Mechanisms of electroless metal plating: II. Decomposition of formaldehyde

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A detailed investigation of the decomposition of formaldehyde was carried out to account for the fact that formaldehyde decomposition on Group VIII metals, e.g., Pd, occurs without simultaneous hydrogen generation, while on Group IB metals, e.g., Cu, formaldehyde decomposition is accompanied by hydrogen evolution. It was found that in principle metals may be divided into three main classes: (a) metals with positive free energy of hydrogen adsorption, (b) metals with free energy of hydrogen adsorption close to zero, and (c) metals with negative free energy of hydrogen adsorption. In the case of class (a) metals formaldehyde oxidation is accompanied by hydrogen evolution; for class (b) metals there is no simultaneous hydrogen evolution; and class (c) metals show low catalytic activity for formaldehyde oxidation. Hence, formaldehyde cannot be used as a reducing agent for electroless plating of class (c) metals.

Introduction

In electrolytic metal deposition the electrons required for the reduction of the metal ions are supplied by an external current source. In electroless metal deposition, on the other hand, the electrons required for reduction are supplied by the catalytic or electrocatalytic oxidation of a reducing agent. The electrocatalytic oxidation of reducing agents such as methanol has been widely studied [1]. Relatively little work has been done on the oxidation of formaldehyde, an important reducing agent for electroless copper deposition [2]. It is generally agreed, however, that the oxidation of both the organic molecules proceeds via dissociative adsorption leading to dehydrogenation as the precursor reaction. The oxidation of formaldehyde in acid media has been shown [3] to proceed as follows:

$$\mathrm{HCHO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + 2\mathrm{H_2}. \qquad (1)$$

In alkaline media two types of behavior are observed. On Group VIII metals, such as platinum and palladium, formaldehyde oxidation occurs without simultaneous hydrogen generation [4], while on Group IB metals such as copper, silver, and gold, formaldehyde oxidation is accompanied by hydrogen evolution [1(a)]. One of the objectives of the present investigation is to account for this behavior. To this end, a quantitative study of the kinetics and mechanism of formaldehyde oxidation on one metal from each group, namely platinum and copper, has been carried out and the overall stoichiometries of the oxidation reaction on each metal determined.

The second objective has been to determine the effect of the nature of the metal on the electrocatalytic oxidation of formaldehyde. This is a qualitative study in which the catalytic activities of several metals were compared by cyclic voltammetry. The measurements were performed in both acid and alkaline media and the data plotted in the form of the so-called "volcano plots" proposed by Balandin [5] for gas-phase heterogeneous catalytic reactions and by Parsons

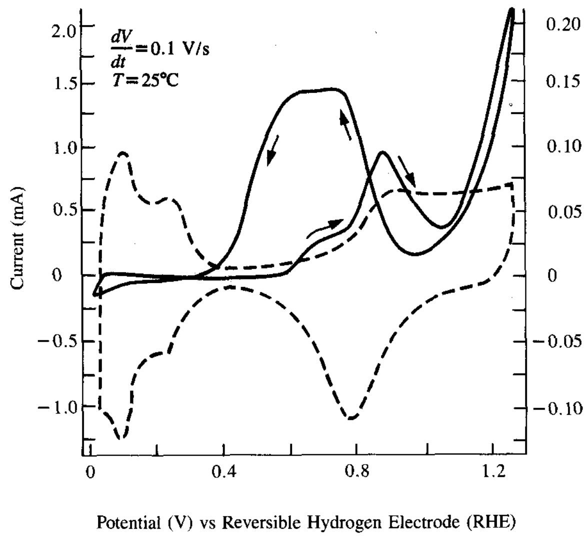


Figure 1

Cyclic voltammetry curves for Pt in 1 M $HClO_4$ (dashed curve, scale on right) and 1 M $HClO_4$ + 0.1 M HCHO (solid curve). Ar saturated; electrode area = 0.458 cm^2.

[6] and Gerischer [7] for electrocatalytic (electrochemical) reactions.

Experimental methods

The electrochemical measurements were performed in a standard three-compartment cell. The auxiliary electrode chamber and the reference electrode chamber were separated from the working electrode chamber by sintered glass frits. The potential of the working electrode was monitored via a luggin capillary with its tip placed one mm from the working electrode. Formaldehyde concentrations were estimated using standard quantitative analysis equipment. It is noted that in aqueous (acid) solution formaldehyde exists mainly as a hydrate, methylene glycol, while in alkaline solution the predominant species is methylene glycolate anion [8].

All the solutions were prepared with water purified by running de-ionized water through a Milli-Q Water Purification system, Continental Water Systems. Perchloric acid and sodium hydroxide were Ultra Pure Baker products and were diluted without further purification. Formaldehyde solutions were prepared by dissolving solid paraformaldehyde in pure water to the required concentration and determining the concentration iodometrically [9]. Iodine and thiosulfate solutions were also prepared from Baker chemicals by the methods described by Vogel [10]. Solutions were de-aerated by continuous bubbling with purified argon.

A Pine Instruments rotator and electrodes were used for all rotating disk measurements. The electrodes, which had a geometric area of 0.458 cm^2, were polished to a near mirror finish on a wheel using successively finer grades of alumina abrasive. The electrodes were then degreased with alcohol and thoroughly rinsed with purified water before each measurement.

The counter electrode was a large area (10 cm^2) gold foil and the reference electrodes were Hg/HgO (1 M NaOH) for measurements in alkaline solution and Hg/Hg_2SO_4 for measurements in acid solutions, respectively. The electrode potentials are referred to the reversible hydrogen electrode (RHE) at the solution pH.

