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The Role of CO_{ad} in the Oxidation of Methanol at a Platinum Electrode in an Acid Solution

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The role of the adsorbate CO_{ad} in the oxidation of methanol was studied under a variety of experimental conditions on the basis of the rate-ratio of the path of CO_2 formation via CO_{ad} to the overall oxidation of methanol at a platinum electrode in 0.5 mol dm^{-3} of H_2SO_4. The results: (a) At potentials below 0.55 V and with a short time of oxidation, CO_{ad} inhibited its own formation; (b) at 0.60—0.75 V and with a long time of oxidation, CO_{ad} was a poison to parallel reactions; (c) at above 0.8 V and at $\theta_1 > 0.15$, the formation of CO_2 via CO_{ad} was predominant, and the CO_{ad} never hindered parallel reactions. There was no difference between the role of the CO_{ad} formed from dissolved CO and that of the CO_{ad} formed from methanol, though, in the absence of dissolved CO, the oxidation of methanol was, for some reason, inhibited at small coverages close to the respective limiting values. When the coverage was larger than about 0.85, CO_{ad} remarkably inhibited all the parallel reactions in the methanol oxidation.

This paper will describe the role of the adsorbate CO_{ad} formed from methanol on a platinum electrode during the anodic oxidation of methanol in 0.5 mol dm^{-3} of H_2SO_4.

Chemical analysis[1)] has shown that CO_2 is the final product of the oxidation and that, at high concentrations of methanol, formaldehyde and formic acid are also formed as intermediate products which are soluble in solution and which can be further oxidized to CO_2, depending on circumstances. Several parallel paths producing CO_2 have so far been proposed.[1—3)] However, only the following two seem to be based more or less upon experimental facts; the others appear to be rather speculative for the time being: (1) The path via a stably chemisorbed substance (SCS), and (2) the path via formaldehyde and formic acid. The formation of SCS and its oxidation to CO_2 were confirmed by Breiter[4)] and Petrii et al[2)]. The existence of the latter path was experimentally verified[1)] only when the oxidation of methanol was prolonged and the concentration of methanol was high. Any adsorbate in this path is considered[5,6)] to be so small in surface concentration that can not yet be experimentally identified. Breiter[7)] and Petrii et al.[2)] determined the rate-ratio of the production of CO_2 by the path via SCS to the overall oxidation of methanol. From these data, they[2,6)] concluded that the SCS 'had the effect of a poison on' (Breiter), or 'passivated' (Petrii), the production of CO_2 by covering the surface of the electrode.

Regardless of a number of such papers,[2,6—9)] the present work will also attempt to reexamine the same problem, the role of SCS (CO_{ad}), by a rather similar method. Our main reasons are as follows: (a) Contrary to most previous workers, we consider the SCS to be CO_{ad}.[10,11)] Petrii[2)] regarded it as COH_{ad}, and Breiter[4)], as a mixture of COH_{ad} and $COOH_{ad}$. In their estimation of the rate-ratios stated above, the number of electrons participating in the oxidation of SCS to CO_2 was decisively important. For the oxidation of CO_{ad}, that number is, of course, different. (b) Although many workers[2,6,8—9)] have supported the idea that a SCS can be a poison, no detailed study has been published on the oxidation conditions under which a particular SCS passivates a particular parallel reaction. (c) As is well-known,[11—13)] the presence of trace amounts of impurities such as a chloride anion in a solution reduces the overall rate of methanol oxidation, while the accumulation of reaction products such as formaldehyde in a solution enhances that rate, because these products are more easily oxidized than methanol. These influences are more or less unavoidable in the case of a prolonged electrolysis of methanol, a method which was adopted in most of the previous works in order to bring a process to the stationary state or to collect a gas sample of the products for analysis. (d) It is also known[14)] that the degree of coverage with SCS affects the overall rate of methanol oxidation. On the other hand, previous works[2,7)] on the contribution of the path via SCS to the overall oxidation seldom dealt with cases of a low coverage.

In short, the experimental conditions of most previous works seem inadequate or insufficient to clarify the role of SCS. A platinum electrode with a large roughness factor is affected only a little by the presence of impurities, but much by the accumulation of the soluble intermediate products. The reverse is true for an electrode with a small roughness factor. Consequently, we used a platinized platinum electrode with a moderate roughness factor of about 17. In order to minimize the harmful influence of impurities, the time of methanol oxidation was limited to within 400 s, during which period the coverage with impurities never exceeded a few per cent. Consequently, it follows that the present work deals with the process in which the oxidation of methanol changes from a non-stationary state to an approximately stationary state.

We also assumed that, as have the previous workers,[2,7] that the rates for the path via SCS, which were too hard to measure directly, were equal to the rates of the oxidation of CO_{ad} in the supporting electrolyte containing no methanol. Instead of using these rate values directly, however, we first generalized them in the form of a rate equation. Then, the rates for that path at any set of initial coverages and potentials could be calculated by using the equation.

