Possible thermal effects in CO₂ reduction electrocatalysis

H-Electrolysis cell with applied potential, 20 min into electrolysis

Increasing IR overlay – thermal imaging by Visual IR Thermometry

The Formation of CO by Thermal Decomposition of Formic Acid under Electrochemical Conditions of CO₂ Reduction

Aidan Q. Fenwick,^a Oana R. Luca^{a§}

[§]*corresponding author*

^a*Joint Center for Artificial Photosynthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States.*

Abstract

We report that the thermal decomposition of formic acid to CO may occur under electrochemically-relevant conditions by mild heating. These thermal effects may play a role in the outcome of electrolytic experiments as an artifact of resistive, local heating and illumination. This non-Faradaic reactivity pathway may therefore need consideration in the analysis of electrochemical data on CO₂ reduction to formic acid and CO and may become a hindrance in scaleup efforts of these chemical transformations. IR visual thermometry provides evidence of macroscopic heating effects during electrolytic experiments.

Keywords: Artificial Photosynthesis, Electrocatalysis, Solar Fuels, CO₂ reduction, Thermal Effects, Non-Faradaic Processes, Formic Acid Decomposition

Introduction

Catalysis for the formation of chemical fuels from abundant carbon sources such as CO_2 is now the focus of major efforts [1, 2]. Efficient solar-driven transformations will require significant technological development and some the main challenges in the field have been recently reviewed [3]. This paper describes a series of model studies of formic acid (HCOOH) conversion to carbon monoxide (CO) under electrochemically-relevant conditions with heating. As CO has been shown to be a key intermediate product in electrocatalytic CO_2 reduction [4], we now propose non-Faradaic contributions to CO formation in electrocatalytic systems on the basis of our preliminary observations reported here.

Thermal effects in catalytic processes have been extensively studied in both academic and industrial settings [5] and although they directly affect the rate of a chemical process, they have also been shown responsible for changes in composition of catalyst and drastically alter reaction profiles and intermediates [6]. A large class of such thermal studies are aimed at microwave-induced chemistry where the focus is on local heating effects, as has been described elsewhere.[7] Of relevance to Artificial Photosynthesis, a recent study has now modeled the temperature-dependence of a photoelectrochemical water-splitting device and has shown that a likely operating temperature for an integrated device is around 80°C , thus raising the question of the effect of temperature in the development of device-relevant catalytic processes for the reduction of CO_2 . [8]

Modern research in the field of electrocatalysis, whether at a fixed applied potential or under controlled current conditions, is typically run at ambient temperature and pressure. These electrolyses generally occur in a cell with a separator between the anode and cathode, as recombination of oxidized and reduced products would lead to unproductive chemistry, as well as possible safety problems if O_2 is formed along with H_2 . [9] This separator can either be a proton-conducting membrane, in the case of some aqueous electrolytes [10, 11], but more often in the case of non-aqueous media, the separator is a glass or ceramic frit [12-15]. As such, the separator necessarily introduces resistive effects in the electrochemical cell, which although most times compensated for, may generate thermal effects that as yet remain unexplored.

Results and Discussion

Two of the most common products in the electrocatalytic reduction of CO₂, particularly in the field of molecular catalysis are carbon monoxide (CO, Eq 1) and formic acid (HCOOH, Eq 2), both being accessed through reduction of CO₂ by 2 H⁺ + 2 e⁻. [13, 16-21]

Product analyses of electrolysis experiments often indicate productive pathways of CO₂ reduction to *both* CO and HCOOH. [16-18, 22] We now test the hypothesis that CO could be the product of thermal dehydration of a formate or related species at the electrode surface (**Pathway 1**) as a result of its experiencing an as yet unrecognized local ohmic heating effect.

A secondary, but still accessible, thermal decomposition pathway, **Pathway 2** is the disproportionation of HCOOH to H₂ and CO₂, shown to be competitive by having a mere 2.2.kcal higher energy of activation [23]. The present work has been carried out in three organic solvents with NBu₄PF₆ and trifluoromethanol as a proton source, as they are directly relevant to the electrochemical conditions often used in electrocatalytic work in order to test the hypothesis of thermal contributions to CO formation from thermal decomposition of formic acid.