Cyclic voltammetry and current-potential curves were obtained with a PAR 173 potentiostat in conjunction with a PAR 175 Universal Programmer. The curves were recorded on a Yokogawa X-Y-T Recorder, Model 3033. The charge passed during the formaldehyde decomposition efficiency measurements was recorded with the help of a PAR 179 coulometer. The pH values were measured on a Beckman-Altrex pH meter, with a pH electrode designed for measurement at high pH.

Formaldehyde oxidation on Pt, Pd, and Cu

- *Cyclic voltammetry*

Formaldehyde oxidation on noble metals such as Au, Pt, Pd, Rh, and Ir in 1 M $HClO_4$ was compared by the cyclic voltammetry technique. In 1 M NaOH solution the list of metals was extended to include Ag, Cu, and Ni. Cyclic voltammograms for formaldehyde oxidation on Pt, Pd, and Cu are described below, and the voltammograms for the other metals are described elsewhere [11].

Platinum A typical cyclic voltammetry curve for Pt in 0.1 M HCHO + 1 M $HClO_4$ is shown in **Figure 1**, together with the curve obtained in the base electrolyte. The general features of this voltammogram are similar to the voltammogram for Pt in HCOOH + 0.5 M sulfuric acid [12]. In each case three peaks occur in the anodic scan, though in the case of formaldehyde the first peak occurs at 0.7 V vs RHE instead of at 0.5 V vs RHE as for formic acid. This peak is attributed to a simple charge transfer step:

$$H_2C(OH)_2 \rightarrow H\overset{x}{C}(OH)_2 + H^+ + e^-, \qquad (2)$$

where $H\overset{x}{C}(OH)_2$ represents an adsorbed radical occupying a single site on the substrate. The first anodic peak is followed by a "passive" region (as opposed to an "inhibitive" region in the case of formic acid) before the onset of the second oxidation peak. In the second anodic peak, the strongly adsorbed intermediates of the type $\overset{xxx}{C}OH$ are removed from the substrate by oxidation reactions such as

$$\overset{xxx}{C}OH + Pt(OH) \rightarrow \overset{xx}{C}(OH)_2 + Pt, \qquad (3)$$

$$\overset{xx}{C}(OH)_2 + Pt(OH) \rightarrow \overset{x}{C}OOH + Pt + H_2O, \qquad (4)$$

$$\overset{x}{C}OOH + Pt(OH) \rightarrow CO_2 + Pt + H_2O. \qquad (5)$$

With the removal of the strongly adsorbed intermediates, more Pt(OH) sites are created and solution-phase formaldehyde is oxidized sequentially to give the following overall stoichiometry:

$$H_2C(OH)_2 + 4Pt(OH) \rightarrow CO_2 + 4\ Pt + 4H_2O. \qquad (6)$$

It is not clear whether the decrease in current after the second anodic peak is due to the formation of inactive PtO [13] or due to self-poisoning of the formaldehyde oxidation reaction by some sort of secondary disproportionation reaction [14]. In any case oxidation of formaldehyde does not totally cease after the second anodic peak, as in the case of formic acid. At around 1.1 V the current increases rather abruptly and this increase is attributed to the reaction of a $PtO(O)_{ad}$ species with formaldehyde. At 1.2 V the potential scan was reversed.

In the cathodic scan a broad anodic peak spread over 0.4 V is observed. This peak has a substructure which indicates two peaks at 0.8 V and 0.6 V, and the familiar shoulder also observed in the case of formic acid is observed at 0.4 V. The peak at 0.8 V occurs at approximately the same potential as the first anodic peak and is attributed to the formation of the weakly bound intermediate $H\overset{x}{C}(OH)_2$ via the charge transfer reaction described in Eq. (2). At more cathodic potentials the weakly bound $H\overset{x}{C}(OH)_2$ undergoes a disproportionation reaction to give the strongly bound and "poisonous" species $\overset{xxx}{C}OH$, and the current decreases until it reaches zero at ~0.3 V.

The cyclic voltammetry curves obtained with and without formaldehyde in alkaline solution are shown in **Figure 2**. There is a clear difference in the voltammograms obtained in acid and alkaline media, and it is almost certain that this difference is due to the fact that at pH = 14 the active species in the electrolyte is the methylene glycolate anion, $H_2C(OH)O^-$, while at pH = 0 the active species is the formaldehyde hydrate or methylene glycol, $H_2C(OH)_2$. The fact that surface oxidation on Pt in acid electrolyte commences at 0.8 V and in alkaline electrolyte at 0.6 V does not seem to have much effect. Formaldehyde oxidation currents are much higher in 1 M NaOH than in 1 M $HClO_4$, suggesting that the reaction is base-catalyzed. There is no evidence of strongly adsorbed intermediates either in the hydrogen region or in the double-layer region. Inhibition of the oxidation reaction first begins at 0.7 V. This may be due to the formation of inactive PtO or a self-poisoning reaction described earlier. The peak at 1.0 V in the anodic and cathodic scans is probably due to the formation $PtO(O)_{ads}$, which is able to react with formaldehyde. The reaction totally ceases at 1.5 V. It is tempting to suggest that this is due to the formation of inactive PtO_2 even though it is inconsistent with the results of Biegler et al. [15], which show that a complete PtO_2 layer forms at much more anodic potentials.

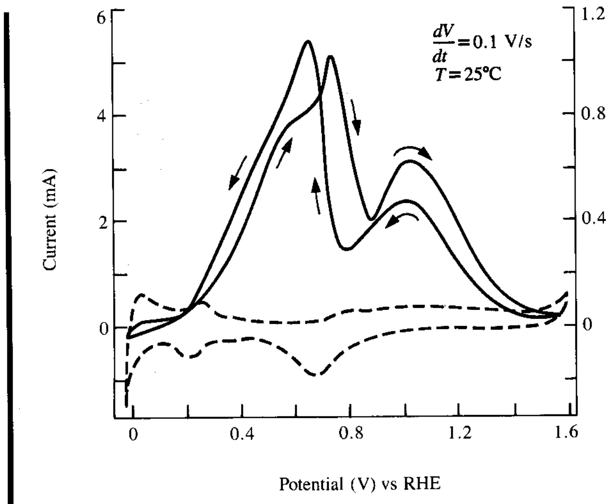


Figure 2

Cyclic voltammetry curves for Pt in 1 M NaOH (dashed curve, scale on right) and 1 M NaOH + 0.1 M HCHO (solid curve). Ar saturated; electrode area = 0.458 cm^2.

