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Electrocatalysis

The Role of Bridge-Bonded Adsorbed Formate in the Electrocatalytic Oxidation of Formic Acid on Platinum**

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The oxidation of formic acid (HCOOH) on platinum electrodes has been extensively investigated as a model electrocatalytic reaction.[1–4] It is generally accepted that HCOOH is oxidized to CO_2 through a dual-pathway mechanism: one pathway (the main pathway) involves a fast reaction via a reactive intermediate and the second pathway includes a step in which a poisoning species is formed. This species, which is oxidized to CO_2 at high potentials, has been identified as adsorbed CO, which is formed by dehydration of HCOOH. Adsorbed hydroxycarbonyl ($COOH_{ads}$) has long been assumed to be the reactive intermediate in the main pathway,[1–4] but the spectroscopic detection of this species has not been reported to date.

By using surface-enhanced infrared absorption spectroscopy in the attenuated total reflection mode (ATR-SEIRAS),[5] Miki et al.[6] observed that formate is adsorbed in a bridge-bonded configuration on Pt electrodes during HCOOH oxidation. On the basis of systematic time-resolved ATR-SEIRAS analysis of the oxidation dynamics, Samjeské et al.[7–9] suggested that adsorbed formate ($HCOO_{ads}$) is a reactive intermediate in the main pathway and its decomposition to CO_2 is the rate-determining step (rds). The adsorbed formate is in equilibrium with HCOOH in the bulk solution and the reaction pathway (formate pathway) can be represented by Equation (1)[8–10]

$$HCOOH + 2^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCOO_{ads} + H^+ + e^- \xrightarrow[\text{rds}]{k_2} CO_2 + 2\,H^+ + 2\,e^- + 2^* \tag{1}$$

where the asterisk represents a free site on the Pt surface and k_n ($n = 1$, -1, and 2) is the rate constant of each step. On the other hand, in a follow-up ATR-SEIRAS investigation under flow conditions, Chen et al. argued that most oxidation current is carried by the direct oxidation of HCOOH via weakly adsorbed molecular HCOOH ($HCOOH_{ads}$)[11,12] [Eq. (2)]

$$HCOOH + p^* \rightarrow HCOOH_{ads} \xrightarrow{\text{rds}} CO_2 + 2\,H^+ + 2\,e^- + p^* \tag{2}$$

and that adsorbed formate is a site-blocking spectator in the reaction rather than the intermediate.

The electrochemical and spectral data obtained under static[6–9] and flow[11,12] conditions are essentially identical, and all the experiments consistently showed that the oxidation current i is not proportional to the coverage of adsorbed formate $\theta_{formate}$. The different conclusions from the two reports stem from different interpretations of the nonlinear relationship between i and $\theta_{formate}$. Samjeské et al.[7–9] suggested that i is represented by the second-order rate equation [Eq. (3)]

$$i \propto k_2\,\theta_{formate}(1-2\,\theta_{formate}-\theta_{CO\_L}-2\,\theta_{CO\_B}) \tag{3}$$

where θ_{CO_L} and θ_{CO_B} are the coverages of linear CO (CO_L) and bridge-bonded CO (CO_B), respectively. Herein, coverage is defined as the number of adsorbed species divided by the number of surface Pt atoms, and the factor of 2 for $\theta_{formate}$ and θ_{CO_B} represents the occupation of two sites by bridge-bonded formate and CO_B. The term given in parentheses represents the requirement of a neighboring free site for the decomposition of a formate species. The rate equation is identical to that proposed to express the kinetics of the vacancy-driven autocatalytic decomposition of formate and acetate to CO_2 (the so-called kinetic surface explosion) observed on metal surfaces under ultrahigh vacuum (UHV) conditions,[13,14] and the neighboring free site is speculated to be necessary for a tilted[15] or monodentate[16] transient state for the decomposition of bridge-bonded formate. The rate equation was successfully used to simulate potential and current oscillations observed in HCOOH oxidation under galvanostatic and potentiostatic conditions, respectively.[7,8,10] However, Chen et al.[11,12] assumed that the oxidation current in formate pathway is proportional to the value of $\theta_{formate}$ and estimated the contribution of this pathway to the total oxidation current to be 25% at most[11] (15% at most for DCOOH oxidation[12]), which led to the proposal of the third additional pathway, which proceeds via $HCOOH_{ads}$ as the main current carrier. This pathway is termed the direct pathway.

