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Photochemical Reduction of Carbon Dioxide to Methanol and Formate in a Homogeneous System with Pyridinium Catalysts

David J. Boston, Chengdong Xu, Daniel W. Armstrong, and Frederick M. MacDonnell*

Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, Texas 76019, United States

Supporting Information

ABSTRACT: Photochemical catalytic CO_2 reduction to formate and methanol has been demonstrated in an aqueous homogeneous system at pH 5.0 comprising ruthenium(II) trisphenanthroline as the chromophore, pyridine as the CO_2 reduction catalyst, KCl, and ascorbic acid as a sacrificial reductant, using visible light irradiation at 470 ± 20 nm. Isotopic labeling with $^{13}CO_2$ yields the six-electron-reduced product $^{13}CH_3OH$. After 1 h photolysis, the two-electron-reduced product formate and the six-electron-reduced product methanol are produced with quantum yields of 0.025 and 1.1×10^{-4}, respectively. This represents 76 and 0.15 turnovers per Ru for formate and methanol, respectively, and 152 and 0.9 turnovers per Ru on an electron basis for formate and methanol, respectively. The system is inactive after 6 h irradiation, which appears largely to be due to chromophore degradation. A partial optimization of the methanol yield showed that high pyridine to Ru ratios are needed (100:1) and that the optimum pH is near 5.0. The presence of potassium salts enhances the yield in formate and methanol by 8- and 2-fold, respectively, compared to electrolyte-free solutions; however, other alkali and alkali earth cations have little effect. The addition of small amounts of solid metal catalysts immobilized on carbon had either no effect (M = Pt or Pd) or deleterious effects (M = Ni or Au) on methanol production. Addition of colloidal Pt resulted in no methanol production at all. This is in notable contrast with the pyridine-based electrocatalysis of CO_2 to methanol in which metallic or conductive surfaces such as Pt, Pd, or p-type GaP are necessary for methanol formation.

Photochemical, photoelectrochemical, and electrochemical processes for the reduction of CO_2 into fuel could play important roles in addressing current environmental and energy challenges associated with the continued use of fossil fuels.[1−13] Transition-metal-based catalysts have been the focus of most homogeneous CO_2 reduction processes. Meyer and co-workers were one of the first to demonstrate that Rh and Ir polypyridyl complexes are competent electrocatalysts for CO_2 reduction in DMF under air-free, but ambient, condition.[14] Since then, there have been significant contributions in both electrocatalytic and photocatalytic CO_2 reduction with homogeneous catalysts by a number of groups including Meyer,[15−20] Fujita,[21−23] and others.[5,24−31] Notably, despite all the advances with CO_2 electro- and photoreduction with homogeneous transition-metal catalysts, products have been largely limited to the two-electron-reduction products (CO or formic acid) with only a few accessing deeper reduction to CH_3OH or CH_4.[32,33] Methanol is a particularly attractive product in that it is a liquid under ambient conditions and can be readily integrated into the existing liquid fuel transportation infrastructure.[2,34] Solar-powered photochemical reduction of CO_2 to liquid fuels would be a particularly attractive and environmentally benign technology, as it could, in theory, lead to a carbon-neutral fuel cycle.

