

Supporting Information:

**Selective Oxidation of 1,2-Propanediol in Alkaline Anion-Exchange
Membrane Electrocatalytic Flow Reactors: Experimental and DFT
Investigations**

*David J. Chadderton,^{‡1a} Le Xin,^{‡a} Ji Qi,^{1a} Brian Brady,^b Julie A. Miller,^b Kai Sun,^c Michael
J. Janik,^{*b} Wenzhen Li^{*1a}*

^a Department of Chemical Engineering Michigan Technological University, Houghton, Michigan 49931,
United States

^b Department of Chemical Engineering Pennsylvania State University, University Park, Pennsylvania
16802, United States

^c Department of Material Science and Engineering University of Michigan, Ann Arbor, Michigan 48109,
United States

Email: Wenzhen Li wzli@iastate.edu; Michael J. Janik mjanik@engr.psu.edu

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Calculation of conversion, selectivity, and carbon balance:

PDO conversion was calculated by eq S1:

$$\text{PDO Conversion \%} = \frac{N_{\text{PDO,initial}} - N_{\text{PDO}}}{N_{\text{PDO,initial}}} \times 100\% \quad (\text{S1})$$

Where N_{PDO} is the amount of PDO (moles) determined by HPLC. Product selectivity was calculated as a molar fraction of total identified products by eq S2:

$$\text{Product selectivity \%} = \frac{N_i}{\sum_i N_i} \times 100\% \quad (\text{S2})$$

Where N_i is the amount of product species i (moles). Total carbon balances were calculated to confirm that the majority of products had been identified, given by eq S3:

$$\text{Carbon balance \%} = \frac{3N_{\text{PDO}} + 3N_{\text{C}_3} + 2N_{\text{C}_2} + N_{\text{C}_1}}{3N_{\text{PDO,initial}}} \times 100\% \quad (\text{S3})$$

Where N is the molar amount of PDO, C₃, C₂, or C₁ products.

Physical Characterizations of Prepared Catalysts:

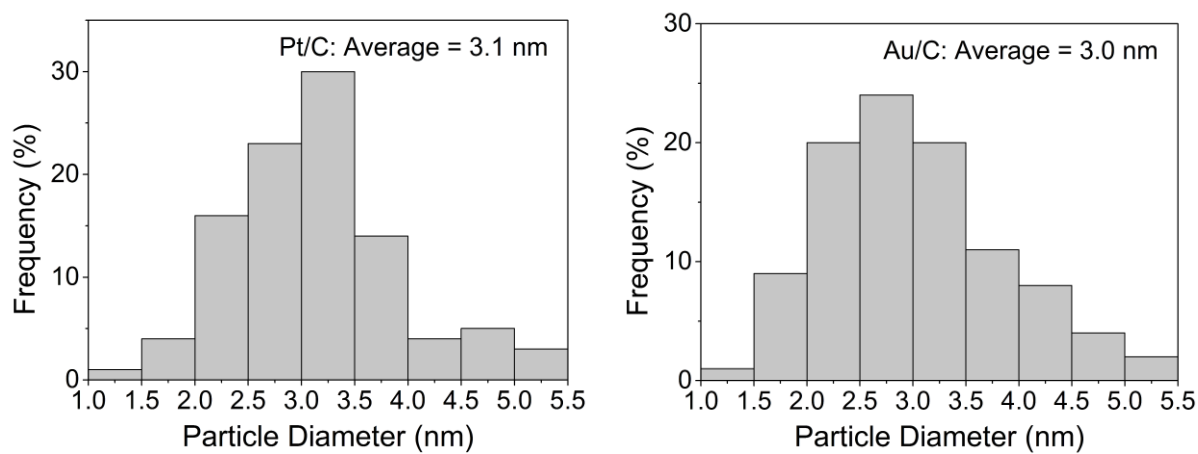


Figure S1. TEM particle size histograms of Pt/C (left) and Au/C (right)

