalytic oxidation of alcohols in alkaline media. At sufficiently high pH, where "sufficiently" depends on the pK_a of the alcohol, the alcohol deprotonates into its corresponding alkoxide through reaction 1. The alkoxide is thought to be more active toward oxidation and therefore acts as a precursor to aldehyde formation:

$$H_\beta R\text{-}O^- \rightarrow R\text{=}O + H_\beta^+ + 2e^- \tag{3}$$
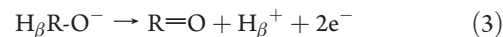
We believe that some of the deviations from the simple Hammett relationship may be traced back to the different leaving ability of the H$_\beta$. For instance, methanol, having a pK_a of 15.5, would be expected to be more reactive than ethanol (pK_a = 15.9), but the C−H$_\beta$ bond in methanol is stronger than the C−H$_\beta$ bond in ethanol[28] (we have not been able to find similar data for the corresponding alkoxides). In reaction 3, there may therefore be an important role of the catalyst, though Figure 2 strongly suggests that base catalysis dominates the overall reactivity. As mentioned, Cong and Masel[23] found that β-elimination is

enhanced on platinum oxide versus platinum, and recent DFT calculations suggest that adsorbed OH on gold lowers the barrier for β-elimination significantly,[9] suggesting that some interaction of the alkoxide with the (hydroxylated) gold surface is mandatory. This is also evidenced by the inhibiting role of strongly adsorbing anions in the electrochemical oxidation reaction, and by the fact that carbon is not a good electrode material for alcohol oxidation in alkaline media. However, if the alcohol is to be oxidized catalytically, a "real" catalyst, such as Pt or Pd, is needed. Aldehydes are not stable in alkaline media, and will react quickly in the presence of oxygen or other electron acceptors, such as positively polarized gold. These reactions determine the final products of the oxidation reaction on gold. Still, the activity of gold in alkaline media can be very high, even higher than that of platinum. The main reason for this is that gold is much less prone to the formation of poisoning oxides. Under electrochemical conditions, gold oxidizes at 0.4−0.5 V more positive potentials than platinum. For an electron transfer reaction with a Butler−Volmer transfer coefficient of 0.5, this translates into a rate enhancement of 3 to 4 orders of magnitude! This effect has been observed for the oxidation of glycerol, which shows much higher current densities (turnover numbers) on gold than on platinum in alkaline media,[14,15,21] but only at high overpotentials for which Pt is oxidized and hence not active.

In conclusion, the oxidation of the alcohol to an aldehyde involves the transfer of two protons and two electrons. The first "alpha" proton transfer is base catalyzed, with no essential role of the (gold) catalyst. The second combined "beta" proton−electron transfer (reaction 3) is fast, provided the leaving ability of the "beta" hydrogen is good, and gold primarily acts as an electron acceptor, although this step likely involves a catalytic interaction with surface bonded hydroxide. If the H_β is bound strongly, deviations to the "pK_a rule" are expected, to the extent that oxidation activity can even be completely absent (such as for fluoroethanol). This picture of alcohol oxidation is similar to that recently suggested by Davis et al.,[9] who suggest that both solution-mediated and metal-catalyzed steps are involved. This paper makes an important and crucial addition by the establishment of a Hammett relationship as illustrated in Figure 2c, which shows that the OH⁻ in solution could be more important for the overall reactivity than OH bound to the gold catalyst. We emphasize that OH can be formed on gold in acidic media at a sufficiently positive potential (for instance, CO may be oxidized on gold in perchloric acid at potentials as low as 0.6 V_{RHE}[10,29]), but it does not lead to any appreciable alcohol oxidation activity such as that observed in alkaline media. The further reaction of the aldehyde into other products is also strongly if not entirely base catalyzed. Certain implications of this model can be transferred to the platinum- or palladium-catalyzed alcohol oxidation in alkaline media, even if such reactions involve additional catalyzed steps, especially related to C−C bond breaking. One often reads that alkaline media are highly active for the oxidation of alcohols on Pt and Pd because of the high coverage of hydroxide on the electrocatalyst surface. However, OH is adsorbed on a Pt electrode in acidic and alkaline in the same potential region (vs RHE), and still alkaline media are significantly more reactive toward ethanol oxidation than acidic media.[30,31] Therefore, we believe that it is really the solution hydroxide that promotes the initial deprotonation, and thereby the important first step of the overall oxidation reaction, and that the explicit formulation of this idea is important for the future development of alkaline electrocatalysts.

To summarize our main points once more:

- The first deprotonation step in the electrocatalytic oxidation of an alcohol is base catalyzed, resulting in the reactive alkoxide intermediate.
- The second deprotonation (to the aldehyde) depends on the ability of the electrode material to abstract the H_β. If this is fast, the "pK_a rule" applies.
- On gold, the overall reaction rate is determined by the more sluggish of the two. On the other metals, further oxidation pathways will be important. However, in alkaline media, aldehydes are not stable and their degradation products should not be misinterpreted as resulting from the catalytic activity of gold.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Further material, as referred to in the text This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
m.koper@chem.leidenuniv.nl

Present Addresses
†Department of Chemistry, University of Warwick, Coventry, CV4 7AL, U.K.

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