

Supporting Information

Formate to Oxalate: A Crucial Step for the Conversion of Carbon Dioxide into Multi-carbon Compounds

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Index:

Section 1:	Computational details	Page 2
Section 2:	Raman Experiments	Page 5
Section 3:	Thermal Reaction Experimental Details	Page 9
Section 4:	Reference	Page 10
Figure S1:	Computational details	Page 6
Figure S2, S3,	S4: Experimental Raman spectra	Page 6, 7
Figure S5:	Theoretical Raman Spectra	Page 8

Section 1: Computational details

Density functional theory (DFT) calculations were performed using the hybrid B3LYP^{*I*, 2} exchange-correlation functional and 6-311⁺⁺G(2d,2p)^{3, 4} basis set with unrestricted Kohn-Sham wave functions as implemented in Gaussian 09 package.⁵. For thermodynamics calculations, thermal contributions to molecular free energies included the ideal-gas, rigid-rotator, and harmonic oscillator approximations.⁶ Solvation effects were accounted for by using the SMD continuum solvation model^{7, 8}. We carried out calculations using two different dielectric constants: $\varepsilon = 26$ to effectively represent the molten salt dielectric and $\varepsilon = 80$ to track the changes in thermochemistry in a hypothetic case of aqueous solution. The reported reaction free energies in solution were calculated using the following cycle:

$$\begin{array}{c} A_{g} \xrightarrow{\Delta G_{r}(g)} B_{g} \\ \Delta G_{solv}(A) \bigvee A_{aq} \xrightarrow{\Delta G_{r}(aq)} B_{aq} \end{array} \begin{array}{c} B_{g} \\ A_{aq} \xrightarrow{\Delta G_{r}(aq)} B_{aq} \end{array}$$

Figure S1. Thermodynamic cycle to estimate the free energy changes in aqueous solution $\Delta G_r(aq)$ based on gas phase optimized geometries and solvation free energies $\Delta G_{solv.}$

Relaxed potential energy surfaces PES scans were performed in internal coordinates using z-matrices. The types of stationary points on the PES were determined from the analysis of Hess matrix; second derivatives were calculated analytically. Transition states were (TS) located according to the procedure of eigenvector following with the Berny algorithm.⁹ The structures of the TS were confirmed by calculating the

intrinsic reaction coordinate¹⁰ through the mode corresponding to a single imaginary frequency.

Thermodynamics of the hydride pathway

Using our computational models, we calculated changes in Gibbs Free energy, Enthalpy, Entropy, Solvation Free energy for each step in the mechanism presented in Figure 2.