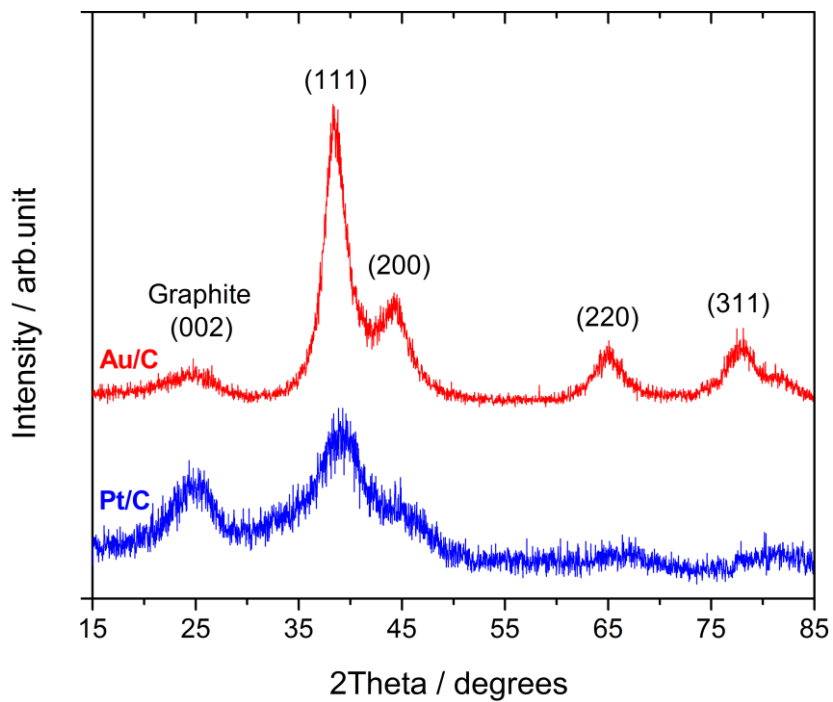


Figure S2. XRD patterns of self-prepared Pt/C and Au/C catalysts.

Cyclic Voltammograms on Prepared Catalysts:

Cyclic voltammetry was performed in a glass electrochemical reactor (AFCELL3, Pine Instruments) in a three-electrode-configuration controlled by a potentiostat (Versastat MC, Princeton Applied Research). Electrolyte was nitrogen purged 1.0 M KOH. Potential sweep rate was 50 mV s^{-1} . Catalysts were dispersed in isopropanol by ultrasonication to form a uniform ink (1.0 mg mL^{-1}). With a microsyringe, $20 \mu\text{L}$ of ink were deposited onto a mirror polished glassy carbon rotating disk electrode (Pine Instruments, 5.0 mm diameter). A Hg/HgO (1.0 M KOH) reference electrode and platinum-wire counter electrode were used. Tests were conducted at room temperature.

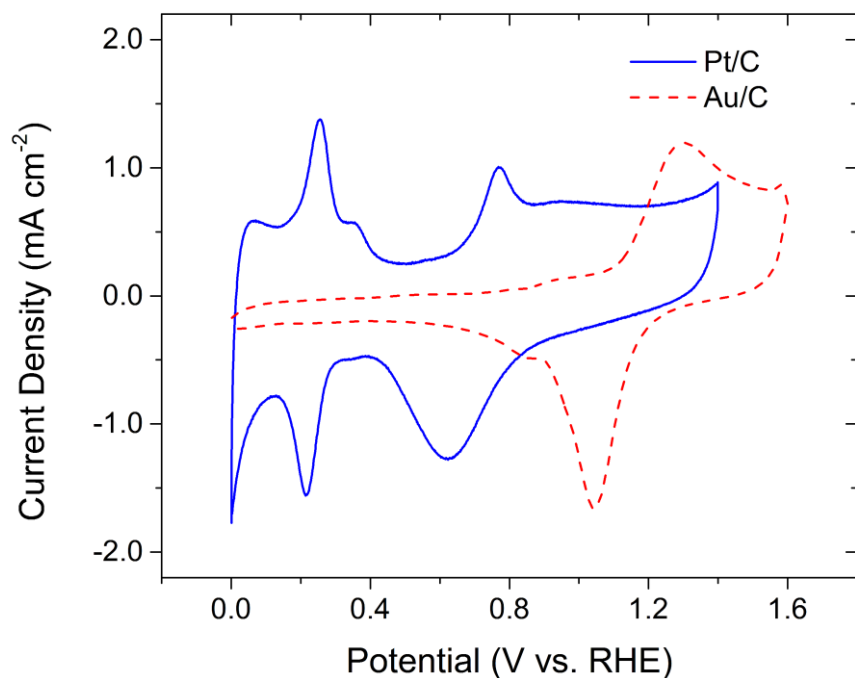


Figure S3. Cyclic voltammograms recorded with a sweep rate of 50 mV s^{-1} on Pt/C and Au/C catalyst in 1.0 M KOH.

Detailed Product Analysis of PDO oxidation in AEM-based Reactors:

Table S1. PDO Oxidation in AEMFC^a

catalyst	PDO conversion (%)	lactate (%)	pyruvate (%)	acetate (%)	formate (%)	carbon balance (%)
Pt/C	20.4	86.8	0.4	12.1	0.7	98.9
Au/C	6.4	42.3	29.7	25.9	2.1	97.3

^a two hour reaction, cell voltage = 0.1 V.

Table S2. PDO Oxidation in AEM-Electrocatalytic Cell^a

catalyst	applied potential (V vs RHE)	PDO conversion (%)	lactate (%)	pyruvate (%)	acetate (%)	formate (%)	carbon balance (%)
Pt/C	0.2	3.8	88.0	0	6.2	5.8	97.1
	0.3	4.8	86.0	0	8.0	6.0	97.1
	0.4	7.2	90.0	0.3	8.7	1.0	95.8
	0.5	7.7	89.4	0.5	9.9	0.2	96.7
	0.6	10.5	86.8	1.0	11.6	0.6	95.5
	0.7	12.3	85.7	1.2	12.4	0.7	96.3
Au/C	0.35	1.6	49.0	20.1	28.0	2.9	98.9
	0.4	1.9	47.5	33.3	17.5	1.7	99.4
	0.5	7.8	36.9	47.8	14.9	0.4	95.5
	0.6	8.3	35.1	53.5	11.3	0.1	96.7
	0.7	9.2	35.3	54.5	10.0	0.2	93.4
	0.75	12.5	33.2	55.9	10.8	0.1	95.2

