

# The reaction of formic acid with clean and water-covered Pt(111)

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We have studied the interaction of formic acid with clean and water-covered Pt(111) in vacuum, using the technique of thermal desorption. We find that formic acid dissociates on clean Pt(111), forming gaseous CO<sub>2</sub> and H<sub>2</sub> exclusively at low exposure. At higher exposure, molecular formic acid begins to desorb at 200 K; simultaneously, the yields of CO<sub>2</sub> and H<sub>2</sub> saturate. At twice this exposure, the 200 K state saturates and multilayer desorption begins in a state centered at 165 K. Coadsorbed water does not measurably influence formic acid adsorption and dissociation. Finally, water is displaced from its own normal, high-temperature state by formic acid. This displacement is never complete, suggesting that formic acid or its dissociation products may not completely exclude water from metal sites.

## 1. Introduction

Within the field of surface science, there have been many studies of formic acid and its reactions at metal surfaces (e.g. refs. [1–22]). These studies have been designed to clarify heterogeneous catalytic reactions which involve oxygenated hydrocarbons. However, the electrochemical community is also very active in this area. It is driven by the desire to develop fuel cells which utilize methanol and oxygen, and to identify the self-poisoning reaction which prevents such cells from attaining commercial viability (e.g. refs. [23–25]). Platinum is the best known electrocatalyst for this reaction, and oxidation of formic acid at platinum is believed to produce the same poison as oxidation of methanol [25,26]. This has motivated many electrochemical studies of formic acid oxidation at platinum, and platinum-group metals.

We hope to shed light on the fundamental processes which occur in this class of fuel cells, using the techniques of surface science. In this paper we report results on the reaction of formic acid at clean Pt(111), using thermal desorption

spectroscopy. We also describe the effect of coadsorbed water, as a first step toward understanding the role which solvent may play at a real electrode surface.

## 2. Experimental details

Details of the experimental apparatus and procedures have appeared, or will appear, elsewhere [27–30]. In brief, the experiments are conducted in a stainless steel ultrahigh vacuum chamber, base pressure typically  $(1-2) \times 10^{-10}$  Torr. The chamber is equipped with a cylindrical mirror analyzer and coaxial electron gun for Auger electron spectroscopy, an ion bombardment gun, and an electron energy loss spectrometer. During thermal desorption, the partial pressures of up to eight different ions are monitored (effectively simultaneously) using a computer-interfaced, apertured quadrupole mass spectrometer. The sample is exposed to formic acid through a gas doser consisting of a conductance-limiting aperture and a spatially-collimating aperture in series. This doser is designed to be used with gas pressures of 100 mTorr or below in the backing line, thus preventing dimerization of formic acid in the gas phase [18]. Water exposure is achieved with a different

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gas doser, used with pressures of about 18 Torr behind the conductance-limiting aperture. Exposures are reported in units of Torr · s, the product of the average pressure behind the conductance-limiting aperture during the dose and the length of the exposure. An exposure of 25 Torr · s of CO, obtained with the doser, is equivalent to 1 Langmuir obtained by backfilling the chamber, based upon desorption peak areas. In other words, the effective pressure at the sample is  $4 \times 10^{-8}$  Torr using the doser, while the pressure in the chamber never rises above  $7 \times 10^{-10}$  Torr. The sample is held at temperatures of 80–100 K during all exposures.

The Pt crystal is cut and polished using established metallurgical techniques and aligned to within  $0.5^\circ$  of the (111) face as verified by Laue diffraction. Initial cleaning in vacuum involves several cycles of heating to 1200 K and ion bombardment (400 eV in  $5 \times 10^{-5}$  Torr Ar). This procedure significantly reduces all contaminant levels except for carbon. Carbon is removed by prolonged heating; up to 1000 K, in  $1 \times 10^{-6}$  Torr O<sub>2</sub>, followed by flashes in vacuum to 1600 K. Auger electron spectroscopy and reproduction of published thermal desorption results for H<sub>2</sub>, CO, O<sub>2</sub> and H<sub>2</sub>O [31–34] serve to verify surface cleanliness. Carbon which accumulates overnight is removed by heating in  $1 \times 10^{-7}$  Torr O<sub>2</sub> at 1100 K followed by flashing to 1600 K to remove oxygen. Cleaning between thermal desorption experiments consists of exposing the crystal to 1 L O<sub>2</sub> at 1100 K followed by heating in vacuum to 1600 K.

