Energetics of Methanol and Formic Acid Oxidation on Pt(111): Mechanistic Insights from Adsorption Calorimetry

Trent L. Silbaugh^a, Eric M. Karp^a, Charles T. Campbell^{a,b,*}

^aDepartment of Chemical Engineering, University of Washington, Seattle, WA 98195 USA

^bDepartment of Chemistry, University of Washington, Seattle, WA 98195-1700 USA

* Corresponding author email = charliec@uw.edu

Abstract

The catalytic and electrocatalytic oxidation and reforming of methanol and formic acid have received intense interest due to potential use in direct fuel cells and as prototype models for understanding electrocatalysis. Consequently, the reaction energy diagram (energies of all the adsorbed intermediates and activation energies of all the elementary steps) have been estimated for these reactions on Pt(111) by density functional theory (DFT) in several studies. However, no experimental measurement of these energy diagrams have been reported, nor is there a consensus on the mechanisms. Here, we use energies of key intermediates on Pt(111) from single crystal adsorption calorimetry (SCAC) and temperature programmed desorption (TPD) to build a combined energy diagram for these reactions. It suggests a new pathway involving monodentate formate as a key intermediate, with bidentate formate only being a spectator species that slows the rate. This helps reconcile conflicting proposed mechanisms.

Keywords: methanol fuel cell, formic acid fuel cell, formate, monodentate formate, adsorbed intermediates, energy diagram, adsorption calorimetry, platinum

Direct methanol fuel cells (DMFC's) offer the possibility for direct conversion of methanol to electricity without the Carnot efficiency limitation of conventional, combustion-based power generation. Platinum-based catalysts are amongst the best, and thus are the subject of intense research related to this reaction.[1-9]. Formic acid fuel cells using Pt-based catalysts also show great promise for similar applications, and thus have been widely studied as well [10-15]. The mechanisms for both reactions are closely related, but remain in debate. Evidence supports a two-path reaction scheme for the electrooxidation of methanol on Pt, whereby it first converts to CO, which can be further oxidized to CO₂, or directly oxidized to CO₂,[4, 5] with adsorbed bidentate formate observed during reaction and proposed as the active intermediate in this latter pathway to CO₂ [6, 16, 17]. Bidentate formate is also thought to be an intermediate in the oxidation and electrooxidation of formic acid on Pt [18-20]. The reforming of methanol and the electrocatalytic reduction of CO₂ to methanol or formic acid must involve a similar set of intermediates, so the mechanisms of these reactions are all intimately interrelated. Thus, there is great motivation to understand the energetics of the adsorbed intermediates and elementary-step transition states that might be involved. Consequently there have been many calculations, mainly by density functional theory (DFT), of various aspects of these energetics [21-28]. These have usually concluded that bidentate formate [19, 20, 23-25] or carboxyl (-COOH) [28, 29] is the key adsorbed intermediate in the pathway to CO₂ that does not involve CO.

We present here the most comprehensive analysis yet reported of *experimental* measurements of these energetics, many from our own lab, and compare these experimental results to DFT results. We find that, while most aspects are well reproduced by DFT calculations using GGA, DFT generally seems to underestimate the stability of monodentate formate, HCOO_{mono,ad}, relative to the other intermediates (including bidentate formate, HCOO_{bi,ad}), to the extent that it is often ignored completely or found not even to be a stable intermediate[28, 29]. In contrast, these experimental energetics suggest that monodentate formate is more stable and may be a key intermediate in these reactions on Pt-based catalysts and electrocatalysts. An important role of monodentate formate in methanol synthesis over Cu has also been suggested by recent studies of Cu surfaces indicating that monodentate formate is involved in the production of bidentate formate from CO₂ plus H₂ [30, 31], often proposed as a key step in methanol synthesis[30-32].