^a one hour reaction

¹H NMR Analysis of Hydroxyacetone / Lactaldehyde Equilibrium:

¹H NMR spectra were collected with a Bruker 600 MHz NMR (AVIII6000) for the analysis of a 1 mM hydroxyacetone solution in deuterium oxide at various pH, and the results are shown in Table S3. Concentrations of KOH or HClO₄ were varied and ionic strength was held constant at 0.1 M by the addition of KCl. At pH 12 (0.01 M KOH) the equilibrium strongly favored lactaldehyde with a ratio of 10.3 to 1, and at pH 13 hydroxyacetone was below the detection limit. In contrast, at pH 11 (0.001 M KOH) and in neutral solution (0.1 M KCl) the species were found in relatively equal amounts with a hydroxyacetone/lactaldehyde ratio of 0.62–0.65. In acidic solution (0.1 M HClO₄) the equilibrium strongly favored hydroxyacetone. ¹H NMR spectra are shown in Figure S4.

Table S3. ¹H NMR Analysis of Hydroxyacetone / Lactaldehyde Equilibrium

solution	¹ H NMR signals			[hydroxyacetone]	[lactaldehyde]	K ratio ^a
	4.33 ppm	2.11 ppm	1.16 ppm	(M)	(M)	
0.1 M KOH	0	0	3	0	0.001	-
0.01 M KOH	0.28	0.16	3	9.667×10^{-5}	0.001	10.34
0.001 M KOH	1.17	1.82	1.17	0.0005958	0.00039	0.65
0.1 M KCl	1.27	1.93	1.19	0.0006392	0.0003967	0.62
0.1 M HClO ₄	2.03	2.98	0.16	0.001004	5.333×10^{-5}	0.05