Despite the promise of such technology, there is only one known selective electrocatalyst for CO_2 to methanol, which is the surprisingly simple pyridine molecule. Bocarsly and co-workers have shown that pyridine, at pH 5, will selectively reduce CO_2 to methanol in a series of one-electron steps and at low overpotentials.[1,6,35,36] Other deep reduction products such as formaldehyde or higher alcohols are only produced in trace quantity. While mechanistic studies are incomplete, evidence points to the formation of a carbamate-type intermediate between the CO_2 and a pyridinium radical and subsequent sequential electron and proton transfer processes to ultimately yield methanol. The electrode surface appears to be intimately involved in the reduction mechanism as only Pt or Pd electrodes are active in electrocatalytic systems[3] and p-type GaP in photoelectrochemical systems.[36] It is clear that there is a significant positive shift in the pyridinium reduction potential ($E_{red} = -0.34$ V vs NHE)[6] when Pt and Pd electrodes are used compared to Hg electrodes ($E_{red} = -0.95$ V vs NHE)[38] and theoretical calculations of $E_{red} = -1.1$ V vs NHE.[37] This unusual positive shift with Pt and Pd electrodes has been used to support the argument that the surface is involved in the CO_2 reduction mechanism (beyond simply supplying electrons). It is notable that other working electrodes, such as glassy carbon or Hg, do not drive the pyridine-catalyzed CO_2 to methanol reduction even at more negative potentials.[38] These data suggested that homogeneous pyridine-based reduction of CO_2 to methanol may not be possible and the performance of the pyridine-based system would be tied to issues such as electrode surface area and composition. We sought to address this issue and ideally directly couple this system with solar energy by examining a homogeneous photochemical system in which the electrode is replaced by a homogeneous visible light chromophore and electrons are supplied, in this case, by a sacrificial donor (ascorbate).

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Herein, we report on the homogeneous photochemical reduction of CO_2 to formic acid and, to a lesser extent, methanol using pyridine as the CO_2 reducing catalyst and $[Ru(phen)_3]^{2+}$ as the chromophore. This complex and the closely related $[Ru(bpy)_3]^{2+}$ complex are well-known photosensitizers for photochemical reduction and oxidation reactions. Both possess strong MLCT absorptions in the 400−500 nm region which yield long-lived ^{3}MLCT states that transiently localize the electron on one of the phen or bpy ligands and the hole on the metal center {i.e., $[Ru^{III}(phen)_2(phen^{\bullet -})]^{2+*}$} to form a powerful excited state oxidant and reductant.[39,40] As shown in the black line in Figure 1, irradiation of a CO_2-saturated, aqueous solution of pyridine (50 mM), $[Ru(phen)_3]Cl_2$ (0.20 mM), 0.1 M KCl, and ascorbic acid (0.2 M), at pH 5.0 and 25.0 °C at 470(±20 nm) in a custom-built LED photoreactor (see Supporting Information) steadily produces methanol for a 3−4 h period, after which activity falls off. While formic acid was the dominant product, we focused our initial optimization studies exclusively on methanol as this is the more desirable product. Methanol was detected by taking aliquots at various time points and analyzing for methanol by GC-MS. Samples were trap-to-trap distilled to remove all salts prior to GC-MS. Attempts to use ion-exchange resins for desalting[36] gave spurious peaks in the GC which interfered with the analysis. Methanol was detected at a *m*/*z* of 31 using single-ion mode. Experiments using isotopically labeled $^{13}CO_2$ (99% enriched) gave $^{13}CH_3OH$, confirming that the CO_2 is the carbon source for methanol production (see Supporting Information).

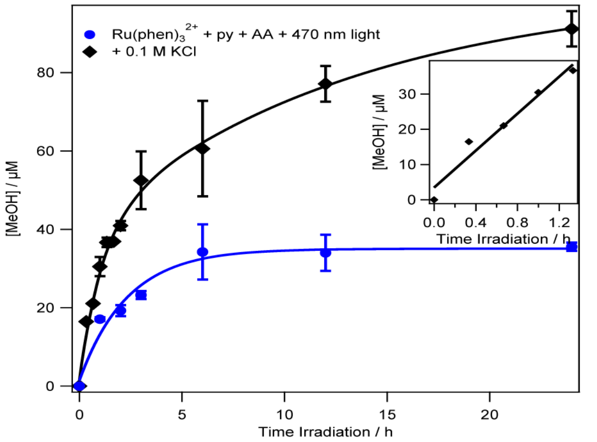

Figure 1. Growth of methanol with irradiation time for a solution (blue circles) of 50 mM pyridine, 0.20 mM $[Ru(phen)_3]Cl_2$, 0.2 M ascorbic acid, at pH 5.0, 25.0 °C, and irradiation with 470 nm light. Black diamonds: Performance of the same system with the additional component of 0.1 M KCl. The inset shows the initial growth of methanol for the first 1.3 h of irradiation in the system with KCl, where methanol production is linear.