One set of DFT calculations on Pt(111) which modeled the effect of solvent by including a few coadsorbed water molecules found that the monodentate formate gains relative stability in the presence of coadsorbed water, and concluded that the oxidation of bidentate formate on Pt to CO₂ may occur through a monodentate formate intermediate but that the carboxyl intermediate is not a favorable path.[24]

Table 1 lists the experimental standard enthalpies of formation (ΔH_f^0) of the relevant adsorbed species along with the coverages and temperatures at which they were measured, and literature citations. Table 1 also lists the standard enthalpies of formation of the gas phase species at 150 K, and the literature citations. “Standard” here simply means at 1 bar pressure (using the ideal gas law to correct the PV term in enthalpies to 1 bar via $PV/n = RT$). For many adsorbates, these enthalpies of formation were determined from measurements of the heats of adsorption of gases on clean Pt(111) that produce this single adsorbate. For some adsorbates, however, the reactions whose experimental enthalpies were reported in those citations are not so simple, and so their enthalpies had to be combined with the standard heats of formation of both gas-phase species and other adsorbed species to get the heats of formation listed here. Table 2 lists the actual reactions whose enthalpies were measured in those cases, the measurement temperatures and coverages, the measurement method, and the reported standard reaction enthalpies.

Note that OH_{ad} is a common product listed here. It is likely that these OH_{ad} products disproportionate immediately upon production to make the (H₂O-OH)_{ad} complex via the reaction $3 \text{ OH}_{\text{ad}} \rightarrow (\text{H}_2\text{O-OH})_{\text{ad}} + \text{O}_{\text{ad}}$, but since this reaction is nearly thermoneutral, this would not affect this reaction’s enthalpy nor any of the corresponding enthalpies of formation by more than 7 kJ/mol (or less, depending upon the coverage of O_{ad} produced). We list the reaction enthalpy here for the simpler reactions with OH_{ad} as the product, to simplify the analysis of the overall reaction energy diagram. The enthalpies of formation of (H₂O-OH)_{ad} and O_{ad} are also listed in Table 1, in case the interested reader wishes to refer to those products instead. The values in Tables 1 and 2 are a self-consistent enthalpy set, assuming the heat capacity differences of adsorbates are negligible over the range of temperature differences here. Note that the errors on these energies are <7 kJ/mol.

The experimental activation energies (E_{act}) for the relevant elementary reaction steps are listed in Table 3, along with the measurement temperatures, methods and very approximate coverages.

Figure 1 shows the standard reaction enthalpy diagram for methanol and formic acid oxidation and decomposition based on experimental measurements of the standard enthalpies of formation of the adsorbates and their elementary-step activation energies on Pt(111) listed in Tables 1-3. Figure 1 strictly refers to enthalpies at 150 K but which is not expected to vary strongly with temperature. In making it, we assumed that the heat capacities of adsorbates and transition states (or at least their differences) are negligible between 150 K and their measurement temperatures listed in Tables 1-3. Note that these enthalpies and activation energies were all measured by SCAC and TPD in ultrahigh vacuum (UHV). In discussing these in the context of electrochemical reactions, we assume below that the enthalpies of these adsorbed species are not affected by the coadsorbed solvent present in the electrochemical environments, as has also been assumed for most DFT studies of the energetics of these reactions [22, 23].

It is known from UHV studies that upon heating an adlayer of HCOOH_{ad} coadsorbed with atomic oxygen, it first loses its acid hydrogen to form $\text{HCOO}_{\text{mono,ad}}$ plus OH_{ad} , and that $\text{HCOO}_{\text{mono,ad}}$ later converts to $\text{HCOO}_{\text{bi,ad}}$ [33]. TPD experiments show that formic acid decomposes to give CO_2 , H_2O and H_2 (depending on relative exposures of formic acid to O_{ad}) as the only gaseous products [33, 34]. The CO_2 peak temperature was 320 K at low coverage and 280 K at high coverage, with no CO_2 desorption at temperatures below the onset of this peak. The intermediate peak temperature of 300 K yields an activation energy (E_{act}) of 65 kJ/mol for the decomposition of bidentate formate on Pt(111), assuming the prefactor $A = (1.9 \text{ to } 4.0) \times 10^{11} \text{ s}^{-1}$, which was the A value measured on Cu(111) [35]. This prefactor for formate decomposition on Cu(111) is several orders of magnitude lower than the prefactor on Cu(110) [35, 36], in fitting with the structure sensitivity of formate decomposition on Cu(111) versus (110). The E_{act} thus determined for Pt(111) using the prefactor from Cu(111) is essentially identical to the barrier for the conversion of bidentate to monodentate formate of 64 kJ/mol determined from SCAC by summing the difference in stability monodentate versus bidentate formate (Table 2 and Figure 1) (35 kJ/mol) and the activation barrier for the conversion of monodentate to bidentate formate of 29 kJ/mol (Table 3).

