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To be cited as: *ChemCatChem* 10.1002/cctc.201600765

Link to VoR: http://dx.doi.org/10.1002/cctc.201600765

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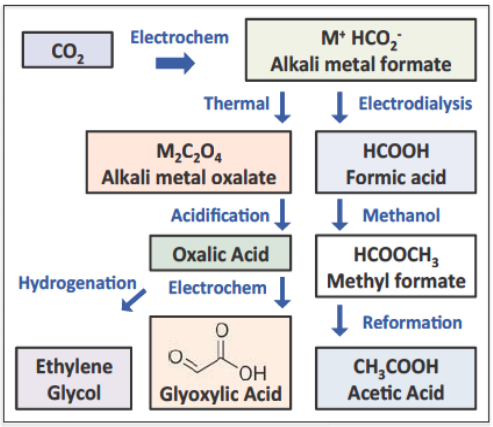
Formate to Oxalate: A Crucial Step for Conversion of CO_2 into Multi-carbon Compounds

Prasad S. Lakkaraju*, Mikhail Askerka, Heidie Beyer, Charles T. Ryan, Tabbetha Dobbins, Christopher Bennett, Jerry J. Kaczur, and Victor S. Batista*

Abstract: *Efficient conversion of formate into oxalate could enable the industrial-scale synthesis of multi-carbon compounds from CO_2 by C-C bond formation. We find conditions for highly selective catalytic conversion of molten alkali formates into pure solid oxalate salts. Nearly quantitative conversion is accomplished by calcination of sodium formates with sodium hydride. A catalytic mechanism through a carbonite intermediate, generated upon H_2 evolution, is supported by density functional theory (DFT) calculations, Raman spectroscopy and the observed changes in catalytic performance upon changing the nature of the base, or reaction conditions. While the formate to oxalate conversion using hydroxide ion catalyst has been studied before, the hydride ion catalysis and the chain reaction mechanism for the conversion involving carbonite ion intermediate are being reported for the first time.*

The production of chemicals and fuels from CO_2 could provide viable solutions to challenges of global relevance. Reducing the amount of CO_2 in the atmosphere could mitigate global warming. Converting CO_2 into fuels could produce carbon-neutral renewable fuels for energy storage, while synthesizing multi-carbon chemicals from CO_2 could enable the sustainable production of precursors or feed stocks for organic synthesis.[1,2] Therefore, there is great interest in the conversion of CO_2 into formate and oxalate products.[3-10] However, economically viable and environmentally benign methods are yet to be established. Outstanding challenges include Faradaic efficiency, electrocatalyst stability, product selectivity, isolation and purification of the products.

Over the past six years, research at Liquid Light Inc. (LL) has been focused on the development of electrochemical and chemical methods for the conversion CO_2 into value added products on a large scale.[11-14] Scheme 1 illustrates some of the pathways of interest for bulk synthesis of C_2 compounds from CO_2, relying upon conversion of formate to oxalate, including synthetic routes for production of highly utilized chemicals such as ethylene glycol and glyoxylic acid. The pathways are particularly attractive since an efficient method for generation of alkali metal formates by electrochemical reduction of CO_2 has been demonstrated.[11] Specifically, potassium and sodium formates are produced with Faradaic efficiencies >60% in 100 cm^2 cells, with current densities as high as 120 mA cm^{-2} and cell potentials lower than 4 Volts.[11,12] The alkali metal formate salts may be converted to formic acid by either electrodialysis or electrochemical acidification (Scheme 1).



Scheme 1. *Conversion of CO_2 into value-added products.*

While formic acid has been explored as a fuel and in applications to commercial chemistry, the development of viable synthetic routes to generate C2 and higher order carbon compounds from formate salts remains an outstanding challenge. In this communication, we report a highly useful catalytic conversion of formates into oxalates:

$$2\,NaHCO_2(l) \xrightarrow[\Delta]{cat} Na_2C_2O_4(s) + H_2(g) \qquad (1)$$

with high selectivity for C-C coupling chemistry achieved by calcination with alkali hydroxide, or hydride catalysts. The two main products $H_2(g)$ and $Na_2C_2O_4(s)$ are spontaneously separated, making the synthetic process simple and practical when by-products such carbon monoxide and carbonates are curtailed, as in a recently disclosed integrated process.[13,14]