These improved circumstances led to the following conclusions. At potentials below ca. 0.55 V, the CO_{ad} species were formed rapidly and oxidized slowly. They inhibited mainly their own formation. At 0.6—0.75 V, reactions parallel to the reaction via CO_{ad} became predominant; the CO_{ad} hindered mainly these parallel reactions. At potentials and coverages higher than 0.8 V and 0.15 respectively, the oxidation of CO_{ad} was fast, and no hindrance of any reaction by CO_{ad} was any longer seen.

The adsorbate CO_{ad} is formed also from dissolved carbon monoxide,[2,15] which is well-known[15—18] to be a poison to the oxidation of hydrogen. At first sight, therefore, it is strange that CO_{ad} is not always a poison to the oxidation of methanol, which involves the oxidation of the hydrogen atoms of a methanol molecule. Accordingly, the role of CO_{ad} in the methanol oxidation in the presence of dissolved carbon monoxide was also studied. There was no difference between the role of CO_{ad} formed from dissolved CO and that of the CO_{ad} formed from methanol, though, in the absence of dissolved CO, the oxidation of methanol was, for some reason, inhibited at small coverages that were close to the respective limiting values.

Experimental

The procedures for measuring the overall rate of the methanol oxidation and the coverage with CO_{ad} were almost the same as those described in the previous papers.[11,14]

The formation of CO_{ad} from dissolved CO in a test solution of methanol was very fast.[2,15] Consequently, the duration of Step D for the last cleaning of the electrode in the potential sequence (illustrated in Fig. 1 in Ref. 11) was extremely shortened (to 10 ms) in order to suppress the formation of CO_{ad} at that step to approximately nothing. Otherwise, the electrode surface was almost fully covered with CO_{ad}; i.e., the observation of the methanol oxidation at low coverages became impossible. A trace amount of O_2 present in the commercial CO gas was removed with the aid of an alkaline pyrogallol solution.

The coverages with CO_{ad}, θ_1 and θ_2, were expressed, respectively as:

$$\theta_1 = Q^{ox}/Q^{ox}_{max} \tag{1}$$

$$\theta_2 = (Q^{0}_{H} - Q_{H})/Q^{0}_{H} \tag{2}$$

where Q^{ox} was the electric quantity required to oxidize an amount of CO_{ad} to CO_2 and where Q^{ox}_{max} was the maximum Q^{ox}. Q^{0}_{H} was the quantity required to cover the electrode surface fully with a monolayer of adsorbed hydrogen atoms in the absence of CO_{ad}, and Q_H was that required to do so in the presence of CO_{ad}.

Proper Use of θ_1 and θ_2. On a particular electrode, the Q^{ox}_{max} for the CO_{ad} formed from methanol differs in value from that for the CO_{ad} formed from dissolved carbon monoxide. The former is always smaller; the cause[14] of this lies in the process of the formation of the CO_{ad} from methanol. A considerable number of single sites remain unoccupied, even at the saturated coverage in the methanol system; these sites can be further occupied by hydrogen atoms or the CO_{ad} molecules from dissolved carbon monoxide. When the original substances are the same as each other, θ_1, unlike θ_2, is proportional to the number of moles of CO_{ad}; hence, the use of θ_1 is reasonable in the case of, e.g., determining the amount of CO_{ad}. However, the use of θ_2 is more reasonable when the roles of the two kinds of CO_{ad}, originating from methanol and carbon monoxide, are compared.

Washing-Electrode Method. The rate of the oxidation of CO_{ad} in a supporting electrolyte solution, 0.5 mol dm^{-3} of H_2SO_4, was measured by means of the washing-electrode method.[2] The apparatus and the pretreatment of the electrode were almost the same as those reported previously.[19] A platinized-platinum electrode with a true surface area of 3.8 m^2 was used. After CO_{ad} had been formed from a methanol solution, the electrode was washed several times with an electrolyte solution containing no methanol, while the potential was kept at about 0.1—0.06 V in order to prevent the oxidation of CO_{ad}. It was confirmed that the height and shape of the oxidation wave of the CO_{ad} were scarcely altered by the washing. After the washing, the adsorbate was potentiodynamically oxidized in the electrolyte solution containing no methanol at a scan rate of

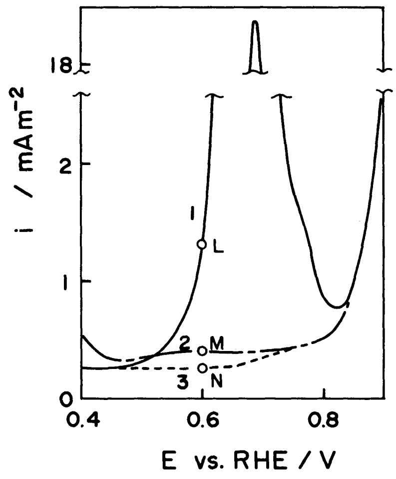

Fig. 1. Potentiodynamic current-potential curve for oxidation of CO_{ad} in 0.5 mol dm^{-3} H_2SO_4, Scan rate = 0.86 mV s^{-1}, CO_{ad} was formed by 10 min-oxidation at 0.6 V in 0.01 mol dm^{-3} CH_3OH + 0.5 mol dm^{-3} H_2SO_4:
(1) i''_c at $\theta_1^{t=0} \doteqdot 1$; (2) i_{d1} at $\theta_1^{t=0} = 0$; (3) i_{d1} calculated.

