Supporting Information for:

Identification of reaction intermediates in the decomposition of formic acid on Pd

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S1.Speed Distributions of CO₂



Figure S1: Typical experimental speed distributions of CO_2 (grey dots) from formic acid decomposition on Pd(111) (left column) and on Pd(332) (right column). The black solid line shows the 3D-Maxwell-Boltzmann-distribution at the corresponding surface temperature.

In Figure S1 we show speed distributions of CO_2 from formic acid decomposition on Pd(111) (left column) and on Pd(332) (right column) for two different surface temperatures as indicated. On Pd(111) we see a bimodal speed distribution, one sub- and one hyperthermal component. On Pd(332) we observe only a subthermal speed distribution at these surface temperatures. The hyperthermal speed distribution on Pd(111) indicates an activated adsorption process while the subthermal speed distributions indicate a non-activated adsorption where the initial sticking probability decreases as a function of translational energy.

S2. The Effect of Transient H* and CO* Build-up

Sequential scans of the CO₂ formation rate reveal a drop of ~10 % in the reactive signal at 393 K on Pd(332) as the reaction proceeds in our experiments, as shown in Figure S2a. However, as shown in Figure S2b, the peak normalized kinetic traces show the same shape and look indistinguishable within our resolution. We therefore conclude that the barriers and rates for CO₂ formation are not changed by this drop in reactive signal.



Figure S2: Sequential scans for CO_2 formation from DCOOH decomposition at 393 K on Pd(332). In panel a) we show sequential scans for CO_2 formation from DCOOH decomposition on Pd(332). The real time to acquire these kinetic traces are given in the legend. Panel b) show the same kinetic traces as in panel a) but peak normalized. We conclude that within the resolution of our experiment these kinetic traces look the same.

The drop could be due to a decrease in the initial sticking probability of formic acid changes on Pd(332) as a function of co-adsorbed hydrogen that builds up during the decomposition reaction. To check this hypothesis, we conducted experiments with different coverages of hydrogen by leaking background hydrogen gas in the chamber, see Figure S3a. We see a larger but qualitatively the same effect because in these background gas experiments the steady-state coverage of hydrogen is much larger than the hydrogen build up in the formic acid decomposition experiments. Although the hydrogen coverage is significantly larger in these experiments, the peak normalized kinetic traces look the same, see Figure S3b indicating that hydrogen co-adsorption has no significant effect on the barriers.

The hydrogen coverage from background experiments is estimated by solving the following equation to get the steady state coverage.

$$\frac{d[H]}{dt} = 2S_0 \left(1 - \frac{[H]}{1 ML}\right)^2 \frac{p_{H_2}}{\sqrt{2\pi m_{H_2} k_b T}} - 2k_{rec} [H]^2$$
Eq. S1

where k_{rec} is the recombination rate constant of hydrogen, T is 298 K, $m_{H_2}^{m_{H_2}}$ is the mass of H₂ and [*H*] is the hydrogen coverage in monolayers (ML).¹

The background pressures of hydrogen in the experiments that led to 0.22 ML and 0.32 ML coverages were 6.6×10^{-7} mbar and 1.8×10^{-6} mbar respectively. The steady state coverage is established after a few seconds.

In the case of letting only the formic acid beam run, we estimate the upper limit of the hydrogen coverage by assuming that all the formic acid molecules react and considering a continuous beam with the same flux as the pulsed formic acid beam used in the experiments. A single molecular beam pulse has a dosage of $\sim 10^{-4}$ ML per pulse at a repetition rate of 25 Hz so the average flux of the equivalent continuous beams is $F^{Formic Acid} = 2.5 \times 10^{-3}$ ML/s. We get the steady state coverage by solving

$$\frac{d[H]}{dt} = 2S^{Formic\ Acid} \left(1 - \frac{[H]}{1\ ML}\right)^2 F^{Formic\ Acid} - 2k_{rec}[H]^2 \qquad \qquad Eq.\ S2$$

for steady state. Here $S^{Formic Acid}_{0}$ is the initial sticking probability of formic acid².