The conversion of formate into oxalate has been a long-standing challenge.[15-24] Thermal approaches were explored[16] and factors determining the conversion efficiency into oxalates and other by-products were analysed by using varying amounts of sodium hydroxide, under various temperatures and partial vacuum conditions.[17] Products of decomposition including carbonates, oxalates, CO and CO_2 were determined from dynamic thermo-analytical analysis of thermal decomposition of $LiHCO_2$, $NaHCO_2$, $KHCO_2$, $RbHCO_2$ and $CsHCO_2$.[18] However, conditions for achieving high product yields have yet to be established. For example, Baraldi[19] analyzed the IR spectra of twelve metal formates under heating in air at atmospheric pressure, and under a dynamic vacuum of 10^{-2} Torr. Formation of oxalate was suggested by IR features when formate was heated in vacuum at 300°C. However, decomposition into carbonate was observed at 475°C.

Górski[20,21] explored the influence of gaseous and solid reactants on the yields of oxalates and carbonates, during thermal

[*] J.J. Kaczur
Liquid Light, Inc.
11 Deer Park Drive, Suite 121
Monmouth Junction, NJ, 08852
Email: jkaczur@LLchemical.com

Prof. P. Lakkaraju, Heidie Beyer, Charles T. Ryan
Chemistry & Biochemistry Department
Georgian Court University
900 Lakewood Ave, Lakewood, New Jersey 08701
Email: Lakkaraju@georgian.edu

Dr. Tabbetha Dobbins, Christopher Bennett
Department of Physics, Rowan University
201 Mullica Hill Road, Glassboro, NJ 08028

M. Askerka, Prof. V. S. Batista
Department of Chemistry, Yale University
225 Prospect St, New Haven, Connecticut 06520-8107
Email: victor.batista@yale.edu

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decomposition of $LiHCO_2$, $NaHCO_2$ and $KHCO_2$. Addition of $NaBH_4$ to $NaHCO_2$ resulted in 88% conversion yield, which declined to 0% conversion when using a 1:1 molar ratio. Thus, reaction conditions for quantitative yields have not reported. In addition the underlying reaction mechanism remains uncertain. While Górski proposed oxalate formation upon decomposition of formate, as follows:

$$2HCO_2^- \rightarrow CO_2 + CO_2^{2-} + H_2 \quad (2)$$

$$CO_2 + CO_2^{2-} \rightarrow C_2O_4^{2-} \quad (3)$$

It remains to be explored whether such a reaction, or an alternative mechanism, is consistent with theoretical studies and direct comparisons with experimental measurements, as reported below.

Reaction Times and Product Yields: We find reaction conditions for the best yield conversion of formate into oxalate when alkali formate salts are melted at high temperatures in the presence of a strong base, such as NaH or NaOH by varying both the catalyst amount and the temperature. A porous solid, self-rising NaC_2O_4 is produced with hydrogen gas evolved as a by-product. DFT calculations support a mechanism based on a hydride catalytic pathway (Figure 1), consistent with Raman spectroscopy and the observed changes in reaction times and product yields produced by changing the base (e.g., NaH or NaOH) or the reaction conditions. In particular, the reaction times are much shorter for the stronger base (NaH) than for NaOH at the same temperature. These observations are consistent with a rate-limiting step due to the primary deprotonation of formate upon H_2 evolution, followed by C-C bond formation (*vide infra*).

Table 1 (NaOH) reports the product yields obtained for different reaction times with NaH and NaOH. We find nearly quantitative conversion into oxalate for NaH and yields >80% with NaOH at 390°C but negligible conversion at lower temperatures (330 - 350°C).