0.8—4 $mV\,s^{-1}$. Neither higher rates nor lower ones were adequate, because both resulted in unreliable data. Figure 1 shows an example of these current -potential curves.

The potentials were quoted with respect to the reversible hydrogen electrode in 0.5 $mol\,dm^{-3}$ of H_2SO_4. All the measurements were made at 0 °C.

Derivation of Equations

Several reaction paths composing the oxidation of methanol will frequently be referred to hereafter. To avoid misunderstandings caused by the descriptions, the reactions and rates will often be expressed by the symbols shows in Table 1.

Rate of Reaction C′ (i'_C). The net rate of Reaction C′ in the supporting electrolyte containing no methanol, i'_C, was determined by subtracting the double-layer-charging current density, i_{dl}, from the directly measured current density, i''_C:

$$i'_C = i''_C - i_{dl}. \tag{3}$$

According to Frumkin,[16]

$$i_{dl} = i^0_{dl}(1-\theta_1) + i^1_{dl}\theta_1, \tag{4}$$

where i^0_{dl} and i^1_{dl} are i_{dl} values at $\theta_1=0$ and $\theta_1=1$ respectively. To determine the i_{dl} values according to Eq. 4, θ_1 values were needed. These values of i_{dl} and θ_1 were determined by the ordinary trial-and-error method of calculation. An example of the calculation will be shown at the end of this section. In the first calculation, the initial value of i_{dl} at a particular potential was assumed to be i^0_{dl}, i.e., the current density indicated by Curve 2 in Fig. 1, while the Q^{ox} value at the potential was determined by the graphical integration of the following equation:

$$Q^{ox} = v^{-1}\int_E^{0.9}(i''_C - i^0_{dl})\,dE, \tag{5}$$

where v was the scan rate and where 0.9 was the potential at which the adsorbate was completely removed by oxidation. This Q^{ox} value and Eq. 1 gave a first approximate value of θ_1. When this θ_1 value was substituted in Eq. 4, the second approximate value of i_{dl} at the potential E was obtained. The determination of the i_{dl} values in this way at intervals of 0.025 V gave a plot of i_{dl} against E (Curve 3 in Fig. 1). The higher-order calculations were no longer necessary, because they brought about only a negligibly small change in the i_{dl} value. Thus, the variation in i'_C with the potential and the coverage was determined.

Rates of Reaction A and B. When the oxidation of CO_{ad} is slower than the formation, CO_{ad} is accumulated on the electrode surface; i.e., the coverage with CO_{ad} increases. Taking into account the mass balance for CO_{ad}, the rate of methanol consumption can be approximately represented as i_A+i_B, where i_A is the net rate of CO_{ad} formation when no further oxiation of CO_{ad} is assumed and where i_B is the net rate of Reaction B, which is assumed not to contribute at all to the accumulation of CO_{ad} (Table 1). In other words, the CO_{ad} formed by Reaction B is immediately oxidized to CO_2. In the same way, the whole number of moles of CO_{ad} formed at any given moment can be represented as the sum of the number of moles of CO_{ad} contributing to the increase in the coverage (N_A) and that contributing to the formation of CO_2 (N_B).

The formation of CO_{ad} is written as:

$$CH_3OH = CO_{ad} + 4H^+ + 4e \tag{6}$$

therefore, its net rate i_A is:

$$i_A = 4F\mathrm{d}N_A/\mathrm{dt}. \tag{7}$$

The oxidation of CO_{ad} is expressed as:

$$CO_{ad} + H_2O = CO_2 + 2H^+ + 2e \tag{8}$$

By use of the pulse anodic stripping method, N_A at any instant during the formation of CO_{ad} can be determined. Therefore,

$$N_A = Q^{ox}/2F = (Q^{ox}_{max}/2F)\theta_1. \tag{9}$$

Hence, the time dependence of N_A is:

$$\mathrm{d}N_A/\mathrm{d}t = (Q^{ox}_{max}/2F)\mathrm{d}\theta_1/\mathrm{d}t. \tag{10}$$

From Eqs. 7 and 10, we obtain:

$$i_A = 2Q^{ox}_{max}(\mathrm{d}\theta_1/\mathrm{d}t). \tag{11}$$

Thus, i_A can be determined by using the experimental values of Q^{ox}_{max} and d θ_1/dt.