Palladium **Figures 3** and **4** show the cyclic voltammetry curves for Pd in the presence and absence of formaldehyde in 1 M $HClO_4$ and 1 M NaOH, respectively. In acid solution there is only one anodic peak in the anodic scan, which occurs at 0.95 V. Hydrogen adsorption on Pd is suppressed in the presence of formaldehyde in the electrolyte, indicating the presence of strongly absorbed intermediates on the surface. Between 0.4 V and 0.7 V the anodic current in the presence and absence of formaldehyde has the same value. From 0.7 V until the anodic peak at 0.95 V the current in the presence of formaldehyde is much lower than the base electrolyte current. This confirms the presence of strongly adsorbed intermediates which prevent the formation of Pd(OH) or PdO. At 0.95 V there is an abrupt increase in current, and an asymmetrical peak is observed. This peak is most likely due to the reaction between $PdO(O)_{ads}$ and the "poisonous" intermediates as well as bulk phase $H_2C(OH)_2$, just as in the case of Pt in acid solution. The current due to formaldehyde oxidation ceases around 1.2 V, presumably due to the formation of inactive PdO_2.

In the cathodic scan, one large anodic peak is observed. This peak commences at the threshold of oxide reduction on Pd. The acceleration of oxide reduction by strongly adsorbing organic intermediates has been described by Capon and Parsons [12]. The oxidation peak, however, is

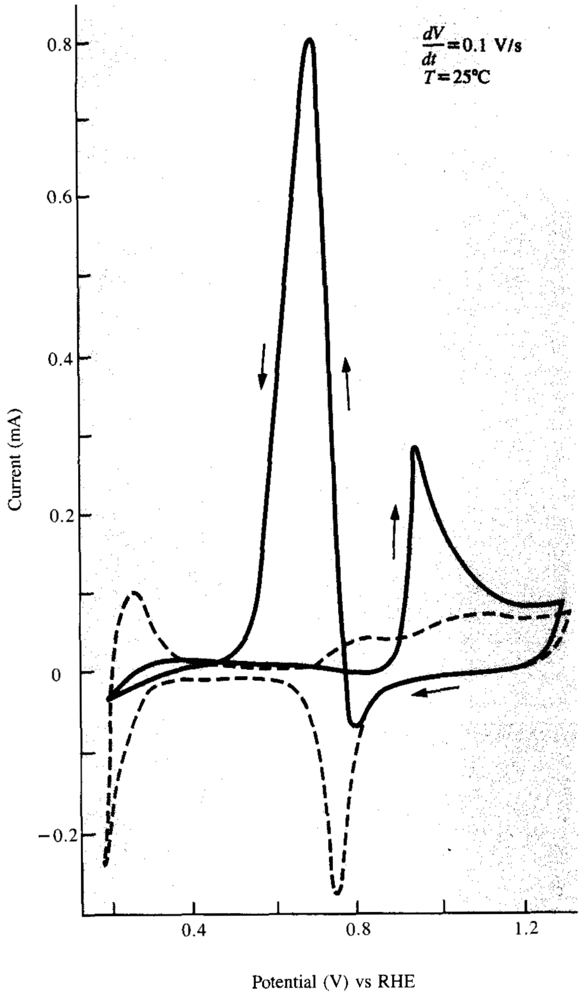


Figure 3

Cyclic voltammetry curves for Pd in 1 M $HClO_4$ (dashed curve) and 1 M $HClO_4$ + 0.1 M HCHO (solid curve). Ar saturated; electrode area = 0.458 cm^2.

rather narrow, suggesting Langmuirian adsorption of the intermediate.

The voltammogram obtained in alkaline solution (Fig. 4) is quite different from that obtained in acid solution. It is clear from Fig. 4 that the anodic and the cathodic scans show some hysteresis, although the general formaldehyde oxidation characteristics are the same. In the anodic scan the first anodic peak occurs at 0.5 V. This peak is attributed to the first charge-transfer reaction of the type described in Eq. (2). The reduction in current following the peak is due to surface coverage by strongly adsorbed intermediates. The large peak at 0.85 V, as in the case of Pt in alkaline solution, is due to the interaction of Pd(OH) with formaldehyde. The reduction in current is due either to the formation of inactive PdO or a self-poisoning secondary reaction. In the cathodic scan there is one large anodic peak at 0.7 V and two shoulders at 0.65 V and 0.4 V. The anodic peaks in the cathodic and anodic scans are approximately of the same magnitude. The cyclic voltammetry curves for formaldehyde oxidation in 1 M NaOH on Pt and Pd are quite similar. The catalytic activity is slightly greater for Pd.