We therefore assembled all of the components of an electrochemical experiment: solvent, supporting electrolyte, proton source and added formic acid in order to examine their possible decomposition under thermal conditions to mimic electrode-heating effects, but in the absence of any applied potential or current flow. The samples were heated for two hours in round-bottom flasks, under N₂ and the reaction headspace was then sampled and analyzed *via* GC-TCD (details in the methods section). We now report the formation of CO in the presence of all the components of this electrochemical system as detailed below.

Table 1. Results of thermal-induced formic acid decomposition in acetonitrile after 2 hours at 50 °C under N₂ .

Entry	Comment	μ moles CO formed	μ moles H ₂ formed
1	6 mL acetonitrile /trifluoroethanol 4:1 v:v), 5 mL formic acid (FA) and 0.2 M NBu ₄ PF ₆	216 ± 3.2%	0.46 ± 8.2%
2	6 mL acetonitrile/trifluoroethanol 4:1 v:v), 5 mL formic acid (FA) and no NBu ₄ PF ₆	177 ± 6.3%	0.84 ± 18%
3	6 mL acetonitrile and 5 mL FA, no trifluoroethanol, no NBu ₄ PF ₆	188 ± 4.4%	0.59 ± 14%
4	5.6 mL acetonitrile, 5 mL FA, 0.4 mL water and 0.2M NBu ₄ PF ₆ , no trifluoroethanol, water as proton source	198 ± 13.3%	0.77 ± 10%
5	5 mL FA and 6 mL water	0	0.85 ± 15%

Before we proceeded with our analyses, we first wanted to account for any contributions from dissolved gases under our conditions. We were happy to observe that under our conditions, no dissolved gases were detectable by NMR spectroscopy of the liquid phases. No H₂ was observed by ¹H NMR in our conditions and no ¹³CO was detected in the thermal decomposition control of H¹³COOH by ¹³C NMR after heating at 50° C for two hours (SI for details).

Table 1 summarizes our formic acid decomposition results in acetonitrile as analyzed by sampling of the headspace above a volume-calibrated reaction vessel. After heating 6 mL solution acetonitrile/trifluoroethanol 4:1 (v:v), 5 mL formic acid and 0.2 M NBu₄PF₆, we observed the formation of 216 μ moles CO in the headspace with only 0.5 μ moles H₂ present (Entry 1), thus indicating **Pathway 1** is preferred in the presence of all the components of an electrochemical experiments under thermal conditions by **orders of magnitude**. A similar set of conditions were used in Entry 4, but with water, a weaker proton source instead of trifluoroethanol. Although a comparable amount of CO was observed in this case, the contributions from **Pathway 2** are significantly enhanced, the ratio of observed products for **Pathway 1** over **Pathway 2** now **being greatly reduced**. Interestingly, the absence of salt additive (Entry 2) and of proton source (Entry 3) produce a similar amount of CO, with H₂ production slightly enhanced in the presence of water as a proton source (0.59 vs 0.77 μ moles). A control experiment was performed under the standard conditions with only 5 mL HCOOH and 6 mL water and no CO was observed in that case (Entry 5 Table 1).

Table 2. Results of thermal-induced formic acid (FA) decomposition experiments after 2 hours in tetrahydrofuran (THF) at 50 °C under N₂

Entry	Comment	μ moles CO formed	μ moles H ₂ formed
1	6 mL THF /trifluoroethanol 4:1 v:v), 5 mL formic acid (FA) and 0.2 M NBu ₄ PF ₆	150 $\pm$ 5.8%	0.56 $\pm$ 22%
2	6 mL THF/trifluoroethanol 4:1 v:v), 5 mL formic acid (FA) and no NBu ₄ PF ₆	NA	1.6 $\pm$ 30%
3	6 mL THF and 5 mL FA, no trifluorethanol, no NBu ₄ PF ₆	NA	0.97 $\pm$ 14%
4	5.6 mL THF, 5 mL FA, 0.4 mL water and 0.2M NBu ₄ PF ₆ , no trifluoroethanol, water as proton source	150 $\pm$ 2.2%	0.64 $\pm$ 36%