Figure S3: CO_2 formation rates from HCOOH decomposition on Pd(332) at 393 K as function of hydrogen coverage. In panel a) we show the non-normalized CO_2 formation rates for different hydrogen coverages, see legend. Panel b) shows the same kinetic traces as in panel a) but peak normalized.

To investigate the effect of co-adsorbed CO, we acquired data for CO₂ formation from formic acid decomposition on Pd(332) with CO background gas ($p_{CO} = 1 \times 10^{-8} mbar$) as shown in Figure S4a). The corresponding steady-state CO coverage is adapted from Eq. S1 as shown in Eq. S3.

$$\frac{d[CO]}{dt} = S_0 (1 - \frac{[CO]}{0.35 \text{ ML}}) \frac{p_{CO}}{\sqrt{2\pi m_{CO} k_b T}} - k_d [CO]$$
 Eq. S3

 S_0 is assumed to be unity, k_d is the desorption rate constant of CO, m_{CO} is the mass of CO and [CO] is the CO coverage in ML.³ The saturation coverage of CO is taken from Ref. ⁴.

The results show that co-adsorption of CO changes the shape of the kinetic trace by making the fast component sharper and the slow component slower. The branching fraction of the fast component is ~ 10 % larger compared to the CO-free experiment.

We attempted to reproduce the effect of co-adsorbed CO by exposing the surface to the formic acid beam for up to 84 minutes. The results are shown in see Figure S4b. Note that no change is observed during the course of exposure to the beam. The " $[CO_{ad}]$ " curve in the figure shows the effect of 0.28 ML of CO co-adsorbed from background gas. We can clearly distinguish the peak normalized kinetic trace for CO₂ with CO background gas from the CO₂ kinetic trace without CO background gas. Since we acquired the data on formic acid decomposition reported in this work in 6 minutes, we conclude that the effect of co-adsorbed CO is negligible in this work.



Figure S4: In panel a) we compare the kinetic trace of CO_2 formation with CO background gas (black line) with the kinetic trace of CO_2 formation without CO background gas. In panel b) we show sequential scans for kinetic traces of CO_2 from formic acid decomposition (for acquisition time, see legend) and the kinetic trace for CO_2 with CO background gas. The surface temperature was 413 K for all experiments.

S3. Non-resonant Photodissociation of Formic Acid

We identify the fast channel of CO formation on Pd(332) from formic acid decomposition to be the photodissociation of the parent formic acid molecule. Photodissociation of formic acid leading to CO⁺ and OH⁺/H or CO⁺ and H₂O⁺ with fs-pulses of a Ti:Sapphire laser has been reported previously.^{5, 6} Additionally, we show Figure S5a that the fast channel of CO has the same time-dependence as the formic acid signal. In Figure S5b, we see more ions with higher velocity than in Figure S5c because for early reaction times with see a higher contribution of photodissociated formic acid.



Figure S5: The kinetic trace of CO and HCOOH on Pd(332) and the raw ion images for different reaction times. a) The kinetic trace of CO (grey dots) and HCOOH (blue line, scaled) at 663 K on Pd(332) is shown. The kinetic trace of HCOOH is scaled such that it fits the kinetic trace of CO. We show for different reaction timings (t_1 and t_2) the raw ion images b) and c). The red line marks the position of the laser. We emphasize that for early reaction time ions are distributed non-thermally all over the detector while we see for later reaction times only ions with thermal accessible velocities ($\langle v \rangle$ (T = 663 K) = 709 ms⁻¹, blue line).

S4.Summary of DFT calculations



Figure S6: Schematic picture of Pd(332) surface, with the lattice box and the vacuum layer. The grey atoms represent the unit cell used for DFT calculations. We replicated the unit cell twice with the dark blue atoms to show the steps.

Table S1: Binding energy and selected geometric parameters of formic acid decomposition intermediates on Pd(111) and Pd(332) surfaces.