Copper The cyclic voltammetry curve for Cu in 1 M NaOH + 0.1 M HCHO is given in **Figure 5** together with the background curve. The first anodic peak in the background curve is attributed to the formation of Cu_2O. At slow scan rates (dV/dt < 10 mV/s), this peak is preceded by a pre-peak at 0.55 V due to $Cu(OH)_2^-$ formation. The current between 0.8 V and 1.0 V increases as $Cu(OH)_2$ is formed and decreases when the passivating species CuO forms. There is some evidence of film dissolution in this potential range. At around 1.2 V the anodic current increases again, probably due to the reaction Cu(II) → Cu(III) [16]. The background curve shows a cathodic peak at 0.5 V. This peak is due to the reduction of Cu_2O. The cathodic peak that starts at around 0.2 V is due to the reduction of a surface layer consisting of more than one species. The Cu/NaOH system

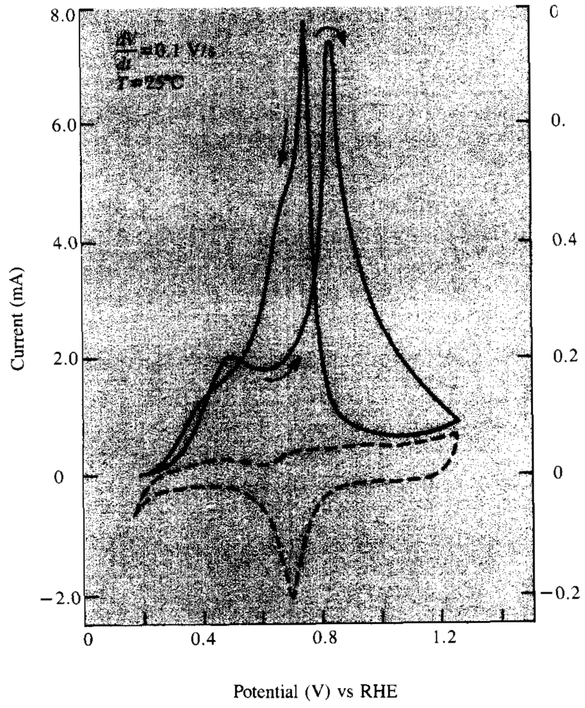


Figure 4

Cyclic voltammetry curves for Pd in 1 M NaOH (dashed curve, scale on right) and 1 M NaOH + 0.1 M HCHO (solid curve). Ar saturated; electrode area = 0.458 cm^2.

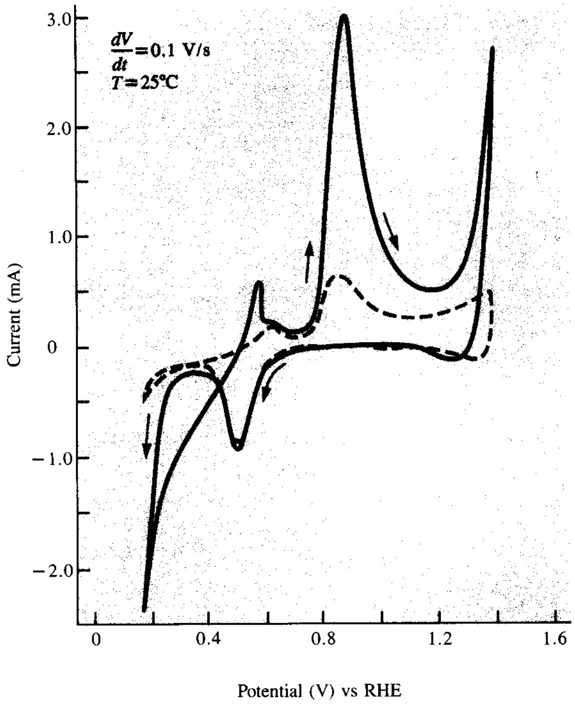


Figure 5

Cyclic voltammetry curves for Cu in 1 M NaOH (dashed curve) and 1 M NaOH+0.1 M HCHO (solid curve). Ar saturated; electrode area = 0.458 cm^2.

is very complex and requires more work for full interpretation than was expended in this study.

In the presence of formaldehyde the first anodic peak occurs at 0.55 V as a result of the reaction of formaldehyde on the freshly reduced Cu surface. This peak has been used for the volcano plots and other analysis. Cu_2O is not catalytically active. The interaction of formaldehyde with $Cu(OH)_2$ causes a large increase in the anodic current at 0.8 V. The current decreases at 0.9 V as a result of the formation of inactive CuO. Once the inactive CuO has been removed via dissolution [16] or the conversion of Cu(II) to Cu(III), a large anodic current due to the oxidation of formaldehyde on the fresh Cu surface appears again. During the cathodic sweep the curve in the presence of formaldehyde coincides with the background curve until 0.25 V, when a large cathodic current due to formaldehyde reduction is seen.

- *Kinetic parameters*

Tafel slopes
A potential step method was used to obtain Tafel plots on Pt substrates free from strongly adsorbed intermediates. The technique involved pretreatment of the electrode at an anodic potential (1.0 V vs RHE) where the strongly adsorbed intermediates are oxidized, prior to stepping the potential into the potential region where oxidation of formaldehyde first begins. Currents were measured on electrodes rotated at 1600 rpm, at a standard time interval of one second after the application of the potential step. Hardly any hysteresis was observed when the potential was retraced. No corrections for the *IR* drop were made as the measurements were performed in the region of low current densities where this correction was found to be insignificant. The Tafel plots for Cu electrode were constructed from polarization data obtained by the potentiodynamic method. The potential scan rate was 100 mV/s. Tafel plots for formaldehyde oxidation on Pt and on Cu are shown in **Figure 6**. These plots yield Tafel slopes of 150 ± 5 mV/decade and 180 ± 5 mV/decade for Pt and Cu, respectively.

Reaction orders
Reaction orders were ascertained with respect to the formaldehyde and hydroxide ions only. The reaction order for the reduction of the formate ion, although desirable, is difficult to measure and therefore was not attempted.

Formaldehyde Peak currents for the large cathodic peak at varying concentrations of formaldehyde yielded a reaction order of 0.9 ± 0.15 for Pt. Confirmation of first order was obtained from rotating disk data which yielded linear plots of $1/i$ vs $1/\sqrt{\omega}$ [17]. The complete rotating disk electrode data are given elsewhere [11]. In the case of a Cu electrode the first anodic oxidation peak current was plotted as a function of formaldehyde concentration. **Figure 7** shows that the reaction order with respect to formaldehyde on Cu is similar to that on Pt and has a value of 0.9 ± 0.1.

