The Kinetics of Oxidation of Formaldehyde at a Platinum Electrode in an Acid Solution

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(Received June 26, 1989)

Three types of the retardation were found for the rate of oxidation of formaldehyde at a platinum electrode in 0.5 mol dm^{-3} sulfuric acid. These rate retardations are attributed to the blocking of individual reaction sites by strongly chemisorbed species, the inhibition of the pairing of adjacent sites indispensable for the oxidation of formaldehyde, and the accumulation of oxidation intermediates. The oxidation rate under conditions excluding these rate retardations was independent of the potential in the potential range of about 0.4—0.6 V vs. a reversible hydrogen electrode and corresponded to first-order kinetics with respect to the formaldehyde concentrations. These kinetic data are explained in terms of a slow adsorption of formaldehyde molecules.

The elucidation of the mechanism of the formaldehyde oxidation helps to understanding the mechanism of methanol oxidation, since formaldehyde is a probable intermediate of the oxidation of methanol.[1–4)]

A Tafel relationship have been observed for the overall oxidation of formaldehyde[5,6)] and a strongly chemisorbed adsorbate (SCS) such as CO_{ad}[7–9)] also has been detected. Although the Tafel relationship has been explained in terms of a consecutive mechanism, the low reactivity of the detected adsorbate suggests a parallel mechanism. According to the parallel mechanism, the overall rate approximately agrees with the rate of a fast reaction not via SCS (this reaction is hereafter called Reaction F), and the rate of Reaction F is retarded by the formation of SCS. Hence, the overall rate of the formaldehyde oxidation will vary due to both the rate retardation and the kinetics of Reaction F. In the present paper, the rate retardation of the formaldehyde oxidation at a platinum electrode in 0.5 mol dm^{-3} sulfuric acid was examined, and the rate equation for Reaction F was derived to explain the reaction mechanism.

Experimental

The surface coverage, θ, with SCS was determined according to the following equation.

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

where the $Q_H{}^\circ$ and Q_H are the electric quantities required to cover fully the electrode surface with adsorbed hydrogen atoms in the absence and the presence of SCS respectively. These quantities were determined by the conventional hydrogen deposition method.

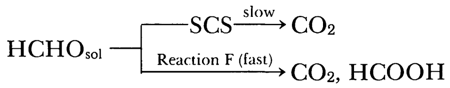
The solution of formaldehyde was prepared by heat decomposition of chemical grade (Wako) paraformaldehyde in deoxygenated water, the solution was cooled to about 0 °C, and then dilute sulfuric acid was added until its concentration became 0.5 mol dm^{-3}. In order to prevent the formation of formic acid from formaldehyde by oxygen oxidation, all the operations were performed under a nitrogen atmosphere.

The rate of the overall oxidation of formaldehyde, i_t, was determined by stepping the potential to given potentials from 0.03 V at which no oxidation occurred. Consequently, the available concentrations of formaldehyde was limited to about 0.02 mol dm^{-3}, because at higher concentrations a considerable amount of SCS was formed even at 0.03 V.

Other experimental conditions and procedures were almost the same as those used in the previous studies.[10,11)] 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

Rate Retardations. Loucka[9)] and other workers[6)] have proposed the parallel mechanism for the oxidation of formaldehyde at a platinum electrode in an acid solution.



According to this reaction scheme, SCS blocks the sites of the fast reaction, and consequently the overall rate, i_t, decreases. When only the blocking effect of SCS is exerted, the rate, i_F, of Reaction F can be expressed by