Table 2 summarizes our results in tetrahydrofuran (THF). In contrast with the observations in acetonitrile, the differences between the two decomposition pathways in the presence of different proton sources are no longer observed. Both pathways show a similar amount of CO formed (150 μ moles in both Entries 1 and 4)) as well as a similar amount of H₂ (0.56 and 0.64 μ moles for Entries 1 and 4 respectively). Surprisingly, in the absence of NBu₄PF₆ electrolyte, no CO formation was observed after the two hours of heating, with slightly more H₂ formed when trifluoroethanol was present (Entry 2: 1.6 μ moles vs Entry 3: 0.97 μ moles).

Table 3. Results of thermal induced formic acid decomposition in dimethylformamide (DMF) after 2 hours at 50 °C under N₂

Entry	Comment	μ moles CO formed	μ moles H ₂ formed
1	6 mL DMF /trifluoroethanol 4:1 v:v), 5 mL formic acid (FA) and 0.2 M NBu ₄ PF ₆	154 $\pm$ 15%	0.13 $\pm$ 28%
2	6 mL DMF/trifluoroethanol 4:1 v:v), 5 mL formic acid (FA) and no NBu ₄ PF ₆	153 $\pm$ 15%	0.18 $\pm$ 16%
3	6 mL DMF and 5 mL FA, no trifluoroethanol, no NBu ₄ PF ₆	158 $\pm$ 10%	0.16 $\pm$ 31%
4	5.6 mL DMF, 5 mL FA, 0.4 mL water and 0.2M NBu ₄ PF ₆ , no trifluoroethanol, water as proton source	151 $\pm$ 10%	0.58 $\pm$ 20%

Table 3 describes our results in dimethylformamide (DMF). In contrast with the observations in acetonitrile and THF, the formation of H₂ by Pathway 2 is now much less predominant in the presence of all components and in the absence of electrolyte and proton source, the observed molar ratio of CO/H₂

being much higher than in the other solvents. This may likely be due to decreased proton availability in the solvent and competing hydrogen-bonding. We believe that in order to rationalize our results further, a better understanding of ionic dissociation would be necessary in the different solvents. The presence of organic salt at a high concentration likely interferes with the dissociation of formic acid into a formate anion and proton. This effect is pronounced in the ratios of **Pathway 1** vs **Pathway 2** in acetonitrile and THF, but is not as pronounced in DMF, where hydrogen bonding effects may overcome these effects. It is likely that **Pathway 1** is more greatly affected by speciation of ions in solution.

In order to provide supporting evidence of heating effects in electrolysis experiments for CO₂ reduction, we provide a heatmap of a standard H-electrolysis cell under operating conditions. This map was produced using a Visual IR Thermometer. The experiment was set up under the standard conditions of Sampson *et al*[24] with a GC plate as a working electrode and a reticulated vitreous carbon counter electrode in a standard H-Cell during CO production conditions. To the best of our knowledge, this is the first instance of IR thermometry being used to provide evidence of heating effects during electrolysis measurements.

Figure 1. Observed heatmap image overlays of an H electrolysis cell with applied potential during a standard catalytic run for CO₂ reduction with Mn(bpy)(CO)₃⁺. Photographs were taken with a Fluke FT04 Visual IR thermometer. a. Image of electrolysis cell with applied potential with no IR overlay b. Image of electrolysis cell without applied potential at 75% IR, contrast observed c. Image of electrolysis cell with applied potential at 100% IR, significant contrast observed.

Conclusion

In conclusion we now report thermal decomposition of formic acid to CO under electrochemically-relevant conditions in acetonitrile, THF, dimethylformamide and water, all solvents of relevance to electrochemical work on the reduction of CO₂. While not directly modeling a local heating effect and more a macroscopic manifestation of resistive or heating under illumination, the work shows the distinct

formation of CO under the chosen conditions. The observation raises questions regarding chemical speciation and the chemical rates of reaction of intermediates generated under electrochemical conditions as a possible pathway limiting the reduction of CO₂ to a 2e⁻ product. CO may limit the catalytic system either by bonding strongly to the catalyst or possibly leaving the system instead of carrying on to further reduction pathways.