### 3. Experimental results

Exposure of formic acid to clean Pt(111) at low temperature and heating leads to desorption of H<sub>2</sub> ( $m/e = 2$ ), CO<sub>2</sub> ( $m/e = 44$ ), and HCOOH ( $m/e = 29$  and 46). Fig. 1 illustrates thermal desorption traces for these three products, obtained after various exposures of formic acid. We do not observe generation of H<sub>2</sub>O ( $m/e = 18$ ) or CO ( $m/e = 28$ ), other than that which can be attributed to fragmentation of formic acid within the mass spectrometer ionizer.

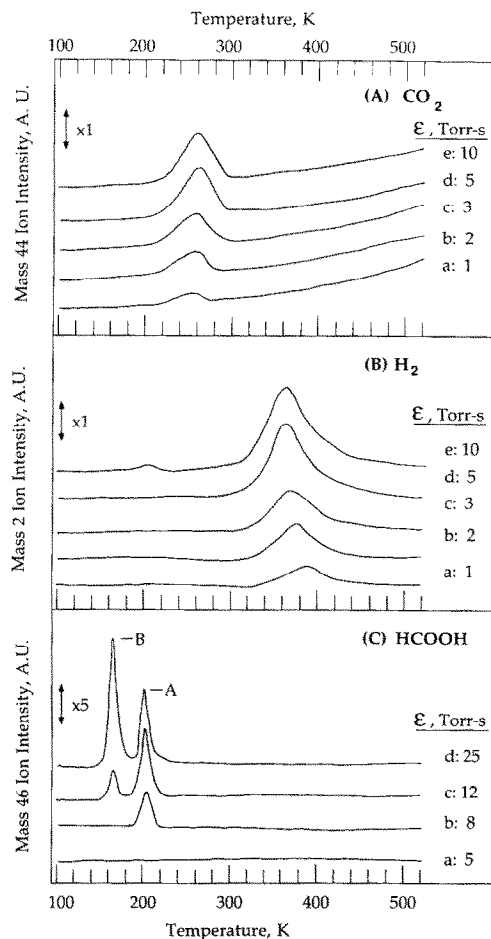


Fig. 1. Thermal desorption traces of various gases following adsorption of formic acid at 80–100 K. The heating rate is constant at 11 K/s between 100 and 200 K, then drops continuously to 5.5 K/s at 350 K. (A)  $m/e = 44$ , CO<sub>2</sub> desorption traces. (B)  $m/e = 2$ , H<sub>2</sub> desorption traces. (C)  $m/e = 46$ , HCOOH desorption traces.

Figs. 1A and 1B illustrate that CO<sub>2</sub> and H<sub>2</sub> evolve from the surface even after the very shortest exposures. (The small features in the range 170–200 K, visible after 10 Torr · s exposure in fig. 1B, are probably due to fragmentation of molecular formic acid within the mass spectrometer ionizer. Compare these small features with the data of fig. 1C.) The desorption peak temperature of CO<sub>2</sub> is invariant, within experimental error, at  $260 \pm 3$  K, and that of hydrogen decreases from 390 to  $365 (\pm 2)$  K. Based upon previous work by

Avery, gaseous  $\text{CO}_2$  is probably released immediately upon dissociation of adsorbed formate species, i.e. desorption of  $\text{CO}_2$  is reaction-rate limited [1,2]. By contrast, hydrogen evolution appears to be desorption-rate-limited, rather than reaction-rate-limited, based on the fact that the positions and shapes of the hydrogen desorption traces compare favorably with those obtained by other authors following hydrogen adsorption on clean Pt(111) [31,32]. We estimate that the saturation coverage of hydrogen produced by formic acid decomposition is 10 to 20% of the saturation hydrogen coverage on Pt(111). Assuming that the absolute coverage of hydrogen at saturation is unity [32,35], this corresponds to 0.1 to 0.2 monolayers of hydrogen and 0.05 to 0.1 monolayers of parent formic acid.