^a molar ratio of hydroxyacetone to lactaldehyde at equilibrium

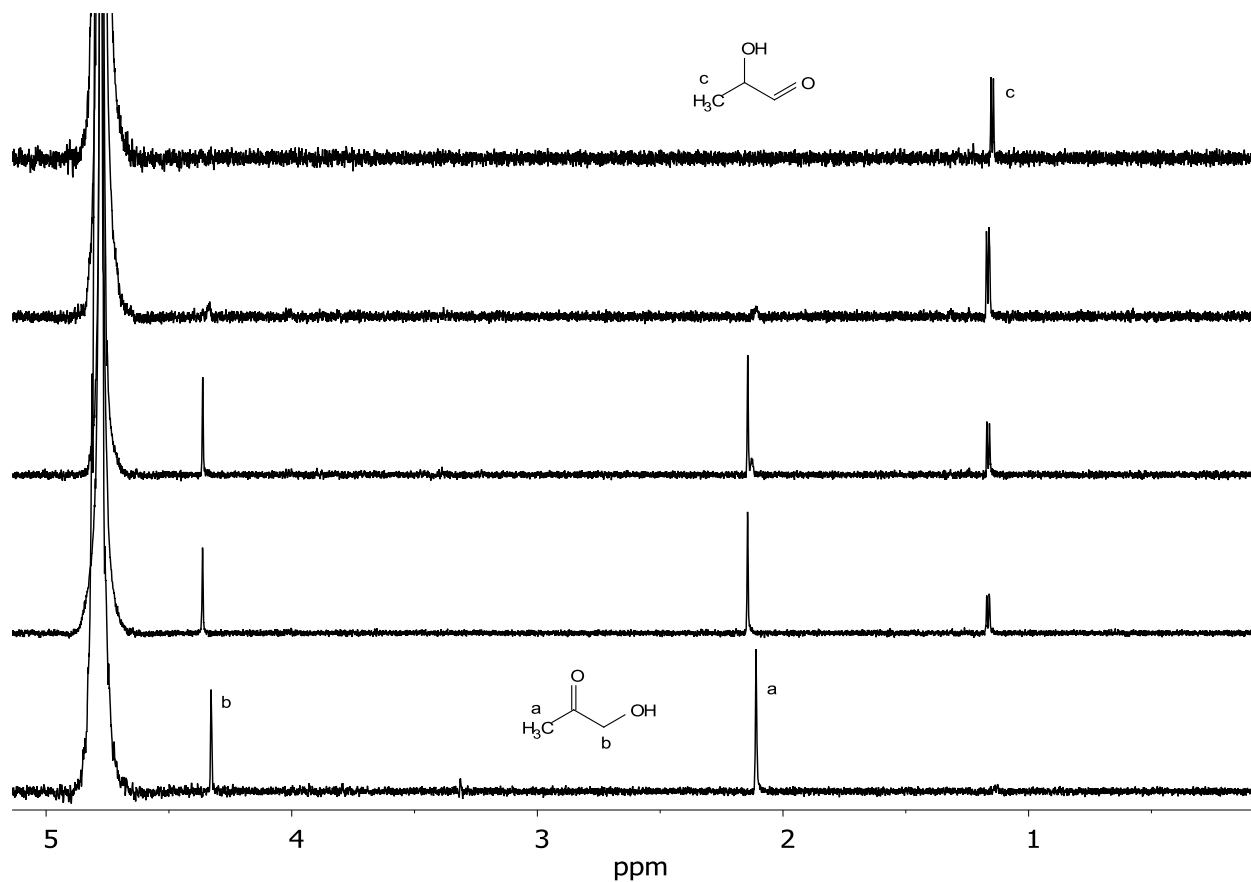
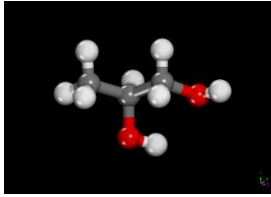
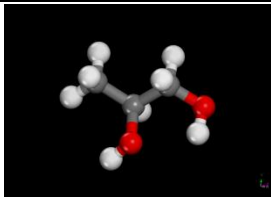
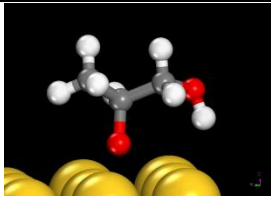
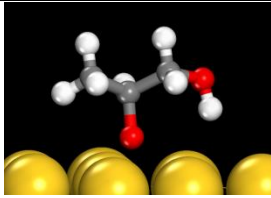
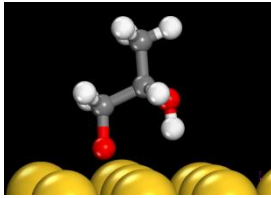
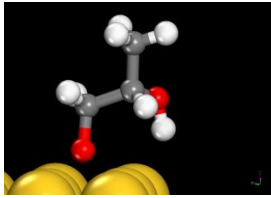
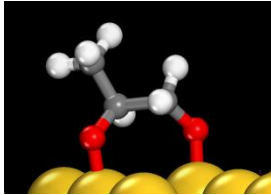
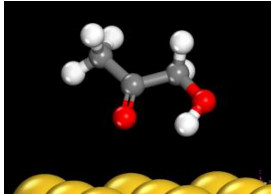
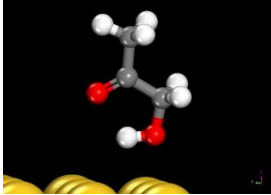
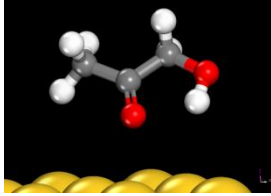
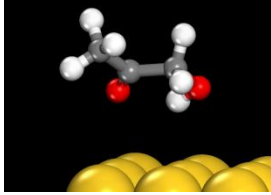
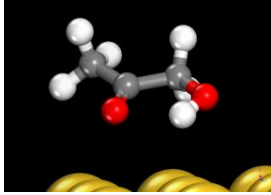
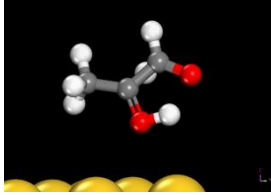
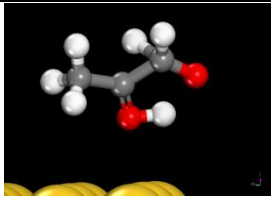
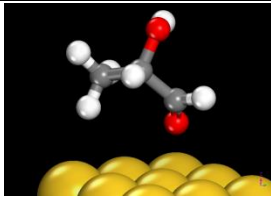
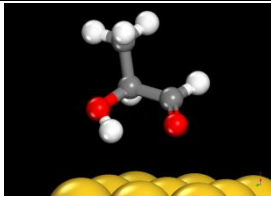
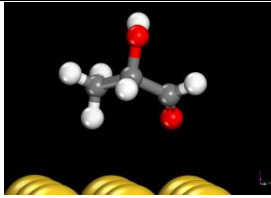
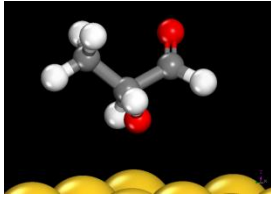
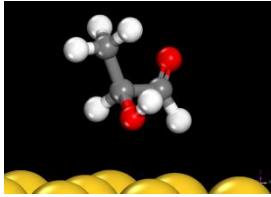
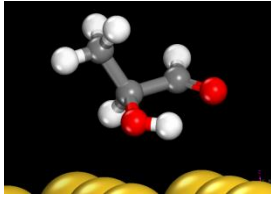


