Acknowledgment. We would like to acknowledge the help of Drs. Gwen Bauman, Asbed Vassilian, and Bruno van Hemelryck in the early stages of this work. We also gratefully acknowledge the support of the National Institutes of Health by Grant GM 26234. S.S.I. is the recipient of a National Institutes of Health Career Development Award (AM 00732) (1980–1985) and a Camille and Henry Dreyfus Teacher–Scholar Award (1981–1985).

Effective Photoreduction of CO_2/HCO_3^- to Formate Using Visible Light

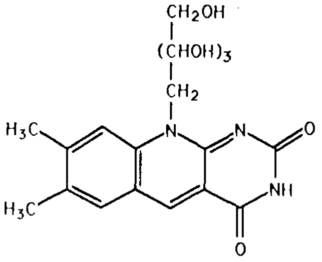
Daniel Mandler and Itamar Willner*

Department of Organic Chemistry
The Hebrew University of Jerusalem
Jerusalem 91904, Israel

Received April 6, 1987

Photoreduction of CO_2 and its aqueous forms to organic products is a challenging subject as a means of mimicking photosynthesis and solar energy conversion and storage.[1,2] Photoreduction of CO_2 to formate has been reported with use of homogeneous catalysts,[3] semiconductor powders[4] or electrodes,[5] and the enzyme formate dehydrogenase.[6] Recently, we were able to photoreduce CO_2 to methane,[7] although in low yields. Electrocatalyzed reductions of CO_2 have been extensively studied,[8,9] but these do not occur at the thermodynamic potential for formate formation. Wrighton et al. have examined[10] the reduction of HCO_3^- to formate by hydrogen and the electroreduction of HCO_3^-, in the presence of various supported palladium catalysts, in which effective formate production has been accomplished at room temperature close to the thermodynamic potential. Interestingly, the photosensitized reduction of CO_2/HCO_3^- using Pd-based heterogeneous catalysts has not been reported. Here we wish to report on the design of a novel heterogeneous Pd colloid stabilized by β-cyclodextrin (β-CD)[11] and its application in the effective reduction of CO_2/HCO_3^- to formate. High quantum yields, $\phi = 1.1$ are reported for formate production. We find that the β-CD support strongly affects the catalyst activity.

Photoreduction of *N,N'*-dimethyl-4,4'-bipyridinium salt, methyl viologen, MV^{2+}, with various sensitizers and sacrificial electron donors, has been extensively explored in recent years.[12,13] Krasna has found[14] that deazariboflavin, dRFl (**1**), acts as an effective photosensitizer for the reduction of MV^{2+}. For example, in the presence of oxalate as electron donor, $MV^{\bullet+}$ is photogenerated in quantum yields $\phi > 1$. Comparison of the reduction potential of $MV^{\bullet+}$ ($E°(MV^{2+}/MV^{\bullet+}) = -0.45$ V vs NHE[15]) to the thermodynamic potential for formate formation ($E°(HCO_3^-/HCO_2^-) = -0.42$ V vs NHE,[16] at pH 7) suggests that the thermodynamic balance for the process outlined in eq 1 corresponds to $\Delta G° \approx$



1

$$2M\;{}^{\bullet+} + HCO_3^- + 2H^+ \rightleftharpoons 2MV^{2+} + HCO_2^- + H_2O \qquad (1)$$

0. [illegible] us, by the light-driven generation of $MV^{\bullet+}$ high concent[illegible] s of formate could, in principle, be accumulated. Yet, this [illegible] is kinetically unfavored, and no formate is formed in [illegible] that include CO_2/HCO_3^- and photogenerated $MV^{\bullet+}$. [illegible] ind that Pd supported on β-CD acts as an effective catalyst [illegible] photoreduction of CO_2/HCO_3^-, by $MV^{\bullet+}$. The system [illegible] nposed of an aqueous sodium bicarbonate solution (3 mL), [illegible], that included deazariboflavin, dRFl (**1**), as photosensitizer, 8 [illegible] $^{-5}$ M, MV^{2+}, 2×10^{-3} M, as primary electron acceptor, a[illegible] xalate as sacrificial electron donor, 0.06 M. Pd-β-CD colloid (30 mg·L^{-1}) was added to the solution, and CO_2 was bubbled through the system (final pH 6.8). Illumination of the system (λ > 400 nm), at 30 °C, results in the formation of formate, HCO_2^-, and trace amounts of hydrogen. Figure 1 shows the rate of HCO_2^- and H_2 formation at time intervals of illumination.[17] The quantum yields correspond to $\phi(HCO_2^-) = 1.1$ and $\phi(H_2) = 0.03$. Control experiments reveal that in the absence of CO_2/HCO_3^- the major photoproduct is H_2 (eq 2), $\phi = 0.12$, and