Table 1. *Formate to oxalate conversion yields, obtained by using NaH and NaOH as a catalyst for various experimental conditions of temperature and reaction times under a N_2 atmosphere.*

Catalyst	Sample Number	Temp °C	Calcination Time, min.	Cat Wt%	Oxalate % Yield (±1%)
NaH	1	390	10	2	92
	2	390	10	2	99
	3	390	8	2	93
NaOH	1	390	20	2.5	74
	2	390	30	2.5	68
	3	390	40	2.5	86
	5	350	15	0	0.9
	6	350	30	0	0.5

Shorter reaction times, higher product yields and superior quality of the oxalate product are obtained when using NaH as a catalyst (Table 1, NaH). In contrast, NaOH catalyzed reactions typically yielded a mixture of products, including oxalate, carbonate, carbon monoxide and hydrogen. The maximum oxalate yield, obtained with NaOH, was about 80%, including as much as 10% of carbonate. The reaction times were typically 4 times longer for NaOH when compared to the NaH. When the formate to oxalate conversion is carried out using NaH or NaOH at temperatures >420C, charring of the sample occurs affecting the quality of the product.

In addition, we find that the nature of the alkali metal ion significantly affects the product yield and optimum reaction conditions. For comparison shown in Table 2 reports the product yields obtained with (or without) KOH by calcination at 420-480°C for various reaction times. Clearly, KOH increases the yield obtained at 420-440°C, although it requires higher temperature than NaOH, or NaH, to obtain yields >75%. At higher temperatures (>500 °C) the reaction yields are not affected by the addition of a catalyst and the reaction times are significantly reduced, even without addition of a catalyst base.

Table 2. *Formate to oxalate conversion yields, obtained by using KOH as a catalyst for various reaction times at 420-520°C under a N_2 atmosphere.*

Sample Number	Temp °C	Calcination Time (min)	KOH Wt% Added	% Yield to Oxalate (±1%)
1	420	30	0	8
2	420	30	5	76
3	420	30	8	74
4	420	45	8	74
5	420	60	5	78
6	440	30	0	14
7	440	30	8	77
8	440	60	5	78
9	480	30	0	73
10	480	30	2	76
11	520	5	0	71

Formate to Oxalate Conversion Mechanism: DFT calculations support a simple mechanism (Figure 1), initiated by hydrogen evolution and formation of the carbonite (CO_2^{2-}) intermediate, upon reaction of formate with the hydride catalyst. Carbonite reacts with formate to produce oxalate by C-C bond formation, regenerating the hydride catalyst.

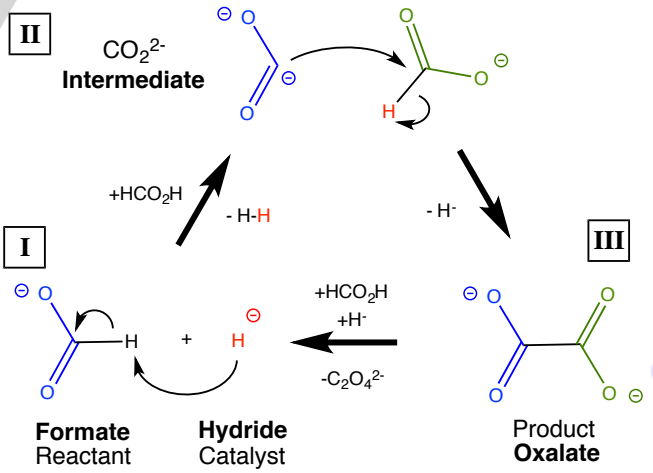

Figure 1. Catalytic conversion of formate to oxalate. Using the hydride base, one mole of the formate is converted to a carbonite ion (blue color) that nucleophilically attacks the second mole of formate, releasing the hydride catalyst.

We probed the catalytic thermal conversion of formate into oxalate by Raman spectroscopy at 350°C (*i.e.*, the highest temperature allowed by our variable temperature system). As the reaction proceeded, we monitored the bands at 1357 cm^{-1}, 1072 cm^{-1} and 770 cm^{-1} (see Supplemental material), assigned

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to the CO_2 symmetric stretch, formate C-H bending and CO_2 bending, respectively. Simultaneously, two bands emerged at 1457 cm^{-1} and 884 cm^{-1} assigned to the oxalate C-O symmetric stretch and oxalate C-C stretch, respectively. The bands observed for products were identical to those observed for an authentic sample of sodium oxalate.