Methods

All reagents were received from commercial sources and used without further purification unless otherwise specified. Solvents were dried by passage through a column of activated alumina followed by storage under dinitrogen. NMR spectra were recorded at room temperature on Varian 400 MHz spectrometers unless otherwise specified. Chemical shifts are reported with respect to residual internal protio solvents for ¹H and ¹³C NMR spectra. NMR Spectra were worked up in MNova 9.1.0-14011.

GC-TCD measurements were performed using an Agilent Technologies 7890A GC system with two TCD detectors and He carrier gas. The oven was held at 50° C for 9 minutes, then the temperature was increased 8°C/min to 80°C with the following column configuration: G3591-81143 0.5m x 1/8", Ultimetel, Hayesep T 80/100 mesh , G3591-81144 0.5m x 1/8", Ultimetel, Hayesep Q 80/100 mesh, G3591-81145 1.5m x 1/8", Ultimetel, Molsieve 13X 80/100 mesh , G3591-81146 1m x 1/8", Ultimetel, Hayesep Q 80/100 mesh , G3591-81149 1m x 1/8", Ultimetel and a Molsieve 5A 60/80 mesh.

Volumes of round bottom flasks were calibrated prior to use. Reactions were set up under atmospheric conditions and degassed with the corresponding inert atmosphere.

Acknowledgements

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993.

Supporting Information

Detailed experimental information and NMR spectra are available in the supplementary information.

References

- [1] D. Gust, D. Kramer, A. Moore, T. A. Moore, and W. Vermaas, "Engineered and artificial photosynthesis: human ingenuity enters the game," *MRS bulletin*, vol. 33, pp. 383-387, 2008.
- [2] J. J. Concepcion, R. L. House, J. M. Papanikolas, and T. J. Meyer, "Chemical approaches to artificial photosynthesis," *Proceedings of the National Academy of Sciences*, vol. 109, pp. 15560-15564, 2012.
- [3] A. Q. Fenwick, J. M. Gregoire, and O. R. Luca, "Electrocatalytic Reduction of Nitrogen and Carbon Dioxide to Chemical Fuels: Challenges as Opportunities for a Solar Fuel Device," *J Photochem Photobiol B: Biology*, 10.1016/j.jphotobiol.2014.12.019.
- [4] K. P. Kuhl, T. Hatsukade, E. R. Cave, D. N. Abram, J. Kibsgaard, and T. F. Jaramillo, "Electrocatalytic Conversion of Carbon Dioxide to Methane and Methanol on Transition Metal Surfaces," *Journal of the American Chemical Society*, vol. 136, pp. 14107-14113, 2014/10/08 2014.
- [5] F. S. Karn, J. F. Shultz, and R. B. Anderson, "Measuring Thermal Effects in Catalytic Reactions," *Industrial & Engineering Chemistry Process Design and Development*, vol. 4, pp. 266-270, 1965/07/01 1965.
- [6] R. J. Farrauto, J. K. Lampert, M. C. Hobson, and E. M. Waterman, "Thermal decomposition and reformation of PdO catalysts; support effects," *Applied Catalysis B: Environmental*, vol. 6, pp. 263-270, 1995.
- [7] A. de la Hoz, A. Diaz-Ortiz, and A. Moreno, "Microwaves in organic synthesis. Thermal and non-thermal microwave effects," *Chemical Society Reviews*, vol. 34, pp. 164-178, 2005.
- [8] S. Haussener, S. Hu, C. Xiang, A. Z. Weber, and N. S. Lewis, "Simulations of the irradiation and temperature dependence of the efficiency of tandem photoelectrochemical water-splitting systems," *Energy & Environmental Science*, vol. 6, pp. 3605-3618, 2013.
- [9] A. Steinfeld and A. Meier, "Solar fuels and materials," *Encyclopedia of energy*, vol. 5, pp. 623-637, 2004.
- [10] W. Grot, "Use of Nafion perfluorosulfonic acid products as separators in electrolytic cells," *Chemie Ingenieur Technik*, vol. 50, pp. 299-301, 1978.
- [11] M. Carmo, D. L. Fritz, J. Mergel, and D. Stolten, "A comprehensive review on PEM water electrolysis," *International Journal of Hydrogen Energy*, vol. 38, pp. 4901-4934, 2013.
- [12] J. Huang, L. Cheng, R. S. Assary, P. Wang, Z. Xue, A. K. Burrell, *et al.*, "Liquid Catholyte Molecules for Nonaqueous Redox Flow Batteries," *Advanced Energy Materials*, 2014.
- [13] D. C. Lacy, C. C. McCrory, and J. C. Peters, "Studies of Cobalt-Mediated Electrocatalytic CO₂ Reduction Using a Redox-Active Ligand," *Inorganic chemistry*, 2014.
- [14] O. R. Luca, D. L. Huang, M. K. Takase, and R. H. Crabtree, "Redox-active cyclopentadienyl Ni complexes with quinoid N-heterocyclic carbene ligands for the electrocatalytic hydrogen release from chemical fuels," *New J. Chem.*, vol. 37, pp. 3402-3405, 2013.
- [15] O. R. Luca, J. D. Blakemore, S. J. Konezny, J. M. Praetorius, T. J. Schmeier, G. B. Hunsinger, *et al.*, "Organometallic Ni Pincer Complexes for the Electrocatalytic Production of Hydrogen," *Inorganic Chemistry*, vol. 51, pp. 8704-8709, 2012/08/20 2012.
- [16] C. Costentin, S. Drouet, M. Robert, and J.-M. Savéant, "A local proton source enhances CO₂ electroreduction to CO by a molecular Fe catalyst," *Science*, vol. 338, pp. 90-94, 2012.