Inspection of fig. 1A and 1B reveals that, at exposures below 4 Torr·s, the yields of  $\text{H}_2$  and  $\text{CO}_2$  increase with increasing exposure. Fig. 1C shows that in this same exposure range, there is no desorption of molecular formic acid. Between about 4 and 6 Torr·s ( $\sim 0.2$  Langmuir equivalents), the yields of  $\text{H}_2$  and  $\text{CO}_2$  saturate. At exactly the same exposure, desorption of molecular formic acid begins, in a state centered at  $200 \pm 2$  K. The peak position is invariant with increasing exposure. This state (which we label A) continues to intensify until about 10 Torr·s (about 0.4 Langmuir equivalents), where a lower-temperature state appears. The latter state, which we label B, is centered at about 165 K, and we assign it to sublimation from a bulk-like multilayer (condensed phase). Note that the exposure at which the B-state appears, and the A-state saturates, is just *twice* the exposure at which the A-state appears, and the  $\text{CO}_2$  and  $\text{H}_2$  yields saturate. If we assume constant sticking coefficient, then these data indicate that the number of formic acid molecules which dissociate to  $\text{CO}_2$  and  $\text{H}_2$  is the same as that required to saturate the molecular A-state.

The exposure-dependence of the desorption yields is shown more clearly in fig. 2, where the integrated areas of various thermal desorption features are illustrated as a function of exposure for clean Pt(111).

We have also investigated the role which coadsorbed water plays in adsorption and decomposi-

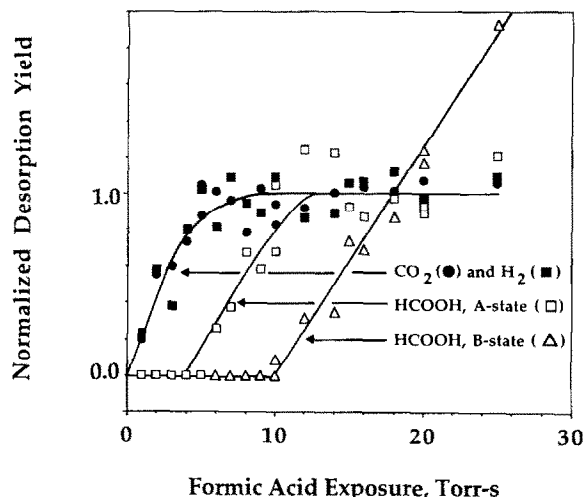


Fig. 2. Desorption yields (integrated desorption peak areas) of  $\text{CO}_2$ ,  $\text{H}_2$ , and the A- and B-states of formic acid as a function of formic acid exposure on clean Pt(111). The yields are obtained by integrating desorption peak areas, such as those shown in fig. 1, which result from adsorption of  $\text{HCOOH}$  on clean Pt(111). The integrated desorption peak areas of  $\text{CO}_2$ ,  $\text{H}_2$ , and A-state  $\text{HCOOH}$  are independently normalized to unity at saturation. The yield of the B-state of  $\text{HCOOH}$  is multiplied by the same factor as the A-state of  $\text{HCOOH}$ , even though the B-state does not saturate.

tion of formic acid on Pt(111). Fisher and Gland (FG) have previously reported that thermal desorption of water from Pt(111) occurs in two main states, centered at 170–180 K and at 160 K [33]. We have reproduced their work, and agree with the major aspects of their results. For the clean Pt surface, we observe two main states, one centered at 175 K (this shifts upward as exposure increases, by about 5 K) and the other at 150 K (again, this shifts upward with increasing exposure). The state at  $\sim 180$  K has also been described by Wagner and Moylan [34]. FG's interpretation, and ours, is that the 175–180 K state represents a water layer (or layers) stabilized by interaction with the metal surface, whereas the 150 K state is due to multilayer sublimation [33,36].