The rate limiting step in $\text{HCOO}_{\text{bi,ad}}$ decomposition to CO_2 plus H_{ad} could therefore be the breaking of a surface bond to one of its oxygens to make $\text{HCOO}_{\text{mono,ad}}$, since the activation barrier for the overall decomposition of formate to CO_2 equals the barrier for the conversion of bidentate to monodentate formate, within error bars. This conclusion is consistent with the known oxidation behavior of formic acid during TPD, whereby formic acid is adsorbed on an O-Pt(111) surface at low temperature (100 K) where little to no reaction occurs, and then the temperature is ramped slowly (e.g. 10 K/s). The decomposition of formic acid in this model is then described by the sequence of reactions: (i) HCOOH_{ad} oxidizes to $\text{HCOO}_{\text{mono,ad}}$, (ii) $\text{HCOO}_{\text{mono,ad}}$ converts mostly to $\text{HCOO}_{\text{bi,ad}}$, with some low equilibrium concentration of $\text{HCOO}_{\text{mono,ad}}$, (iii) $\text{HCOO}_{\text{mono,ad}}$ decomposes to CO_2 , (iv) bidentate formate converts to monodentate formate to reestablish equilibrium, and steps (iii) and (iv) are continuously repeated until all formate is removed. Given the barriers in Fig. 1, this can only be true if the prefactor for the decomposition of $\text{HCOO}_{\text{mono,ad}}$ to CO_2 is lower than the prefactor for its conversion to $\text{HCOO}_{\text{bi,ad}}$, otherwise CO_2 would have been observed in TPD at the lower temperature where it converts to bidentate formate. From the values in Table 1, the enthalpy of the reaction $\text{HCOO}_{\text{mono,ad}} \rightarrow \text{CO}_{2,\text{gas}} + \text{H}_{\text{ad}}$ is -80 kJ/mol, and the enthalpy of $\text{HCOO}_{\text{mono,ad}} + \text{O}_{\text{ad}} \rightarrow \text{CO}_{2,\text{gas}} + \text{OH}_{\text{ad}}$ is -152 kJ/mol. These are quite exothermic, consistent with the small barrier of ~29 kJ/mol or less required in this model for the decomposition of monodentate formate by one of these reactions. This description also would mean that bidentate formate is not an active intermediate in the overall formic acid oxidation pathway, but rather acts as a spectator in the net reaction whose existence actually would slow down the net rate. This is consistent with a recent study [37] that proves bidentate formate acts only as a spectator in methanol synthesis from CO_2 and H_2 on Cu surfaces, which is closely related mechanistically to the reverse of methanol combustion.

This model is consistent with DFT studies on Pt(111) [23, 29] and Cu surfaces[31], indicating that the decomposition of $\text{HCOO}_{\text{bi,ad}}$ proceeds through a monodentate configuration.[29, 31] In the studies on Cu [30, 31], the reaction of $\text{CO}_{2,\text{g}}$ with H_{ad} was proven to lead first to the formation of $\text{HCOO}_{\text{mono,ad}}$, which then afterwards converts to $\text{HCOO}_{\text{bi,ad}}$. The insensitivity of this formate synthesis reaction rate upon changing the crystal face of Cu seen experimentally is due to similar transition states and $\text{HCOO}_{\text{mono,ad}}$ binding energies for all Cu surfaces.[31] However, the binding strength of $\text{HCOO}_{\text{bi,ad}}$, and consequently the conversion from

bidentate to monodentate formate, was found to vary markedly between different crystal faces of Cu. This explained the experimentally observed structure sensitivity of formate decomposition on different crystal faces of Cu, and showed that this step is rate determining in bidentate formate decomposition to CO₂ plus H₂. [30] It seems the role of monodentate formate may be similarly important in catalysis on Pt.