The experimental Raman peak at 1076 cm^{-1} was assigned to the O-C-O symmetric stretch of the carbonite intermediate, supported by DFT calculations (Supporting Information) and with the steady-state concentration of carbonite established during the course of the catalytic reaction upon continuous purging of H_2(g) with N_2(g) in the variable temperature system. Another observation that supports the assignment to carbonite is that the intensity of the 1076 cm^{-1} band diminishes upon exposure of the sample to air or water, enhancing the intensity of the oxalate bands. The 1076 cm^{-1} intensity also correlates with hydrogen evolution during the course of the reaction and increases when increasing the concentration of the hydride catalyst, as expected for an increased steady state concentration of carbonite.

The formation of oxalate from the reaction of carbonite with water (Table 3, k) is likely spontaneous because of a large negative reaction Gibbs free energy predicted by DFT. We are conducting additional Raman spectroscopy studies on the reaction using ^2H and ^{13}C isotope enriched formate samples, and the results of these investigations will be reported in a future publication.

The temperature dependence of the reaction rates, shown in Figure 2, allowed for estimation of the activation enthalpy and activation entropy, according to the Eyring-Polanyi equation. The slope of the plot (Figure 2) yields an activation enthalpy of 41 kcal mol^{-1} and the intercept corresponds to activation entropy of -6 cal K^{-1} mol^{-1}. As discussed below, these results are fully consistent with the mechanism introduced in Figure 1, as supported by DFT calculations of the reaction free energy profile and direct comparisons to experimental data.

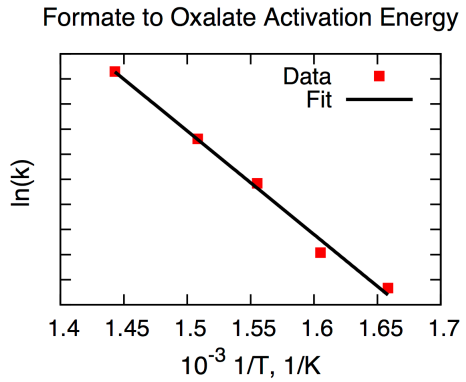

Figure 2. Eyring-Polanyi graph for thermal conversion of sodium formate to sodium oxalate in the 330 - 420°C temperature range, using sodium hydride as a catalyst base (2.5% by mass).

DFT exploration of low free energy pathways supports the proposed reaction mechanism, shown in Figure 1, as indicated by the thermodynamics of elementary steps summarized in Table 3 (details of the DFT methodology are given in the Supporting information).

We first analyzed the thermodynamics of formate to oxalate conversion in terms of the simplest possible mechanism, the direct reaction of two formate ions in the absence of the catalyst base (Table 4, a). We found that while the reaction is certainly thermodynamically feasible, it is kinetically hindered (with a high-energy barrier >70 kcal mol^{-1}) when leading to H_2 evolution through a single transition state. Oxalate formation according to (2) and (3), as suggested by Gorski [20,21], (Table 3, i and j) was also found to be thermodynamics unflavored due to the decomposition of formate into carbonite and carbon dioxide (Table 3, i). Therefore, alternative reaction pathways were explored, including the pathway outlined in Figure 1 where the catalyst plays an important role.

Table 3. Reaction free energies (kcal mol^{-1}) in aqueous solution for various possible elementary steps associated with formate to oxalate conversion.

	Reaction	ΔG_r No ion	Na^+	K^+
a)	$2HCO_2^- \rightarrow C_2O_4^{2-} + H_2$	8	-1	2
a^{TS})	$2HCO_2^- \rightarrow [TS_1]^{\neq} \rightarrow C_2O_4^{2-} + H_2$	--	70	72
b)	$HCO_2^- \rightarrow OH^- + CO$	21	21	25
c)	$HCO_2^- \rightarrow H^- + CO_2$	35	33	35
d)	$HO^- + HCO_2^- \rightarrow H_2O + CO_2^{2-}$	52	33	30
e)	$H^- + HCO_2^- \rightarrow H_2 + CO_2^{2-}$	32	15	14
e^{TS})	$H^- + HCO_2^- \rightarrow [TS_2]^{\neq} \rightarrow H_2 + CO_2^{2-}$	35*	28	26
f)	$HCO_2^- + CO_2^{2-} \rightarrow H^- + C_2O_4^{2-}$	-26	-18	-14
g)	$OH^- + 2HCO_2^- \rightarrow H_2O + H^- + C_2O_4^{2-}$	26	16	16
h)	$H_2O + H^- \rightarrow H_2 + OH^-$	-18	-16	-14
i)	$2HCO_2^- \rightarrow CO_2 + CO_2^{2-} + H_2$	69	50	53
j)	$CO_2 + CO_2^{2-} \rightarrow C_2O_4^{2-}$	-61	-51	-49
k)	$2CO_2^{2-} + 2H_2O \rightarrow C_2O_4^{2-} + 2OH^- + H_2$	-95	-67	-58