We have repeated the experiments illustrated in figs. 1 and 2, substituting a water-covered surface for the clean metal. The coverage of water which we use is sufficient to populate the 175–180 K state of  $\text{H}_2\text{O}$ , and just below that necessary for the  $\text{H}_2\text{O}$  multilayer state to emerge. We find that

adsorption and desorption of formic acid are not affected in any major way by the presence of coadsorbed water. Specifically, both  $\text{H}_2$  and  $\text{CO}_2$  are again observed as decomposition products, and are the only gas-phase products (except for  $\text{H}_2\text{O}$ ) below about 4 Torr · s exposure. The temperatures of the desorption peak maxima at saturation are within  $\pm 2$  K of their corresponding values on clean Pt(111). The saturation yields of  $\text{H}_2$  and  $\text{CO}_2$  are independent of water, within experimental error. This is shown by fig. 3, where the  $\text{CO}_2$  yield as a function of exposure is compared for the clean surface and the water-covered surface. No CO is released, indicating that water does not change the decomposition pathway. At exposures past saturation of the  $\text{H}_2$  and  $\text{CO}_2$  desorption yields, both the A- and B-states are observed, at the same temperatures (to within  $\pm 2$  K) as on the clean surface. Their relative intensity is changed by the presence of the water, indicating that water may interfere with these more weakly-bound states of formic acid. The main point, however, is that pre-adsorbed water does not hinder adsorption and decomposition of formic acid in any measurable way.

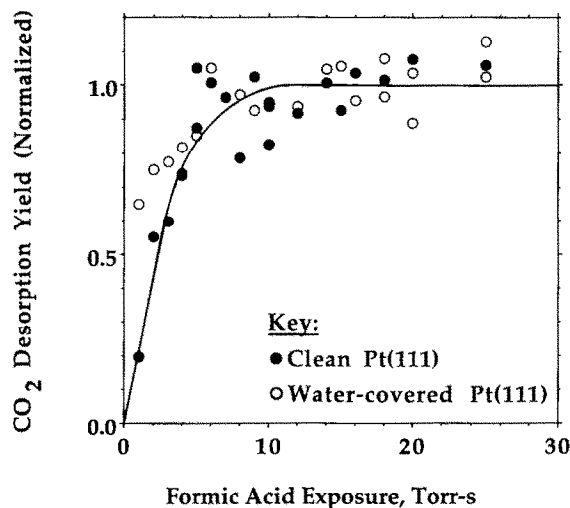


Fig. 3. Desorption yields (integrated desorption peak areas) of  $\text{CO}_2$  as a function of exposure, following adsorption of formic acid on clean and water-covered Pt(111). The yields are normalized to unity at saturation. The same normalization factor is used for both sets of data, i.e. the saturation yield of  $\text{CO}_2$  is virtually independent of water.

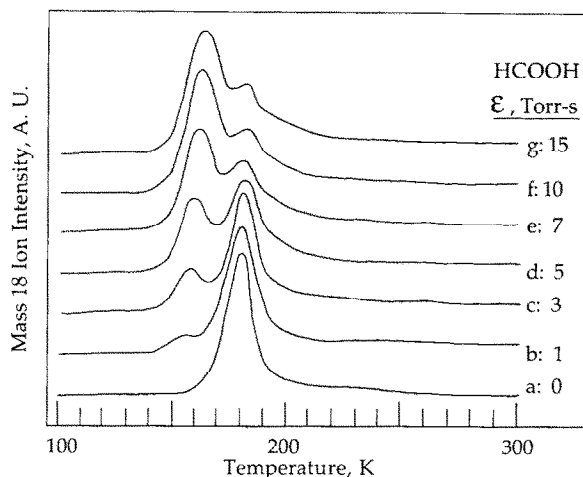


Fig. 4. Desorption traces of  $\text{H}_2\text{O}$  ( $m/e = 18$ ) following adsorption of formic acid on water-covered Pt(111). The exposure of water is constant, while the exposure of formic acid varies as indicated by the labels.

Water itself is affected by formic acid quite markedly. As formic acid exposure increases, water is progressively displaced from its high-temperature desorption state to its low-temperature, multi-layer state. (The latter is not populated at all in the absence of formic acid, at this selected coverage.) This displacement is illustrated in fig. 4. The peak temperatures of both water states may be shifted upward by as much as 5 K in the presence of formic acid, but this effect is in any case very small. In other experiments, we have confirmed that the displacement occurs also when water is isotopically labelled, i.e. the data of fig. 4 are reproduced very closely when  $\text{D}_2\text{O}$  is substituted for  $\text{H}_2\text{O}$ . Displacement proceeds until the ratio of peak heights (multilayer: first layer) reaches a constant value, in these experiments, of 2; in other experiments, the value falls between 2 and 3.