$$i_F = i_t/(1-\theta) \qquad (2)$$

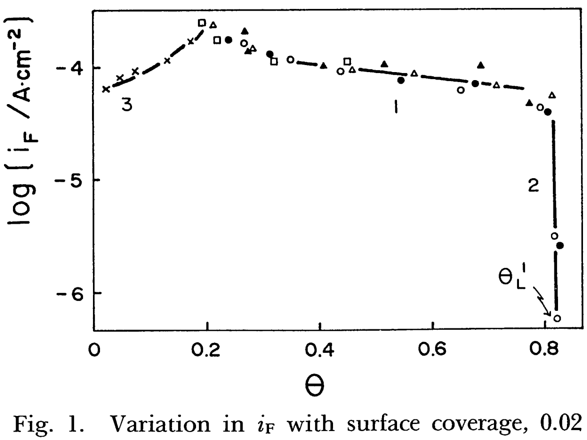


Fig. 1. Variation in i_F with surface coverage, 0.02 mol dm^{-3} HCHO+0.5 mol dm^{-3} H_2SO_4. Potentials (V): ○ 0.400; ● 0.425; ▲ 0.500; □ 0.650; × 0.800.

In order to confirm the presence of the other rate retardations, the relationship between the i_F and the θ was examined at a constant potential. As may be seen from curves 1, 2, and 3 in Fig. 1, the rate retardation of the formaldehyde oxidation can be classified into the following three types.

Rate Retardation A: i_F was roughly independent of θ as indicated by curve 1. This means a linear decrease in the i_t with increasing θ, i.e., the rate retardation was due to a simple blocking effect of SCS on the sites of Reaction F. The θ increased with increasing time and decreasing potential at potentials below about 0.6 V, as shown in Fig. 2. Consequently, the i_t at the low potentials remarkably decreased by increasing θ, even after the i_F reached a stationary value at each surface coverage. The stationary i_F was realized a few seconds after the start of the oxidation. At potentials higher than about 0.7 V, no rate retardation A occurred, since θ was small, and decreased with increasing time.

Curve 1 was a straight line with a small slope, the observed rate retardation A was more remarkable than that due to the simple blocking effect. Mathematically, curve 1 can be expressed by an Elovich equation.[12)]

$$i_F = i_{\theta=0} \cdot \exp(-\alpha\theta/RT) \qquad (3)$$

where $i_{\theta=0}$ is the i_F at θ=0, and α 1.4 RT. The small α value indicates a slight variation in the adsorption heat with the θ.

Rate Retardation B: i_F decreased remarkably as the θ approached a limiting coverage, θ_L^1, as indicated by curve 2. Similar decrease in the i_F was observed also in the case of the methanol oxidation,[13)] and attributed to a special blocking effect of SCS. In this effect, the pairing of adjacent sites that is indispensable for the oxidation of methanol is inhibited by the partial occupation of the sites. Curve 2 in Fig. 1 had the same shapes as the calculated curves which had been derived[13)] from the blocking effect on the pairing of the adjacent sites. Therefore, rate retardations B can be attributed to the blocking effect of SCS on the pairing of adjacent sites.

From the comparison of Figs. 1 and 2, the $\theta_L{}^1$ in the kinetics of Reaction F agreed with the $\theta_L{}^2$ in the SCS formation from formaldehyde. Probable causes of the $\theta_L{}^2$ in the SCS formation are (1) a steric hindrance[14)] among adsorbate molecules and (2) the blocking effect[13,14)] of preadsorbed species on the pairing of adjacent sites indispensable for the formation of SCS. According to Loucka[9)] and other workers,[7,8)] the SCS is adsorbed carbon monoxide. This adsorbate will have explicitly no steric hindrance, because θ=1.0 is attained[15)] in the adsorption from carbon monoxide gas. Therefore, a steric hindrance among SCS molecules was excluded from the probable causes of the limiting coverage. Abstruction of two hydrogen atoms from the formaldehyde molecule is necessary for the SCS formation. Probably, the pairing of adjacent sites is indispensable for this abstruction.

Rate Retardation C: The i_F decreased at small surface coverages, as indicated by curve 3. The causes of the rate retardation was confirmed as follows. Figure 3 shows potentiodynamic i-E curves from 0.2 V immediately after the preoxidation of formaldehyde at 0.8 V. The waves of the oxidation of adsorbed hydrogen and formaldehyde appeared in the potential ranges of about 0.2—0.3 and 0.35—0.9 V respectively. Although the hydrogen wave was little influenced by the preoxidation, the wave height for the formaldehyde oxidation decreased with increasing time of preoxidation. Since the θ is almost zero at the preoxidation potential of 0.8 V, no rate retardations A and B explicitly occurred.