$$2MV^{\bullet+} + 2H^+ \xrightarrow{\text{Pd-}\beta\text{-CD}} 2MV^{2+} + H_2^{\bullet} \qquad (2)$$

only trace amounts of HCO_2^- are formed by in situ generation of CO_2 by the oxidation of oxalate (vide infra). Also, in the absence of the Pd-β-CD colloid no HCO_2^- or H_2 are produced, and $MV^{\bullet+}$ is the only photoproduct, $\phi(MV^{\bullet+}) \approx 3.5$. Illumination of an aqueous system that includes dRFl (**1**), MV^{2+} as electron acceptor, oxalate as electron donor, and a Pt colloid stabilized by β-CD results in the formation of H_2, and no formate is formed. These results clearly indicate that formate is not formed by the sacrificial oxidation of oxalate and that Pd-β-CD is a specific catalyst for the photoreduction of CO_2/HCO_3^- to formate.[18] Comparison of the amount of photogenerated formate to the

---

[1] (a) Inoue, S.; Yamazaki, N. *Organic and Bio-organic Chemistry of Carbon Dioxide*; Kodansha Ltd.: Tokyo, Wiley: New York, 1982. (b) Ziessel, R. *Nouv. J. Chim.* **1983**, *7*, 613.

[2] (a) Keene, F. R.; Creutz, C.; Sutin, N. *Coord. Chem. Rev.* **1985**, *64*, 247. (b) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 56. (c) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536. (d) Kitamura, N.; Tazuke, S. *Chem. Lett.* **1983**, 1109.

[3] Ziessel, R.; Hawecker, J.; Lehn, J.-M. *Helv. Chim. Acta* **1986**, *69*, 1065.

[4] (a) Aurian-Blanjeni, B.; Halmann, M.; Manassen, J. *Sol. Energy* **1980**, *25*, 165. (b) Halmann, M. *Nature (London)* **1978**, *275*, 115.

[5] Bradley, M. G.; Tysak, T.; Graves, D. J.; Vlachopoulos, N. A. *J. Chem. Soc., Chem. Commun.* **1983**, 349.

[6] Parkinson, B. A.; Weaver, P. F. *Nature (London)* **1984**, 148.

[7] Maidan, R.; Willner, I. *J. Am. Chem. Soc.* **1986**, *108*, 8100.

[8] (a) Russell, P. G.; Kovac, N.; Srinivasan, S.; Steinberg, M. *J. Electrochem. Soc.* **1977**, *124*, 1329. (b) Amatore, C.; Saveant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 5021. (c) Kaiser, V.; Heitz, E. *Ber. Bunsen. Gesell.* **1973**, *77*, 818.

[9] (a) Tezuka, M.; Yajima, T.; Tsuchiya, A. *J. Am. Chem. Soc.* **1982**, *104*, 6834. (b) Slater, S.; Wagenknecht, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5367. (c) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1984**, 328.

[10] (a) Stalder, C. J.; Chao, S.; Summers, D. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 6318. (b) Chao, S.; Stalder, C. J.; Summers, D. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 2723.

[11] The colloid of Pd stabilized by β-CD was prepared by heating a 1.5×10^{-3} M $PdCl_4^{2-}$ solution that included β-CD (1% w/w) at 70 °C for several minutes till the color changed. Heating was continued another 2–3 min. The colloid was then deionized (with Amberlite MB-1) and centrifugated (5000 rpm, 30 min). The mean particle diameter of the colloid was estimated to be 150 Å by electron microscopy measurements. Preparation of metal colloids stabilized by cyclodextrins has been previously reported. Cf. Komiyama M.; Hirai, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2833.

[12] (a) Willner, I.; Ford, W. E.; Otvos, J. W.; Calvin, M. In *Bioelectrochemistry*; Keyzer, H., Gutmann, F., Eds.; Plenum Press: New York, 1980. (b) Moradpour, A.; Amouyal, E.; Keller, P.; Kagan, H. *Nouv. J. Chim.* **1978**, *2*, 547. (c) Kalyanasundaram, K.; Gratzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720.

[13] (a) Amouyal, E.; Zidler, B.; Keller, P. *Nouv. J. Chim.* **1983**, *7*, 725. (b) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.

[14] Krasna, A. I. *Photochem. Photobiol.* **1980**, *31*, 75.

[15] Ito, M.; Kuwana, T. *J. Electroanal. Chem. Interfac. Electrochem.* **1971**, *32*, 415.

[16] Latimer, In *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd ed.; Prentice Hall: New York, 1952.