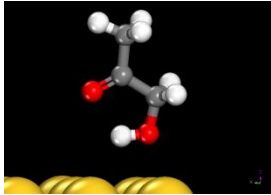
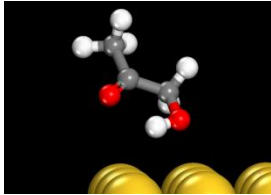
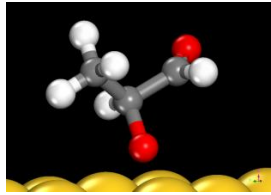
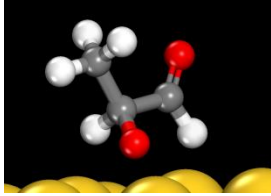
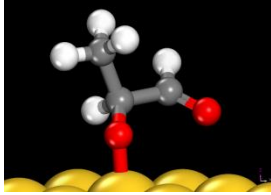
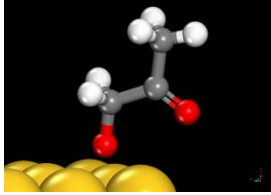
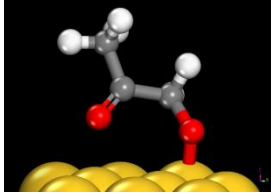
Figure S4. ^1H NMR (600 MHz, D_2O) of 1 mM hydroxyacetone with varying amounts of KOH or HClO₄. Ionic strength held constant at 0.1 M with KCl. Solutions contain (bottom to top): 0.1 M HClO₄, 0.1 M KCl, 0.001 M KOH, 0.01 M KOH, and 0.10 M KOH. Note, no signal is expected for H bound to C-2 on lactaldehyde as the isomerization in D_2O would incorporate ^1H NMR silent ^2H at that position.

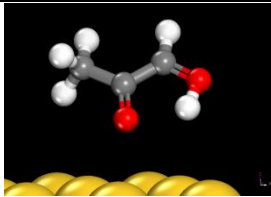
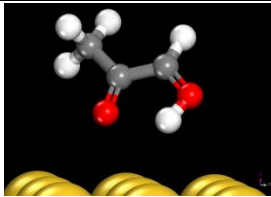
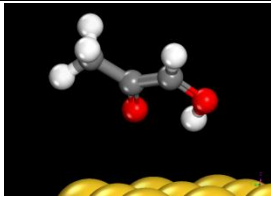
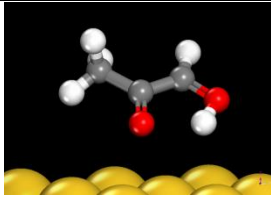
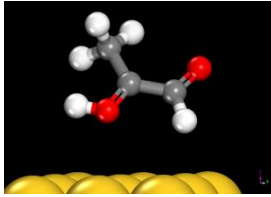
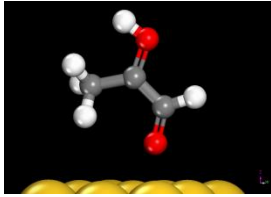
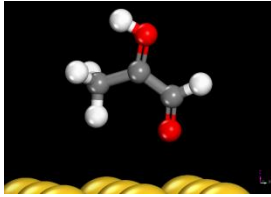
Table S4. Optimized intermediate structures and relative energies (eq 2) along the path of PDO oxidation on the Au(111) surface. Most favorable structures of a given intermediate are in bold. Energies in this table were determined with a 3x3x1 Monkhorst-Pack k-point mesh, and single-point energies with 4x4x1 mesh are included for preferred structures.

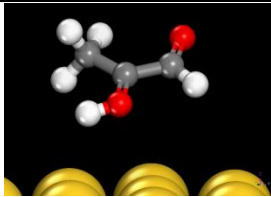
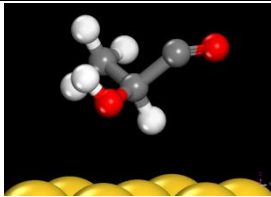
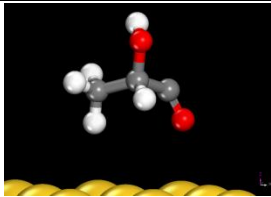
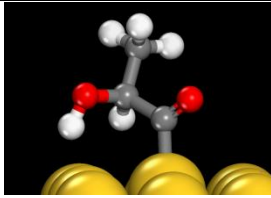
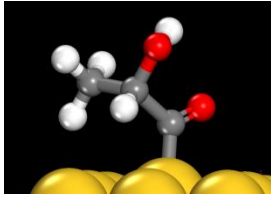
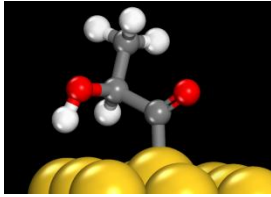
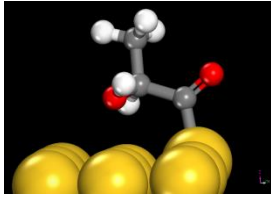
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0	0B		
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1	1B		0.00 (0.00)
1	1C		0.03 (0.02)
1	1D		0.06