Hydroxide ion The pH dependence of formaldehyde oxidation was examined over the range 12.0–13.7 by adding varying amounts of concentrated $HClO_4$ to 0.1 M HCHO in 1 M NaOH. Plots of peak currents against pH (the large cathodic peak for Pt and the first anodic peak for Cu) yielded a reaction order of 0.5 in hydroxide ion for Cu and of 0 for Pt. These plots are displayed in **Figure 8.** A fractional reaction order implies participation of the hydroxide ion via an adsorbed state, thus confirming that in the case of Cu substrate, the anodic peak is due to catalysis by $Cu(OH)_2^-$. A reaction order of 0, as in the case of Pt, implies that the reaction is independent of hydroxide ion concentration in the solution.

Stoichiometric number ν
The stoichiometric number ν is generally evaluated either by the activation polarization resistance method [18] or from the anodic and cathodic transfer coefficients [19]. These methods could not be applied here because neither the

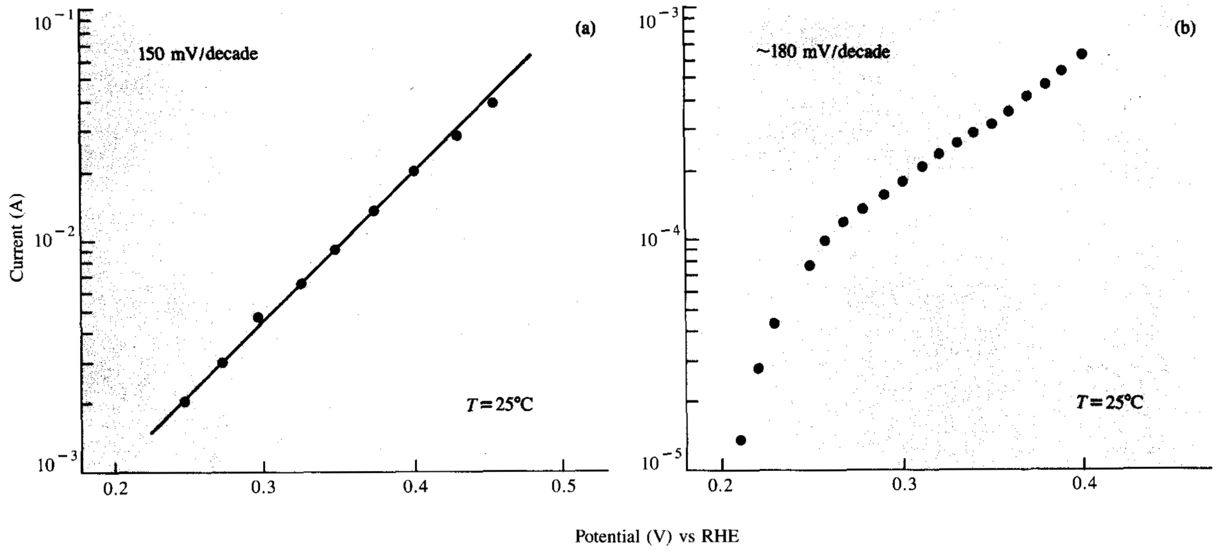


Figure 6

Tafel plots for HCHO oxidation in 1 M NaOH. Ar saturated; electrode area = 0.458 cm^2. (a) Platinum; (b) Copper.

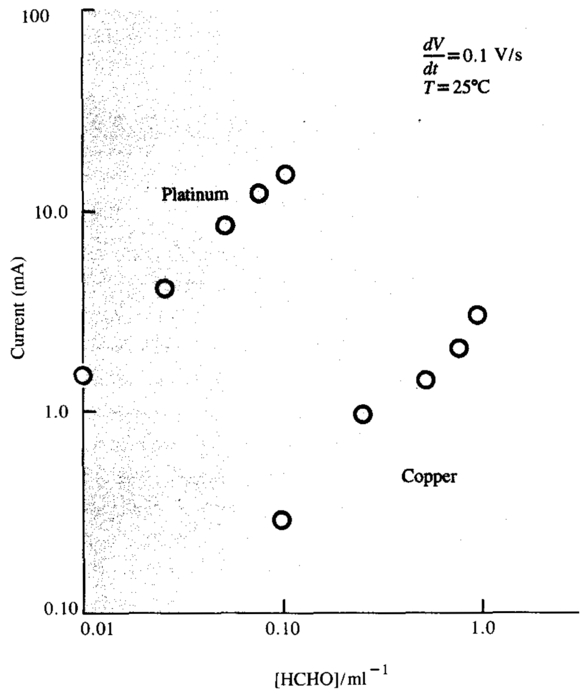


Figure 7

Reaction order for oxidation of HCHO in Ar-saturated 0.1 M HCHO + 1 M NaOH. Electrode area = 0.458 cm^2.

current-potential curves for formaldehyde oxidation at low overpotentials nor the transfer coefficient for formate reduction could be measured. Therefore ν was evaluated by applying the Allen and Hickling [20] graphical treatment to the general equation for a multistep reaction [21]. This equation has the form

$$i = i_0 \left\{ \exp\left[\left(\frac{n - \vec{\gamma}}{\nu} - r\beta\right)\frac{F\eta}{RT}\right] - \exp\left[-\left(\frac{\vec{\gamma}}{\nu} + r\beta\right)\frac{F\eta}{RT}\right]\right\}, \qquad (7)$$

where η is the overpotential, $\vec{\gamma}$ is the number of electrons transferred before the rate-determining step (rds) in the electronation reaction or the number of electrons transferred after the rds in the de-electronation reaction; n is the number of electrons involved in the overall reaction; β is the symmetry factor of the rds; and r is the number of electrons involved in the rds. The graphical treatment of Allen and Hickling [20] gives a linear plot of log $[i/1 - \exp(-nF\eta/\nu RT)]$ against η for the appropriate value of ν. Plots of $\nu = 1$ and $\nu = 2$ are shown in **Figure 9** for Pt and for Cu. It is evident from Fig. 9 that $\nu = 1$ for Pt and $\nu = 2$ for Cu. The slope of these plots is $[(n - \gamma)/\nu - r\beta]RT/F$. The numerical values observed in Fig. 9 are 150 mV/decade for Pt and 180 mV/decade for Cu, similar to the Tafel slopes observed in Fig. 6.

