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The Retardation of Methanol Oxidation at a Platinum Electrode in an Acid Solution

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The rate retardation of the oxidation of methanol at the potential range of about 0.65—0.8 V vs. a reversible hydrogen electrode on a platinum electrode in 0.5 mol dm^{-3} H_2SO_4 was studied. The rate retardation of the overall oxidation was caused by that of the oxidation, Reaction D, not via CO_{ad}. From the relationship among the rate of Reaction D, the CO_{ad} coverage, and the potentials, three types of rate retardation were found out: Type 1— Reaction D is not accelerated by the potential, and the rate of the reaction is determined by the CO_{ad} coverage and the methanol concentration. Type 2— the rate of Reaction D decreases at stationary CO_{ad} coverages as the oxidation is prolonged. Type 3— the rate decreases at CO_{ad} coverages close to the limiting value. It is proposed that Types 1 and 2 of the rate retardations take place when the adsorption of methanol molecules is rate-determining, and when the formaldehyde and formic acid formed from methanol are accumulated in the vicinity of the electrode, respectively. Type 3 of the rate retardation has been explained in a preceding paper in terms of the aggregate damaging effect of CO_{ad}.

It has been known[1-3] that a plot of log *i* vs. *E* gives a straight line for the oxidation of methanol at a platinum electrode in an acid solution in the potential range lower than about 0.6—0.7 V, but the downward deviation from the straight line takes place at higher potentials than about 0.65 V. Such a deviation for the rate of the methanol oxidation has been interpreted in terms of the formation of stably chemisorbed species (SCS),[2,4,5] the formation of platinum surface oxide,[6] and the accumulation of adsorbed impurities from a solution.[7,8] Furthermore, the rate deviation has been reported[1,9] to occur when the dissociative adsorption of methanol is rate determining. This information was based on the assumption that methanol was always oxidized to CO_2 via SCS. However, recent investigations[2,4,5] have revealed that methanol is oxidized via at least two parallel reactions; one via SCS (Reaction B), and the other not via SCS (Reaction D).

Two types of SCS are generally proposed: COH_{ad},[10,11] and CO_{ad}.[12,13] For example, mass spectroscopic measurements[10,11] gave results suggesting COH to be adsorbable. On the other hand, in situ IR spectroscopic investigations[12] gave strong evidence for the existence of CO_{ad}. Furthermore, our results[13] obtained by means of the electrochemical methods confirmed that SCS is CO_{ad}. In the present paper, therefore, the downward deviation of methanol oxidation is discussed by assuming CO_{ad} as SCS. Of course, the conclusions derived by the present investigation are not altered even when another chemical kind of SCS instead of CO_{ad} is assumed.

The present investigation was undertaken in order to determine the origin of such a downward deviation, i.e., the rate retardation in the electrooxidation of methanol to carbon dioxide at platinum in a 0.5 mol dm^{-3} H_2SO_4 solution in the potential range of 0.65—0.8 V vs. RHE. The upper limit of 0.80 V was taken in order to eliminate the rate retardation of methanol oxidation due to the formation of platinum oxide.

Experimental

The coverage θ, with CO_{ad} is expressed as:

$$\theta = (Q_H{}^0 - Q_H)/Q_H{}^0 \qquad (1)$$

where $Q_H{}^0$ and Q_H are the charge required to cover fully the electrode surface with adsorbed hydrogen atoms in the absence and in the presence of CO_{ad} respectively. These charges were determined by the conventional hydrogen deposition method.

The rate of Reaction D was determined by the following procedure. As has been reported in a previous paper,[5] the overall rate, i_T, of the methanol oxidation can be expressed by:

$$\begin{aligned} i_T &= i_A + i_B + i_D \\ &= 2\,\mathrm{d}Q^{ox}/\mathrm{d}t + 3i_B + i_D \qquad (2) \end{aligned}$$

where i_A and i_B are the rates of the formation and the further oxidation of CO_{ad} respectively. i_D is the rate of the methanol oxidation not via CO_{ad}, and Q^{ox} is the charge required to oxidize CO_{ad} to CO_2. When the methanol concentration is smaller than about 0.5 mol dm^{-3}, $i_B \ll i_T$ at potentials below about 0.8 V, as has been described in the previous work[5]. Consequently,

$$i_D \fallingdotseq i_T - 2\,\mathrm{d}Q^{ox}/\mathrm{d}t \qquad (3)$$

Here, Q^{ox} can be approximated by $Q_H{}^0\,\theta$ (see Fig. 8 in Ref. 15). Thus,

$$i_D \fallingdotseq i_T - 2\,Q_H{}^0\,\mathrm{d}\theta/\mathrm{d}t \qquad (4)$$

In the present investigation, i_D was determined under both potentiostatic and potentiodynamic conditions.

(A) Potentiostatic Conditions: The current and θ at a constant potential were measured by using the potential sequence of (a) in Fig. 1. i_T at the potential is equal to the observed current for the methanol oxidation, while dθ/d*t* was determined from the time-variation in θ. Then, i_D was

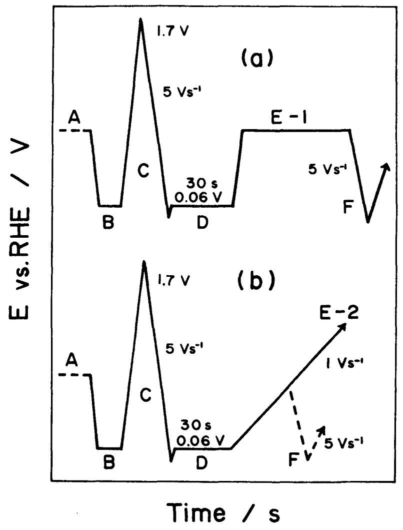


Fig. 1. Potential sequence for measurements of oxidation rate and surface coverage. Oxidation: (a) potentiostatic; (b) potentiodynamic. Steps: (A) introduction of deoxygenated solution; (B) reduction of remaining oxygen; (C) cleaning of electrode surface; (D) recovering equilibrium of concentrations; (E-1) measurement of oxidation rate at a constant potential; (E-2) potential scan; (F) measurement of surface coverage.

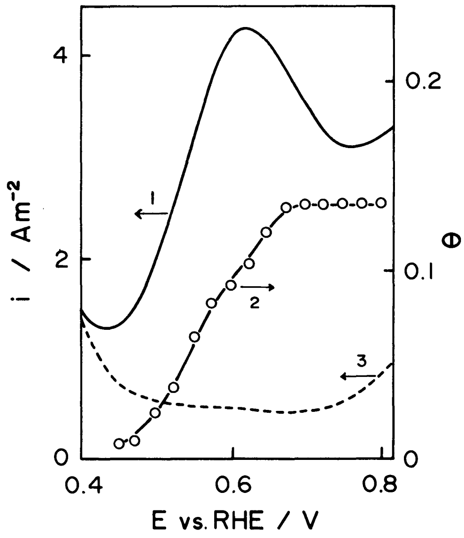


Fig. 2. Potentiodynamic i-E and θ-E curves for oxidation of methanol in 0.1 mol dm^{-3} CH_3OH +0.5 mol dm^{-3} H_2SO_4, scan rate 1 V s^{-1}. Curves: (1) currents; (2) surface coverages; (3) currents in the absence of CH_3OH and CO_{ad}. Platinized platinum (roughness factor=134).

calculated according to Eq. 4.

(B) Potentiodynamic Conditions: The i-E curves and θ values were obtained by using the potential sequence of (b) in Fig. 1. The potential was scanned after the preadsorbed CO species had been removed at Step C of the pretreatment in Fig. 1. Curves 1 and 3 in Fig. 2 show examples of i-E curves in the presence and the absence of methanol respectively, when the scan rate is 1 V s^{-1} and the methanol concentration is 0.1 mol dm^{-3}. The values of i_T were determined from the differences in the current between Curves 1 and 3. Curve 2 in Fig. 2 is the θ-E curve obtained under the same experimental conditions as Curve 1. $d\theta/dt$ during the anodic scan is proportional to $d\theta/dE$, because the scan rate, s, is constant:

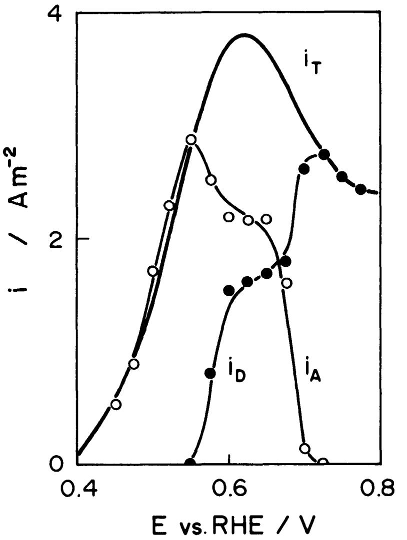


Fig. 3. Variation in i_A, i_D, and i_T with potential, 0.1 mol dm^{-3} CH_3OH+0.5 mol dm^{-3} H_2SO_4, scan rate 1 V s^{-1}. These values were obtained on the basis of Fig. 2.

$$d\theta/dt = s\, d\theta/dE \tag{5}$$

Thus, $d\theta/dt$ was determinable from the slope of the θ-E curve, and then i_D was calculated from Eqs. 4 and 5. Figure 3 shows the potential dependence of the i_D value thus obtained. The i_D was approximately equal to i_T in the potential range of about 0.7—0.8 V, while $i_T \fallingdotseq i_A$ at potentials below about 0.55 V. Therefore, the order of Reaction D with respect to the methanol concentration was determined from the relationship between i_T at 0.7 V and the concentration.

The effects of the presence of formaldehyde and formic acid on the i-E curve and θ were also examined by using the potential sequence of (b) in Fig. 1. The other experimental conditions and procedures were almost the same as those used in the previous studies.[5,14] All the reaction rates and the charges were measured at 0 °C. The potentials were referred to a reversible hydrogen electrode (RHE) in 0.5 mol dm^{-3} H_2SO_4.

Results and Discussion

Figure 4 shows the relationship between the potential and i_D in the prolonged oxidation of methanol under potentiostatic conditions. Since the methanol oxidation, Reaction D, not via CO_{ad} does not occur at the electrode surface occupied by CO_{ad}, the rate of Reaction D was expressed by the current per the surface not occupied by CO_{ad}, $i_D/(1-\theta)$. As may be seen from Fig. 4, there is a linear relationship between

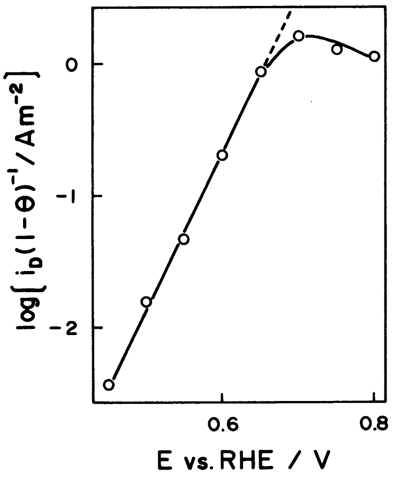


Fig. 4. Variation in stationary i_D with potential, oxidation time at a constant potential 300 s, 0.1 mol dm^{-3} CH_3OH+0.5 mol dm^{-3} H_2SO_4.

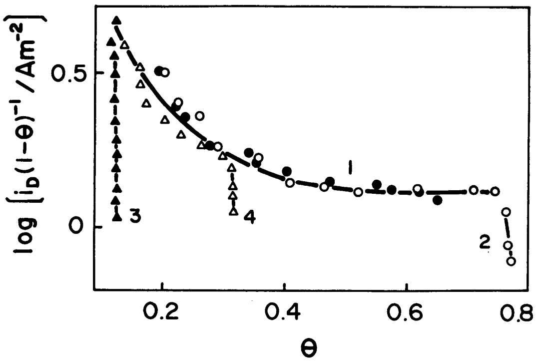


Fig. 5. Variation in $i_D/(1-\theta)$ with CO_{ad} coverage, 0.1 mol dm^{-3} CH_3OH+0.5 mol dm^{-3} H_2SO_4. Potential (V): ○ 0.65; ● 0.70; △ 0.75; ▲ 0.80. All of part of the rates at every potential belong to curve 1.

the potential and the logarithm of $i_D/(1-\theta)$ in the potential range of 0.45—0.65 V. The rate of Reaction D at the higher potentials, however, deviates downward from the straight line. In order to clarify the causes of this rate deviation, the relationship between $i_D/(1-\theta)$ and θ during the controlled potential oxidation of methanol at different potentials was examined. The results are presented in Fig. 5.

Figure 5 indicates three types of rate retardation: Type 1; $i_D/(1-\theta)$ directly deviates from the Tafel straight line without any other rate retardations at potentials above about 0.7 V. The resulting $i_D/(1-\theta)$ is at constant surface coverages, independent of the potential, as Curve 1 in Fig. 5 shows. Type 2: at potentials above about 0.75 V, the CO_{ad} coverage soon becomes stationary, although with small values, and then $i_D/(1-\theta)$ falls, as in indicated by Curves 3 and 4. Type 3: at a coverage close to about 0.8, $i_D/(1-\theta)$ begins to fall abruptly, as Curve 2 shows.

The rate retardation of Type 3 has already been presented in the preceding paper[15] as being due to the aggregate demaging effect on reaction sites indispensable for the methanol oxidation. The causes of the rate retardations of Types 1 and 2 will be discussed below.

Rate Retardation of Type 1. As Curve 1 in Fig. 5 shows, the rate retardation of Type 1 occurs at the same CO_{ad} coverage, although CO_{ad} has a retarding effect on Reaction D. Hence, the rate retardation of Type 1 is explicitly caused by some factor other than the formation of CO_{ad}.

Breiter et al.[7,8] reported that the rate of the oxidation of methanol at platinum electrodes could be retarded by the presence of not only CO_{ad}, but also easily desorbable surface substances, such as chloride anions. Although such desorbable adsorbates can not be detected by the conventional hydrogen-deposition method, the adsorbates are detectable by an anodic stripping method in which the potential scan is very rapid. In this method,[9] the hardly and easily oxidizable adsorbates are detected by the hindrance of the formation of the platinum oxide and the appearance of a new oxidation wave in the potentiodynamic *i*–*E* curve. In the present investigation, a potential scan of 718 V s^{-1} was applied to the electrode immediately after the methanol oxidation at 0.8 V in 0.01 mol dm^{-3} CH_3OH+0.5 mol dm^{-3} H_2SO_4. The wave of the dotted line 3 around 1.5 V is due to the formation of the platinum oxide, while the wave of the solid line 1 around 1.8 V is due to both the formation of the surface oxide and the oxidation of the CO_{ad} which was formed during the previous oxidation at a constant potential. The presence of methanol had little effect on the formation of the oxide; also, no appreciable wave for the oxidation of new adsorbates was detected. Hence, both hardly and easily oxidizable surface substances, even if these substances are easily desorbable, can be eliminated as possible causes of the rate retardation of Type 1. The remaining cause of the rate retardation is a change in the reaction mechanism.

In Fig. 5, $i_D/(1-\theta)$ goes down on Curves 2—4 as the oxidation time passed. Consequently, the extent of the rate retardations of Types 2 and 3 were slight at a short oxidation time. Hence, provided that the oxidation time is short, the reaction order with respect to the methanol concentration can be examined without any effect of rate retardations of Types 2 and 3. These experimental conditions were approximately satisfied by oxidizing methanol at a potential scan of a few V s^{-1} after the removal of CO_{ad}. That is, the oxidation time was short at this scan rate, and the retardation of Type 1 occurred at potentials of about 0.7—0.8 V, as is indicated by Fig. 3. Figure 7 shows the dependence of $i_D/(1-\theta)$ at 0.7 V on the methanol concentration obtained when the scan rate is 3 V s^{-1}. As may be seen from this figure, there was a

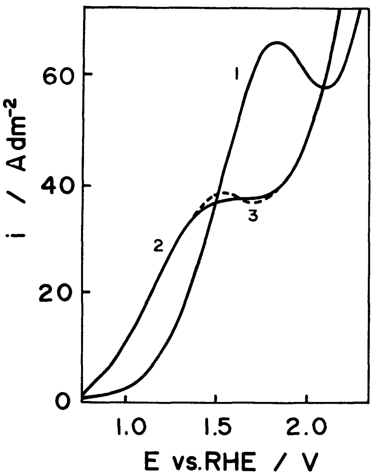


Fig. 6. i-E curves at rapid potential scan after 100 second oxidation of methanol at a constant potential, scan rate 718 V s^{-1}, 0.01 mol dm^{-3} CH_3OH +0.5 mol dm^{-3} H_2SO_4, smooth platinum. Potential (V): (1) 0.6; (2) 0.8; (3) in the absence of CH_3OH.

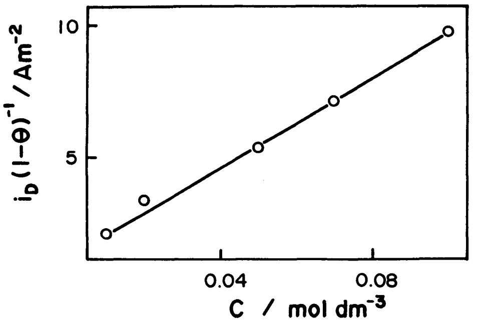


Fig. 7. Variation in i_D with methanol concentration, C. The rates were taken from potentiodynamic (3 V s^{-1}) i-E curves.

linear relationship between $i_D/(1-\theta)$ and the methanol concentration; i.e., the reaction order with respect to the methanol concentration was first.

An $i_D/(1-\theta)$ value independent of the potential and the first reaction order with respect to the methanol concentration would result, when one of the following nonelectrochemical processes of methanol molecules becomes rate-determining: (1) the diffusion to an electrode, (2) the adsorption on an electrode, and (3) a chemical reaction at the electrode surface, e.g., the dehydrogenation of methanol molecules. The maximum value of the observed rate of the methanol oxidation was smaller by a few orders of magnitude than the limiting diffusion rate previously estimated.[16] For example, the maximum value of i_D in Fig. 4 is less than about one hundredth of the estimate. Consequently, Process 1 can be rejected as a possible rate-determining step. Process 3 can also be ruled out as the rate-determining step, because no product of the surface reaction involved in Reaction D could be detected at the open circuit. Furthermore, the adsorption of methanol molecules has been proposed[2,4,17] as an elementary process in the electrooxidation. From these facts, it was concluded that the rate retardation of Type 1 is caused when the adsorption of methanol molecules is rate-determining.

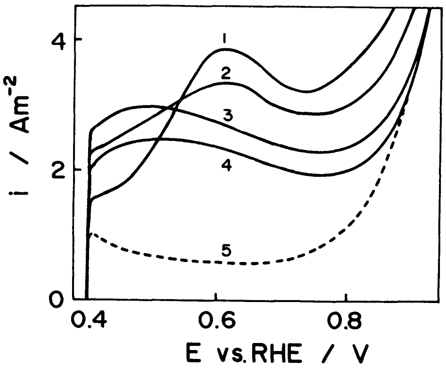


Fig. 8. Potentiodynamic i-E curves immediately after preoxidation at 0.8 V, 0.1 mol dm^{-3} CH_3OH +0.5 mol dm^{-3} H_2SO_4, scan rate 1 V s^{-1}. Preoxidation times (s): (1) 0; (2) 1; (3) 10; (4) 100; (5) in the absence of CH_3OH.

Table 1. Current Efficiencies for the Formation of Formaldehyde and Formic Acid in CH_3OH+ 0.5 mol dm^{-3} H_2SO_4; Oxidation Time, (300 s)

Potential	CH_3OH	HCHO	HCOOH
V	mol dm^{-3}	%	%
0.7	1.0	34	14
0.7	0.5	35	13
0.7	0.3	29	11
0.7	0.2	17	6
0.7	0.1	13	6
0.8	1.0	35	15
0.8	0.1	14	7

Rate Retardation of Type 2. In order to clarify the cause of the rate retardation of Type 2, the effect of the preoxidation on i_D was examined by means of the potential scan of 1 V s^{-1}. Figure 8 shows the potentiodynamic i-E curves for the oxidation of methanol when a prolonged oxidation at 0.8 V is undertaken prior to the potential scan. By the preoxidation, i_T at 0.7—0.8 V, i.e., i_D decreased, and a new wave appeared at about 0.4—0.5 V. This finding suggests that some products retarding Reaction D are formed from methanol and are accumulated in the vicinity of the electrode.

Formaldehyde and formic acid are known[4,16] to be formed in the anodic oxidation of methanol. Under the present experimental conditions also, their formation was confirmed, as Table 1 shows. The effect of the presence of these substances on i_D was examined in mixed systems of methanol-formaldehyde and methanol-formic acid. As Table 1 shows, the current efficiencies for the production of these

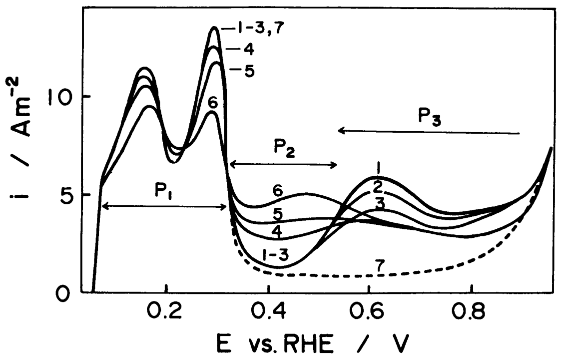


Fig. 9. Potentiodynamic *i*-*E* curves in the presence of formaldehyde added to solution, HCHO $+0.1\,mol\,dm^{-3}$ $CH_3OH+0.5\,mol\,dm^{-3}$ H_2SO_4, scan rate $1\,V\,s^{-1}$. HCHO ($mol\,dm^{-3}$): (1) 0; (2) 0.001; (3) 0.002; (4) 0.01; (5) 0.02; (6) 0.05; (7) in the absence of HCHO and CH_3OH.

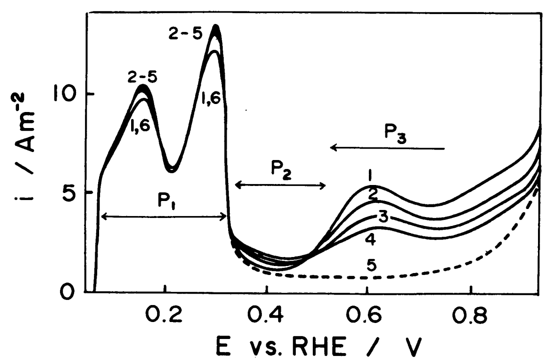


Fig. 10. Potentiodynamic *i*-*E* curves in the presence of formic acid added to solution, HCOOH $+0.1\,mol\,dm^{-3}$ $CH_3OH+0.5\,mol\,dm^{-3}$ H_2SO_4, scan $1\,V\,s^{-1}$. HCOOH ($mol\,dm^{-3}$): (1) 0; (2) 0.0005; (3) 0.002; (4) 0.005; (5) in the absence of HCOOH and CH_3OH.

substances are small at low methanol concentrations. Therefore, in order to reduce the accumulation of formaldehyde and formic acid from methanol, the methanol concentration of $0.1\,mol\,dm^{-3}$ was used to examine the effect of the addition of formaldehyde and formic acid.

Figures 9 and 10 shows the potentiodynamic *i*-*E* curves in mixed systems of methanol-formaldehyde and methanol-formic acid. As these curves indicate, methanol was oxidized at potentials above about 0.45 V, while formaldehyde and formic acid were oxidized at potentials above 0.35 V, at the scan rate of $1\,V\,s^{-1}$. Consequently, the new wave observed around 0.4 V in Fig. 8 is ascribed to the oxidation of the formaldehyde and formic acid which are formed during the oxidation of methanol at 0.8 V. It is particularly interesting that, in the mixed system, the overall rate in the potential range of about 0.5—0.8 V decreased as the concentration of formaldehyde and formic acid increased up to about $0.02\,mol\,dm^{-3}$. As

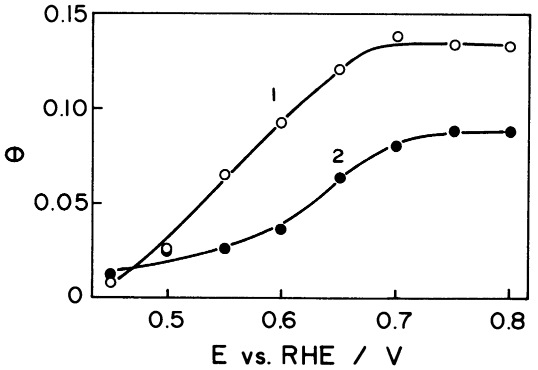
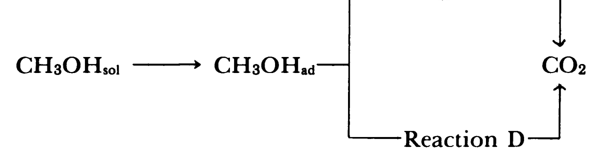


Fig. 11. Potentiodynamic *θ*-*E* curves for oxidation of methanol in (2) $0.02\,mol\,dm^{-3}$ HCOOH $+0.1\,mol\,dm^{-3}$ CH_3OH; (1) in the absence of HCOOH, scan rate $1\,V\,s^{-1}$.

has been described in the Experimental section, the i_T values in the potential range of 0.7—0.8 V are approximately equal to i_D. Therefore, it seems certain that Reaction D is retarded by the formation of formaldehyde and formic acid. The effects of these substances are most remarkable in the concentrations of 0.02—0.03 $mol\,dm^{-3}$. At higher concentrations, the overall rate increased with an increase in the concentration. Since the oxidation of formaldehyde and formic acid was enhanced at high concentrations, the increase in the overall rate at the higher concentrations is probably due to the oxidation of these substances.

As has been described above, the adsorption of methanol molecules precedes both the CO_{ad} formation and Reaction D, and the accumulation of adsorbed molecules is very slight:



Consequently, the rate of the adsorption of methanol molecules, r_{ad} is the sum of the rates of the CO_{ad} formation and Reaction D, when each rate is expressed in $mol\,s^{-1}\,m^{-2}$:

$$r_{ad} = i_A/4F + i_D/6F \qquad (6)$$

where i_A can be expressed in terms of $d\theta/dt$ by the same method as in the Experimental section:

$$i_A \fallingdotseq 2sQ_H^0\,d\theta/dE \qquad (7)$$

Figure 11 shows the relationship between the CO_{ad} coverage and the potential in the presence and in the absence of formic acid under potentiodynamic conditions. In the potential range of about 0.7—0.8 V, the slope of the *θ*-*E* curve, i.e., $d\theta/dE$ was little influenced by the presence of formic acid, and i_D decreased, as may be seen from Fig. 9. Consequently, i_D and also r_{ad} are decreased by the presence of formic acid. A smilar decrease in r_{ad} was observed also in the case of formaldehyde, so long as the formaldehyde concentration was lower than about 0.05 mol dm^{-3}. At higher concentrations, however, the CO_{ad} formation from formaldehyde was remarkable at the pretreatment step D in Fig. 1b; therefore the effect of the presence of formaldehyde on i_D could not be examined.

To sum up, the rate retardation of Type 2 was related to the retardation of the adsorption of methanol molecules. The retardation occurred when small amounts of formaldehyde and formic acid were added to a solution of methanol, or when these substances were formed at the electrode by the preoxidation of methanol, although the adsorption of these substances was not confirmed by either the method of hydrogen deposition and by that of anodic stripping. From these results, it was concluded that the rate retardation of Type 2 was due to the accumulation of formaldehyde and formic acid in the vicinity of the electrode without adsorption.

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16) The limiting current density, i_L, for the linear diffusion was determined by means of the following equation:

$$i_L = nFDC/\delta$$

where each of the symbols represents its ordinary meaning. When n, D, C, and δ are 6, 1×10^{-9} m^2 s^{-1}, 0.1 mol dm^{-3}, and 5×10^{-4} m respectively, one obtains $i_L=1\times10^2$ A·m^{-2}. With a platinized platinum electrode, the limiting diffusion current per unit of apparent surface area would be equal to or a little larger than, this value* because of the roughened surface, though it appears that any exact estimation would be very complicated.

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