	On Pd(111)				On Pd(332)					
Species	BE (eV)	Pd-X (Å)	C-O (Å)	О-Н (Å)	С-Н (Å)	BE (eV)	Pd-X (Å)	C-O (Å)	O-H (Å)	С-Н (Å)
HCO*OH*	-0.77	2.29 ^b	1.24 ^c , 1.32 ^d	1.02	1.10	-0.98	2.19 ^b	1.24°, 1.32ª	1.02	1.10
HCO*O*	-2.74	2.15 ^b	1.27	-	1.11	-3.14	2.11 ^b	1.27	-	1.11
C*OOH	-2.58	1.97 ª	1.24 ^c , 1.34 ^d	0.99	-	-2.69	1.96 ª	1.24°, 1.34 ^d	0.98	-
C*O	-2.18	2.07ª	1.19	-	-	-2.33	2.05ª	1.19	-	-
CO2	-0.25	-	1.18	-	-	-0.39	-	1.18 ª	-	-
O*H	-2.69	2.20 ^b	-	0.98	-	-2.99	2.12 ^b	-	0.98	-
Н*	-0.71*	1.82 ^e	-	-	-	-0.82*	1.79°	-	-	-

^a Pd-C ^b Pd-O

° C=O

^d C-OH

° C-OH ° Pd-H

* H₂ in the gas phase is used as reference.

Molecules are more strongly bounded to (332) surfaces than to (111) surfaces. In Table S1, the binding energy increases from 0.11 eV and 0.12 eV for C*OOH and H* to 0.29 eV and 0.40 eV for HCO*OH* and HCO*O*. This increase is due to more active sites on the (332)

surface. The palladium atoms on the edge of the step have only 7 nearest-neighbor atoms against 9 for the flat (111) surface. The lack of nearest neighbor enhances their reactivity and so the preferred sites, for (332) surface, are all in the vicinity of these low neighbor Pd atoms (see Main text, Figure 4 to Figure 8).

Table S2: Comparison of binding energy for formic acid decomposition intermediates on Pd(111) surface with Mavrikakis and coworkers and Jiao and coworkers.^{7, 8} For better comparability, the binding energy of H^{*} is reference to H in the gas phase.

Species	This work	Mavrikakis and coworkers	Jiao and coworkers
HCO*OH*	-0.77	-0.41	-0.39
HCO*O*	-2.74	-2.34	-2.37
С*ООН	-2.58	-2.22	-
C*O	-2.18	-1.99	-
CO ₂	-0.25	-0.05	-
O*H	-2.69	-2.16	-
H*	-2.97	-2.83	-

The adsorption sites are the same for Pd(111) surface as for Mavrikakis and coworkers⁸. However, the binding energy is systematically higher in this study (see Table S2). It increases by 0.28 eV, 0.40 eV, 0.36 eV, 0.20 eV for HCO*OH*, HCO*O*, C*OOH and CO₂ respectively. Similarly, the binding energy of H* is about 2.97 eV which is 0.14 eV higher than the value obtained with PW91 GGA functional. We pointed out in Fingerhut et. al.² the influence of dispersive interaction on the formic acid binding energy. Van der Waals interactions add attractive forces between species and the surface that enhance the adsorption. Luo and coworkers reported only the binding energies for formic acid and bidentate formate. Their values are close to the ones from Mavrikakis et al, because the GGA functional they used (PBE without VdW interactions) gives results like PW91. Then, our binding energies also overestimate their reported binding energies.

The intramolecular distances for Pd(111) are identical to Mavrikakis and coworkers⁸. The increase of the binding energy due to the dispersive interactions leads to species closer to the surface by 0.02-0.03 Å and is systematic for all species. There are no differences for intramolecular distances between Pd(111) and Pd(332) surfaces. Because molecules are more strongly bounded, they are also slightly closer to the metallic surface. The biggest change is for formic acid where the Oxygen atom is 0.10 Å closer to the nearest Palladium atom.

S4.1. Initial State Structures and Harmonic Frequencies

Table S3: Harmonic frequencies of formic acid (HCOOH, -H; DCOOH, -D1; HCOOD, -D2) on Pd(111) and Pd(332).