- [17] A. M. Herring, B. D. Steffey, A. Miedaner, S. A. Wander, and D. L. DuBois, "Synthesis and characterization of water-soluble [Pd (triphosphine)(CH₃CN)](BF₄)₂ complexes for CO₂ reduction," *Inorganic Chemistry*, vol. 34, pp. 1100-1109, 1995.
- [18] H. Ishida, K. Tanaka, and T. Tanaka, "Electrochemical CO₂ reduction catalyzed by ruthenium complexes [Ru(bpy)₂(CO)₂]²⁺ and [Ru (bpy)₂(CO) Cl]⁺. Effect of pH on the formation of CO and HCOO⁻" *Organometallics*, vol. 6, pp. 181-186, 1987.
- [19] A. J. Morris, G. J. Meyer, and E. Fujita, "Molecular approaches to the photocatalytic reduction of carbon dioxide for solar fuels," *Accounts of chemical research*, vol. 42, pp. 1983-1994, 2009.
- [20] E. Fujita, "Photochemical carbon dioxide reduction with metal complexes," *Coordination chemistry reviews*, vol. 185, pp. 373-384, 1999.
- [21] E. E. Benson, C. P. Kubiak, A. J. Sathrum, and J. M. Smieja, "Electrocatalytic and homogeneous approaches to conversion of CO₂ to liquid fuels," *Chemical Society Reviews*, vol. 38, pp. 89-99, 2009.
- [22] M. Azuma, K. Hashimoto, M. Hiramoto, M. Watanabe, and T. Sakata, "Electrochemical Reduction of Carbon Dioxide on Various Metal Electrodes in Low-Temperature Aqueous KHCO₃ Media," *Journal of the Electrochemical Society*, vol. 137, pp. 1772-1778, 1990.
- [23] J. S. Francisco, "A comprehensive theoretical examination of primary dissociation pathways of formic acid," *The Journal of Chemical Physics*, vol. 96, pp. 1167-1175, 1992.
- [24] J. M. Smieja, M. D. Sampson, K. A. Grice, E. E. Benson, J. D. Froehlich, and C. P. Kubiak, "Manganese as a Substitute for Rhenium in CO₂ Reduction Catalysts: The Importance of Acids," *Inorganic Chemistry*, vol. 52, pp. 2484-2491, 2013/03/04 2013.

Figure 1