Table 1. Symbols of Reactions and Rate

Symbol of Reaction	Rate	Path	Remark
A	i_A	CH_3OH-CO_{ad}	The CO_{ad} is never oxidized
B	i_B	CH_3OH-CO_{ad}-CO_2	The CO_{ad} never accumulates
C′	$i_{C'}$	CO_{ad}-CO_2	The rate in the absence of methanol
C	i_C	CO_{ad}-CO_2	The rate in the presence of methanol
D	i_D	CH_3OH-HCHO- HCOOH-CO_2	The path suggested by Breiter[7]
	i_T		The overall rate of methanol oxidation

From Eqs. 6 and 8, i_B and i_C are deduced as:

$$i_B = 6F\mathrm{d}N_B/\mathrm{d}t, \quad (12)$$

$$i_c = 2F\mathrm{d}N_c/\mathrm{d}t. \quad (13)$$

From Eqs. 12 and 13, we obtain:

$$i_B = 3i_c, \quad (14)$$

where i_C is the rate of oxidation of CO_{ad} 'in the presence of methanol'. The trouble is that neither N_B nor i_C can be directly measured, because the formation and the oxidation of CO_{ad} occur concurrently in the presence of methanol. Out of necessity, therefore, we assumed, following Petrii et al.[2,7] that i_C is equal to i'_C, the net rate of the oxidation of CO_{ad} in the supporting electrolyte containing no methanol.

Reaction C. As may be seen in Fig. 2, the plot of log (i'_C/θ_1) against E under the same experimental conditions as those in Fig. 1 was a straight line with a slope of 0.073 *V*/decade over the potential range of about 0.50—0.73 V, i'_C/θ_1 corresponding to the rate of the oxidation of one CO_{ad} molecule. The line was expressed as:

$$E = 0.073 \log (i'_c/\theta_1) + 0.794. \quad (15)$$

The potential range over which Eq. 15 held depended both on the coverage at the beginning of the oxidation, $\theta_1^{t=0}$, and on the scan rate of the potential. However, the equation was valid irrespective of the values of $\theta_1^{t=0}$, provided that the momentary coverage, θ_1, during the oxidation was larger than about 0.15 and that the rate was 0.8—4 mV s^{-1}.

The rearrangement of Eq. 15 gave:

$$i'_c = \theta_1 \exp (31.4E-24.9) \quad (\theta_1 > \text{ca. } 0.15). \quad (16)$$

The coverage range will soon be discussed. This experimental equation was substantially the same as the equation[20] proposed for an electron-transfer process without reactant transport; i.e., the reactants are preadsorbed species alone.

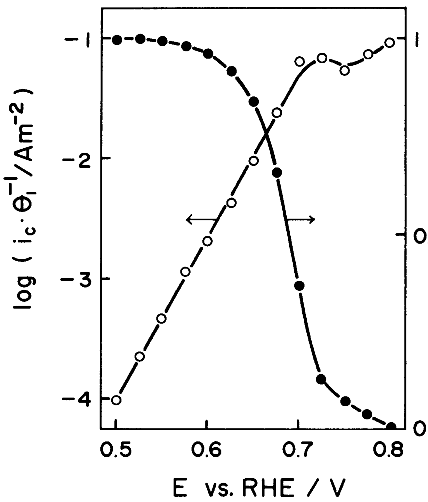

Fig. 2. Relaionship among i'_c/θ_1, potential, and θ_1 (reconstructed curves from Fig. 1.).

When θ_1 was smaller than about 0.15, the values of log (i'_C/θ_1) deviated in the direction of the decrease from the straight line (Fig. 3). As is shown in Fig. 4, an approximately linear relationship was found between θ_1 and the magnitude of the deviation, *D*, which was expressed as:

$$D = \log (i'_c/\theta_1) - (31.4E-24.9)/2.30. \quad (17)$$

Thus, the linear relationship of Fig. 4 was formulated as:

$$D = 6.95\theta_1 - 0.994 \quad (18)$$

The combination of Eq. 17 with Eq. 18 gave Eq. 19:

$$i'_c = \theta_1 \exp (16\theta_1) \exp (31.4E-27.2) \quad (\theta_1 < 0.15). \quad (19)$$

Equation 16 or 19 can be used for the estimation of i_C $(=i'_C)$ when the values of E and θ_1 are given.

Example of the Determination of i'_C, i_A, and i_B. (a) i'_C at 0.6 V (see Fig. 1): The value of i''_C at 0.6 V is

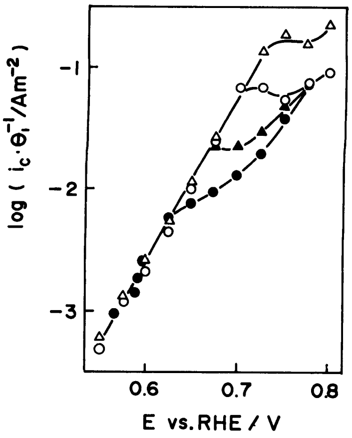

Fig. 3. Relationship between i'_c/θ_1 and potential at different scan rates (mV s^{-1}) and $\theta_1^{t=0}$: △ 2.3, 0.94; ○ 0.86, 1; ▲ 0.86, 0.22; ● galvanostatic oxidation at 0.94 mA m^{-2}, $\theta_1^{t=0}$=0.97.

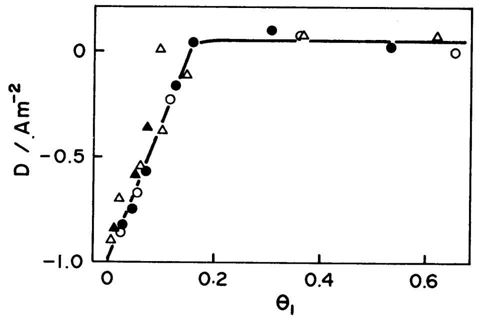

Fig. 4. Relationship between θ_1 and magnitude of deviation, *D*, from linear line in Fig. 3, $D = \log (i'_c/\theta_1) - 13.6E + 10.8$, symbols have the same meaning as in Fig. 3.

indicated by Point L, i.e., $i''_C = 1.35\ \mathrm{mA\,m^{-2}}$. To determine i'_C, the value of i_{dl} at 0.6 V is necessary (Eq. 3): the i_{dl} can be calculated by the trial-and-error method according to Eq. 4, which requires the values of i^0_{dl}, i^1_{dl}, and θ_1. The i^0_{dl} value at 0.6 V is 0.40 $\mathrm{mA\,m^{-2}}$, as is indicated by Point M. The θ_1 value at 0.6 V can be obtained if Q^{ox} and Q^{ox}_{max} are given. The graphical determination of the area bounded by Curves 1 and 2 gives the first approximate value of Q^{ox} at 0.6 V, i.e., $Q^{ox}=7.65$ C. Here, Curve 2, representing i^0_{dl}, is assumed to be the curve of the first approximate values of i_{dl}. The value of Q^{ox}_{max} is measured by an additional experiment at $\theta_1=1$, i.e., $Q^{ox}_{max}=7.74$ C. Consequently, the substitution of these coverage values into Eq. 1 gives the first approximate value of θ_1 (7.65/7.74=0.988). The value of i^1_{dl} is also found to be 0.23 $\mathrm{mA\,m^{-2}}$ by an additional measurement at $\theta_1=1$ and at 0.4 V. Therefore, by the substitution of the values of θ_1, i^0_{dl}, and i^1_{dl} into Eq. 4 $\{0.40\ (1-0.988)+0.23\times0.988=0.23\ \mathrm{mA\,m^{-2}}\}$, the second approximate value of i_{dl} is obtained. The i_{dl} value is represented by Point N on Curve 3. Consequently, the subtraction of the i_{dl} value from the observed i''_C value gives the i'_C value of 1.12 $\mathrm{mA\,m^{-2}}$. (b) i_A and i_B at 0.55 V, 1 mol $\mathrm{dm^{-3}}$ methanol, and 11 s (see Fig. 5): From the curve of θ_1 vs. the time, the $d\theta_1/dt$ value, 0.0076 $\mathrm{s^{-1}}$, at 11 s is obtained. The substitution of this value and $Q^{ox}_{max}=2.05\ \mathrm{C\,m^{-2}}$ into Eq. 11 gives the i_A value of 0.031 $\mathrm{A\,m^{-2}}$. This value is represented by Point F in Fig. 5. At 11 s, the θ_1 value is 0.91, as is indicated by Point G. Consequently, the i'_C value of 0.0020 $\mathrm{mA\,m^{-2}}$ is obtained from Eq. 16, and the i_B value of 0.0059 $\mathrm{A\,m^{-2}}$, from Eq. 14. The latter is represented by Point H.

Results and Discussion

Effects of Methanol and Its Oxidation Products on i_C. Petrii et al.[2,7] implicitely assumed that the oxidation rate of SCS (COH_{ad}) was not affected by the presence of methanol and its oxidation products, such as hydrogen ions. We consider this assumption to be reasonable, though we differ from them with regard to the kind of SCS. Among the probable products of the oxidation of methanol, the substances not participating in the reaction (Eq. 8) would not affect the rate of the oxidation of CO_{ad} directly. Although some unidentified SCS are formed from formaldehyde and formic acid at low potentials, we found that only very small amount of such SCS was formed at potentials above about 0.5 V in a mixed solution of methanol and formaldehyde or formic acid. The formation of no other influential adsorbate from these two products has ever been reported. According to our test, CO_2 has no effect on the rate so long as the potential is higher than 0.3 V.

Among the products, only the hydrogen ion directly participates in the oxidation of CO_{ad}. However, the effect of the 'increase' in the hydrogen-ion concentration during the oxidation of methanol would be relatively small for the following reasons: (1) The solution originally contains sulfuric acid as the supporting electrolyte at a high concentration of 0.5 mol $\mathrm{dm^{-3}}$. (2) The duration of oxidation is 400 s at the most; hence, the amount of hydrogen ions accumulated on the electrode surface is not very large. (3) The limiting rate of methanol oxidation is relatively small compared with the limiting diffusion rate of methanol; hence, the formation rate for hydrogen ion is relatively small. The amount of hydrogen ions accumulated on a very roughened surface of electrode is larger than that on a smooth surface. However, the roughness factor of the electrode used in the present work is not so large, i.e., 17. Considering this roughness together with the reasons above described, it might safely be said that the effect of hydrogen-ion formation on the rate of CO_{ad} oxidation is relatively small.