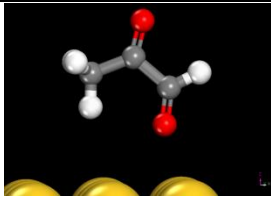
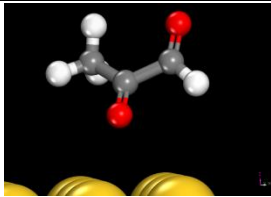
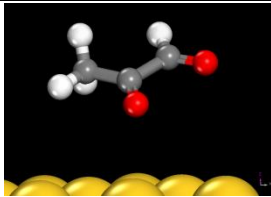
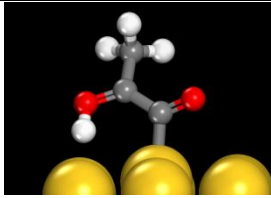
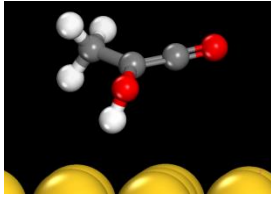
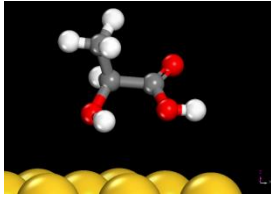
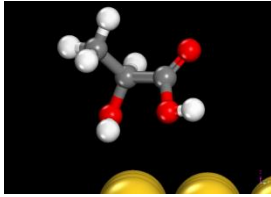
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2	2H		-1.58 (-1.46)
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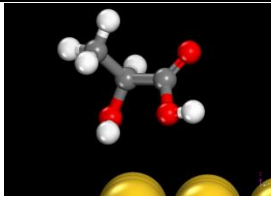
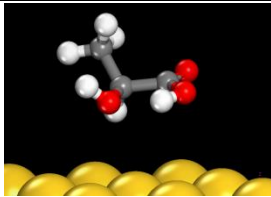
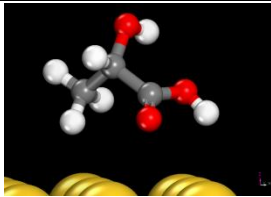
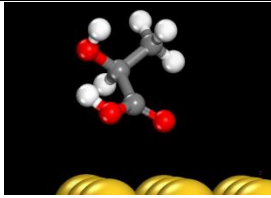
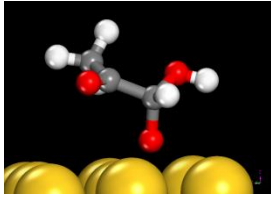
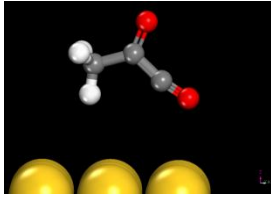
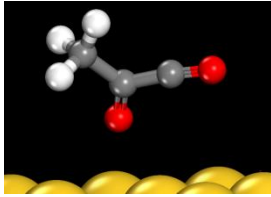
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2	2L		-1.29
2	2M		-1.15
2	2N		-1.16
2	2O		-1.17
2	2P		-1.34 (-1.21)

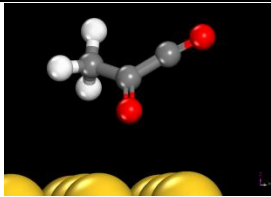
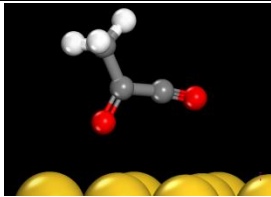
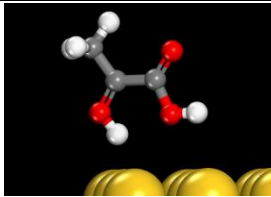
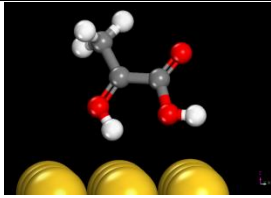
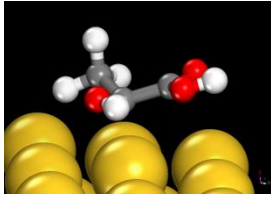
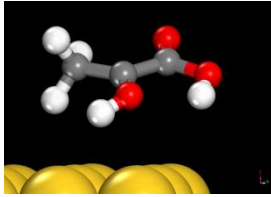
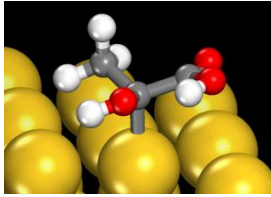
2	2Q		-1.47
2	2R		-1.56
3	3A		-0.34
3	3B		-0.37
3	3C		-0.33
3	3D		-0.55
3	3E		-0.58

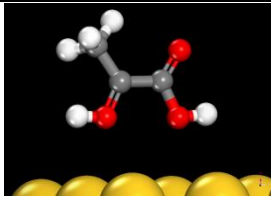
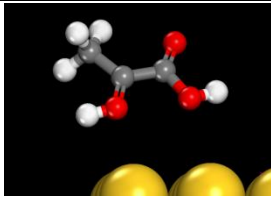
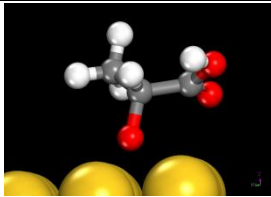
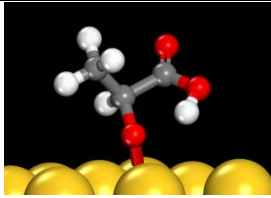
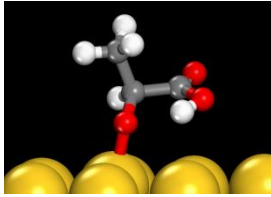
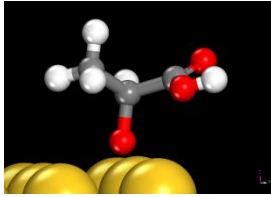
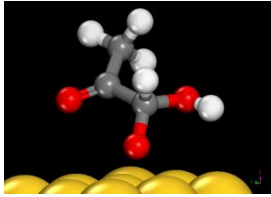
3	3F		-1.01
3	3G		-0.99
3	3H		-0.98
3	3I		-0.99 (-0.89)
3	3J		-0.77
3	3K		-0.65
3	3L		-0.64