We discuss herein whether adsorbed formate is a reaction intermediate or a site-blocking spectator in the electro-

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oxidation of HCOOH. This issue is also very important for the electrooxidation of methanol and formaldehyde (a partially oxidized product of methanol[17,18]) on Pt because adsorbed formate is commonly observed during the oxidation of all these small organic molecules.[19–21] If adsorbed formate were a site-blocking spectator, then catalysts should be designed to suppress its adsorption. We will show that the adsorbed formate is actually the reaction intermediate in the electro-oxidation of HCOOH (and hence also of methanol and formaldehyde) and that the contribution of the direct pathway proposed by Chen et al. is negligible at best.

The formate and CO pathways are kinetically coupled:[9] adsorbed CO not only inhibits the adsorption of formate but also suppresses the decomposition of adsorbed formate [Eq. (3)], while adsorbed formate suppresses the oxidation of CO by blocking the neighboring sites that are necessary for the adsorption of the oxygen-containing species (water or OH) that are required for CO oxidation. The kinetic coupling of the pathways hampers the elucidation of the reaction mechanism.[9,22] For examining the pathways in which CO is not produced (i.e., the formate and direct pathways) in detail, the influence of adsorbed CO must be eliminated. For this purpose, we employed potential-step chronoamperometry coupled to time-resolved ATR-SEIRAS. Specifically, the electrode potential was stepped to a desired potential E_s after oxidizing adsorbed CO at 0.9 V versus the reversible hydrogen electrode (RHE) for 2–5 s, and the subsequent current transient and infrared spectra of the electrode surface were recorded simultaneously. Since CO accumulates rather slowly,[8] the voltammetric behavior and the kinetics of HCOOH oxidation can be examined with negligible influence of adsorbed CO by sampling the data immediately after the potential step to E_s.[23] Following the procedure of Lu et al,[23b] the current was sampled at 0.5 s to avoid the contributions of double-layer charging and the reduction of Pt surface oxides to the HCOOH oxidation current, and also to minimize the effect of mass transport. A thin Pt film electrode chemically deposited on a Si ATR prism[6,20] was used as the working electrode. Other experimental details are described elsewhere,[5b,8,9,24] and potentials are quoted versus the RHE except where otherwise noted. Current densities were calculated with respect to the real surface area of the electrode as determined from the hydrogen adsorption peaks in a cyclic voltammogram recorded in 0.5 M H_2SO_4 without HCOOH.

A typical chronamperogram for a double-potential step from 0.05 to 0.9 V and then to $E_s = 0.6$ V in 10 mM HCOOH with 0.5 M H_2SO_4 is shown in Figure 1a. Ar was bubbled through the solution during the measurements to facilitate the mass transport of HCOOH to the electrode surface. The oxidation current increases immediately after the potential step to E_s and then gradually decreases (the latter behavior will be discussed later).