Vibrational modes (meV)	Pd(111)-H	Pd(332)-H	Pd(111)-D1	Pd(332)-D1	Pd(111)-D2	Pd(332)-D2
C-H stretching	373.1	375.3	275.5	277.1	372.7	375.1

O-H stretching	356.7	345.5	357.3	345.8	260.4	252.3
C=O stretching	203.5	202.3	201.6	200.6	202.8	201.5
C-H bending	166.7	167.2	119.2	119.8	165.4	166.1
C-O stretching	159.0	158.7	157.4	156.8	152.0	152.3
O-H bending	140.7	140.5	143.4	143.1	121.6	117.8
C-H bending	122.0	121.7	102.6	102.1	118.6	121.3
O-H bending	82.6	84.4	78.6	83.7	65.2	66.0
OCO bending	79.3	79.7	81.7	79.0	71.7	72.1
Rotation	23.2	28.4	21.6	27.8	21.7	28.1
Rotation	22.1	27.1	20.6	23.7	21.7	25.3
Normal translation	14.5	17.1	14.4	17.0	14.2	16.7
Translation	7.7	9.9	7.3	9.6	7.6	9.8
Translation	6.3	4.7	6.2	4.6	6.2	4.6
Normal rotation	3.3	8.2	3.3	8.1	3.2	7.9

Table S4: Harmonic frequencies of bidentate formate intermediate (HCOO, -H, and DCOO, -D) on Pd(111) and Pd(332).

Vibrational modes (meV)	Pd(111) - H	Pd(332) - H	Pd(111) - D	Pd(332) - D
C-H stretching	365.5	365.3	268.9	268.8
OCO asym stretching	185.8	186.0	185.8	186.0
C-H bending	161.0	163.4	118.7	120.5
OCO sym stretching	159.6	160.5	156.8	157.7
C-H bending	119.1	121.0	89.73	89.40
OCO bending	90.68	90.31	101.3	102.4
Rotation	36.25	39.23	31.09	38.10
Rotation	35.31	35.87	34.35	30.99
Normal translation	32.64	36.90	32.26	36.14
Normal rotation	12.59	10.62	12.05	6.52
Translation	12.21	12.09	12.58	10.61
Translation	8.98	6.683	8.704	11.95

Vibrational modes (meV)	Pd(111) - H	Pd(332) - H	Pd(111) - D	Pd(332) - D
O-H stretching	435.4	444.1	316.9	323.2
C-O stretching	193.5	192.9	192.1	191.5
O-H bending	150.4	149.2	112.4	111.3
OCO stretching	138.2	137.2	142.1	142.0
OCO bending	83.14	84.19	80.37	81.12
O-H bending	72.70	71.75	61.75	62.10
Rotation	56.36	55.76	49.01	47.64
Normal translation	35.76	38.49	35.71	38.48
Rotation	30.36	28.18	28.72	26.70
Normal rotation	12.37	9.784	12.19	9.569
Translation	7.008	13.01	6.909	12.79
Translation	3.152	2.048	3.063	2.003

Table S5: Harmonic frequencies of carboxyl intermediate (COOH, -H, and COOD, -D) on Pd(111) and Pd(332).

Table S 6: Harmonic frequencies of carbon dioxide on Pd(111) and Pd(332).

Vibrational modes (meV)	Pd(111)	Pd(332)
Asym stretching	292.5	290.7
Sym stretching	162.5	162.9
Bending	76.97	77.34
Normal bending	73.87	75.40
Normal translation	7.274	5.970
Rotation	7.191	3.491
Translation	4.596	1.956
Translation	1.860	0.275
Normal rotation	1.563	3.380i

Table S 7: Harmonic frequencies of carbon monoxide on Pd(111) and Pd(332)

Vibrational modes (meV)	Pd(111)	Pd(332)
C=O Stretching	219.6	217.8

Rotation	42.70	42.82
Rotation	39.53	39.61
Normal translation	38.70	38.57
Translation	18.47	19.30
Translation	17.47	17.48

Table S 8: Harmonic frequencies of hydroxide radical (OH, -H, and OD, -D) on Pd(111) and Pd(332).