[17] Formate was analyzed by two complementary methods: ion chromatography (Wescan ion exclusion column, 2×10^{-3} N H_2SO_4 as eluent) and by an enzymatic assay with use of formate dehydrogenase.

[18] At pH ≤ 5 no formate is photogenerated, and the only photoproduct is H_2. This suggests that HCO_3^- is the substrate being reduced to formate rather than CO_2. In the specified systems, pH 6.8, CO_2 is included to maintain constant pH and HCO_3^- concentration.

0002-7863/87/1509-7884$01.50/0

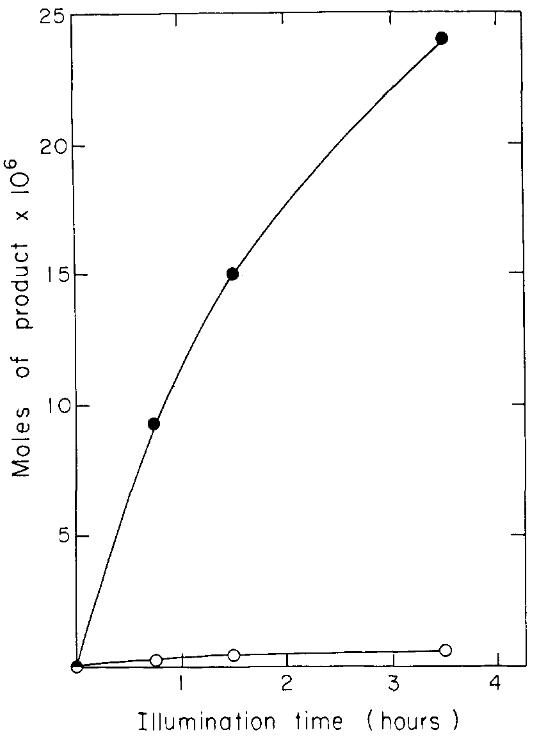


Figure 1. Rate of formate (●) and hydrogen (○) formation as a function of illumination time.

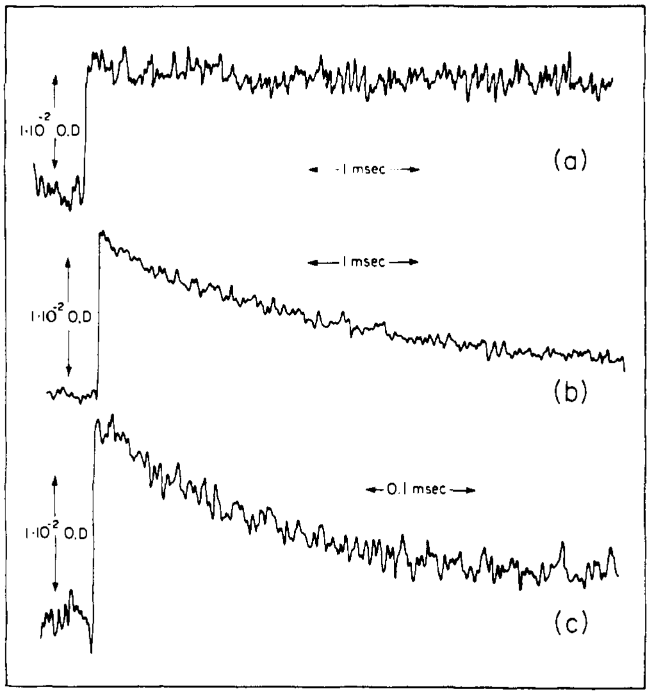


Figure 2. Transient decay of $MV^{•+}$ followed at λ = 602 nm in systems composed of dRFl, 4×10^{-5} M; MV^{2+}, 1×10^{-3} M; and oxalic acid, 6.7 $\times 10^{-2}$ M. (a) Without CO_2/HCO_3^- or Pd-β-CD. (b) Without CO_2/HCO_3^- and with Pd-β-CD (30 mg·L^{-1}). (c) With CO_2/HCO_3^- (6.7×10^{-2} M) and with Pd-β-CD (30 mg·L^{-1}). All systems were adjusted to pH 7 and degassed by either CO_2 (b) and (c) or by Ar (a).

amount of Pd-β-CD catalyst included reveals that the catalyst performs ca. 10 turnovers.