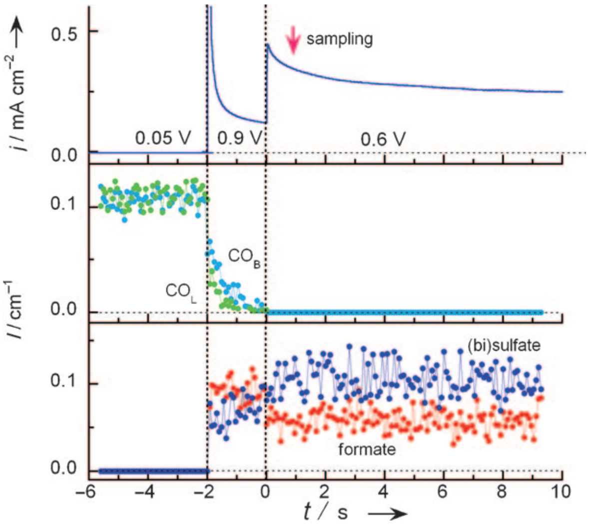

Figure 1. a) Current transient for a double-potential step from 0.05 to 0.9 (2 s) and then to 0.6 V (vs. RHE) in 10 mM HCOOH with 0.5 M H_2SO_4. b, c) Transients of the integrated band intensities of CO_L, CO_B, formate, and (bi)sulfate taken from a set of time-resolved IR spectra of the Pt electrode surface collected simultaneously with the current transient at 80 ms intervals.

Infrared spectra of the electrode surface recorded simultaneously with the chronoamperogram at every 80 ms interval (Figure S1 in the Supporting Information) were identical to those observed under potential sweep conditions.[6–9] The C–O stretching modes of CO_L and CO_B, the symmetric O–C–O stretching mode of bridge-bonded formate, and the S–O stretching modes of sulfate and/or bisulfate were observed in the spectral range of 4000–1000 cm^{-1}, in addition to the stretching and bending modes of water. Transients of the integrated band intensities of the adsorbates during the double-potential step are shown in Figure 1 b, c, in which the sum of the two bands at approximately 1180 and 1100 cm^{-1} is shown as the intensity of adsorbed (bi)sulfate because the relative intensities of the two bands were time- and potential-dependent, and the sum of the intensities of the two bands was almost proportional to the coverage of adsorbed (bi)sulfate.[25] As can be observed, adsorbed CO is almost completely oxidized within 2 s (a longer time was required at higher θ_{CO} values and at lower potentials) and the bands of bridge-bonded formate and (bi)sulfate emerge. After the second potential step to $E_s = 0.6$ V, the formate band intensity decreases and the (bi)sulfate band intensity increases quickly to constant values (i.e., the steady state is reached quickly). No CO accumulation is observed at this potential.

Current–potential curves obtained by varying the value of E_s exhibited maxima at 0.45 and 0.6 V for HCOOH concentrations of 10 and 100 mM, respectively, (Figure S2 in the Supporting Information), which are in good agreement with previously reported values.[23b] When the HCOOH concentration was 10 mM, the formate and (bi)sulfate bands appeared at around 0.2 V in the corresponding spectra. The formate band intensity increased almost linearly with increasing potential up to approximately 0.9 V and then decreased at more positive potentials because of the oxidation of the electrode surface (which is evidenced by the shift of the baseline level of the spectra[9]). On the other hand, the (bi)sulfate band intensity reached a maximum at approximately 0.6 V and then decreased at higher potentials. A similar trend was found when the HCOOH solution was 100 mM, but coadsorption of (bi)sulfate was hardly observed in this case (and for higher HCOOH concentrations), thus indicating that formate is adsorbed more strongly than (bi)sulfate.

When the same experiments were performed with HCOOH concentrations ranging from 5 mM to 1 M, the potential of the maximum current systematically shifted to higher potentials as the concentration increased (Figure S3 in the Supporting Information). The formate band intensity A_{formate} and the oxidation current at 0.6 V are plotted as a function of HCOOH concentration (c_{HCOOH}) in Figure 2. The formate band intensity almost saturates at around 0.1 M, while the oxidation current keeps increasing. The nonlinear relationship between the oxidation current and A_{formate} is seen more clearly in the inset of Figure 2.