3	3M		-0.83
3	3N		-0.11
3	3O		-0.06
3	3P		-1.42 (-1.34)
3	3Q		-1.36
3	3R		-1.42
3	3S		-1.26

4	4A		-1.61
4	4B		-1.68 (-1.55)
4	4C		-1.51
4	4D		-0.98
4	4E		-1.09
4	4F		-2.81
4	4G		-2.81

4	4H		-2.85
4	4I		-2.88 (-2.75)
4	4J		-2.81
4	4K		-2.75
4	4O		-2.28
5	5A		-0.9
5	5B		-0.89

5	5C		-0.89
5	5D		-0.82
5	5E		-2.34
5	5F		-2.34
5	5G		-2.43 (-2.40)
5	5H		-2.19
5	5I		-2.41

5	5J		-2.05
5	5K		-2.12
5	5L		-1.72
5	5M		-1.95
5	5N		-1.9
5	5O		-1.87
5	5P		-1.37

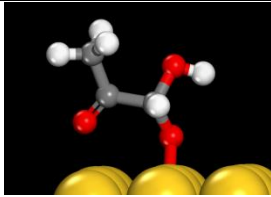
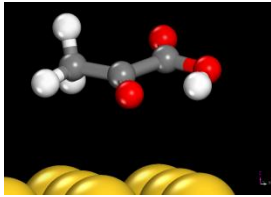
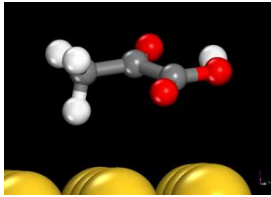
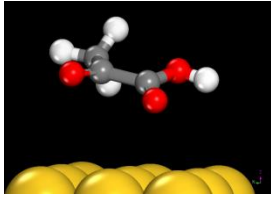
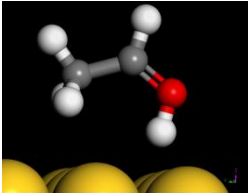
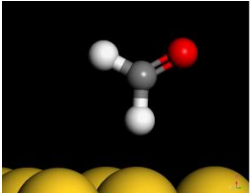
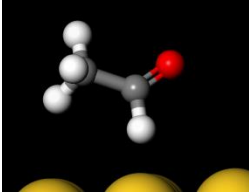
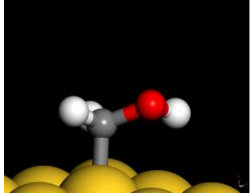
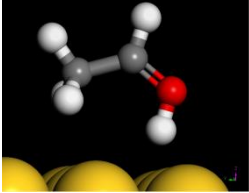
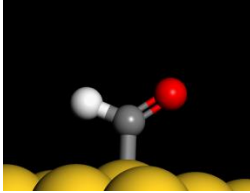
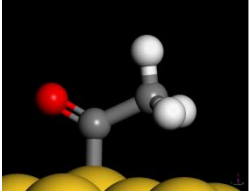
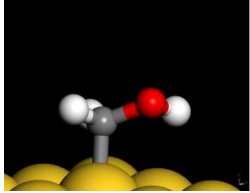
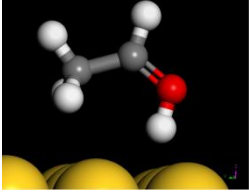
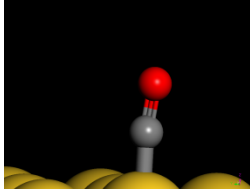
5	5Q		-1.36 (-1.36)
6	6A		-3.38 (3.25)
6	6B		-3.38
6	6C		-3.22

Table S5. Optimized Structures of Fragments Considered Following C-C Dissociation of C₃ Intermediates on the Au(111) Surface. Relative energies (eq 2) are included, allowing calculation of dissociation energies by comparison with species energies in Table S3.