Vibrational modes (meV)	Pd(111)-H	Pd(332)-H	Pd(111)-D	Pd(332)-D
O-H Stretching	456.6	457.4	332.4	332.7
Rotation	49.5	79.3	41.7	58.7
Rotation	48.6	74.5	41.3	55.0
Normal translation	41.5	45.0	40.3	44.1
Translation	15.6	27.4	13.0	26.3
Translation	13.8	9.8	11.5	9.4

Table S 9: Harmonic frequencies of adsorbed H-/D-atom on Pd(111) and Pd(332)

Vibrational modes (meV)	Pd(111)-H	Pd(332)-H	Pd(111)-D	Pd(332)-D
Normal vibration	124.3	120.1	87.87	84.89
Vibration	101.7	117.7	71.90	83.21
Vibration	101.0	98.96	71.40	69.98

S4.2. Transition State Structures and Harmonic Frequencies

Table S10: Selected geometric parameters for transition states of formic acid decomposition on Pd(111) and Pd(332).

	Pd(111)				Pd(332)			
Reactions	Pd-X (Å)	C-0	O-H (Å)	C-H (Å)	Pd-X (Å)	C-0	O-H (Å)	C-H
		(Å)				(Å)		(Å)
HCO*OH*→HCO*O* + H*	2.10 💷	1.28	1.71	1.11	2.08 💷	1.30 1	1.97	1.12
		1.25 "				1.24 "		
HCO*OH*→H*CO*OH	2.62 💷	1.36 ⁱ	0.98	1.11	2.28 💷	1.341	0.98	1.10
		1.21 "				1.23 "		
H*CO*OH→C*OOH + H*	2.62 💷	1.36 ⁱ	0.98	1.11	2.19 🗉	1.341	0.98	1.73
		1.22 "				1.24 "		
HCO*O*→COO + H* a)	2.07 💷	1.30 ⁱ	-	1.19	2.83 11	1.321	-	1.15
		1.23 "				1.24 "		
HCO*O*→COO + H* b)	2.55 Ⅲ	1.25	-	1.29	2.41 11	1.25	-	1.26
		1.25				1.26		
C*OOH→COO + H*	1.99 Ⅳ	1.26 ⁱ	1.89	-	1.95 1	1.36 ⁺	1.95	-
		1.22 "				1.22 "		
C*OOH→C*O + O*H	2.11 1	1.45	0.98	-	1.95	1.36	1.07	-
		1.22 "				1.22		

l) C-O ll) C=O

III) Pd-O IV) Pd-C

Table S11: Harmonic frequencies of transition	state of formic acid (HCOOH, -H and HCOOD, -D)
reaction to the bidentate formate intermediate of	n Pd(111) and Pd(332).

Vibrational modes (meV)	Pd(111)-H	Pd(332)-H	Pd(111)-D	Pd(332)-D
C-H stretching	366.2	353.5	366.3	353.5
Asym OCO stretching	194.7	194.3	193.0	193.8
C-H bending	159.4	159.6	159.3	159.5
Sym OCO stretching	157.6	151.6	157.3	151.5
O-H bending	100.4	107.5	70.9	76.1
C-H bending	116.9	121.1	116.9	121.1
O-H bending	92.1	102.0	65.8	72.2
OCO bending	90.0	90.4	90.8	90.5
Rotation	45.4	79.9	40.0	56.8
Normal rotation	32.6	39.9	31.2	39.2
Normal translation	28.9	35.9	27.7	35.9
Rotation	10.6	17.6	10.3	17.6
Translation	6.6	6.7	6.6	6.7
Translation	5.6	5.1	5.6	5.1
O-H dissociation	22.5i	4.7i	20.4i	4.7i

Table S12: Harmonic frequencies of transition state of the formic acid (HCOOH, -H and DCOOH, -D) reaction to carboxyl intermediate on Pd(111) and Pd(332).

Vibrational modes (meV)	Pd(111)-H	Pd(332)-H	Pd(111)-D	Pd(332)-D
O-H stretching	441.8	449.8	441.8	449.8
C-H bending	212.8	207.0	161.6	146.7
Asym OCO stretching	191.8	196.7	191.1	196.8
O-H bending	148.7	148.3	145.4	148.4
Sym OCO stretching	141.7	137.3	132.2	137.0
C-H bending	123.9	59.86	93.50	58.66
O-H bending	113.7	72.58	90.55	71.96
OCO bending	75.58	82.43	73.88	82.37

Rotation	62.85	46.41	62.57	38.54
Rotation	24.04	34.26	23.62	33.71
Normal translation	20.12	25.13	19.78	22.80
Normal Rotation	9.630	5.327	9.592	5.126
Translation	8.870	16.27	8.812	16.35
Translation	5.977	6.022	5.859	6.011
C-H dissociation	21.20i	79.08i	19.81i	57.48i

Table S13: Harmonic frequencies of transition state of the formate intermediate (HCOO, -H and DCOO, -D) reaction to CO_2 on Pd(111) and Pd(332), pathway a).