## 4. Discussion

### 4.1. Formic acid adsorption on clean Pt(111)

There have been three other studies of formic acid adsorption on Pt(111) surfaces [1–3]. In two,

Avery used electron energy loss spectroscopy to identify adsorbed formate at temperatures of 130–260 K, both on clean and oxygen-dosed Pt(111) [1,2]. Formate has also been observed spectroscopically on Pt(110) at 155 K [4], and on surfaces of other metals, including Ag, Cu, Ni, Rh, and Ru (e.g. refs. [5–15,19,20]). Several reaction schemes have been proposed for the formation, and/or decomposition, of this formate intermediate. These mechanisms can be broadly divided into dehydrogenation to gaseous  $\text{H}_2$  and  $\text{CO}_2$ , and dehydration to gaseous  $\text{H}_2\text{O}$  and CO [13,16,17]. Thus, the identification of the gaseous dissociation products is important to determine which of these broad classes of mechanisms is operative.

The identity of the gas-phase products of formic acid adsorption on clean Pt(111) is controversial. On clean Pt(111), Avery has described  $\text{CO}_2$  (with  $T_p$ , desorption peak temperature, = 260 K) and  $\text{H}_2$  ( $T_p$  = 370 K) as desorption products, following adsorption at 130 K. (Although Avery also observes gaseous CO, he attributes this to desorption from the edges and back of the crystal, since electron energy loss spectroscopy fails to detect chemisorbed CO on the front face.) This result would indicate that formic acid only dehydrogenates on Pt(111). Abbas and Madix (AM), however, report CO and  $\text{H}_2\text{O}$  as additional desorption products from clean Pt(111), following exposure at 200 K [3]. They propose that one out of every four formic acid molecules dissociates via dehydration at saturation coverage.

Our work is a more complete description of the desorption products of formic acid on clean Pt(111), and the conditions of exposure necessary to produce them, than has been previously published [1–3]. Using an apertured mass spectrometer to reduce or eliminate spurious desorption features, we observe no evolution of CO on clean Pt(111) at any exposure. On this point we are in agreement with Avery [1,2]. This suggests that formic acid dehydrogenates, but does not dehydrate, on Pt(111).

Furthermore, our peak temperatures for  $\text{CO}_2$  and  $\text{H}_2$  agree well with those of Avery, while the hydrogen peak temperatures reported by AM at saturation are 44–56 K lower than ours [3]. The lower peak temperatures reported by AM are con-

sistent with the fact that AM report excess hydrogen adsorption from background, which would lead to a higher hydrogen coverage than in our work. This could also be related to the observation of CO and  $\text{H}_2\text{O}$  as dissociation products in AM's experiments, since excess adsorbed hydrogen (a dehydrogenation product) might shift the reaction equilibrium significantly in favor of dehydration.

Our work, showing no CO as a vacuum decomposition product of formic acid, contrasts with electrochemical research, where CO has been identified in-situ as an adsorbed by-product of formic acid oxidation on polycrystalline Pt surfaces (e.g. refs. [37,38]). Our work also contrasts with recent results by Kizhakevariam and Stuve [39], who find *no* decomposition of formic acid on Pt(100). These comparisons suggest that the decomposition pathway of formic acid may be quite structure-sensitive on Pt surfaces, and/or dependent upon differences in the chemical environment such as those provided in the electrochemical cell.

Another discrepancy in the published literature regards the molecular desorption states of formic acid. Avery observes molecular desorption of  $\text{HCOOH}$  only at  $T_p$  = 170 K, following exposure at 130 K [1,2]. Abbas and Madix report desorption of molecular formic acid,  $T_p$  = 235 K, following exposure at 200 K. We do not observe the 235 K state reported by AM at any exposure, although in our experiments adsorption takes place at considerably lower temperature, 80–100 K. We do observe the 170 (165) K state of Avery, and an additional state at 200 K. There have been similar reports of two desorption states, at ~170 and 190–210 K, on other surfaces. These include Ag(110) [5], Au(110) [22], and Rh(111) [19]. The low-temperature state is unanimously attributed to multilayer sublimation, while the high-temperature state (which always saturates with increasing exposure) is usually attributed to a first (non-dissociative) layer.