DFT calculations of the oxidation of formic acid on clean Pt(111) [23] and Pt(111) preadsorbed with water molecules [24] (i.e. 1, 2, or 4 H₂O_{ad} per unit cell), to simulate the presence of solvent, qualitatively match the experimental energetics in Figure 1. Referencing all energies to gas phase formic acid, we find that DFT on clean Pt(111) predicts both adsorbed formic acid and bidentate formate to be ~20 kJ/mol less stable than SCAC, while it predicts monodentate formate to be 66 kJ/mol less stable, with a large barrier of 123 kJ/mol for the conversion of HCOO_{bi,ad} to HCOO_{mono,ad}. However, in the presence of two adsorbed water molecules, these intermediates, including monodentate formate, are all found by DFT to be consistently only ~20 kJ/mol less stable than experiment, with the activation barrier for the conversion of HCOO_{bi,ad} to HCOO_{mono,ad} now falling to 63 kJ/mol, close to the experimental value of 64 kJ/mol. Since our SCAC experiments produce monodentate formate plus OH_{ad}, and since some or all of this OH_{ad} disproportionates to make coadsorbed water (see above), these DFT calculations which include two water molecules per formate are possibly more similar to our SCAC experiments than are the DFT calculations with no water present. So the agreement of the calculation with water present to SCAC values (except for the 20 kJ/mol offset) is not surprising. This also suggests that the active intermediate is not simply monodentate formate, but rather monodentate formate coordinated through hydrogen bonding with coadsorbed water or OH in a more complex structure. Comparing energetics between experiment and theory should always be done with caution, considering that while water is found by DFT to be less stable compared to experiments by 21 kJ/mol, CO_{ad} is more stable by ~40 kJ/mol (i.e. adsorption enthalpy of 160 kJ/mol by DFT [23] versus 115 kJ/mol by SCAC [38]).

At elevated temperatures and pressures, or in an electrochemical environment where surface-bound formate is in equilibrium with formate in solution, a short-lived monodentate formate species, perhaps unable to convert to bidentate due to site availability or stabilized by surrounding water molecules, may serve as the active intermediate in the direct pathway, rather than the carboxyl species (-COOH) commonly cited [28, 29] (which has yet to be observed

experimentally). Monodentate formate has been discussed as a possible intermediate from DFT, but always in the context of a conversion from $\text{HCOO}_{\text{bi,ad}}$ [24]. It is often overlooked that formic acid has already been shown experimentally to react first to monodentate rather than bidentate formate.[33] The reaction scheme in Figure 2 modifies the triple pathway commonly presented in the literature to show that the “formate path” acts as a dead end for the active monodentate formate direct path. It is unknown whether the conversion of methoxy to formate in the non-CO pathway proceeds directly to bidentate formate, monodentate formate, or first to formic acid.

We suggest that bidentate formate is a spectator species. Since it is quite stable, it may serve mainly to poison surface sites. A route to minimizing the buildup of unwanted bidentate formate by decreasing the equilibrium ratio of bidentate to monodentate formate may be to utilize a bimetallic surface consisting of Pt and a metal that binds oxygen species more weakly, resulting in fewer adjacent Pt sites and therefore a larger equilibrium constant for the conversion of bidentate to monodentate formate.

The route to methanol oxidation that goes through CO probably proceeds by elementary steps that are well known from UHV studies [39, 40], and indicated in Fig. 1: First, adsorbed methanol cleaves its O-H bond to make methoxy and either OH_{ad} or H_{ad} , depending on the oxygen coverage. The methoxy then loses its hydrogens (stepwise) to make $\text{CO}_{\text{ad}} + 3 \text{H}_{\text{ad}}$ with a low activation barrier. The CO_{ad} and H_{ad} then combine with O_{ad} to make CO_2 and water, respectively. At low coverage of O_{ad} , they desorb as CO and H_2 , respectively.”

In conclusion, we have presented for the first time an experimentally determined energy landscape for the oxidation of methanol and formic acid on Pt(111). From the insights gained, we propose a new reaction scheme with monodentate formate as a key intermediate in the direct oxidation pathway.

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References

- [1] A.S. Arico, S. Srinivasan, V. Antonucci, DMFCs: From Fundamental Aspects to Technology Development, Fuel Cells, 1 (2001) 133-161.
- [2] Y.G. Guo, J.S. Hu, L.J. Wan, Nanostructured materials for electrochemical energy conversion and storage devices, Adv. Mater, 20 (2008) 2878-2887.