Discussion

- *Reaction mechanisms*

The mechanism of formaldehyde oxidation on Pt and on Cu in alkaline media is discussed in this section. Under

Langmuir adsorption conditions, the transfer coefficient obtained from the Tafel plot is equal to the transfer coefficient yielded by the Allen-Hickling analysis (Fig. 9), i.e.,

$$\alpha_a = \frac{n - \vec{\gamma}}{\nu} - r\beta. \tag{8}$$

Equation (8) is solved for $\vec{\gamma}$ by inserting the appropriate values for the other parameters. The quantity n was evaluated by measuring the coulombic efficiency for formaldehyde oxidation on Pt and Cu (Fig. 12, shown later), while the value of ν on each metal was obtained from the Allen-Hickling plots. The values of r and β were assumed to be 1 and 0.5, respectively, for each substrate. The value $r = 0$ is rejected because a symmetry factor is needed for an electron transfer step and $r = 2$ is improbable, as a two-electron transfer would require very high activation energy. The values of the kinetic and mechanistic parameters are collected in **Table 1**.

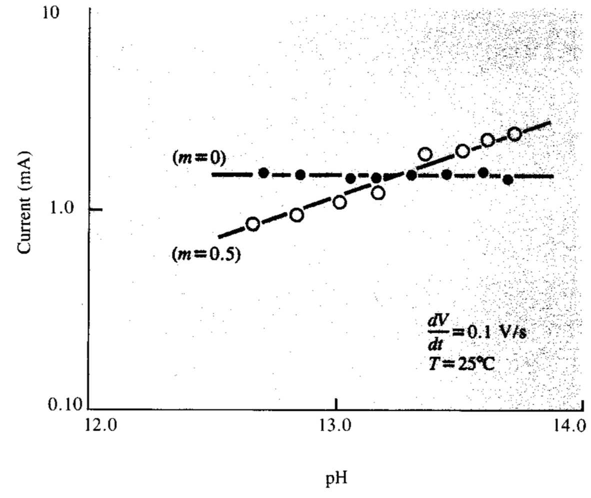


Figure 8

Dependence of HCHO oxidation on pH for (●) Pt and (○) Cu in Ar-saturated 1 M NaOH + 0.1 M HCHO. Electrode area = 0.458 cm^2.

It is clear from Table 1 that the Tafel slope for formaldehyde oxidation both on Pt and on Cu is $RT/\alpha F$,

Table 1 Values of kinetic and mechanistic parameters for formaldehyde oxidation on Pt and on Cu in alkaline media.

	$\frac{\partial V}{\partial \log i}$	$\frac{\partial \log i}{\partial \log C_F}$	$\frac{\partial \log i}{\partial \log C_{OH^-}}$	α_a	n	ν	r	β	γ
Platinum	150 ± 5	1	0	0.4	2	1	1	0.5	0
Copper	180 ± 5	1	0.5	0.33	1	2	1	0.5	1

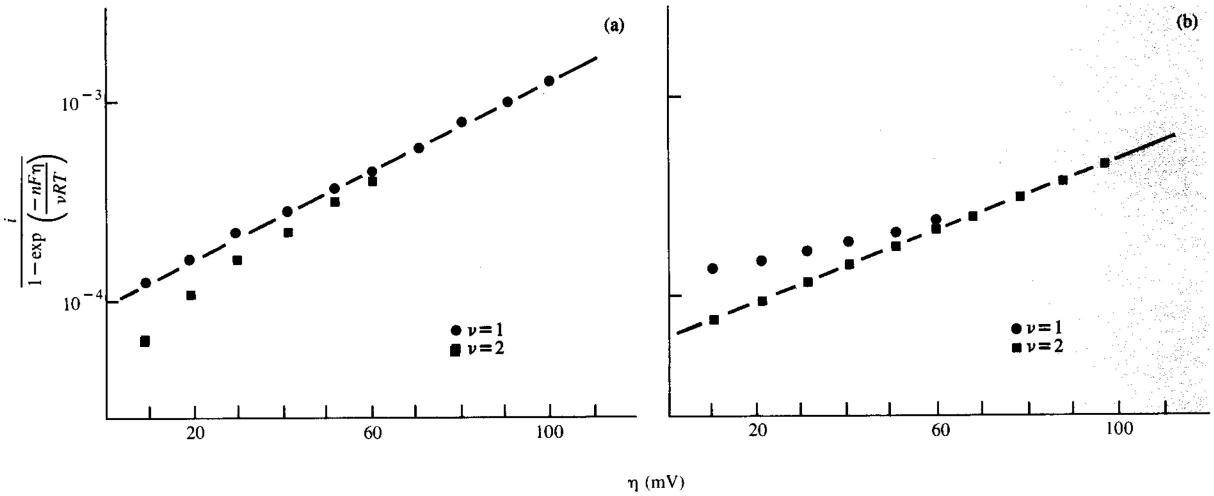


Figure 9

Allen and Hickling type plots for stoichiometric number determination for (a) Pt; (b) Cu.