We propose two possible explanations for our molecular state at 200 K. One is that formic acid layers grow sequentially on the surface. The first layer, in direct contact with the metal, dissociates to formate and hydrogen, perhaps upon adsorption at 80 K, but at least by 130 K [1,2]. The formate decomposes further at about 260 K, yield-

ing  $\text{CO}_2$  as a direct gas-phase product at this temperature. The acyl hydrogen must be released simultaneously to form additional adsorbed hydrogen but the atomic hydrogen does not combine and desorb until higher temperature (365–390 K) because the adsorption bond strength of hydrogen is much higher than that of  $\text{CO}_2$ . When the first dissociative layer is saturated, at exposures between 4 and 6 Torr·s, a second layer begins to fill. Upon heating, this layer desorbs, without dissociation, in the A-state. After the second layer is filled, at about 10 Torr·s, the multilayer appears and grows. This hypothesis of sequential layer filling is supported by the data of fig. 2, if one assumes that the sticking coefficient is constant, and that the space occupied by a second-layer formic acid molecule is about the same as that occupied by an adsorbed formate particle or formate-precursor. Under these assumptions, it is reasonable that the formic acid exposure necessary to saturate the first layer (as measured by the yields of  $\text{CO}_2$  and  $\text{H}_2$ ) should be just half that necessary to saturate the second layer (as measured by the yield of the molecular A-state). The coverage within each layer then equals 0.05 to 0.1 monolayers. Larson and Dickinson also proposed this hypothesis to explain similar behavior, which they observed on Ru(100) [21].

The second possibility is that the A-state represents formic acid molecules which are in direct contact with the metal, but which intermingle with adsorbed formate, or formate-precursor. This model resembles those which have been proposed for the other metallic surfaces with states analogous to the A-state (e.g. refs. [5,19,22]). Making the same assumptions as those described above, the data of fig. 2 then suggest that there is a 1:1 stoichiometry between the molecules which eventually dissociate, and those which do not, within the first layer.

#### *4.2. Adsorption on water-covered Pt(111)*

Ours is the first study of the interaction between formic acid and water on a metal surface. We find that water does not measurably hinder adsorption and dissociation of the acid. Further, the absence of CO evolution both with and without

water indicates that water does not change the dissociation pathway of the acid, i.e. dehydrogenation still occurs but not dehydration. These results suggest that water probably exerts little influence on formic acid chemistry at a Pt surface in aqueous solution.

We also find that water is displaced from its metal-stabilized, high-temperature state to its multilayer, low-temperature state by the acid. The water coverage used is sufficient to saturate the high-temperature state but not sufficient to initiate the low-temperature state in the absence of formic acid. Subsequent adsorption of formic acid displaces the water from the high-temperature state to the low-temperature state until the ratio of peak heights between these two states reaches a value of 2. This intriguing result suggests that there may be empty "pockets" in a well-ordered first layer formed by the adsorption products of formic acid, into which water molecules can fit without interference. Alternatively, there may be a specific, stoichiometric hydrogen-bonded complex which forms between the first-layer formic acid products and the water molecules. This will be the subject of continuing investigation in our laboratory.

#### **5. Summary**

We find that formic acid dissociates on clean Pt(111), forming gaseous  $\text{CO}_2$  and  $\text{H}_2$  exclusively at low exposure. At higher exposure, molecular formic acid begins to desorb at 200 K; simultaneously, the yields of  $\text{CO}_2$  and  $\text{H}_2$  saturate. At twice this exposure, the 200 K state (the A-state) saturates and multilayer desorption begins. Assuming constant sticking coefficient, this means that the number of molecules necessary to saturate the dissociative state equals that necessary to saturate the molecular, A-state. The A-state may represent a second layer, or formic acid molecules intermixed with dissociation products (formate plus hydrogen) or their precursors, in the first layer.

Coadsorbed water does not measurably inhibit formate adsorption and dissociation. It also does not change the decomposition pathway, judging by the constant distribution of decomposition

products. ( $\text{CO}_2$  and  $\text{H}_2$ , but not  $\text{CO}$ , are evolved.) Finally, water itself is displaced from its high-temperature state but this displacement is never complete, suggesting that formic acid or its dissociation products may not completely exclude water from metal sites.

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