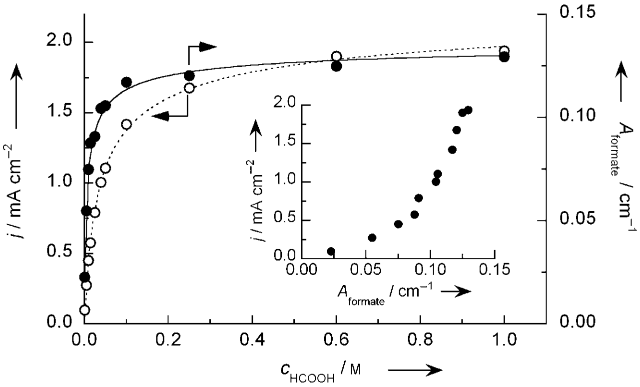

Figure 2. Current density j (open symbols) and A_{formate} (closed symbols) sampled at $t = 0.5$ s after stepping the potential to 0.6 V and plotted as a function of c_{HOOH}. The solid trace is a fit of Equation (5) to the $A_{\text{formate}}-c_{\text{HOOH}}$ plot. The dashed trace is a guide. The inset shows the nonlinear relationship between j and A_{formate}. A_{formate} is the average of 10 spectra around $t = 0.5$ s.

We now discuss which pathway better explains the results when assuming that A_{formate} is proportional to θ_{formate}. This assumption is generally applicable if the orientation of the adsorbate is unchanged with coverage[5] and the adsorbate–adsorbate interaction is not so strong, as for CO adsorbed on Pt, except at very high coverage.[26] In the case of the formate band, the spectral features and vibrational frequency were independent of HCOOH concentration and potential, and dipole–dipole coupling was not observed in the experiments where mixed solutions of HCOOH and DCOOH were used. Therefore, the assumption will be reasonable. The c_{HCOOH} dependence of the oxidation current and A_{formate} (i.e., θ_{formate}) at 0.6 V (Figure 2) is discussed first in order to avoid the complexity arising from the potential dependence of the rate constant k ($= k^0\exp(n\alpha\eta F/RT)$, where k^0, n, α, and η are the standard rate constant, the number of electrons involved, transfer coefficient, and overpotential, respectively).

The direct pathway model [Eq. (2)] has not been supported by experimental evidence to date, and is not convincing. For example, the different oxidation rates of HCOOH and DCOOH led Chen et al.[12] to conclude that the C–H bond cleavage of $\text{HCOOH}_{\text{ads}}$ is the rate-determining step in the direct pathway. However, the kinetic isotope effect can also be explained by the formate pathway mechanism (i.e., the C–H bond breaking of adsorbed formate), as will be discussed later. In addition, $\text{HCOOH}_{\text{ads}}$ has not been detected by IR spectroscopy. Chen et al. argued that $\text{HCOOH}_{\text{ads}}$ decomposes very quickly and hence cannot be detected, but another interpretation of this result is that $\text{HCOOH}_{\text{ads}}$ is quickly converted to adsorbed formate. One more serious problem of the direct pathway model is that the coadsorption of (bi)sulfate was not taken into account. As shown in Figure 1, the electrode surface is densely covered not only by formate but also by (bi)sulfate, that is, the amount of free sites for the direct pathway is very limited. Therefore, the contribution of the direct pathway must be negligible at best in H_2SO_4. Even if adsorbed (bi)sulfate would not inhibit the adsorption of $\text{HCOOH}_{\text{ads}}$, the contribution of the direct pathway to the total oxidation current is estimated to be 25 % at most (see the Supporting Information).

We now quantitatively discuss the kinetics of HCOOH oxidation in terms of the formate pathway model. In the steady state, the θ_{formate} value is determined by the rates of adsorption, desorption, and decomposition of formate as [Eq. (4)].

$$\begin{aligned} \mathrm{d}\theta_{\text{formate}}/\mathrm{d}t = {} & k_1(1-2\,\theta_{\text{formate}})^2\, c_{\text{HCOOH}} - k_{-1}\,\theta_{\text{formate}} \\ & - k_2\,\theta_{\text{formate}}(1-2\,\theta_{\text{formate}} - q\,\theta_{\text{(bi)sulfate}} - \theta_{\text{OH}}) \end{aligned} \tag{4}$$