The proposed mechanism is consistent with the various outcomes under different experimental conditions. We note that a small amount of oxalate is obtained at 420°C (8% yield) even without addition of any kind of catalyst base, and higher yields (>70%) are produced without catalyst at higher temperatures (>480°C) (Table 2). However, at the lower temperatures (e.g., 420°C), obtaining significant yields required addition of a base. Also, the resulting product yields are quite different when using NaH, NaOH or KOH (Tables 1 and 2). These observations are all consistent with generation of the base catalyst *in situ* at the higher temperatures (>480°C). In particular, the catalyst base OH^- can be generated by thermal decomposition of formate (Table 3, b). The reaction involves a free energy change of 21 and 25 kcal mol^{-1} for sodium and potassium salts, respectively.

Formation of hydride by thermal decomposition of formate is ruled out since it is thermodynamically a lot more demanding (Table 3,c). However, the hydride catalytic species are readily generated from OH^-, upon reaction with formate (Table 3, g). These results are thus consistent with generation of the hydride catalyst base *in situ* from OH- at high temperatures. Formate to oxalate conversion proceeds according to Figure 1 (Table 3, e and f), after generation of the H^- catalyst. A detailed mechanism is described by the DFT free energy profile, shown in Figure 3.

Figure 3 (top panel) shows that the first step ($\mathbf{I}_1 \rightarrow \mathbf{I}_2$) involves electrostatic complexation of NaH (or KH) with formate. Then, H_2 evolves upon nucleophilic attack of hydride on formate ($\mathbf{I}_2 \rightarrow \mathbf{I}_3$). The transition state TS_1 is reached through rotation of the sodium (or potassium) hydride fragment, which relaxes into the weakly bound H_2 + CO_2Na_2 intermediate, $\mathbf{I}_3$. The H_2 fragment

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spontaneously exchanges with formate (I_4), forming the more stable intermediate I_5.

Our calculations of the complete thermodynamic cycle (Supporting Information, Table S1 and Table S2) show that $I_2 \rightarrow TS_1$ is the rate-limiting step for oxalate formation (Table S2), with a barrier of 41.0 kcal mol^{-1} in excellent agreement with the experimental value estimated from the observed temperature dependence (Figure 2).

Figure 3 (top panel) shows that out-of-plane rotation of formate in I_5, brings together the two carbon atoms, forming the transition state TS_2 which forms the C-C bond in the $(OOCHCOO)Na_3$ complex (I_6) before relaxing into the isomeric complex I_7 through a 90° rotation of the O-C-C-O torsion angle and a slight rearrangement of the Na^+ counter ions. The C-H bond is then elongated, forming NaH + $Na_2C_2O_4$ (I_8) through the transition state TS_3. The separation of these electrostatically bound species, upon precipitation of $Na_2C_2O_4$(s) forms I_9 and regenerates NaH for the next turn of the catalytic cycle.