Vibrational modes (meV)	Pd(111)-H	Pd(332)-H	Pd(111)-D	Pd(332)-D
C-H stretching	245.8	303.3	176.9	221.5
C=O stretching	202.8	195.5	203.1	194.1
C-H bending	148.6	151.7	105.6	111.1
C-O bending	139.1	140.5	139.2	137.7
C-H bending	112.4	106.2	94.0	92.0
C-O stretching	82.9	82.4	82.4	81.5
Normal translation	36.9	39.5	36.4	39.5
Rotation	31.1	25.3	28.0	23.2
Translation	17.5	10.1	16.7	9.9
Rotation	9.0	7.5	9.0	7.4
Translation	5.1	2.2	5.1	2.2
Rotation	12.2i	27.2i	12.1i	24.3i

Table S14: Harmonic frequencies of transition state of the formate intermediate (HCOO, -H and DCOO, -D) reaction to CO_2 on Pd(111) and Pd(332), pathway b).

Vibrational modes (meV)	Pd(111)-H	Pd(332)-H	Pd(111)-D	Pd(332)-D
Asym stretching	202.1	213.8	202.1	213.8
C-H bending	175.6	172.9	104.7	152.5
Sym stretching	133.9	119.9	152.2	103.0
C-H bending	127.5	117.8	94.65	86.5
OCO bending	108.2	97.4	93.24	79.9

Rotation	74.16	62.1	73.62	55.8
Normal translation	33.58	31.6	30.99	30.6
Normal rotation	18.46	15.1	17.94	14.7
Translation	8.508	10.4	8.458	10.4
Translation	8.091	5.7	7.990	5.6
Rotation	14.30i	9.9i	14.30i	9.8i
C-H dissociation	32.60i	44.1i	30.42i	41.3i

Table S15: Harmonic frequencies of transition state of the carboxyl intermediate (COOH, -H, and COOD, -D) reaction to CO_2 on Pd(111) and Pd(332).

Vibrational modes (meV)	Pd(111) - H	Pd(332) - H	Pd(111) - D	Pd(332) - D
C-O stretching	212.8	199.4	210.8	198.1
O-H stretching	182.5	404.2	129.7	294.2
OCO stretching	143.8	132.7	144.0	138.0
OCO bending	97.77	83.42	84.43	80.84
O-H bending	81.45	155.6	61.50	113.5
Rotation	64.94	59.66	64.78	62.54
Normal translation	37.67	36.10	37.48	35.76
Rotation	29.65	30.96	29.64	29.66
Normal rotation	11.11	4.931	11.10	4.872
Translation	8.758	0.6105i	8.757	0.607i
Translation	6.100i	7.943i	6.080i	7.630i
O-H bending	58.99i	71.88i	41.87i	50.93i

Table S 16: Harmonic frequencies of transition state of carboxyl intermediate (COOH,	, -H and COOD,	-
D) reaction to CO on Pd(111) and Pd(332).		

Vibrational modes (meV)	Pd(111) - H	Pd(332) - H	Pd(111) - D	Pd(332) - D
O-H stretching	453.2	348.6	329.6	253.0
C=O stretching	196.8	197.1	196.7	195.9
O-H bending	133.7	158.0	107.9	126.8
C-O bending	94.15	125.3	91.15	124.0
O-H bending	74.42	99.87	69.62	73.50
Normal translation	35.21	36.00	34.94	35.24

Normal Rotation	31.32	82.42	29.18	74.74
Rotation	28.50	39.01	27.95	38.11
Rotation	22.33	24.52	21.19	24.41
Translation	13.43	15.74	13.39	15.63
Translation	11.43	13.26	11.25	13.10
C-O dissociation	14.50i	13.31i	11.44i	13.18i

1. References

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