Adsorbed (bi)sulfate and OH do not inhibit the adsorption of formate[8] but can suppress formate decomposition by blocking neighboring free sites. The factor q for $\theta_{\text{(bi)sulfate}}$ is the number of sites occupied by an adsorbed (bi)sulfate (most likely three, that is, coordination with three oxygen atoms). If the desorption of formate is assumed to be much faster than its decomposition,[27] the Langmuir-type isotherm [Eq. (4)] is approximated by Equation (5).

$$k_1(1-2\,\theta_{\text{formate}})^2\, c_{\text{HCOOH}} = k_{-1}\,\theta_{\text{formate}} \tag{5}$$

In fact, the plot of A_{formate} against c_{HCOOH} shown in Figure 2 reasonably fits the isotherm (solid trace). For $c_{\text{HCOOH}} \geq 0.1$ M (i.e., $\theta_{\text{(bi)sulfate}} \approx 0$) and at 0.6 V ($\theta_{\text{OH}} \approx 0$),[28] the oxidation current in the formate pathway i_{formate} is given by Equation 6.

$$i_{\text{formate}} \propto k_2\theta_{\text{formate}}(1-2\theta_{\text{formate}}) = \frac{k_3}{\sqrt{(k_1/k_{-1})c_{\text{HCOOH}}}}\theta_{\text{formate}}^{3/2} \tag{6}$$

The analysis of the data presented in Figure 2 (that is, the plot of j vs. $A_{\text{formate}}{}^{3/2}/(c_{\text{HCOOH}})^{1/2}$ in Figure 3) shows that Equation (6) is valid for c_{HCOOH} values between 0.1 and 1 M, thus strongly supporting the formate pathway mechanism and the second-order rate equation. The deviation from the linearity for $c_{\text{HCOOH}} < 0.1$ M can be ascribed to the negative shift of the current–potential curve as c_{HCOOH} decreases (Figures S2 and S3 in the Supporting Information).

Any proposed mechanism must explain the observed bell-shaped current–potential curves with peaks at 0.4–0.6 V (Figures S2 and S3 in the Supporting Information). The second-order rate equation [Eq. (3)] was originally introduced to explain such a voltammetric feature observed under potential sweep conditions (i.e., on CO-covered Pt surfaces) in terms of the formate pathway model.[7–9] This model predicts that the oxidation current increases as the value of

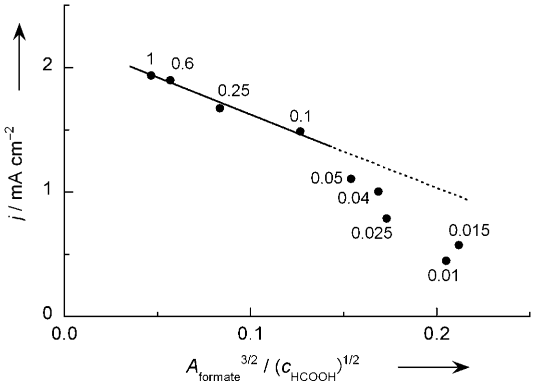

Figure 3. Analysis of the data given in Figure 2 by applying Equation (6). Values on the plot are in M.