for diagram						relative to the previous step														
index	Δ0	aq	ΔG(e=26)	ΔG	aq	ΔG(e	e=26)	Δ	E	Δ	Н	T	۸S	ΔZI	PVE	ΔΔC wa	Gsol ter	ΔΔ((e=	Gsol 26)
	Κ	Na	K	Na	Κ	Na	Κ	Na	Κ	Na	Κ	Na	Κ	Na	K	Na	Κ	Na	K	Na
$I_1 {\rightarrow} I_2$	-2.3	-5.6	-5.5	-13.2	-2.3	-5.6	-5.5	-13.2	-34.0	-38.4	1.2	1.4	-8.4	-8.5	1.4	1.7	20.8	21.1	17.5	13.6
$I_2 {\rightarrow} TS_1$	28.3	29.6	28.4	22.0	30.5	35.3	33.9	35.2	44.5	48.6	-3.1	-3.1	-0.3	-0.7	-2.9	-2.9	-8.2	-8.1	-4.9	-8.1
$TS_1 {\rightarrow} I_3$	21.1	17.0	22.5	9.3	-7.1	-12.7	-5.9	-12.7	-8.8	-9.4	1.6	1.2	2.7	3.8	0.5	-0.1	2.2	-0.6	3.5	-0.6
$I_3 {\rightarrow} I_4$	16.1	17.0	19.3	18.7	-5.1	0.0	-3.2	9.4	7.6	9.4	-1.0	-1.0	5.1	4.8	-1.3	-1.4	-5.3	-2.3	-3.4	7.2
$I_4 {\rightarrow} I_5$	8.1	-0.4	4.6	-10.8	-8.0	-17.4	-14.7	-29.5	-44.5	-52.8	0.9	1.1	-9.7	-10.4	0.3	-9.3	25.6	25.8	18.9	21.1
$I_5 {\rightarrow} TS_2$	31.2	24.6	35.3	21.0	23.1	25.0	30.7	31.8	38.2	42.1	-1.0	-1.6	-4.3	-3.9	0.4	0.2	-18.8	-20.3	-11.2	-12.8
$TS_2 {\rightarrow} I_6$	20.4	13.6	27.4	13.9	-10.8	-11.1	-7.9	-7.1	-8.1	-6.0	1.4	1.8	-0.6	-0.2	1.6	1.3	-6.2	-7.8	-3.4	-4.4
$I_6 {\rightarrow} I_7$	21.5	5.9	26.2	13.1	1.1	-7.6	-1.2	-0.8	-6.2	-18.7	-0.6	0.6	-1.0	0.9	-0.2	0.6	7.2	10.7	4.8	17.6
$I_7 \rightarrow TS_3$	30.2	30.1	30.3	22.6	8.7	24.2	4.1	9.5	10.5	27.4	-2.7	-3.8	0.7	-0.8	-3.1	-3.9	4.7	3.8	0.1	-11.0
$TS_{3} {\rightarrow} I_{8}$	8.9	-2.7	3.8	-15.8	-21.3	-32.8	-26.5	-38.4	-21.0	-38.5	-0.2	0.6	1.0	1.1	-0.5	0.3	1.5	5.9	-3.8	0.3
$I_8 \rightarrow I_9$	11.3	-0.6	0.9	-9.6	2.4	2.1	-2.9	6.2	25.0	36.0	-0.6	-1.3	10.7	9.9	-1.1	-1.7	-19.5	-21.0	-15.5	-16.9

Table S1. Thermodynamics of the hydride pathway at 298 K

for diagram							relative to the previous step													
index	ΔG	laq	ΔG(e	e=26)	ΔG	laq	ΔG(e	e=26)	Δ	E	Δ	Н	T	۱S	ΔZI	PVE	ΔΔC wa	Gsol ter	ΔΔ((e=	Gsol 26)
	Κ	Na	Κ	Na	Κ	Na	Κ	Na	Κ	Na	K	Na	Κ	Na	Κ	Na	Κ	Na	Κ	Na
$I_1\!\!\rightarrow I_2$	9.5	4.7	6.2	-2.8	9.5	4.7	6.2	-2.8	-34.0	-38.4	1.2	1.4	-20.1	-18.9	1.4	1.7	20.8	21.1	17.5	13.6
$I_2 \rightarrow TS_1$	40.5	40.8	40.5	33.3	31.0	36.1	34.3	36.1	44.5	48.6	-3.1	-3.1	-0.7	-1.6	-2.9	-2.9	-8.2	-8.1	-4.9	-8.1
$TS_1 {\rightarrow} I_3$	29.5	23.4	30.8	15.9	-11.0	-17.4	-9.7	-17.4	-8.8	-9.4	1.6	1.2	6.5	8.5	0.5	-0.1	2.2	-0.6	3.5	-0.6
$I_3 {\rightarrow} I_4$	17.4	17.4	20.6	19.4	-12.2	-6.0	-10.3	3.5	7.6	9.4	-1.0	-1.0	12.2	10.7	-1.3	-1.4	-5.3	-2.3	-3.4	7.2
$I_4\!\!\rightarrow I_5$	22.8	5.4	19.3	2.7	5.5	-12.1	-1.2	-16.8	-44.5	-52.8	0.9	1.1	-23.2	-23.1	0.3	-9.3	25.6	25.8	18.9	21.1
$I_5 {\rightarrow} TS_2$	51.9	34.4	56.0	39.2	29.1	29.1	36.7	36.6	38.2	42.1	-1.0	-1.6	-10.3	-8.7	0.4	0.2	-18.8	-20.3	-11.2	-12.8
$TS_2 {\rightarrow} I_6$	42.1	24.2	49.0	32.4	-9.9	-10.3	-7.1	-6.9	-8.1	-6.0	1.4	1.8	-1.4	-0.4	1.6	1.3	-6.2	-7.8	-3.4	-4.4
$I_6\!\!\rightarrow I_7$	44.7	15.4	49.2	30.5	2.6	-8.8	0.2	-1.9	-6.2	-18.7	-0.6	0.6	-2.4	2.0	-0.2	0.6	7.2	10.7	4.8	17.6
$I_7 \rightarrow TS_3$	52.4	40.7	52.3	41.0	7.7	25.3	3.1	10.5	10.5	27.4	-2.7	-3.8	1.7	-1.8	-3.1	-3.9	4.7	3.8	0.1	-11.0
$TS_3 {\rightarrow} I_8$	29.8	6.5	24.4	1.2	-22.6	-34.1	-27.9	-39.7	-21.0	-38.5	-0.2	0.6	2.4	2.4	-0.5	0.3	1.5	5.9	-3.8	0.3
$I_8\!\!\rightarrow I_9$	8.0	-3.5	6.6	-4.7	-21.8	-10.0	-17.8	-5.9	25.0	36.0	-0.6	-1.3	25.6	22.0	-1.1	-1.7	-19.5	-21.0	-15.5	-16.9