Formic acid as formate was also detected by addition of strong base to the solid residue from the trap-to-trap distillation and removal of all volatiles under high vacuum. Dissolution in D_2O and NMR analysis with an internal standard (DDS) revealed considerable quantities of formate, as indicated in Table 1 (TON > 1). Quantitative analysis of formaldehyde was not possible due to interferences and difficulties in its isolation and detection, but NMR data suggest that it is only present in trace quantities at best. Control reactions established that all components, except KCl, were required for methanol production (see Supporting Information, Table S1). The presence of KCl doubles the methanol production, but it is not absolutely required. Its role in this process is discussed later.

As seen in Table 1, the pyridine to chromophore ratio was found to be an important factor, with no methanol detected after 6 h irradiation when the chromophore was in excess, approximately 6 μM methanol detected when the ratio was 1:1 or 2:1, and on the order of 30 μM when pyridine was present in large excess (i.e., 1:100). When converted to turnover numbers (TON), this amounts to ~0.15 methanol per $[Ru(phen)_3]^{2+}$ or 0.9 electrons per $[Ru(phen)_3]^{2+}$, the latter being based on the six-electron stoichiometry for the reaction. The reproducibility was good with the methanol concentration measured at 31 ± 3 μM after 6 h irradiation for three separate runs.

As with the electrochemical systems, the pH was important with optimum methanol production occurring around the pK_a of pyridinium ion (5.3), suggesting both the protonated and deprotonated pyridine are important for the overall process. As shown in Table 1, the optimum pH was 5.0 with no methanol production at pH 4.0 and a significant drop-off in methanol production at pH 6.0. The lack of methanol production at pH 4.0 may be due, in part, to the protonation of the ascorbate present (ascorbic acid $pK_a = 4.1$), as the ability of ascorbic acid to function as a sacrificial donor is less than that of ascorbate.[41−43] The use of a sacrificial donor is a temporary solution to any practical photochemical system, but as it is necessary here, the tight pH range limits the acceptable sacrificial donors to ascorbate as the more commonplace

Table 1. Optimization of $[Ru(phen)_3]^{2+}$ to Pyridine Ratio for Methanol and Formate Production[a]

			MeOH			formate		
Ru/py	*n*	pH	[MeOH] (μM)[b]	TON MeOH[b] (in e^-)	Φ^d ($\times 10^{-5}$)	(mM)[c]	TON formate (in e^-)[c]	Φ^d ($\times 10^{-3}$)
2:1	1	5.0	0.00 ± 1	0.0	0.0	4.7	19 (39)	1
1:1	1	5.0	6.3 ± 2	0.03 (0.19)	0.75	2.6	11 (22)	0.6
1:2	1	5.0	6.1 ± 1	0.03 (0.18)	0.46	0.42	1.8 (3.6)	0.1
1:100	1	5.0	29 ± 3	0.14 (0.87)	2.6	0.26	1.0 (2.0)	0.06
1:200	3	5.0	31 ± 3	0.15 (0.92)	6.3	2.2	9 (18)	3
1:200 (0.1 M KCl)	3	5.0	66 ± 12	0.33 (2.0)	11	18	76 (152)	25
1:200 (pH 4.0)	2	4.0	0.00 ± 2	0.0	0.0	2.9	12 (24)	4
1:200 (pH 6.0)	2	6.0	13 ± 0.3	0.05 (0.31)	2.7	1.1	4.5 (9.0)	0.9

[a] Conditions: pH 5.0, 0.20 mM $[Ru(phen)_3]^{2+}$, 0.1 M ascorbic acid, CO_2, py redistilled. [b] After 6 h irradiation, methanol as a function of ruthenium with electrons as a function of ruthenium in parentheses. [c] After 1 h irradiation, formate as a function of ruthenium with electrons as a function of ruthenium in parentheses. [d] ϕ reported on a per electron basis as a function of the slope of the initial linear portion of the product vs time plot.

donors, such as organic amines, are generally protonated and inactive at these pH values.