- [3] S. Wasmus, A. Kuver, Methanol oxidation and direct methanol fuel cells: a selective review, *J. Electroanal. Chem.*, 461 (1999) 14-31.
- [4] T.D. Jarvi, S. Sriramulu, E.M. Stuve, Potential dependence of the yield of carbon dioxide from electrocatalytic oxidation of methanol on platinum(100), *J. Phys. Chem. B*, 101 (1997) 3649-3652.
- [5] S. Sriramulu, T.D. Jarvi, E.M. Stuve, A kinetic analysis of distinct reaction pathways in methanol electrocatalysis on Pt(111), *Electrochimica Acta*, 44 (1998) 1127-1134.
- [6] Y.X. Chen, A. Miki, S. Ye, H. Sakai, M. Osawa, Formate, an active intermediate for direct oxidation of methanol on Pt electrode, *J. Amer. Chem. Soc.*, 125 (2003) 3680-3681.
- [7] S.H. Joo, S.J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, Ordered nanoporous arrays of carbon supporting high dispersions of platinum nanoparticles, *Nature*, 412 (2001) 169-172.
- [8] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E.S. Smotkin, T.E. Mallouk, Combinatorial electrochemistry: A highly parallel, optical screening method for discovery of better electrocatalysts, *Science*, 280 (1998) 1735-1737.
- [9] N. Kakati, J. Maiti, S.H. Lee, S.H. Jee, B. Viswanathan, Y.S. Yoon, Anode Catalysts for Direct Methanol Fuel Cells in Acidic Media: Do We Have Any Alternative for Pt or Pt-Ru?, *Chem. Rev.*, 114 (2014) 12397-12429.
- [10] C. Rice, S. Ha, R.I. Masel, A. Wieckowski, Catalysts for direct formic acid fuel cells, *J. Power Sources*, 115 (2003) 229-235.
- [11] Y.M. Zhu, Z. Khan, R.I. Masel, The behavior of palladium catalysts in direct formic acid fuel cells, *Journal of Power Sources*, 139 (2005) 15-20.
- [12] W. Chen, J.M. Kim, S.H. Sun, S.W. Chen, Composition effects of FePt alloy nanoparticles on the electro-oxidation of formic acid, *Langmuir*, 23 (2007) 11303-11310.
- [13] X.W. Yu, P.G. Pickup, Recent advances in direct formic acid fuel cells (DFAFC), *Journal of Power Sources*, 182 (2008) 124-132.
- [14] X.L. Ji, K.T. Lee, R. Holden, L. Zhang, J.J. Zhang, G.A. Botton, M. Couillard, L.F. Nazar, Nanocrystalline intermetallics on mesoporous carbon for direct formic acid fuel cell anodes, *Nature Chem.*, 2 (2010) 286-293.
- [15] N.M. Markovic, P.N. Ross, Surface science studies of model fuel cell electrocatalysts, *Surf. Sci. Rep.*, 45 (2002) 121-229.
- [16] Z.Y. Zhou, N. Tian, Y.J. Chen, S.P. Chen, S.G. Sun, In situ rapid-scan time-resolved microscope FTIR spectroelectrochemistry: study of the dynamic processes of methanol oxidation on a nanostructured Pt electrode, *J. Electroanal. Chem.*, 573 (2004) 111-119.
- [17] H. Shiroishi, Y. Ayato, K. Kunitatsu, T. Okada, Study of adsorbed water on Pt during methanol oxidation by ATR-SEIRAS (surface-enhanced infrared absorption spectroscopy), *J. Electroanal. Chem.*, 581 (2005) 132-138.
- [18] G. Samjeske, M. Osawa, Current oscillations during formic acid oxidation on a Pt electrode: Insight into the mechanism by time-resolved IR spectroscopy, *Angew. Chem.-Int. Ed.*, 44 (2005) 5694-5698.
- [19] A. Cuesta, G. Cabello, C. Gutierrez, M. Osawa, Adsorbed formate: the key intermediate in the oxidation of formic acid on platinum electrodes, *Phys. Chem. Chem. Phys.*, 13 (2011) 20091-20095.
- [20] M. Osawa, K.-i. Komatsu, G. Samjeske, T. Uchida, T. Ikeshoji, A. Cuesta, C. Gutierrez, The Role of Bridge-Bonded Adsorbed Formate in the Electrocatalytic Oxidation of Formic Acid on Platinum, *Angew. Chem.-Int. Ed.*, 50 (2011) 1159-1163.