Table S2. Thermodynamics of the hydride pathway at the temperatures of the experiment

(663 K for sodium and 713 K for potassium)

Section 2: Raman Experiments

Raman experiments reported in this article were conducted at Rowan University, Dept. of Physics & Astronomy. In-situ Raman spectroscopy was used to investigate the formate to oxalate reaction at 350°C temperature on the Horiba (Edison, NJ) LabRam HR instrument which is equipped with the TST350 Linkam heating stage. The samples were loaded into the heating stage within a dry N₂ glovebox. Nitrogen gas flow was also maintained through heating stage to ensure that no sample oxidation occurs during the measurement. The laser wavelength used is 520 nm. The samples were heated at a rate of 10°C/min.

Experimental Raman band Assignments:

Oxalate:

(a) Band at 1457 cm⁻¹

The strong Raman band at 1457 cm⁻¹ is assigned to the A1g fundamental, where all the four C-O bonds of oxalate are stretched or compressed simultaneously.

(b) Band at 884 cm⁻¹

The Raman band at 884 cm⁻¹ is assigned to V_{C-C} stretching frequency.

Formate:

(a) Band at 1357 cm⁻¹

The strong band at 1357 cm⁻¹ is assigned to V symmetric CO2 mode.

(b) Band at 1072 cm⁻¹

The weak band at 1072 is assigned to C-H bending (B2) mode.

(c) Band at 770 cm⁻¹

The medium intensity band at 770 cm⁻¹ is assigned to CO2 bending mode (A1).



Figure S2. Raman spectra of sodium formate to sodium oxalate conversion promoted by 10% NaH catalyst. (a) spectrum of sodium formate at room temperature, (b) spectrum of the product after reaction at 350°C, and (c) spectrum of an authentic sample of sodium oxalate. The peak at 1076 cm⁻¹ is assigned to the proposed intermediate for the reaction, carbonite ion.



Figure S3. Raman spectra for the formate to oxalate thermal conversion process as a function of the hydride ion concentration. The spectra shown are post-reaction, after the hydrogen evolution ceases. The intensity of the Raman band at 1076 cm⁻¹ increases as a function of sodium hydride concentration (2%, 10% and 25% sodium hydride by mass). This peak at 1076 cm⁻¹ is assigned to the intermediate, carbonite ion.