It is evident that the Pd-β-CD colloid is a poor catalyst for H_2 evolution. Comparison of the quantum yields obtained under steady-state illumination of $MV^{•+}$ production to those of HCO_2^- and H_2 formation suggests that the catalytic processes are the rate-limiting steps. Laser flash photolysis studies have confirmed that Pd-β-CD is a superior catalyst for CO_2/HCO_3^- reduction as compared to H_2 evolution (Figure 2). Flashing the system that includes dRFl, MV^{2+}, and oxalate results in the steady-state accumulation of $MV^{•+}$ (Figure 2a) as a result of the photoreduction of MV^{2+}. Addition of Pd-β-CD in the absence of CO_2/HCO_3^- (Figure 2b) induced a slow decay of $MV^{•+}$ due to H_2 evolution. Addition of CO_2/HCO_3^- (Figure 2c) to the system effects a rapid decay of $MV^{•+}$, implying that the rate of CO_2/HCO_3^- reduction is substantially faster than H_2 evolution.

Formate, HCO_2^-, reduces MV^{2+} in the dark in the presence of Pd-β-CD (eq 1). This allows us to examine the catalytic activity of the Pd colloid in the presence of various additives, and particularly in the presence of sacrificial electron donors, by means of the reverse formate decomposition process. We find that common electron donors such as thiols and the photodecomposition products of EDTA (formaldehyde) inhibit the catalytic activity of Pd-β-CD toward formate decomposition. Accordingly, no photoreduction of CO_2/HCO_3^- is observed in the presence of these electron donors. Oxalate does not inhibit the catalytic activity of Pd-β-CD and explains the success to photoinduce the reduction of CO_2 in the present system.

In conclusion, we have developed an effective system for the photoreduction of CO_2/HCO_3^- to formate by visible light. It should be noted that the β-CD support for the Pd colloid is extremely important to its catalyst activity and Pd colloids prepared by the reduction with citrate or stabilized by polymers, i.e. poly vinyl alcohol, are inactive toward formate production. Previous studies[19] have indicated that hydroxyl-containing supports, i.e., alumina, participate cooperatively in the activation of CO_2 by Pd metal. Similarly, cyclodextrins have been claimed[20] to associate CO_2, and derivatized cyclodextrins catalyze the hydration of CO_2.[21] The possible cooperative activation of CO_2/HCO_3^- by β-CD and Pd are now being investigated.

Acknowledgment. This research is supported by the Belfer Center for Energy Research, Israel.

Registry No. 1, 19342-73-5; CO_2, 124-38-9; HCO_3, 71-52-3; HCOOH, 64-18-6.

---

[19] (a) Solymosi, F.; Erdohelyi, A.; Lancz, M. *J. Catal.* **1985**, *95*, 567. (b) Solymosi, F.; Erdohelyi, A. *J. Mol. Catal.* **1980**, *8*, 471.

[20] (a) Hadley, J. H.; Hsu, F. H.; Yei, W. *J. Chem. Phys.* **1979**, *70*, 3702. (b) Cramer, F.; Henglain, F. M. *Angew. Chem.* **1956**, *20*, 649.

[21] Tabushi, I.; Kuroda, Y.; Mochizuki, A. *J. Am. Chem. Soc.* **1980**, *102*, 1152.

Incorporation of D-Amino Acids into Peptides via Enzymatic Condensation in Organic Solvents

Alexey L. Margolin, Dar-Fu Tai, and
Alexander M. Klibanov*

Department of Applied Biological Sciences
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received August 4, 1987

A number of biologically active peptides, including important antibiotics, synthetic vaccines, and enkephalins and other hormones, contain D-amino acid residues.[1] Although enzymes, namely proteases, are becoming increasingly popular as catalysts of peptide bond formation,[2] this synthetic methodology (as well

---

[1] Shoji, J. *Adv. Appl. Microbiol.* **1978**, *24*, 187–214. Hansen, P. E.; Morgan, B. A. In *The Peptides: Analysis, Synthesis, Biology*; Udenfriend, S.; Meienhofer, J., Eds.; Academic Press: Orlando, 1984; Vol. 6, pp 269–321. Blanc, J. P.; Kaiser, E. T. *J. Biol. Chem.* **1984**, *259*, 9549–9556. Wolfe, S.; Demain, A. L.; Jensen, S. E.; Westlake, D. W. S. *Science (Washington, D. C.)* **1984**, *226*, 1386–1392. Geysen, H. M.; Rodda, S. J.; Mason, T. J. In *Synthetic Peptides as Antigens*; Ciba Foundation Symposium No. 119; Wiley: Chichester, 1986; pp 130–149.

[2] Fruton, J. S. *Adv. Enzymol.* **1982**, *53*, 239–306. Chaiken, I. M.; Komoriya, A.; Ohno, M.; Widmer, F. *Appl. Biochem. Biotechnol.* **1982**, *7*, 385–399. Jakubke, H.-D.; Kuhl, P.; Konnecke, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 85–93. Kullmann, W. *Enzymatic Peptide Synthesis*; CRC Press: Boca Raton, FL, 1987.

0002-7863/87/1509-7885$01.50/0