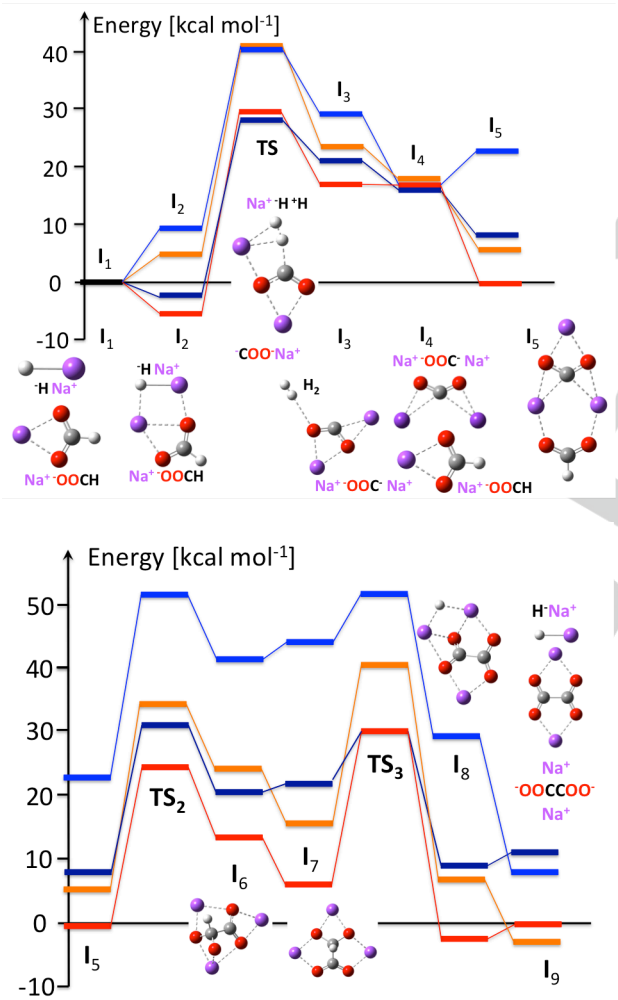

Figure 3. Free energy profile of catalytic conversion of formate to oxalate as salts of sodium (red 663 K, orange 298 K) and potassium (navy 713 K, blue 298 K), computed at the DFT B3LYP level of theory (SI).

Concluding Remarks: We found that quantitative conversion of formate into oxalate can be achieved by simple calcination of molten formate salts in the presence of NaH. DFT calculations support a simple mechanism through a carbonite intermediate, generated upon H_2 evolution by reaction of formate with the catalytic hydride. The mechanism is consistent with thermodynamic parameters, obtained from the temperature dependence analysis and with Raman spectroscopy of the carbonite intermediate. The reported findings are particularly relevant for industrial-scale generation of multi-carbon compounds from CO_2 since formate can be efficiently generated by electrochemical reduction of CO_2.

Further, we are currently investigating the stability and reactivity of carbonite ions by Raman spectroscopy of ^{13}C and ^{2}H enriched samples, and DFT studies. These studies could have significant impact on the utilization of formate as a potential carboxylating reagent via carbonite nucleophile.

Experimental Section

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 N_2 atmosphere by introducing N_2 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 $KMnO_4$ solutions[22,23] as well as by ion chromatography methods for the analysis of formate and oxalate.

Acknowledgements

Georgian Court gratefully acknowledges funding from Liquid Light, Inc. for the undergraduate students who helped conduct the experimental work for this paper. V.S.B. acknowledges the AFOSR grant FA9550-13-1-0020 and high performance computing facilities from NERSC and Yale University.

Keywords: Formate to Oxalate Conversion • Carbon Chain Generation • CO_2 Reduction • Density Functional Theory

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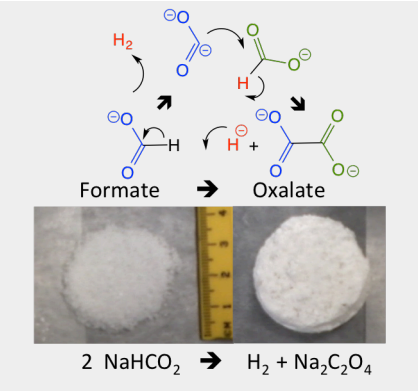

*Author(s), Corresponding Author(s)**

Prasad S. Lakkaraju
Victor S. Batista

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Title

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Text for Table of Contents: *Thermal conversion of formate to oxalate accomplished with quantitative yields by calcination with NaH. The reaction pathway through a carbonite intermediate, generated by upon H_2 evolution is supported by Raman spectroscopy and DFT calculations.*

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