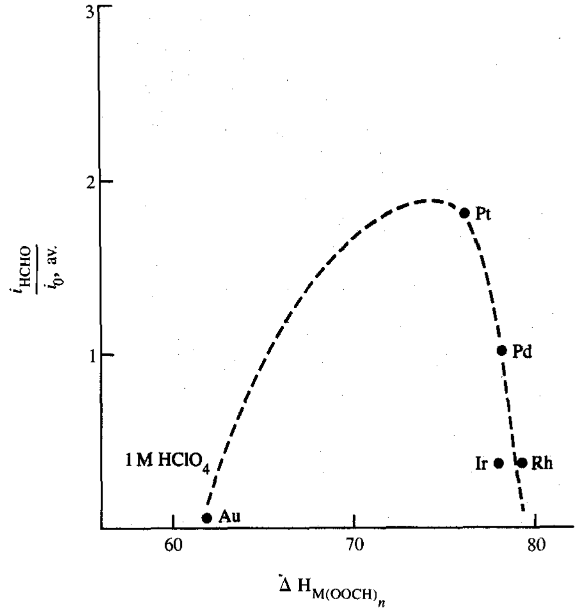
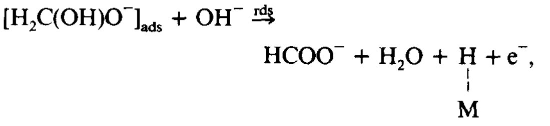


Figure 10

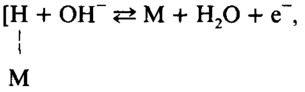
Plot of the relative catalytic activity for HCHO oxidation in 1 M $HClO_4$ as a function of enthalpy of formation of metal formate.

with α values substantially less than 0.5. This indicates specific adsorption of reacting species or intermediates [22] and suggests an *ihp* mechanism in which the first electron transfer is rate-determining. The data given in Table 1 are compatible with a reaction scheme comprising the following sequence of steps:

$$H_2C(OH)O^- \rightleftarrows [H_2C(OH)O^-]_{ads}, \qquad \text{(I)}$$

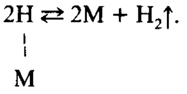


$$[H_2C(OH)O^-]_{ads} + OH^- \xrightarrow{rds} HCOO^- + H_2O + \underset{\underset{M}{\vdots}}{H} + e^-, \qquad \text{(II)}$$



$$[\underset{\underset{M}{\vdots}}{H} + OH^- \rightleftarrows M + H_2O + e^-, \qquad \text{(III)}$$

or



$$2\underset{\underset{M}{\vdots}}{H} \rightleftarrows 2M + H_2\uparrow. \qquad \text{(IV)}$$

M in the above reaction scheme represents the substrate. Steps I, III, and IV are in quasi-equilibrium.

The rate equation for the reaction on platinum, based on the data in Table 1, is

$$\overleftarrow{i} = \overleftarrow{k} FC_F(1 - \theta_F - \theta_H) \exp(1 - \beta) \frac{FE}{RT} \times \exp - (1 - \delta)(r_F\theta_R + r_M\theta_M), \qquad (9)$$

where C_F = concentration of formaldehyde; θ_F and θ_M are the coverages of methylene glycol anion (MGA) and hydrogen, respectively, and r_F and r_M are the interaction coefficients for adsorbed MGA and hydrogen, respectively. The activation coefficient in the case of charge transfer from the adsorbed state is represented by δ and is given by $0 \leq \delta \leq 1$. In the case of Pt, Table 1 shows that $\vec{\gamma} = 1$, that is, one electron is transferred before the rds in the cathodic reaction, or in this case, the anodic rds is followed by a reversible electron transfer step so that the complete stoichiometry of the reaction on Pt is obtained by adding steps I, II, and III, i.e.,

$$H_2C(OH)O^- + 2OH^- \rightarrow 2HCO_2^- + 2H_2O + 2e^-. \qquad (10)$$

The mechanism described in Eq. (10) is similar to that proposed by Buck and Griffith [3] for formaldehyde oxidation on Pt in 1 M KOH.

In the case of Cu, the oxidation current is obtained by multiplying the right-hand side of Eq. (9) by $C_H^{0.5}$, as in this case $\partial i/\partial C_H = 0.5$ (Table 1). The stoichiometry number is two, so that the overall stoichiometry of formaldehyde oxidation on Cu is obtained by adding steps I, II, and IV:

$$2H_2C(OH)O^- + 2OH^- \rightarrow 2HCO_2^- + 2H_2O + H_2\uparrow + 2e^-. \qquad (11)$$

This mechanism is in agreement with the proposal of Lukes [4].

- *Volcano plots*

Volcano plots provide a useful means for comparing the electrocatalytic activities of metals or alloys towards certain reactions. True volcano curves are obtained by plotting the actual catalytic activities as a function of the free energy of adsorption of the reactant or a reaction intermediate [6]. Capon and Parsons [12] have shown that for the electrochemical oxidation of formic acid on various noble metals a plot of the relative catalytic activity against the formate heat of formation, obtained via gas phase measurements by Fahrenfort et al. [23], gives a volcano-type plot. Such a plot therefore suggests that HCOO-M is a likely intermediate in the HCOOH oxidation pathway.