- [21] J. Greeley, M. Mavrikakis, A first-principles study of methanol decomposition on Pt(111), *J. Amer. Chem. Soc.*, 124 (2002) 7193-7201.
- [22] J. Greeley, M. Mavrikakis, Competitive paths for methanol decomposition on Pt(111), *J. Amer. Chem. Soc.*, 126 (2004) 3910-3919.
- [23] W. Gao, J.A. Keith, J. Anton, T. Jacob, Oxidation of formic acid on the Pt(111) surface in the gas phase, *Dalton Trans.*, 39 (2010) 8450-8456.
- [24] W. Gao, J.A. Keith, J. Anton, T. Jacob, Theoretical Elucidation of the Competitive Electro-oxidation Mechanisms of Formic Acid on Pt(111), *J. Amer. Chem. Soc.*, 132 (2010) 18377-18385.
- [25] W. Gao, E.H. Song, Q. Jiang, T. Jacob, Revealing the Active Intermediates in the Oxidation of Formic Acid on Au and Pt(111), *Chem.-Eur. J.*, 20 (2014) 11005-11012.
- [26] S.K. Desai, M. Neurock, K. Kourtakis, A periodic density functional theory study of the dehydrogenation of methanol over Pt(111), *J. Phys. Chem. B*, 106 (2002) 2559-2568.
- [27] D. Cao, G.Q. Lu, A. Wieckowski, S.A. Wasileski, M. Neurock, Mechanisms of methanol decomposition on platinum: A combined experimental and ab initio approach, *J. Phys. Chem. B*, 109 (2005) 11622-11633.
- [28] M. Neurock, M. Janik, A. Wieckowski, A first principles comparison of the mechanism and site requirements for the electrocatalytic oxidation of methanol and formic acid over Pt, *Faraday Discuss.*, 140 (2008) 363-378.
- [29] L.C. Grabow, A.A. Gokhale, S.T. Evans, J.A. Dumesic, M. Mavrikakis, Mechanism of the water gas shift reaction on Pt: First principles, experiments, and microkinetic modeling, *J. Phys. Chem. C*, 112 (2008) 4608-4617.
- [30] I. Nakamura, H. Nakano, T. Fujitani, T. Uchijima, J. Nakamura, Synthesis and decomposition of formate on Cu(111) and Cu(110) surfaces: Structure sensitivity, *J. Vac. Science Technol. a-Vac. Surf. Films*, 17 (1999) 1592-1595.
- [31] G.C. Wang, Y. Morikawa, T. Matsumoto, J. Nakamura, Why is formate synthesis insensitive to copper surface structures?, *J. Phys. Chem. B*, 110 (2006) 9-11.
- [32] T. Fujitani, Y. Choi, M. Sano, Y. Kushida, J. Nakamura, Scanning tunneling microscopy study of formate species synthesized from CO₂ hydrogenation and prepared by adsorption of formic acid over Cu(111), *J. Phys. Chem. B*, 104 (2000) 1235-1240.
- [33] N.R. Avery, Reactions of HCOOH with a Pt(111)-O surface – Identification of adsorbed monodentate formate, *Appl. Surf. Sci.*, 14 (1983) 149-156.
- [34] M.R. Columbia, A.M. Crabtree, P.A. Thiel, Chemical-Reactions between Atomic Oxygen and Formic-Acid on Pt(111), *J. Electroanal. Chem.*, 351 (1993) 207-226.
- [35] T. Yatsu, H. Nishimura, T. Fujitani, J. Nakamura, Synthesis and decomposition of formate on a Cu/SiO₂ catalyst: Comparison to Cu(111), *J. Catal.*, 191 (2000) 423-429.
- [36] D.H.S. Ying, R.J. Madix, Thermal desorption study of formic acid decomposition on a clean Cu(110) surface, *J. Catal.*, 61 (1980) 48-56.
- [37] Y. Yang, D. Mei, C.H.F. Peden, C.T. Campbell, C.A. Mims, Surface bound intermediates in low temperature methanol synthesis on copper - participants and spectators, *ACS Catalysis* 5 (2015) 7328–7337.
- [38] J.-H. Fischer-Wolfarth, J. Hartmann, J.A. Farmer, J.M. Flores-Camacho, C.T. Campbell, S. Schauermaier, H.-J. Freund, An improved single crystal adsorption calorimeter for determining gas adsorption and reaction energies on complex model catalysts, *Rev. Sci. Instrum.*, 82 (2011) 024102.