We noted that the electrolyte in the electrochemical systems was usually 0.1−0.5 M KCl and decided to see if the electrolyte composition had any effect, beyond simply providing a conductive solution, on the methanol production. The presence of potassium ion (0.1 M KCl) dramatically increased the formate yield (8×) and doubled the methanol yield after 6 h in the photochemical system, as seen in Table 1 and Figure 1 compared to the electrolyte-free reactions. Saveant[44] and Darensbourg[45] have shown in separate systems that ion-pairing between carboxylate functions with alkali and alkali-earth metal cations can stabilize the transition states involving CO_2 reduction in transition-metal complexes coordinating a CO_2 ligand. In our case, the enhanced catalysis was specific for potassium ion as addition of other salts, including LiCl, NaCl, RbCl, CsCl, and $MgCl_2$, had little to no effect (see Table S2).

After calibration of the photochemical system using ferrioxalate actinometry, quantum yields were determined for the early linear region of methanol production (0−2 h). Quantum yields for methanol increase from 4.6×10^{-6} to 1.4×10^{-4} with the optimization of Ru:py ratios and added potassium electrolyte. The larger quantum yields are comparable with those reported for the photochemical reduction of CO_2 to CH_4 catalyzed by the combination of $[Ru(bpy)_3]^{2+}$ and noble metal colloids ($\phi = 1 \times 10^{-4}$)[44] and only slightly less than that reported for the photochemical reduction of CO_2 to CO as catalyzed by $[Ru(bpy)_3]^{2+}$ with Ni-cyclams ($\phi = 1 \times 10^{-3}$).[41,45] In all of these comparisons, quantum yields are reported in moles of electrons produced per mol photons absorbed.

While methanol was the desired product, formate was the dominant reduction product. TON ranged from 1 to 76 depending on conditions which give quantum yields for formate production as high as 0.02 (see Table 1). These quantum yields are on par with those of various intermolecular systems for formate production which range from 0.01 to 0.09 and reach as high as 0.15.[46] As seen from Table 1, formate yields improve at low pyridine to Ru ratios, in contrast to the methanol trend; however, the most significant component for formate production appears to be the presence of the KCl. Addition of this component to the 200 py/1 Ru photolysis solution increased TON from 9 to 76 formates per Ru, the largest increase seen. While the effect of added K^+ is not completely understood, it appears that ion-pairing stabilization of the carbamate radical or carbamate greatly improves the reaction yield. It is notable that the buildup of formic acid in our system is in agreement with Bocarsly and co-workers' findings that formic acid reduction is the RDS for the pyridine-catalyzed CO_2 reduction to methanol.[6] Optimization of this system for formate production was beyond the scope of this work and is planned in upcoming studies.

At present, the productivity of this system is limited by the stability of the chromophore. Photolabilization of the diimine ligand in $[Ru(phen)_3]^{2+*}$ and $[Ru(bpy)_3]^{2+*}$ systems has been reported as the most common decomposition pathway, and this process is usually exacerbated in aqueous solution. Examination of the visible spectrum of the solution shows significant changes in the chromophore spectrum consistent with ligand labilization (see Supporting Information), and these decomposition products, such as $[Ru(phen)_2(H_2O)_2]^{2+}$, are photochemically inactive.