Step Number	Structure Name	2C End	1C End	Relative Energy at 0.75 V* (eV)
1	1A			0.85
1	1B			0.04
2	2A			0.58
2	2B			-0.17
3	3A			-0.23

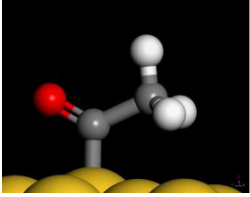
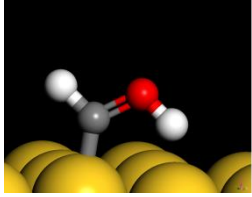
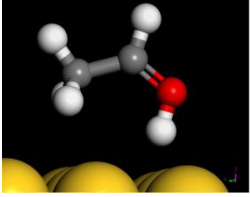
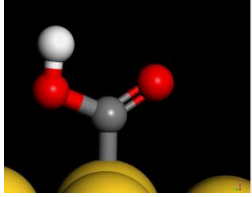
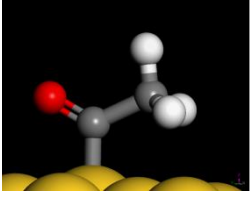
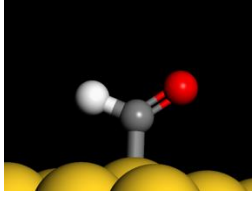
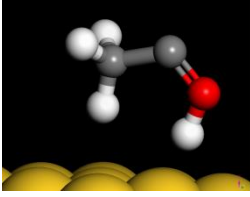
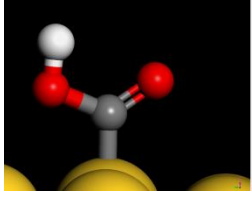
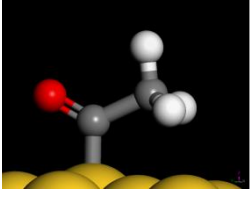
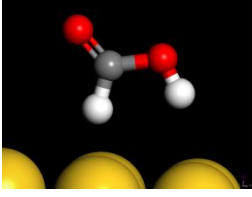
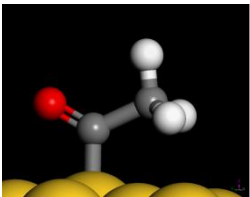
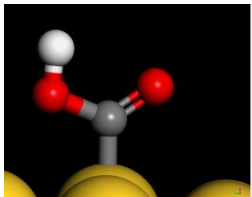
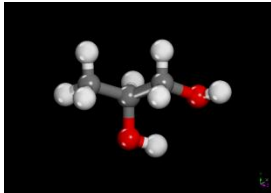
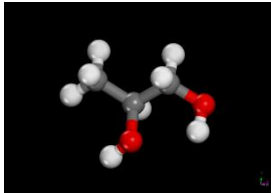
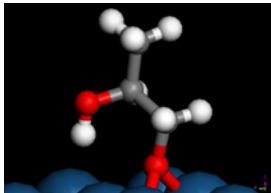
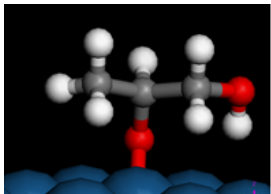
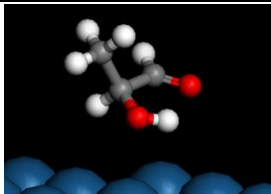
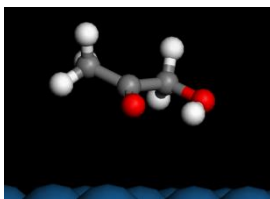
3	3B			0.14
4	4A			-0.79
4	4B			-0.84
5	5A			0.00
5	5B			-2.16
6	6A			-2.20

Table S6. Optimized Intermediate Structures and Relative Energies (eq 2) Along the Path of PDO Oxidation on the Pt(111) Surface.

Step Number	Structure Name	Structure	Relative Energy at 0.75 V* (eV)
0	0A		
0	0B		
1	1A		0.07
1	1B		0.00
2	2A		-0.78

2

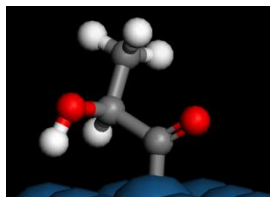
2B



-1.01

3

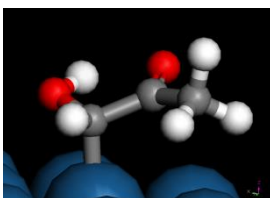
3A



-1.92

3

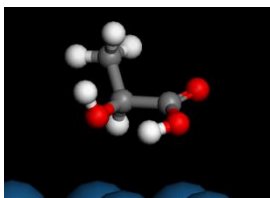
3B



-1.62

4

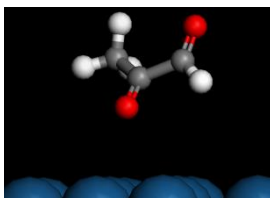
4A



-2.26

4

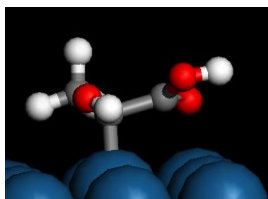
4B



-1.10

5

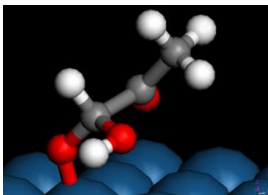
5A



-2.71

5

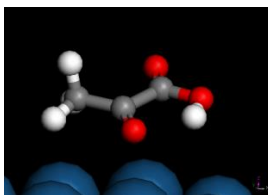
5B



-1.42

6

6A



-2.80