$\theta_{\mathrm{formate}}$ increases, and starts to decrease when the value of $\theta_{\mathrm{formate}}$ exceeds 0.25 (at $\theta_{\mathrm{formate}} < 0.25$ in the presence of coadsorbed species). The systematic negative shift of the peak potential with decreasing c_{HCOOH} (Figure S3 in the Supporting Information) is reasonably explained by the coadsorption of (bi)sulfate. In this context, when $c_{\mathrm{HCOOH}} = 0.1\,\mathrm{M}$, the value of $\theta_{\mathrm{formate}}$ is believed to be close to 0.25 at 0.6 V, at which point the oxidation current reaches the maximum. Additionally, the almost symmetric voltammetric feature suggests that the potential dependence of the rate constant k_2 is weak (i.e., the transfer coefficient α is much smaller than the typical value of 0.5). Otherwise, the curve would be superposed on an exponentially increasing baseline. In fact, Mukouyama et al.[10] estimated $\theta_{\mathrm{formate}} \approx 0.3$ at 0.6 V and $\alpha = 0.16$ for $c_{\mathrm{HCOOH}} = 1\,\mathrm{M}$ from mathematical simulations of potential oscillations in galvanostatic HCOOH oxidation and showed that these parameters simulate well with the observed current–potential curves. The estimated value of α is in good agreement with the experimental values on single-crystal Pt surfaces (0.1–0.25).[29]

The formate pathway model can also be used to reasonably explain the previously reported experimental results and our data (Figure S4 in the Supporting Information):

1) The oxidation current for measurements in $HClO_4$ solution is larger than those in H_2SO_4 solution.[23b] Since perchlorate is only weakly adsorbed on Pt (or not at all) and does not suppress the decomposition of adsorbed formate, a larger current flows when $HClO_4$ is the electrolyte.
2) Impedance analysis for $c_{\mathrm{HCOOH}} = 0.25\,\mathrm{M}$ showed that HCOOH oxidation is controlled by kinetics and not by mass transport.[30] The result is consistent with the formate pathway model, in which the decomposition of adsorbed formate is rate-determining. Nevertheless, the formate pathway can also be limited by mass transport for low c_{HCOOH} values, for which the supply of HCOOH from the bulk solution is slower. In fact, for $c_{\mathrm{HCOOH}} < 0.1\,\mathrm{M}$, the oxidation current and the formate band intensity were found to increase when the solutions were agitated by Ar bubbling (Figure S4 in the Supporting Information). The impact of Ar bubbling was more significant in $HClO_4$ than in H_2SO_4 because of the faster oxidation in $HClO_4$. In marked contrast, Ar bubbling did not affect the current at all for $c_{\mathrm{HCOOH}} \geq 0.1\,\mathrm{M}$ in both $HClO_4$ and H_2SO_4, in accordance with the impedance analysis. Although the mass transport effect makes quantitative kinetic analysis over a wide concentration rage difficult, it is noted that the quickly sampled oxidation current at 0.5 s in H_2SO_4 (Figure 1 a) was not affected by mass transport even for $c_{\mathrm{HCOOH}} < 0.1\,\mathrm{M}$ (Figure S4 a in the Supporting Information).
3) Chen et al.[12] observed that HCOOH was oxidized twice as fast as DCOOH, while the coverages of $HCOO_{\mathrm{ads}}$ and $DCOO_{\mathrm{ads}}$ were identical (in H_2SO_4). A similar result was also obtained in $HClO_4$ (Figure S4 d in the Supporting Information). The interpretation of this kinetic isotope effect was that the C–H bond activation of $HCOOH_{\mathrm{ads}}$ is rate-determining and it was argued that the result conflicts with the formate pathway mechanism because i_{formate} was assumed to be proportional to the value of $\theta_{\mathrm{formate}}$. This argument is apparently questionable because the kinetic isotope effect is expected also for the C–H bond activation of adsorbed formate and the direct pathway is negligible at best, as discussed above. Since an isotope effect is not expected for formate adsorption, the equal coverages of $HCOO_{\mathrm{ads}}$ and $DCOO_{\mathrm{ads}}$ are a reasonable consequence, and hence the kinetic isotope effect is ascribed to the faster decomposition of $HCOO_{\mathrm{ads}}$ than $DCOO_{\mathrm{ads}}$. In fact, the faster decomposition of $HCOO_{\mathrm{ads}}$ was confirmed by the experiments for low HCOOH (DCOOH) concentrations in $HClO_4$ (Figure S4 in the Supporting Information).
4) The IR absorption band of adsorbed formate was observed very weakly on Pd[31] and Sb-modified Pt[32] electrodes that are more active than Pt toward HCOOH oxidation. Such a result has often been interpreted as oxidation of HCOOH through a pathway that is different from the formate pathway,[32] but it should be noted that the $\theta_{\mathrm{formate}}$ value becomes smaller as formate decomposition becomes faster, as is found from Equation (4). For HCOOH oxidation on Pd, the oxidation current was observed to decrease and the formate band intensity to increase at potentials at which (bi)sulfate is adsorbed.[31] This result also can reasonably be explained by the formate pathway model. Furthermore, adsorbed formate has been proposed to be the intermediate in the HCOOH oxidation reaction on Au electrodes.[33]