While all the details of the CO_2 reduction mechanism are still unknown, reduction of the pyridinium ion by the ruthenium chromophore is thought to be an essential initial step. Reductive quenching of the photoexcited complex by ascorbate followed by electron transfer to the pyridinium ion is the most probable path, however oxidative quenching by the pyridinium ion, followed by reduction of the Ru(III) complex by ascorbate is also possible (see Figure S6). We postulate that once the pyridinium radical is formed; the subsequent steps for CO_2 insertion and reduction to methanol are similar to those postulated by Bocarsly and coworkers.

Our results show that metal surfaces are not a requirement for pyridine-catalyzed deep CO_2 reduction. However, this does not necessarily mean that they could not participate or even enhance these processes. The exact role of the surface in the electrochemical systems is a matter of debate with various theoretical studies suggesting the Pt and Pd surfaces are necessary for the formation of surface hydrides[49] or that pyridinium radicals are incapable of reducing CO_2 in homogeneous solution at such low overpotentials.[37] This latter study has been countered by other theoretical work showing the pyridinium radical to be competent for CO_2 reduction. It is also possible that the positive shift in the reduction potential on these particular electrodes is unrelated to the CO_2 reduction mechanism other than to lessen the extent of other side reactions which occur at more negative potentials. To examine this, we added 0.08 mg/mL of metallic Pt, Pd, Ni, or Au (45−50% by mass) on carbon black as heterogeneous cocatalysts or ∼0.01 mg/mL quantity of colloidal Pt solution to the typical 200:1 pyridine/ruthenium mixture (total volume 25 mL). As shown in Table 2, addition of Pt and Pd metal cocatalysts lowered methanol yield by ∼15%, whereas Ni on carbon and Au on carbon cut yields by 50%. Addition of colloidal Pt shut down methanol production completely. Thus, the role of these surfaces in the electrochemical process is still unclear, but it is obvious that they are not a requirement for the pyridine-based CO_2 reduction process.

Table 2. Runs of the Photosystem Containing Various Metal Cocatalysts[a]

cocatalyst	n	MeOH (μM)	TON MeOH/Ru	TON MeOH/e^-	Φ (10^5)
Pt/CB	2	30 ± 3	0.15	0.91	2.1
Pt colloid	1	0			
Pd/CB	2	32 ± 1	0.16	0.97	2.2
Ni/CB	1	16 ± 0.8	0.08	0.48	3.8
Au/CB	1	13 ± 7	0.06	0.40	3.3

[a] Conditions: pH 5.0, 0.20 mM $[Ru(phen)_3]^{2+}$, 40 mM pyridine, 0.1 M ascorbic acid, 0.08 mg/mL ∼45−50% metal catalyst on carbon black support or 0.01 mg/mL colloidal Pt.

In summary, the photochemical reduction of carbon dioxide to formate and methanol has been observed in an aqueous system containing a chromophore, ascorbic acid, and pyridine. While the dominant product is the two-electron-reduced formate, to the best of our knowledge, this is the first homogeneous photochemical system capable of direct reduction of CO_2 to methanol and clearly demonstrates the ability of pyridine, in the presence of a suitable chromophore, to catalyze the deep reduction of CO_2 to methanol without a metal surface. The presence of group 1 metal cations in solution aids the reduction of carbon dioxide to methanol and formate possibly by stabilizing the py-CO_2 adduct that forms through ion-pairing with the oxygen of one or more of the intermediate species formed during the reduction process. In the presence of potassium ion, the 8-fold increase in formate production is mirrored by a 2-fold increase in methanol yield, supporting the supposition that formate (or formic acid) undergoes subsequent pyridinium-based reduction to methanol.[6] However, a more detailed analysis of this latter step is now warranted to firmly demonstrate that this "intermediate" is further reduced to methanol. We are continuing our studies of this system with the goals of improving chromophore stability, improving selectivity for methanol, and replacing the sacrificial donor with more practical donors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, tables, and figures regarding methanol detection, system optimization, and isotopic labeling. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

macdonn@uta.edu

Notes

The authors declare no competing financial interest.

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