In this investigation the relative catalytic activities of various metals towards formaldehyde oxidation were obtained from cyclic voltammograms by the Capon and Parsons [12] method. When these approximate catalytic activities are correlated with the formate heats of formation, volcano-type curves are obtained, as shown in **Figures 10** and **11**. In acid media (Fig. 10) the convex relation obtained is quite similar to the curve obtained by Capon and Parsons for HCOOH oxidation. It is therefore logical to assume that HCOO-M is also the weakly bound intermediate in the formaldehyde oxidation pathway. Under the circumstances formaldehyde oxidation in acid media may simply be described as

$$H_2C(OH)_2 \rightarrow HCOOH \rightarrow CO_2 . \qquad (12)$$

In alkaline media there is little doubt that $HCOO^-$ is an intermediate. In fact, on metals such as Pt a larger overpotential is necessary to oxidize the $HCOO^-$ further to CO_3^{2-} [1a]. It is therefore quite appropriate that Fig. 11 should show a volcano-type correlation. The shapes of the volcano curves are, however, not very helpful in determining the reaction mechanism [6]. Consequently, Fig. 11 does not explain why on certain metals, such as Ag and Cu, formaldehyde oxidation is accompanied by hydrogen evolution while on metals such as Pt and Pd formaldehyde oxidation proceeds without simultaneous hydrogen generation. An explanation for this behavior can be found by examining the detailed mechanism of formaldehyde oxidation on the two types of metals described in the previous section. On Pt the dehydrogenation reaction and rds are followed by hydrogen ionization reaction (reaction scheme I–IV). At the potentials at which formaldehyde oxidation on Pt occurs, the hydrogen oxidation reaction is entirely possible. On Cu the rds occurs twice and this is then followed by a hydrogen radical recombination reaction. Presumably at the potential at which formaldehyde oxidation on copper takes place, hydrogen recombination and evolution is kinetically more favorable than hydrogen ionization, though thermodynamically at these potentials hydrogen ionization is the favored reaction. This suggests that whether formaldehyde oxidation on a substrate is accompanied by hydrogen evolution or not depends entirely on the catalytic activity of the substrate towards the hydrogen ionization reaction, i.e., on the free energy of adsorption of hydrogen on the substrate. This is verified in **Figure 12**, which shows a linear relationship between the coulombic efficiency of the formaldehyde oxidation reaction on various metals (or the number of electrons realized per formaldehyde molecule decomposed) and $-\log i^0_H$. The exchange current density for the hydrogen reaction on these metals, i^0_H, is taken to represent the free energy of adsorption for hydrogen [24]. The correlation between simultaneous hydrogen evolution during formaldehyde oxidation and the heat of adsorption for hydrogen on the metals was first suggested by Van den Meeraker [25]; but the heat of adsorption for hydrogen was erroneously calculated by the Eley-Stevenson [26, 27] method for both transition and *sp* metals. It has been shown by Trasatti [28] that while this method can give satisfactory results for transition metals, it does not hold at all with *sp* metals. The correct parameter to be used for the reactivity scale towards hydrogen of the various metals (transition and *sp* metals) is i^0_H. This parameter relates to the free energy of adsorption for hydrogen in the presence of the solvent and the field in the double layer.

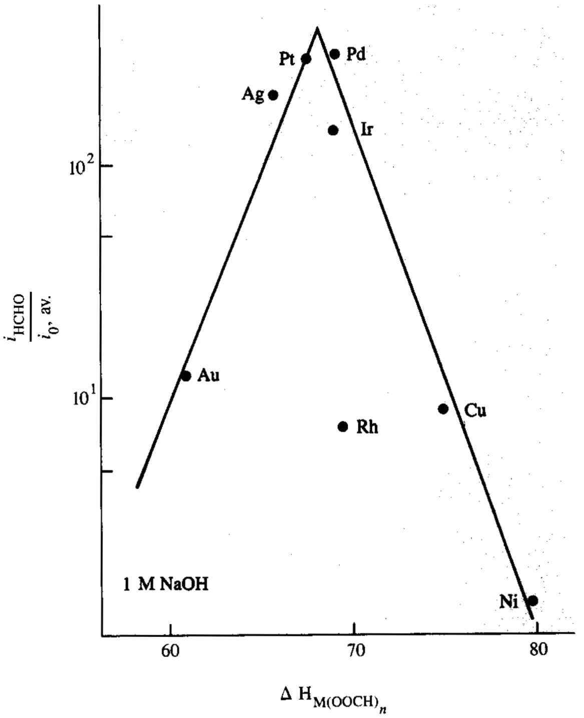


Figure 11

A plot of HCHO oxidation currents in 1 M NaOH vs enthalpy of formation of metal formate.

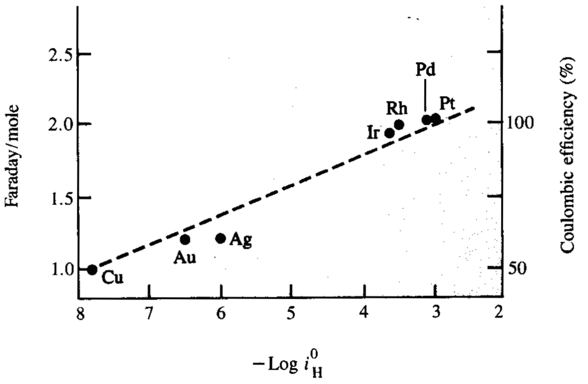


Figure 12

Plot of coulombic efficiency for HCHO oxidation in 1 M NaOH against i^0_H on various metals.

It is interesting to note in Fig. 12 that the Group IB metals or the *sp* metals such as Cu, Au, and Ag show low coulombic efficiency even though Ag exhibits approximately the same catalytic activity for formaldehyde oxidation as Pt and Pd (cf. Fig. 11). The Group VIII metals or metals with unfilled *d* bands exhibit high coulombic efficiency, giving two electrons per formaldehyde molecule oxidized. Clearly, according to the data in Fig. 12, metals may in principle be divided into three main classes: class (a), metals with positive free energy of hydrogen adsorption, class (b), metals with free energy of hydrogen adsorption close to zero, and class (c), metals with negative free energy of hydrogen adsorption. In the case of class (a) metals, formaldehyde oxidation is accompanied by hydrogen evolution. For class (b) metals, there is no simultaneous hydrogen evolution during the formaldehyde oxidation. Class (c) metals, such as Ni, show very low catalytic activity for formaldehyde oxidation to allow accurate measurements of the coulombic efficiency.

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