An addition of formic acid to the solution of formaldehyde caused some rate retardation of the formalde-

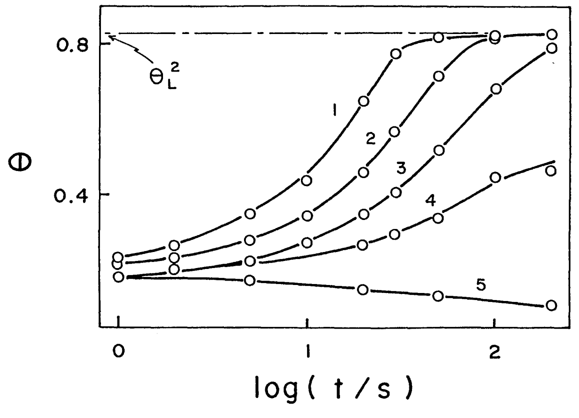


Fig. 2. Variation in surface coverage with time, 0.02 mol dm^{-3} HCHO+0.5 mol dm^{-3} H_2SO_4. Potentials (V): (1) 0.40; (2) 0.45; (3) 0.50; (4) 0.60; (5) 0.70.

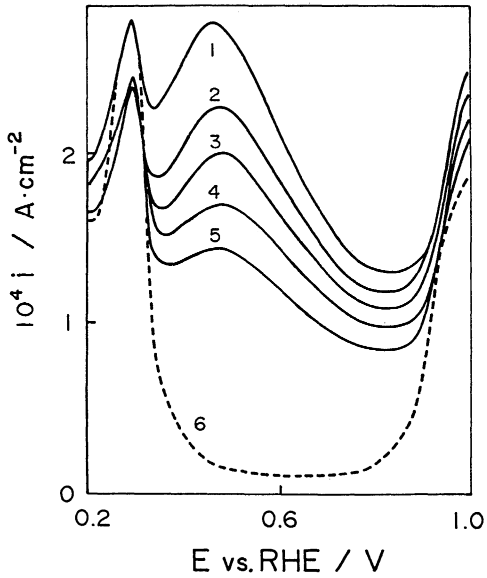


Fig. 3. Potentiodynamic i-E curves immediately after preoxidation at 0.80 V, scan rate 0.3 V s^{-1}, 0.02 mol dm^{-3} HCHO+0.5 mol dm^{-3} H_2SO_4. Preoxidation times (s): (1) 0; (2) 3; (3) 10; (4) 30; (5) 100, ---- in the absence of HCHO.

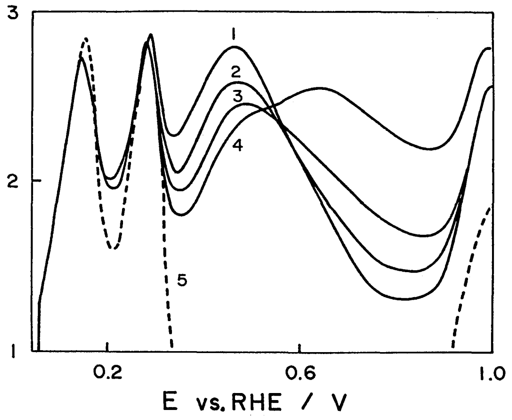


Fig. 4. Effect of formic acid on potentiodynamic *i-E* curves, HCOOH+0.02 mol dm^{-3} HCHO+0.5 mol dm^{-3} H_2SO_4. HCOOH (mol dm^{-3}): (1) 0; (2) 0.005; (3) 0.01; (4) 0.02, ---- in the absence of HCHO.