Figure S4. Raman spectra of 1:1 mole ration sample of sodium formate and sodium hydride. (top) spectrum of the mixture at room temperature, showing peaks from formate and the hydride, (middle) spectrum of the product after reaction at 350°C, showing the carbonite peak and the residual hydride peaks and (bottom) spectrum obtained upon the reaction of the carbonite sample with water at room temperature showing the formation oxalate and a drastic decrease in concentration of the carbonite peak.

DFT Raman Spectra:

In order to identify the reaction intermediates and confirm the mechanism proposed in Fig. 2 and 3, we compared the post reaction Raman spectrum to the spectra predicted by DFT. Panel A and E show that DFT reliably predicts Raman spectra for the standard sodium formate and sodium oxalate compounds. According to an extensive DFT analysis, the peak at 1076 cm⁻¹ can be assigned to the carbonite dianion (Panel B). Alternatively, a similar band (panel C) arises from the reaction intermediate I₇ (Figure 3, main text). Panel D shows that sodium carbonate cannot be either the intermediate or a product of the reaction.



Frequency, cm⁻¹

Figure S5. DFT simulated spectra (in color) of sodium formate (A), carbonite dianion (B), I₇ reaction intermediate (C), sodium carbonate (D) and sodium oxalate (E) compared to experimental spectra (grey). A and E are compared to the corresponding standards, B-D are compared to the post-reaction experimental Raman spectrum.

Species	Experimental (cm ⁻¹)	Theoretical (cm ⁻¹)
Oxalate	1457	1444
Oxalate	884	896
Formate	1357	1360
Formate	1072	1090
Formate	770	781
Carbonite	1075	1091

Comparison of experimental and theoretical peak positions:

Section 3: Thermal Reaction Experimental Details

The thermal reactions were explored by using a Thermo Scientific Thermolyne Benchtop Muffle Furnace that could reach a maximum temperature of 1200°C. Reactions were performed under a flowing N₂ atmosphere by introducing N₂ gas through a vent port since oxygen lowers the yield of oxalate formed. A series experiments were designed using reaction temperature, reaction time and the amount of catalyst as the reaction condition variables to obtain the best possible yields. A typical bench-scale reaction was conducted using a 4.0 g. formate sample placed into a 50 mL nickel crucible and calcined between 300 - 480°C. All chemicals were reagent grade obtained from Sigma Aldrich including NaOH, sodium hydride, KOH, sodium and potassium formate, sodium and potassium oxalate, sulfuric acid, and potassium permanganate (J. T. Baker). The catalyst (e.g., NaH, NaOH, KOH) in weighed amounts of 2.5% by mass were mixed thoroughly using a mortar and pestle in a nitrogen glove box. The quantitative analysis of oxalate formation was performed by volumetric titrations using standardized KMnO₄ solutions^[11,12] as well as by ion chromatography methods for the analysis of formate and oxalate.

A comparison between NaH and NaOH catalysts at the same temperature is shown in the publication. We have not investigated potassium hydride due to its very high reactivity with air. However, we have carried out a comparison between NaH and KOH at 440 oC wherein we have best possible yields of oxalate for the potassium hydroxide catalyst. Comparison of Sodium and Potassium Formate at 440 °C, 2.5% by mass catalyst

Sodium Formate + Hydride Catalyst									
Sample	Reaction Time (m)	Oxalate	Average						
1	3.75	89%							
2	3.75	84%	86%						
3	3.75	85%							
Potassium Formate + Hydroxide Catalyst									
Sample	Reaction Time (m)	Oxalate	Average						
1	30	80%							
2	30	73%	75%						
3	30	72%							

In summary the NaH, NaHCO₂ reaction is nearly eight times as fast as the KOH, KHCO₂ reaction at 440 °C, and NaH reaction gives better yields.

Section 4: REFERENCES

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