Contribution of Reactions A and B to the Overall Oxiation of Methanol. The symbol i_T represents the overall rate of the oxidation of methanol and a quantity directly measured.

As may be seen in Fig. 5, i_B attained a stationary value a short time after the beginning of the oxidation under the conditions described in the figure caption.

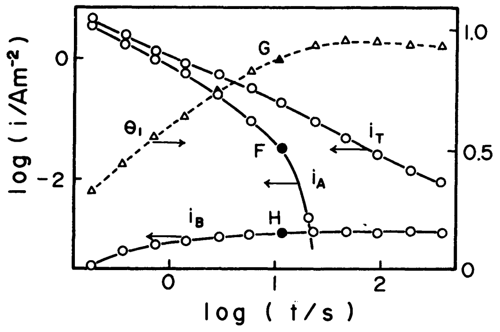

Fig. 5. Variation in i_A, i_B, i_T, and θ_1 with time, 1 mol $\mathrm{dm^{-3}}$ CH_3OH+0.5 mol $\mathrm{dm^{-3}}$ H_2SO_4, 0.55 V.

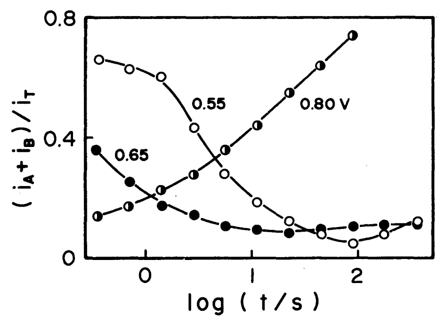

Fig. 6. Variation in $(i_A+i_B)/i_T$ with time, 1 mol $\mathrm{dm^{-3}}$ CH_3OH+0.5 mol $\mathrm{dm^{-3}}$ H_2SO_4.

On the contrary, i_A and i_T were decreased towards zero and i_B respectively. The $(i_A+i_B)/i_T$ ratio depended upon the potential, the time of oxidation, and the concentration of methanol, as may be seen in Figs. 6 and 7. The essential points about the ratio were as follows:

(1) When the potential was lower than 0.55 V and the time of oxidation was short, e.g., within 2 s, $(i_A+i_B)/i_T>0.5$ (Fig. 6) and $i_A \gg i_B$ (Fig. 5). That is, the formation of CO_{ad} was predominant over Reaction B. Moreover, i_A and i_T decreased with an increase in θ_1. This indicates that molecules of the CO_{ad} hinder their own formation, and hence i_T decreases. As the oxidation time went by, i_A decreased remarkably (Fig. 5) and $(i_A+i_B)/i_T$ became smaller than 0.5 (Fig. 6). Taking into consideration the fact that the yield of CO_2 at low concentrations of methanol was about 100 per cent,[1,21] together with the low value of the i_B/i_T ratio, we must decidedly support the idea of Breiter et al.[2,6] that a parallel reaction D exists, producing CO_2 without going through SCS. It would also exist at high concentrations and high potentials.

(2) When the potential was about 0.6—0.75 V, $(i_A+i_B)/i_T \ll 0.5$ except for the earliest oxidation stage of a few seconds (Figs. 6 and 7). At these potentials, the electrode surface was a quite thoroughly covered with CO_{ad}. Therefore, reactions other than A and B must take place on the surface free from CO_{ad}. Its rate can be expressed by $(i_T-i_A-i_B)/(1-\theta_1)$, i.e., the current density per unit free surface area. This rate did not decrease with an increase in θ_1, as may be seen in Fig. 8, while, on the contrary, $(i_T-i_A-i_B)$ and i_T did decrease. These findings indicate that at least one of the causes of the decreases in the latter two quantities is the occupation of reaction sites by CO_{ad}. θ_1 is generally large at high concentrations of methanol, as is well known,[22] when the other conditions are maintained constant. Consequently, the inhibition by CO_{ad} of parallel reactions such as Reaction D would become remarkable at high concentrations of methanol.

(3) At potentials higher than about 0.8 V and at high concentrations of methanol, i_B increased as the time of oxidation went by (Fig. 9), and $(i_A+i_B)/i_T$ increased beyond 0.5 (Fig. 6). In this case, CO_{ad} was not longer the inhibitor; rather the adsorbate was an intermediate in Reaction B, which was contributing predominantly to the overall oxidation of methanol. Breiter[7] and Pletcher et al.[23] also observed that CO_{ad} was no longer a poison under similar conditions. At low concentrations, however, i_B/i_T $\{\fallingdotseq(i_A+i_B)/i_T\}$ is small even at higher potentials, as is shown in Fig. 10.