The decay of the oxidation current (deactivation) after the potential step to 0.6 V (Figure 1 a) is an important issue for fuel cell applications. In the present experiments, the decay is not due to CO accumulation, as shown in Figure 1 b. Chen et al.[12] ascribed this decay to the suppression of the direct pathway by coadsorption of formate, (bi)sulfate, and OH. However, this explanation is not convincing because the adsorption–desorption of formate and (bi)sulfate quickly reach the steady state (Figure 1 c) and OH adsorption is negligible at 0.6 V.[28] The decay can partially be ascribed to mass transport limitation for $c_{\mathrm{HCOOH}} < 0.1\,\mathrm{M}$, but was observed even under flow conditions.[11,12] Since the decomposition of adsorbed formate is slower in tightly packed domains, we speculate that such domains grow with time.

Recently, Neurock et al.[34] carried out first-principles calculations to investigate the two possible routes of HCOOH oxidation on Pt via either adsorbed formate or $COOH_{ads}$ (which correspond to the formate and direct pathways, respectively) and reported that $HCOOH_{ads}$ is spontaneously converted with a negligible activation energy to bridge-bonded formate ($E_{HCOOH}-E_{formate} = -1.0$ eV at 0.5 V vs. SHE), but its decomposition requires a rather high activation energy of 1.1 eV. On the other hand, although 0.47 eV is required for the C–H activation of $HCOOH_{ads}$ to form $COOH_{ads}$, which is unstable and easily decomposes with a small activation energy to form CO_2. From these results, it was concluded that $COOH_{ads}$ is the intermediate in the main reaction pathway and adsorbed formate is a site-blocking spectator. However, this interpretation is flawed because $HCOOH_{ads}$ is almost fully converted to formate, as can be found from a simple calculation: $\theta_{HCOOH}/\theta_{formate} = \exp[(E_{HCOOH}-E_{formate})/RT] = 1.2\times10^{-17}$. The negligible coverage of $HCOOH_{ads}$ cannot provide the observed large oxidation current via $COOH_{ads}$. Although the calculations suggest that formate decomposition is kinetically difficult, it should be noted that the apparent activation energy of the formate pathway with respect to $HCOOH_{ads}$ is only 0.1 eV ($=9.6\ \mathrm{kJ\,mol^{-1}}$) at low $\theta_{formate}$ limits (Figure S5 in the Supporting Information). More recent DFT calculations by Wang and Liu[35] suggested that the direct pathway is facilitated at the free sites that neighbor the adsorbed formate. This mechanism would not work in H_2SO_4 because such sites are blocked by coadsorbed (bi)sulfate.

In conclusion, the kinetics of HCOOH oxidation on Pt is reasonably explained by the formate pathway model proposed by Samjeské et al.,[6–9] in which the adsorption–desorption equilibrium of adsorbed formate is quickly established and a part of the adsorbed formate is decomposed to CO_2 and H^+ ions. On the other hand, the contribution of the direct oxidation of HCOOH to CO_2 proposed by Chen et al.[11,12] is negligible at best. Similarly, it is also very likely that adsorbed formate is an important intermediate in the electrooxidation of methanol, although we still do not know the steps involved in the formation of the intermediate.

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