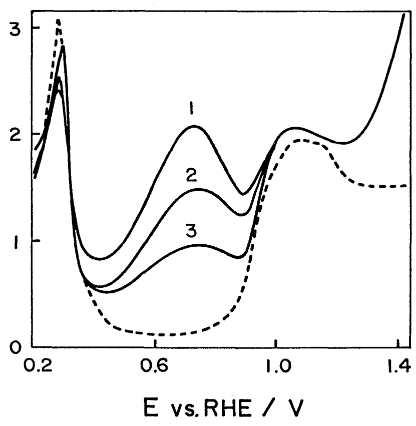


Fig. 5. Potentiodynamic *i-E* curves immediately after preoxidation at 0.8 V, 0.02 mol dm^{-3} HCOOH+0.5 mol dm^{-3} H_2SO_4. Preoxidation times (s): (1) 0; (2) 1; (3) 10, ---- in the absence of HCOOH.

hyde oxidation at low potentials, whereas at potentials higher than about 0.55 V it increased considerably, as shown in Fig. 4. Since formic acid is more slowly oxidized at low potentials than formaldehyde, the rate retardation and increase in the overall rate in Fig. 4 can be explained in terms of the formation of retarding adsorbates from formic acid and the further oxidation of formic acid respectively. Figure 5 shows the *i-E* curves for the oxidation of formic acid immediately after the preoxidation at 0.8 V and the potential step to 0.2 V. The effect of the preoxidation on the *i-E* curve of formic acid was similar to the case of formaldehyde. Kita et al.[16] interpreted the rate retardation in terms of formic acid molecules which were stabilized in the vicinity of the electrode surface by means of hydrogen bonding. Rate retardation C also can be interpreted as similar stabilization of formic acid molecules, though a further investigation is needed to confirm this interpretation.

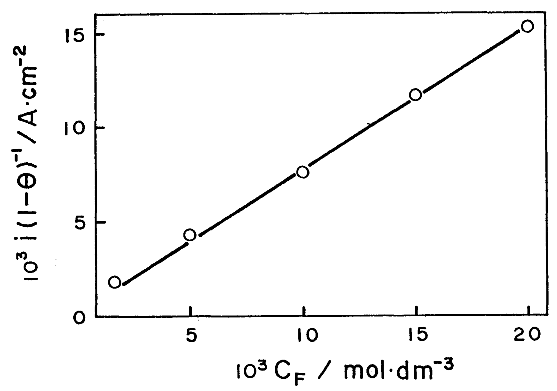


Fig. 6. Variation in i_t with formaldehyde concentration, HCHO+0.5 mol dm^{-3} H_2SO_4, 0.50 V, oxidation time 5 s.

Kinetics of Reaction F. In order to elucidate the reaction mechanism, the rate equation of Reaction F was examined. As described above, the i_F was approximated by Eq. 2 at a constant potential and formaldehyde concentration. Moreover, the i_F was almost independent of the potential in the coverage range of 0.2—0.75. Outside this coverage range, the i_F deviated from curve 1 due to rate retardations B and C. Therefore, the relationship between the i_F and the formaldehyde concentration was examined within the coverage range. Concretely, the observed coverage was within the coverage range when the potential, the oxidation time, and the formaldehyde concentration were 0.5 V, 5 s, and within the concentration range of 0.001—0.02 mol dm^{-3} respectively. As shown in Fig. 6, reaction order with respect to the formaldehyde concentration was explicitly first order. From these findings, the i_F can be expressed by

$$i_F = i_t/(1-\theta) \fallingdotseq k\cdot C \qquad (4)$$

where C and k are the concentration of formaldehyde and a constant respectively. The potential independence of the i_F means that the i_F is determined by a non-electrochemical step such as an adsorption of formaldehyde molecules and some surface reaction of adsorbed intermediates. Several adsorbed intermediates were presumed[5,6] for the oxidation of formaldehyde but none of these were detected. This may be due to the fact that the amount of reactive adsorbate is too small to be detected by the usual methods. From these findings, it was concluded that the adsorption of formaldehyde molecules is slow in the overall oxidation without any rate retardation.

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