- [39] S. Akhter, J.M. White, A static-SIMS TPD study of the kinetics of methoxy formation and decomposition on O/Pt(111), *Surf. Sci.*, 167 (1986) 101-126.
- [40] B.A. Sexton, Methanol Decomposition on Platinum (111), *Surf. Sci.*, 102 (1981) 271-281
- [41] T.R. Center, Selected Values of Properties of Chemical Compounds, Texas A&M University, College Station, Texas, 1997.
- [42] M.W.J. Chase, NIST-JANAF thermochemical tables, fourth edition, 1998.
- [43] J. Chao, K.R. Hall, K.N. Marsh, R.C. Wilhoit, Thermodynamic properties of key organic compounds in the carbon range C1 to C4 .2 ideal gas properties, *J. Phys. Chem. Ref. Data*, 15 (1986) 1369-1436.
- [44] J. Chao, F.D. Rossini, Heats of combustion, formation, and isomerization of 19 alkanols, *J. Chem. Eng. Data*, 10 (1965) 374-379.
- [45] E.M. Karp, T.L. Silbaugh, M.C. Crowe, C.T. Campbell, Energetics of Adsorbed Methanol and Methoxy on Pt(111) by Microcalorimetry, *J. Amer. Chem. Soc.*, 134 (2012) 20388-20395.
- [46] N.D. Lebedeva, 38 (1964) 1435-1437.
- [47] T.L. Silbaugh, E.M. Karp, C.T. Campbell, Energetics of Formic Acid Conversion to Adsorbed Formates on Pt(111) by Transient Calorimetry, *J. Amer. Chem. Soc.*, 136 (2014) 3964-3971.
- [48] E.M. Karp, C.T. Campbell, F. Studt, F. Abild-Pedersen, J.K. Nerskov, Energetics of Oxygen Adatoms, Hydroxyl Species and Water Dissociation on Pt(111), *J. Phys. Chem. C*, 116 (2012) 25772-25776.
- [49] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA key values for thermodynamics, Hemisphere Publishing Corp., New York, 1984.
- [50] W.D. Lew, M.C. Crowe, E. Karp, C.T. Campbell, Energy of Molecularly Adsorbed Water on Clean Pt(111) and Pt(111) with Coadsorbed Oxygen by Calorimetry, *J. Phys. Chem. C*, 115 (2011) 9164-9170.
- [51] A. Schiesser, P. Hertz, R. Schafer, Thermodynamics and kinetics of CO and benzene adsorption on Pt(111) studied with pulsed molecular beams and microcalorimetry, *Surf. Sci.*, 604 (2010) 2098-2105.
- [52] O. Lytken, W. Lew, J.J.W. Harris, E.K. Vestergaard, J.M. Gottfried, C.T. Campbell, Energetics of cyclohexene adsorption and reaction on Pt(111) by low-temperature microcalorimetry, *J. Amer. Chem. Soc.*, 130 (2008) 10247-10257.
- [53] C.T. Campbell, Y.K. Sun, W.H. Weinberg, Trends in preexponential factors and activation-energies in dehydrogenation and dissociation of adsorbed species, *Chem. Phys. Lett.*, 179 (1991) 53-57.

FIGURES

Figure 1: Energy landscape for methanol and formic acid oxidation to CO₂ and their decomposition to CO plus H₂. Energy levels and barriers were determined experimentally (Table S1) and represent key intermediates. Enthalpies are referenced to gas phase methanol and adsorbed oxygen atoms on a Pt(111) surface. The diagram shows bidentate formate decomposing to CO₂ + H_{ad}, but the text shows that this could occur via monodentate formate, such that bidentate formate is only a spectator species.

Figure 2: Reaction scheme for the oxidation of methanol and formic acid to carbon dioxide.

Table 1: Experimentally determined standard enthalpies of formation of gas phase and adsorbed molecules and molecular fragments on Pt(111) from the elements in their standard states. When possible, we have used integral enthalpies of formation, from integral heats of reaction determined at a consistent coverage of 1/4 ML of the adsorbate listed. The label “(and co-adsorbate present)” refers to the coverage of coadsorbates produced during the reaction. The total surface coverage is therefore changing as species are either produced on the surface or desorb. Gases are at 1 bar pressure. Gas phase enthalpies of formation have been adjusted to 150 K using heat capacities from [41-43].