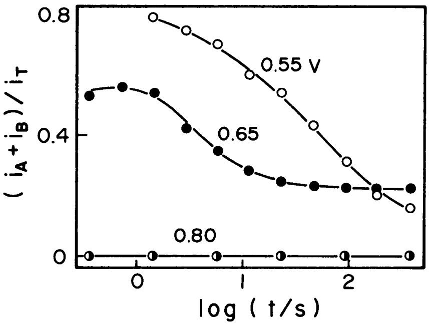

Fig. 7. Variation in $(i_A+i_B)/i_T$ with time, 0.03 mol dm^{-3} $CH_3OH+0.5$ mol dm^{-3} H_2SO_4.

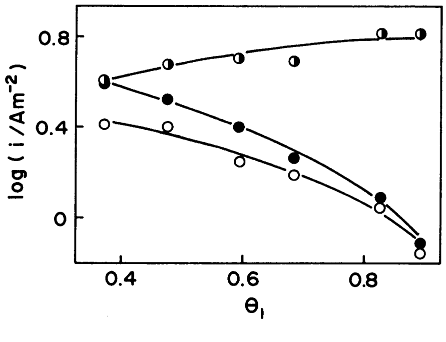

Fig. 8. Variation in i_T[●], $i_T-i_A-i_S$[○], and $(i_T-i_A-i_B)/(1-\theta_1)$[◑] with time, 1 mol dm^{-3} $CH_3OH+0.5$ mol dm^{-3} H_2SO_4, 0.65 V.

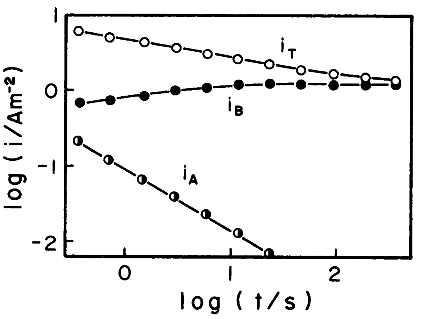

Fig. 9. Variation in i_A, i_B, and i_T with time, 1 mol dm^{-3} $CH_3OH+0.5$ mol dm^{-3} H_2SO_4, 0.80 V.

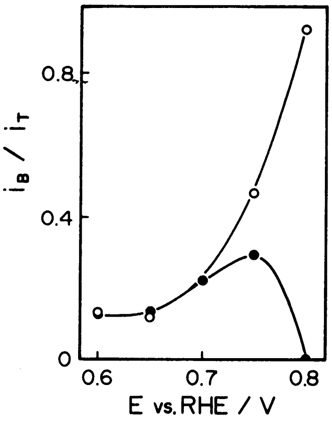

Fig. 10. Variation in i_B/i_T with potential, $CH_3OH+0.5$ mol dm^{-3} H_2SO_4, concentration of methanol (mol dm^{-3}): ○ 1; ● 0.1, oxidation time=360 s.

In this case, θ_1 was small; therefore, the inhibitory action of CO_{ad} seemed negligibly small. At present it is hard to explain why i_B/i_T decreases towards zero or increases remarkably with an increase in the potential, depending upon the low or high concentrations of methanol respectively.

Oxidation of Methanol in the Presence of Dissolved CO. The adsorbate CO_{ad} is also formed on a Pt electrode from the dissolved CO in a solution. Figure 11 showed potentiodynamic i—E curves taken in the respective solutions of methanol, carbon monoxide, and their mixture. When a solution of methanol was saturated with pure CO, the oxidation of methanol was almost completely inhibited at potentials below about 0.9 V, at which CO began to be oxidized. In this case, the coverage θ_2 with CO_{ad} immediately attained the value of 1 (Fig. 12). The use of a CO gas diluted with N_2 resulted in a slower adsorption of CO, as is indicated by Curve 2 in Fig. 13; that was what made the measurement possible at low coverages in the presence of dissolved CO.

As is indicated by Curve 1 in Fig. 13, the coverage with the CO_{ad} formed from methanol has a limiting value, $\theta_2^{\rm L}$. It is known[2,22] that this value is less than or equal to about 0.8 at its maximum, depending upon the potential and concentration of methanol. Curve 1 (taken at 0.75 V) in Fig. 14 has about 0.3 as such a limit, while Curve 3 (0.65 V) has about 0.65. As these curves illustrate, a remarkable fall of i_T took place whenever the θ_2 value fell in the narrow range from $\theta_2^{\rm L}$ to ($\theta_2^{\rm L}$—about 0.1). The fall in a particular case, in which $\theta_2^{\rm L}$ was about 0.8, has been explained[14] by assuming that one CO_{ad} damages a vacant site-aggregate (consisting of two sites) indispensable for the formation of CO_{ad} itself and for the oxidation of methanol to CO_2.

However, the remarkable i_T falls occurring when the $\theta_2^{\rm L}$ values are less than 0.8, e.g., Curves 1 and 3 in Fig. 14, have not yet been explained. Because the falls occur independently of the magnitude of $\theta_2^{\rm L}$, the CO_{ad} is unlikely to be directly connected. Kita[24] reported an i_T decrease at a small coverage and a high potential in a potentiodynamic oxidation of methanol; he suspected that it was caused by some adsorbate other than CO_{ad}. In any event, further investigations are needed.

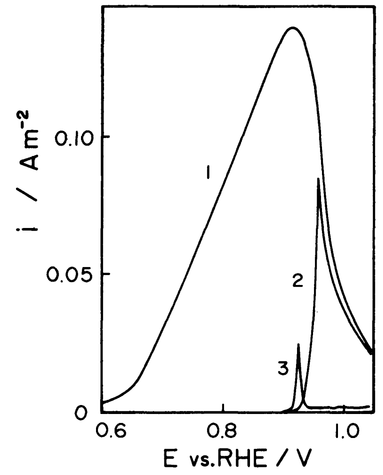

Fig. 11. Potentiodynamic current-potential curve for oxidation of methanol in $CH_3OH+0.5$ mol dm^{-3} H_2SO_4, concentration of methanol (mol dm^{-3}), stauration gas: (1) 0.3, N_2; (2) 0.3, pure CO; (3) 0, pure CO, scan rate=1 mV/s^{-1}.

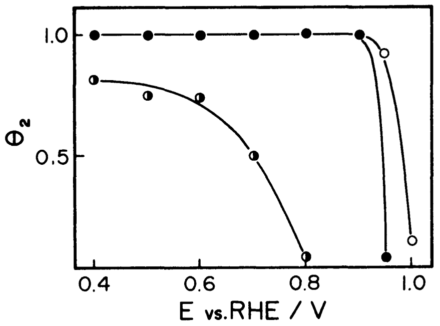

Fig. 12. Variation in θ_2 with potential, methanol was oxidized in $CH_3OH+0.5$ mol dm^{-3} H_2SO_4, concentration of methanol (mol dm^{-3}), saturation gas: (1) 0.03, N_2; (2) 0, pure CO; (3) 0.03, pure CO, oxidation time=90 s.

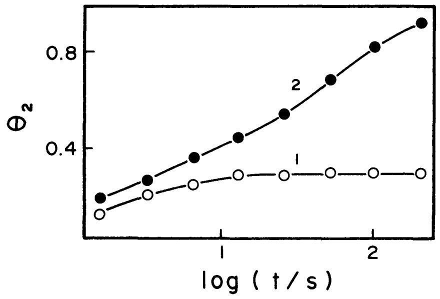

Fig. 13. Variation in θ_2 with time in 0.03 mol dm^{-3} $CH_3OH+0.5$ mol dm^{-3} H_2SO_4, saturation gas: (1) N_2; (2) $CO+N_2$ (vol% of CO=20), 0.75 V.

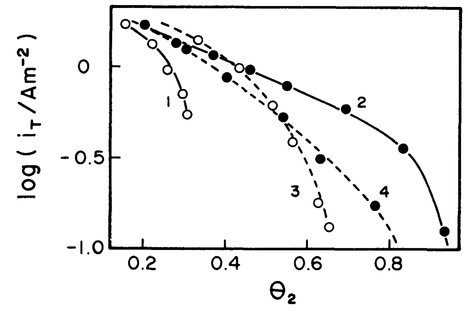

Fig. 14. Variation in i_T with θ_2 in 0.03 mol dm^{-3} $CH_3OH+0.5$ mol dm^{-3} H_2SO_4, vol% CO in saturation gas (N_2+CO), potential (V): (1) 0, 0.75; (2) 0, 0.65; (3) 20, 0.75; (4) 20, 0.065.

The presence of dissolved CO always increased the limiting coverages up to 1 (Fig. 13), though Curves 2 and 4 in Fig. 14 do not show the whole results. Also, in these cases remarkable i_T falls took place before and after the coverage attained about 0.8. The cause of these falls is the same as those discussed above.

Gently sloping parts preceding the remarkably-falling parts just considered always appeared on the $i_T-\theta_2$ curves, though this part was very short in the case of Curve 1. When the coverage was smaller than (θ_2^L—about 0.1), (e.g., $\theta_2<0.2$ for the pair of curves 1 and 2, $\theta_2<0.55$ for 3 and 4 in Fig. 14), the values of i_T/θ_2 in the presence and absence of dissolved CO were approximately the same. This supports the idea that the roles of the CO adsorbates formed from methanol and dissolved CO are same in the oxidation of methanol. The gentle falls of i_T are attributed to the effect of the site occupation of the effective electrode surface by CO_{ad}.

In short, there is no great difference between the role of CO_{ad} in the presence and absence of dissolved CO, though, in the absence of dissolved CO, the oxidation of methanol is, for some reason, inhibited at small coverages that are close to the respective limiting values. Because the coverage, θ_2 is readily able to attain a value of 1 in the presence of dissolved CO, the steady-state oxidation of methanol is remarkably inhibited by the CO_{ad}, which, at high coverages, makes unavailable the site-aggregates indispensable for the oxidation of methanol.

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