Species	Enthalpy of Formation (kJ/mol)	Adsorbate Coverage (and co-adsorbate present)	Temperature
CH ₃ OH _g	-198[44]	-	150 K
CH ₃ OH _{ad}	-256 [45]	1/4 ML	100 K
CH ₃ O _{ad}	-161 [45]	1/4 ML (with 1/4 ML OH _{ad})	150 K
HCOOH _g	-373.4[46]	-	150 K
HCOOH _{ad}	-441[47]	1/4 ML	100 K
HCOO _{mon,ad}	-347[47]	1/4 ML (with 1/4 ML OH _{ad})	130 K
HCOO _{bi,ad}	-375[47]	1/4 ML (with 1/4 ML OH _{ad})	150 K
O _{ad}	-99[48]	1/4 ML	300 K
OH _{ad}	-213[48]	1/3 ML (within (H ₂ O-OH) _{ad} complex, so with 1/3 ML H ₂ O _{ad})	150 K
H ₂ O _g	-248[49]		150 K
H ₂ O _{ad}	-299[48, 50]	~2/3 ML	100 K
(H ₂ O-OH) _{ad}	-513[48]	1/3 ML	150 K
CO _g	-110[49]	-	150 K
CO _{ad}	-115[40, 51]	1/4 ML	130 K
H _{ad}	-36[52]	1/20 ML	300 K
CO _{2,g}	-391[49]	-	150 K

Table 2: Experimental standard enthalpies of reactions on Pt(111) used to get the values in Table 1, and the methods used to measure them.

Reactions Measured from Calorimetry	Enthalpy of Reaction (kJ/mol)	Primary reactant Coverage	Temperature	Exper. Technique
$\text{CH}_3\text{OH}_g \rightarrow \text{CH}_3\text{OH}_{ad}$	-58	$\frac{1}{4}$ ML	100 K	SCAC [45]
$\text{CH}_3\text{OH}_g + \text{O}_{ad} \rightarrow \text{CH}_3\text{O}_{ad} + \text{OH}_{ad}$	-76.4	$\frac{1}{4}$ ML	150 K	SCAC [45]
$\text{HCOOH}_g \rightarrow \text{HCOOH}_{ad}$	-61	$\frac{1}{4}$ ML	100 K	SCAC [47]
$\text{HCOOH}_g + \text{O}_{ad} \rightarrow \text{HCOO}_{mon,ad} + \text{OH}_{ad}$	-81	$\frac{1}{4}$ ML	130 K	SCAC [47]
$\text{HCOOH}_g + \text{O}_{ad} \rightarrow \text{HCOO}_{bi,ad} + \text{OH}_{ad}$	-116	$\frac{1}{4}$ ML	150 K	SCAC [47]
$\text{O}_2 \rightarrow \text{O}_{ad}$	-99	$\frac{1}{4}$ ML	300 K	TPD [48]
$\text{CO}_g \rightarrow \text{CO}_{ad}$	-115	$\frac{1}{4}$ ML	130 K	SCAC [38, 51]

Table 3: Activation barriers for reactions of interest on Pt(111), and the methods used to measure them (in footnotes).

Reaction	Activation Barrier [kJ/mol]	Pre-exponential factor [s^{-1}]	Approx. coverage	Approx. temperature
$CH_3OH_{ad} + O_{ad} \rightarrow CH_3O_{ad} + OH_{ad}$	23 ± 3^a	10^7^a	1/20 ML	125 K
$CH_3O_{ad} \rightarrow CO_{ad} + 3 H_{ad}$	47.7 ± 2.9^a	$5.3 \times 10^{13 \pm 1}^a$	1/20 ML	157 K
$HCOOH_{ad} + O_{ad} \rightarrow HCOO_{mon,ad} + OH_{ad}$	20^b	10^{11}^c	1/4 ML	130 K
$HCOO_{mon,ad} + O_{ad} \rightarrow HCOO_{bi,ad} + OH_{ad}$	29^b	10^{11}^c	1/4 ML	150 K
$HCOO_{bi,ad} \rightarrow CO_{2,g} + \frac{1}{2} H_{2,g}$	65^d	$2 \times 10^{11}^e$	1/8 ML	300 K

^a Determined from TP-SIMS data [39]

^b Determined from fitting of transient SCAC heat signal pulse shape [47].

^c Common pre-exponential factor for adsorbate dissociation assumed here [53].

^d Determined from CO_2 TPD peak temperature of 300 K for formic acid adsorbed on oxygen pre-covered Pt(111) [34].

^e Assumed to be the same pre-exponential factor as experimentally determined for this same bidentate formate decomposition reaction on Cu(111) [35].

Graphical abstract / Table of Contents Image: