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## **PHOTOREDUCTIVE SEQUESTRATION OF CO<sub>2</sub> TO FORM C<sub>1</sub> PRODUCTS AND FUEL**

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## ABSTRACT

Analytical methods for determining formic, acetic and oxalic acids, formaldehyde, and methanol have been evaluated and/or optimized for measuring products from photoreduction of CO<sub>2</sub> in illuminated, aqueous suspensions of photocatalysts. An electrophoresis anion separation method (CIA) can detect aqueous formate and oxalate ions at 22 and 17 μM (1 ppm), respectively. Recalibration of the Nash formaldehyde determination shows that as little as 10 μM (0.3 ppm) can be detected spectrally. Several experiments using suspensions of Pt/TiO<sub>2</sub>, SrTiO<sub>3</sub>, and SrTiO<sub>3</sub> with Cr and Sb were illuminated in CO<sub>2</sub> saturated solutions. No acids were detected in most experiments using CIA; however, ion chromatography (IC) was able to detect formate and acetate at low μM (sub ppm) concentrations in several experiments using Pt/TiO<sub>2</sub> and SrTiO<sub>3</sub> in sunlight and with xenon uv light. Analysis for methanol by gas chromatography showed that not more than 2 ppm methanol could have formed and probably less.

Adding 0.6 mM 2-propanol to an irradiated CO<sub>2</sub>/TiO<sub>2</sub> suspension led to formation of 550 μM formate, but no formaldehyde, probably because re-oxidation of formate by semiconductor holes was competitively blocked. Loss of C<sub>1</sub> products at higher concentrations by re-oxidation may be an important process, limiting the accumulation of products.

Preliminary estimates were made of the physical size of a solar CO<sub>2</sub> photoreduction unit large enough to reduce the CO<sub>2</sub> produced from a 1000 MW coal-fired electricity plant. A perfectly efficient system could be as small as 2 to 3 km<sup>2</sup>.

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## INTRODUCTION

The combustion-based production of CO<sub>2</sub> has evolved into what is perhaps the major environmental challenge of the 21<sup>st</sup> century. Whereas, CO<sub>2</sub> levels in the atmosphere remained stable over the 10,000 years preceding the industrial revolution, that event initiated a steady increase in CO<sub>2</sub> levels over the past 150 years (Stevens, 2000). The resulting accumulation of CO<sub>2</sub> in the troposphere is increasingly linked to global climate warming, with projections of continued warming in the absence of resolute changes in CO<sub>2</sub> management (Revkin, 2000).

To address global warming, the Department of Energy (DoE) has initiated an extensive program to investigate the technology of capture and storage of CO<sub>2</sub> produced by coal fired plants. Sites now being considered for storing produced CO<sub>2</sub> include the deep ocean, depleted oil and gas reservoirs, deep saline aquifers, and unmineable coal beds (DoE, 2001). Although, many of these sites are believed suitable for long-term storage of CO<sub>2</sub>, considerable uncertainties surround their permanence and how to monitor such storage sites for loss of CO<sub>2</sub> over centuries.

Another approach is to capture and reduce CO<sub>2</sub> to organic compounds including alkanes that can be reused for fuel. Reduction diverts CO<sub>2</sub> from the atmosphere to C<sub>1</sub> products and fuel and requires no large-scale storage facilities. CO<sub>2</sub> becomes a partly renewable resource that reduces consumption of new fossil fuels and by recycling, the rate of CO<sub>2</sub> production. Reduction of CO<sub>2</sub> is an endoergic process requiring energy input. Sunlight is an abundant though diffuse source of energy capable of effecting the reduction of CO<sub>2</sub> through the use of semiconductor catalysts such as TiO<sub>2</sub>, SrTiO<sub>3</sub>, or CdS, which form electron/hole pairs on excitation with uv or visible photons (Yoneyama, 1997). If the band gap of the semiconductor exceeds about 2 eV, the conduction-band electrons can reduce CO<sub>2</sub> to a variety of C<sub>1</sub> and C<sub>2</sub> products using hydrogen in water. However, intrinsic photoefficiencies (quantum yields) of photocatalysts currently used for reduction of CO<sub>2</sub> are very low and utilization of the solar spectrum by these catalysts is generally restricted to the uv portion of the spectrum below 400 nm, further reducing overall efficiency.

One objective of this project was to determine if newer photocatalysts reported over the past five-10 years with visible spectral absorbance have improved overall efficiency for reducing CO<sub>2</sub> using solar light. Some of these photocatalysts are claimed to be active in the visible portion of the solar spectrum for splitting water to hydrogen and oxygen, suggesting they also have surface potentials suitable for reducing CO<sub>2</sub>.

Another project objective is to develop process economic estimates for the cost of CO<sub>2</sub> reduction by sunlight in a practical system that uses flue gas as input CO<sub>2</sub>. In this effort, we will determine spatial requirements (km<sup>2</sup>) for reduction of fixed amounts of CO<sub>2</sub>, using realistic estimates of sunlight intensity and capture efficiency to establish possible conditions and reactor design under which sunlight promoted reduction of CO<sub>2</sub> would be competitive with alternative technologies using current technologies for capture and sequestration of CO<sub>2</sub> from flue gas.

## EXECUTIVE SUMMARY

The use of sunlight to reduce CO<sub>2</sub> to C<sub>1</sub> products and to fuel is being investigated as an alternative to sequestration of CO<sub>2</sub> in deep wells or coal beds to effectively make CO<sub>2</sub> a renewable energy source. A number of new photocatalysts have been reported to absorb visible light thereby improving the overall efficiency with which sunlight can be used for effecting chemical reactions and improving the competitive cost for reduction. This project has two main objectives: one is to evaluate some of the newer photocatalysts that absorb in the visible spectrum for their ability to reduce CO<sub>2</sub>. The second objective is to develop a qualitative process economic estimate for the cost of reducing CO<sub>2</sub> with sunlight using CO<sub>2</sub> captured from flue gas emitted from a coal-fired plant and using realistic estimates of sunlight intensity, reduction efficiencies and newer designs for utilizing sunlight in a heterogeneous photocatalytic system.

During the reporting period, formate, acetate, and oxalate ion analyses were done using capillary ion analysis (CIA) with a sensitivity of about 20 μM or 1 ppm, an ion chromatography (IC) method sensitive to about 0.2 μM or 10 ppb and the Nash formaldehyde method recalibrated to improve sensitivity to about 10 μM or 300 ppb. Gas chromatography was used to detect methanol formation down to about 60 μM or 2 ppm. Photocatalyzed reductions of CO<sub>2</sub> saturated in water were conducted using TiO<sub>2</sub>, Pt/TiO<sub>2</sub>, and SrTiO<sub>3</sub> over periods of 2 to 24 hours using a xenon lamp with irradiance equivalent to midwinter sunlight. However, product formation rates were extremely low, only trace amounts (about 10 to 15 μM) of formaldehyde could be detected and IC analysis showed that 2 to 30 μM (0.10 to 1.5 ppm) formate and acetate did form in these experiments. No methanol formation exceeding 60 μM (1 to 2 ppm) was detected. Formate formation was significant 500 μM (a few ppm) when 0.67 mM 2-propanol was added to inhibit re-oxidation of formate to CO<sub>2</sub>. One catalyst that absorbs visible light, SrTiO<sub>3</sub> with Cr and Sb, did not exhibit any reactivity in reducing CO<sub>2</sub> (based on CIA analyses only), although the analyses were complicated by ionic impurities in the catalyst. IC analyses

are in progress. Preliminary estimates were made of the physical size of a solar CO<sub>2</sub> photoreduction unit large enough to reduce the CO<sub>2</sub> produced from a 1000 MW coal-fired electricity plant. A perfectly efficient system could be as small as 2 to 3 km<sup>2</sup>.

## **EXPERIMENTAL**

### **ANALYTICAL METHODS**

#### **CO<sub>2</sub> Analysis**

The method for measuring consumed CO<sub>2</sub> was described in Quarterly Progress Report No. 2 (November 2002), reaction aliquots of 0.1 mL bicarbonate solution were injected into 2 mL stirred 1.0 M H<sub>2</sub>SO<sub>4</sub> solution in a sealed glass vessel previously swept with argon (100 mL/min) for 5 min and also housing a CO<sub>2</sub> infrared gas sensor (Vaisala, Model 6MM22, Woburn, MA). A calibration curve was developed using standard bicarbonate solutions; Figure 1 from QPR no.3 shows the curve.

#### **Formaldehyde Measurements**

The Nash calorimetric method (Nash, 1953) has been used by a number of workers to determine formaldehyde (CH<sub>2</sub>O) and formic acid in photoreaction mixtures ( Ulman et al., 1982a; Sharma et al., 1997). We prepared the calibration curve for formaldehyde using 33% formalin solution diluted to the μM range with Milli Q water. Dilute CH<sub>2</sub>O solutions (0.8 mL) were mixed with 0.5 mL Nash reagent (prepared from 150 g ammonium acetate, 3 mL acetic acid, and 2 mL acetylacetone diluted to 1 L with Milli Q water) and allowed to stand for 90 minutes. A series of CH<sub>2</sub>O-Nash reagent mixtures with concentrations ranging from 0.033 to 6.67 μM CH<sub>2</sub>O were analyzed by UV/VIS spectrophotometry at 412 nm. The new calibration curve is shown in Figure 1.

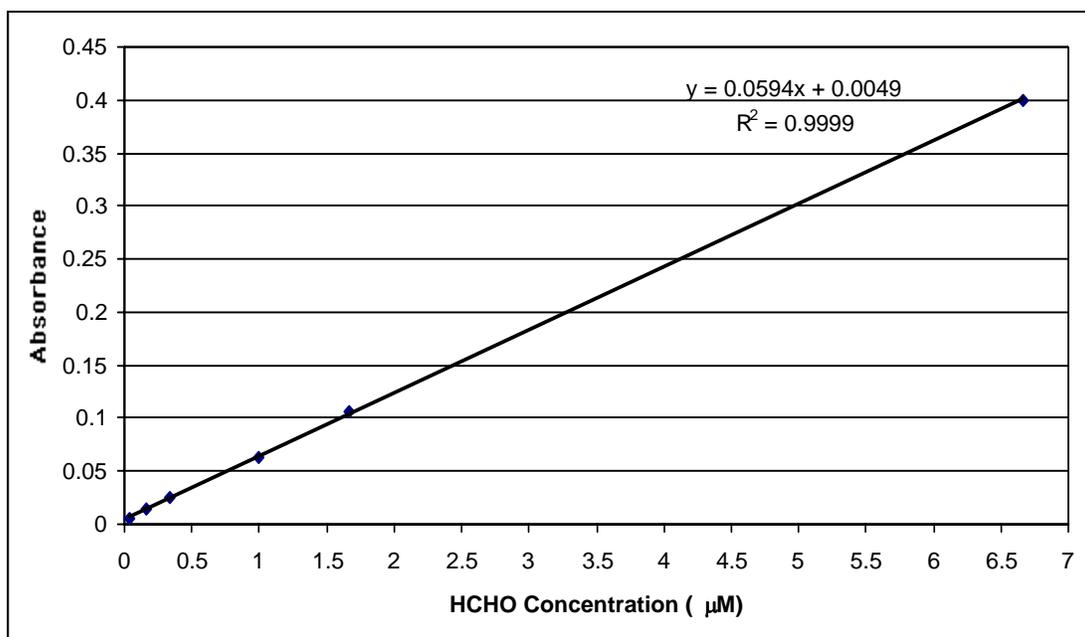


Figure 1. Formaldehyde recalibration using the Nash reagent. Absorbances were measured after 90 minutes.

### Methanol Analyses

Methanol analyses were carried out using a SRI Instruments (location, no connection to SRI) dual oven 8610 chromatograph equipped with a FI detector operating with 250 mL/min air and 27 mL/min H<sub>2</sub>. Separation of methanol from water was accomplished on a Poroplot Q Chrompak wide-bore capillary column (Varian), 25 m x 0.53 mm operating with 25 mL/min argon flow. Elution time for methanol was 3.2 min in a temperature programmed cycle from 80 to 170°C over 6 min. Water produces a false peak and tail starting at 2.1 min, but 5 µL of 10 ppm methanol produces a large peak on the tail. Injections of 5 µL of 65 µM (2 ppm) methanol under these conditions produces a distinct peak, but 1 ppm does not.

### Formate Analysis by Capillary Ion Analysis (CIA)

CIA, an alternative analytical method for low concentration anions available in our laboratory is based on electrophoretic separation. When optimized, the method can be used to detect a wide range of anions in the ~20 µM (1 ppm) concentration range. The detection method depends on the displacement by the anion of a proprietary mobile phase, which does absorb in the uv spectrum at 254 nm; hence, the improved sensitivity over HPLC, which depends on direct uv absorption by the anion around 210 nm.

CIA were conducted with a Waters Quanta 4000 Capillary Ion Analyzer (Waters, Franklin, MA) using a 75  $\mu\text{m}$  x 60 cm fused silica capillary column and a pH 5.6, 0.05 molar phthalate buffer with Waters osmotic flow modifier as the electrolyte. Detection is based on indirect uv absorption at 254 nm. Migration times (approximate) of anions in a standard mixture of 10 ppm each of thiocyanate (internal standard), formate, acetate, oxalate, and bicarbonate are 3.1, 3.22, 3.6, 2.85, and 4.2 min, respectively, at 25°C. The instrument acquired data at the rate of 20 bits/s and integrated peak areas in the time corrected mode. Reproducibility of time corrected peak areas for a standard mixture of 10 ppm of thiocyanate (0.17 mM) and 2 ppm (44  $\mu\text{M}$ ) formate ions in a series of replicate runs conducted on the same day was good: for thiocyanate the peak area was  $429 \pm 11$ ; formate peak area was  $345 \pm 11$  or about a standard deviation  $\pm 3\%$  in both cases. Figure 2 shows a typical CIA plot for thiocyanate and formate.

Although the detectability of formate by CIA in mixtures was close to 10  $\mu\text{M}$  (420 ppb or 0.42  $\mu\text{g/mL}$ ) under ideal conditions, after correcting for background, day to day reproducibility of the instrument is only fair with peak areas changing by as much as 20 to 25%. To account for this variability, all CIA analyses are conducted with standard mixtures of thiocyanate and formate ions. In practice, we could never detect formate or acetate by CIA reliably much below concentrations of 1 ppm (22 and 17  $\mu\text{M}$ , respectively).

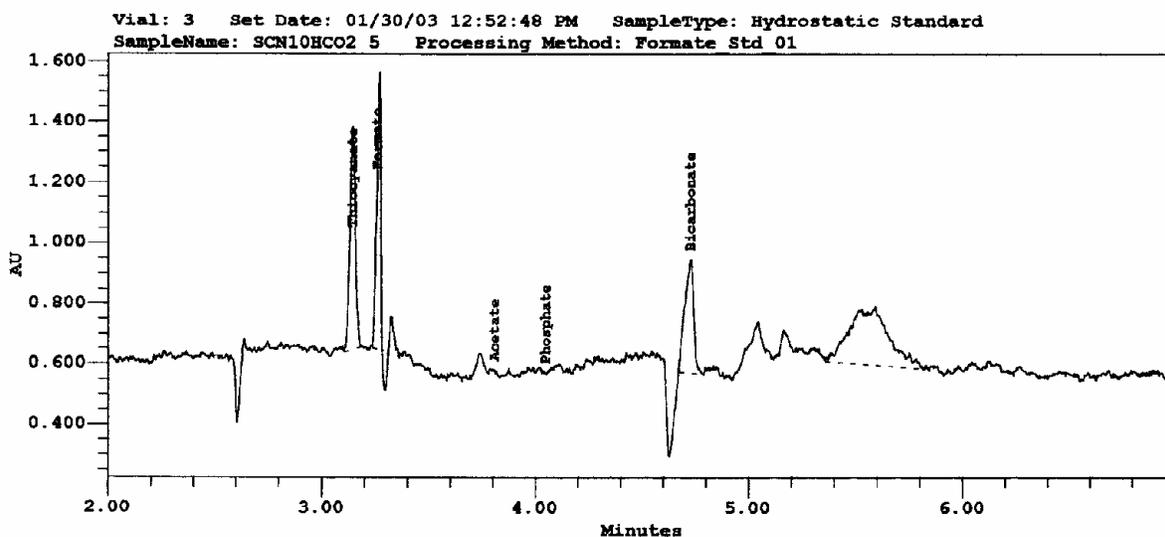


Figure 2. CIA plot for 10 ppm thiocyanate and 2 ppm formate ions.

## **Formate and Acetate Analysis by Ion Chromatography**

Ion chromatographic (IC) analyses for formate and acetate were conducted by West Coast Analytical Services (WCAS, Santa Fe Springs, CA). The IC method can detect formate and acetate reliably to 0.22 and 0.17  $\mu\text{M}$  (10 ppb), or about 100 times lower concentration than can CIA. The WCAS IC analytical method gave retention times for formate and acetate ion of 6.63 and 5.30 min, respectively, with peak areas of 100,000 for 2  $\mu\text{M}$  formate.

## **MATERIALS AND SUPPLIES**

All of the chemicals are reagent grade and used as is. A sample of P-25 anatase  $\text{TiO}_2$  was obtained from DeGussa (DeGussa Corporation, Cameron, NJ) and anatase  $\text{TiO}_2$  and  $\text{SrTiO}_3$  were purchased from Alfa Aesar (Ward Hill, MA) as high surface powders with estimated particle sizes of 30 to 50 nm; both powders are bright white.  $\text{SrTiO}_3$ , doped with Cr and Sb was prepared by sintering a mixture of  $\text{SrCO}_3$ ,  $\text{TiO}_2$  with  $\text{Cr}_2\text{O}_3$ , and  $\text{Sb}_2\text{O}_3$  at 1100°C for 30 hours in an alumina boat (Hirano et al., 2000). The resultant powder is tan colored. Hematite-coated  $\text{TiO}_2$  was prepared from titanium tetrabutoxide ( $\text{Ti}(\text{O}i\text{Bu})_4$ ) and hematite particles following the procedure of Penpolcharoen et al. (1998). The dry catalyst is an ochre-colored fine powder.  $\text{CO}_2$  gas is purified by passing it successively through concentrated sulfuric acid and pure water using gas washing bottles fitted with fritted outlets. Platinized  $\text{TiO}_2$  was prepared by the method of Kim and Choi (2002). The gray powder is estimated to have 2% Pt deposited on the  $\text{TiO}_2$  particles.

## **PHOTOCHEMICAL METHODS**

### **Light Source and Photoreactors**

The light source for these experiments is a Varian/EIMAC air cooled 300 w xenon lamp. A 2-cm thick borosilicate glass cylinder filled with pure water is positioned directly in the light beam to remove uv light below 300 nm and ir light above 1200 nm.

Light intensity from the xenon lamp was measured using two different actinometer solutions in the same reactor tubes used for  $\text{CO}_2$  reductions. One actinometer is 10  $\mu\text{M}$  ammonium dinitramide aqueous solution (ADN, Yao et al., 1995). ADN has a broad absorption from 260 to 360 nm and photolyzes rapidly in uv light with a quantum efficiency of 10% to give products, which do not absorb in the near uv. Loss of ADN was monitored by the loss of absorption at the peak maximum at 284 nm. The half life for ADN was determined to be 140 sec

in borosilicate tubes and 110 sec in quartz tubes. For comparison, ADN has a half life in sunlight in late winter of 240 sec (Mill, 2002). In other words, the xenon source produces about twice the near uv photon flux of winter sunlight under our experimental conditions. We have not yet estimated the actual photon flux with these data.

The second actinometer solution is azoxybenzene (AZB) in ethanol (Bunce et al.,1984). This compound absorbs light strongly from 360 nm into the far uv and forms 2-hydroxyazobenzene on irradiation anywhere in the absorption band with a quantum efficiency of 26%. The product is readily measured by its strong absorption at 458 nm. AZB solutions with concentrations of 5.75, 2.87, and 0.100 mM were irradiated for up to 900 sec. Samples were withdrawn at 10 to 300 sec intervals, quenched and analyzed by uv. The method of Bunce et al. (1984) was used to plot the data and obtain photon fluxes of 0.8-1.8 x 10<sup>-6</sup> Einsteins/sec in the photoreactor. The latter figure is probably the more accurate flux value for the semiconductor experiments since 5.75 mM AZB absorbs almost all light below 360 nm, the same spectral range over which TiO<sub>2</sub> and SrTiO<sub>3</sub> absorb uv light.

The photoreactors used in these experiments are either 20 mL borosilicate cylindrical tubes (1.5 cm path), 100 mL quartz cylindrical tubes (2 cm path), or a 300 mL borosilicate cylindrical reactor (5 cm path). All of the reactors were fitted with serum stoppers and closures and the contents of the reactors were magnetically stirred.

### **Photoreaction Procedures**

In a typical procedure, 10 to 100 mL of Milli Q water is placed in the reactor with a weighed amount of catalyst to give 0.1 to 0.15% by weight and is rapidly stirred at 25°C, while a stream of CO<sub>2</sub> gas is introduced at the bottom of the reactor with a 10 to 20 cm No. 20 hypodermic needle inserted through the serum stopper. A No. 24 needle serves as the outflow. After 30 to 40 min of rapid stirring, an aliquot is removed through the septum as a control through the serum, the inflow needle is moved up into the gas phase and the CO<sub>2</sub> flow continues for the duration of the experiment after the lamp is turned on. In reactors using HCO<sub>3</sub><sup>-</sup> instead of CO<sub>2</sub>, argon is bubbled through a serum stopped-reactor solution using syringe needles for 30 to 50 minutes to remove air. Both the controls and the reaction mixtures are filtered through a 0.45-µm filters to remove catalyst particles; the solutions are then ready for product analysis.

Sunlight experiments with SrTiO<sub>3</sub> and Pt/TiO<sub>2</sub> suspensions in CO<sub>2</sub>-saturated water were conducted in 100 mL sealed quartz tubes, suspended outdoors at about 40° from horizontal, facing south and stirred continuously for 28 hours, corresponding to about 18 hours of sunlight in late May at San Francisco (38° N Lat).

## BACKGROUND, EXPERIMENTAL RESULTS, AND DISCUSSION

### Background Studies

The strategy we have used in this project is to start with catalysts, conditions, and methods used by other workers which were reported to reduce CO<sub>2</sub> in photocatalyzed reactions to C<sub>1</sub> products such as formate, formaldehyde, and methanol. To accomplish this objective, we first developed and tested analytical methods for detecting formate, acetate, and formaldehyde as well as measuring CO<sub>2</sub> lost from the reaction. These efforts were reported in Quarterly Report Nos. 1 and 2. Once we could reproduce some of these earlier results with traditional uv photocatalysts such as TiO<sub>2</sub> and SrTiO<sub>3</sub>, our plan was and is to examine newer catalysts reported to be active photocatalysts in the visible region of the solar spectrum. In Quarterly Report No. 3, we summarized earlier reported photoreductions of CO<sub>2</sub> and presented some of our own results with similar photocatalytic systems. At that time, IC analyses were not available for comparison and CIA showed no detectable amounts of formate, acetate, or oxalate.

Table 1, taken from Quarterly Report No. 3, summarizes reported reduction products from CO<sub>2</sub> using a variety of photocatalysts such as TiO<sub>2</sub>, SrTiO<sub>3</sub>, CdS, and Cu on silicate rock and even the organic dye toluidine blue. Some workers used far uv light, some near uv or solar uv light and in two cases, tungsten lamps were used with visible light- absorbing catalysts. Irradiation times varied from 120 min to 24 hours. Similarly, some experiments used bicarbonate ion, others used flowing or static CO<sub>2</sub>.

In most of these experiments, formate and formaldehyde are formed although in significantly different concentrations, when corrected for differences in times and volumes. For example, formate yields are reported as 28 μM in 24 hrs (0.5 μmoles/hr) using SrTiO<sub>3</sub> as a photocatalyst with a mercury lamp (uv light) and flowing CO<sub>2</sub> gas (Irvine et al., 1990) and 185 μM in 150 min using TiO<sub>2</sub> with a xenon lamp, bicarbonate ion, and oxalate ion as an electron donor (Goren et al., 1990). Sayama et al. (1993) used ZrO<sub>2</sub> and found no formate, only CO. Sharma et al. (1997) used ferrocyanide-modified TiO<sub>2</sub> and claims to have made 2.9 mM formate in 100 min with a Tungsten (visible light) bulb. Sharma et al. also showed that at longer times formate slowly disappeared, presumably reflecting both further reduction as well as reoxidation to CO<sub>2</sub>. Some workers assert that TiO<sub>2</sub> alone does not reduce CO<sub>2</sub>.

**Table 1. Reported Products for CO<sub>2</sub> Photoreduction**

Catalyst	Products	Concentration	Light Source	Conditions/Time	Citation (Cat. No.)
CdS ZnO SrTiO <sub>3</sub>	HCO <sub>2</sub> H, H <sub>2</sub> CO HCO <sub>2</sub> H H <sub>2</sub> CO	28 μM, 2.3 μM 24 μM 5 μM	High pressure Hg lamp with Pyrex or quartz	0.15 g/50 mL CO <sub>2</sub> flow 24 hr	Irvine et al., 1990 (3808)
ZrO <sub>2</sub>	CO	8.6 μM/h	400 W Hg lamp quartz	1 g/350 mL 0.33 M NaHCO <sub>3</sub>	Sayama and Arakawa, 1993 (3809)
SrTiO <sub>3</sub>	HCO <sub>2</sub> H H <sub>2</sub> CO MeOH CH <sub>3</sub> CHO	7.5 μM/h 0.31 μM/h 0.13 μM/h <0.06 μM/h	75 W Hg lamp (high p), 1 g	1 g/160 mL CO <sub>2</sub> flow at 100 mL/min 60°C	Ulman et al., 1982b (3716)
TiO <sub>2</sub> /Pd TiO <sub>2</sub>	HCO <sub>2</sub> H HCO <sub>2</sub> H	8.3 μM/100 min 1.3 μM/100 min	450 W Xenon >360 nm	3 mL 0.05 M NaHCO <sub>3</sub> 0.05 M oxalate	Goren et al., 1990 (3729)
TiO <sub>2</sub> /Fe(CN <sub>6</sub> <sup>4-</sup> )	HCOOH H <sub>2</sub> CO	29 μM/100 min 0.66 μM/100 min	500 W Tungsten	1 g/150 mL CO <sub>2</sub> flow 210 min	Sharma et al., 1997 (3754)
Cu/SiO <sub>2</sub>	HCOOH	10 μM	Sunlight, Pyrex	5 g/5 mL CO <sub>2</sub> (no flow) 10 hr	Ohta et al., 1998 (3750)
Toluidine Blue 1 (-4) M	HCOOH H <sub>2</sub> CO	220 μM 62 μM	500 W Tungsten	50 mL 1 mM CO <sub>3</sub> <sup>=</sup> no pH effect 120 min	Jain et al., 2001 (3749)
CaFe <sub>2</sub> O <sub>4</sub>	H <sub>2</sub> CO CH <sub>3</sub> OH	38 μM 8.2 μM	High pressure Hg lamp	0.3 g/60 mL 0.01 M NaCH CO <sub>2</sub> saturated 4 hr	Matsumoto et al., 1993 (3811)

Initial photochemical experiments reported in Quarterly Report No. 2 were conducted using anatase TiO<sub>2</sub> and SrTiO<sub>3</sub> in the presence of HCO<sub>3</sub><sup>-</sup> ion in an effort to reproduce this earlier work (Miyasaka et al., 1979; Goren et al., 1990; Ulman et al., 1982b). We followed both loss of HCO<sub>3</sub><sup>-</sup> ion from solution and formation of formate and formaldehyde. Although loss of HCO<sub>3</sub><sup>-</sup> ion indicated significant reduction of CO<sub>2</sub>, we were not able to find products using the HPLC analytical methods, which proved to have low sensitivity levels for detecting formate by uv. We then switched to the CIA method for detecting formate and other acid anions and eventually to the IC method for analysis when CIA also proved to be too insensitive to detect products from these photoreductions.

During these latest two reporting periods, we have focused on developing a sensitive method for detecting methanol as well as analyzing a series of reaction mixtures from SrTiO<sub>3</sub>

and from Pt/TiO<sub>2</sub> using UV, IC, and GC methods for acids, formaldehyde and methanol. We also have examined the physical requirements for a photoreduction unit needed to reduce the output from a commercial 1000 MW coal-fired plant.

### **Photoreduction Experiments**

Most initial reaction mixtures consisted of semiconductor powder suspended in 10 to 20 mL of 0.1 M aqueous HCO<sub>3</sub><sup>-</sup> ion solution. However, removing excess HCO<sub>3</sub><sup>-</sup> prior to CIA was difficult and we switched to CO<sub>2</sub> gas and removed excess CO<sub>2</sub> by brief vacuum treatment. Once we started using IC analysis for formate and acetate, CO<sub>2</sub> removal was unnecessary. Table 2 summarizes the experiments conducted with semiconductor catalysts and CO<sub>2</sub>-saturated water (0.033 M) in artificial and real sunlight.

Some CO<sub>2</sub> experiments were carried out with added 2-propanol (2-PrOH) as an electron donor to enhance yields of formate and formaldehyde (No. 4) by inhibiting reoxidation of products to CO<sub>2</sub> by semiconductor holes (h<sup>+</sup>). In one experiment, use of 0.67 mM (40 ppm) 2-propanol did lead to formation of a significant amount of formate (22 μM); whereas, a similar experiment (No. 7) with 2-propanol did not give detectable amounts of formate. Except for the one case (No. 4) where 2-propanol was added, these experiments produced concentrations of formate, acetate or formaldehyde below 1 ppm and detectable only by IC (for the acids).

Experiments 8/9 and 10/11 with SrTiO<sub>3</sub> and Pt/TiO<sub>2</sub> show that similar amounts of formate and acetate are obtained with artificial and real sunlight if differences in photon fluxes are taken into account. With both sources, product formation is very slow, about 2 to 3 μM/hr with the artificial light and 0.3 to 1 μM/hr in sunlight with its more variable intensity. The experiments also show that Pt/TiO<sub>2</sub> consistently produces higher rates of product formation, by a factor of about 3 to 4. Possibly, the greater effectiveness of Pt/TiO<sub>2</sub> is simply because this gray powder absorbs more near uv light than bright white SrTiO<sub>3</sub>.

**Table 2. Experiments on Photoreduction of CO<sub>2</sub>**

Experiment No.	Catalyst (% Loading)	Conditions <sup>a</sup>	Time, h	Results <sup>b</sup>
1	SrTiO <sub>3</sub> (0.10)	0.1 M HCO <sub>3</sub> <sup>-</sup>	24	Formate present in control decreased
2	TiO <sub>2</sub> (0.15)	CO <sub>2</sub> flow	24	No Formate detected No CH <sub>2</sub> O detected
3	TiO <sub>2</sub> (0.15)	0.440 mM HCO <sub>2</sub> <sup>-</sup> under argon	25	320 μM Formate consumed No CH <sub>2</sub> O detected
4	SrTiO <sub>3</sub> (0.15)	CO <sub>2</sub> flow 0.67 mM 2-PrOH	24	Formate 22 μM (1 ppm) No CH <sub>2</sub> O detected
5	SrTiO <sub>3</sub> (0.15)	CO <sub>2</sub> flow 0.75 mM NaOH	24	No CH <sub>3</sub> OH detected No Formate detected No CH <sub>2</sub> O detected
6	SrTiO <sub>3</sub> (0.15)	CO <sub>2</sub> static 0.75 mM NaOH	2 4	No Formate or CH <sub>2</sub> O detected
7	SrTiO <sub>3</sub> (0.1)	CO <sub>2</sub> flow 0.67 mM 2-PrOH 0.75 mM NaOH	20	No Formate detected
8		CO <sub>2</sub> flow	6	Formate 11 μM (0.54 ppm) Acetate 20 μM (1.3 ppm)
9	SrTiO <sub>3</sub>	CO <sub>2</sub> flow	6	Formate 2.5 μM (0.130 ppm) Acetate 5 μM (0.304 ppm)
10	SrTiO <sub>3</sub> (SbO <sub>x</sub> CrO <sub>y</sub> ) (0.15)	CO <sub>2</sub> flow	24	No Formate or CH <sub>2</sub> O detected by CIA
11	Pt/TiO <sub>2</sub> (0.15)	CO <sub>2</sub> static Sunlight	18 <sup>c</sup>	Formate 5.5 μM (0.23 ppm) Acetate 8.5 μM (0.50 ppm); no MeOH
12	SrTiO <sub>3</sub>	CO <sub>2</sub> static Sunlight	18 <sup>c</sup>	Formate 20 μM (0.81 ppm) Acetate 29 μM (1.7) ppm

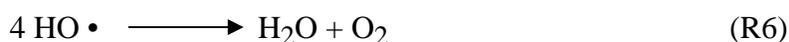
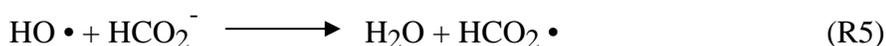
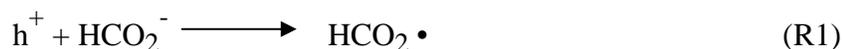
<sup>a</sup>Irradiated with 300 w xenon source at 25 cm.

<sup>b</sup>Detection limits for HCO<sub>2</sub><sup>-</sup> and CH<sub>2</sub>O are 10 and 50 μM.

<sup>c</sup>Sunlight hrs.

To evaluate the reoxidation of formate by semiconductor holes as an explanation for the low rates of production, we irradiated 0.440 mM (19 ppm) formate under argon with 0.15% TiO<sub>2</sub>, Experiment No. 3. After 20 hours, 70% of the original formate had disappeared, but because no formaldehyde was detected (above 30 μM, 1 μM), we conclude that reoxidation is

the most likely explanation for the loss. Sharma et al. (1997) noted that the production of formate declined after 90 minutes irradiation, with a parallel loss of formaldehyde, providing additional evidence that re-oxidation to CO<sub>2</sub> can be an important loss process for C<sub>1</sub> products in the photoreduction. Oxidation of formate (or acetate) likely arises from hole oxidation of formate to the radical, followed by a second oxidation step to form CO<sub>2</sub>.



Reactions (R3) and (R4) indicate that in the absence or near absence of organic material, hole oxidation of water will produce hydroxyl radical (HO or HO •). But as organic compounds build in concentration, h<sup>+</sup> will begin to oxidize them in competition with oxidation of water (R1/R2). HO will with organic compounds to form water and organic radicals as in R5 (Buxton et al., 1988)). The relative importance of competing reactions R1, R3 and R5 is determined by the relation between the rate of formation of HO and the rate of formation of formate through reduction of CO<sub>2</sub>.

### **Spatial Requirements for a Solar Photoreduction Unit**

Any estimate of the spatial requirements for a practical solar reduction unit for CO<sub>2</sub> produced from a power source must begin with an estimate of the photon flux incident on the surface at geographically and seasonally defined place on the earth. We define the location at the 40° N lat in mid summer. Tables of solar insolation data are available from Mill et al. (1982) and Leifer (1988) as a function of wavelength, latitude and season, For the spectral region from 300 to 800 nm, the photon flux at this location and time is about 22 mEinsteins/cm<sup>2</sup> day under clear sky conditions. We further assume that the photoefficiency of reduction of CO<sub>2</sub> to formate is 100% and the quantum yield is 0.5. This value arises from the requirement for two photons (electrons) per CO<sub>2</sub> to form formate.

A 1000-MW coal-fired electric plant produces about 11000 metric tons of CO<sub>2</sub> per day. Given these parameters, it is fairly straightforward to calculate that the spatial requirement for

this unit is  $2.2 \text{ km}^2$ . If photoefficiency is only 0.005, the spatial requirement will increase by 100 to  $220 \text{ km}^2$ . If only half the  $\text{CO}_2$  produced is to be reduced (say only during daylight hours), the spatial requirement is reduced by half. If the catalyst absorbs sunlight only to 600 nm, the photon flux drops to  $11.5 \text{ mEinstein/cm}^2 \text{ day}$ , thus increasing the spatial requirement by a factor of two.

This simplistic analysis only gives a lower boundary estimate of the size of any practical unit, but it does serve to indicate that any photoreduction process that will have practical utility must have a very high photoefficiency over a broad spectrum of sunlight and that the design of the actual unit components must ensure very high efficiency in capturing sunlight photons for the reduction process. A more detailed evaluation is now under preparation.

## CONCLUSIONS AND FUTURE WORK

Use of IC analytical methods have allowed us to measure formation of sub ppm concentrations of formate and acetate starting with 0.033 M (saturated)  $\text{CO}_2$  concentrations. Some published accounts of  $\text{CO}_2$  reduction to formate and formaldehyde describe formation of significantly larger concentrations than we have been able to find in experiments with the same catalysts and under what appear to be similar conditions of light intensity and  $\text{CO}_2$  concentrations. We are continuing to evaluate the reaction conditions in our experiments to more closely replicate results reported earlier. The common practice in earlier investigations of measuring formate formation by reducing it to formaldehyde and using the Nash method to measure formaldehyde could be one cause of the discrepancy between our results and those of others. If reduction of formate also leads to reduction of dissolved  $\text{CO}_2$ , then the yields of formate would be greatly exaggerated.

A first order assessment of the spatial requirements for a solar reduction unit shows that an optimized sunlight capture design, coupled with a very efficient visible light catalyst, could lead to a practical solar unit capable of reducing large volumes of  $\text{CO}_2$ - on the order of several thousand metric tonnes per day, on only a few tens of  $\text{km}^2$  area. Whether the cost of construction on this scale and development of efficient catalysts are possible, remain unknown at this time. More detailed assessment of the spatial requirements will be presented later.

Hole oxidation of  $\text{C}_1$  products could be competitive with oxidation of water at fairly low concentrations of organics. The implications of reoxidation for limiting the efficiency of the overall reduction process and the strategies that might be used to mitigate the effects will be

explored. Use of sacrificial electron donors such as oxalate or 2-propanol to boost yields of C<sub>1</sub> products does not on the face of it appear to be an economically or environmentally attractive option, but one we will examine.

## REFERENCES

- Bunce, N. J., J. LaMarre, and S. P. Vaish. 1984. *Photochem. Photobiol* **39**:532.
- Buxton, G. V., C. L. Greenstock, W. P. Helman, and A. B. Ross. 1988. *J Phys Chem Data* **17**:513-886.
- DoE (2001), Proceed. Conference on CO<sub>2</sub> Sequestration, Washington, DC, May 14-16.
- Eggins, B. R., P.K.J. Robertson, E. P. Murphy, E. Woods, and J.T.S. Irvine. 1998. *J. Photochem. Photobiol. A Chem.* **118**:31.
- Goren, Z., A. J. Nelson, and A. J. Frank. 1990. *J. Phys. Chem.* **94**:3784.
- Hirano, K., E. Suzuki, A. Ishikawa, T. Moroi, H. Shiroishi, and M. Kaneko. 2000. *J. Photochem. Photobiol. A Chem.* **136**:157.
- Irvine, J.T.S., B. R. Eggins, and J. Grimshaw. 1990. *Solar Energy* **45**:27.
- Ishikawa, A., T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, and K. Domen. 2002. *J. Am. Chem. Soc.* **124**:13547.
- Jain, S., J. Vardia, A. Sharma, and S. C. Ameta. 2001. *Int. J. Energy Res.* **25**:107.
- Kato, H. and A. Kudo. 2002. *J. Phys. Chem. B* **106**:5029.
- Kim, S. and W. Choi. 2002. *J. Phys. Chem. B* **106**:13311.
- Leifer, A. 1988. *The Kinetics of Environmental Photochemistry*. ACS Professional Reference Book, Washington, DC.
- Matsumoto, Y., M. Obata, and J. Hombo. 1993. *J. Phys. Chem.* **98**:2950.
- Mill, T., W. R. Mabey, D. C. Bomberger, T. W. Chou, and D. G. Hendry. 1982. *Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water*. U.S. EPA, Washington, DC, EPA 600/3-82-002.
- Mill, T. 2001. Unpublished results.
- Miyasaka, T., T. Watanabe, A. Fujishima, and K. Honda. 1979. *Nature* **277**:637.

- Nash, R. 1953. *Biochem. J.* **55**:416.
- Ohta, K., Y. Ueda, S. Nakaguchi, and T. Mizuno. 1998. *Can. J. Chem.* **76**:228.
- Penpolcharoen, M., R. Amal, and V. Chen. 1998. Proc 25<sup>th</sup> Australasian Chem.Eng. Conf. – CHEMECA '98, p. 222.
- Revkin, A. 2000. Warming effects to be widespread, New York Times, June 12.
- Sayama, K. and H. Arakawa. 1993. *J. Phys. Chem.* **97**:531.
- Sharma, B. K., R. Ameta, J. Kaur, and J. C. Ameta. 1997. *Int. J. Energy Res.* **21**:923.
- Stevens, W. K. 2000. Seas and soils emerge as keys to climate, New York Times, May 16.
- Ulman, M., B. Aurian-Bajeni, and M. Halmann. 1982a. *Isr. J. Chem.* **22**:177.
- Ulman, M., A.H.A. Tinnemans, A. Mackor, B. Aurian-Blajeni, and M. Halmann. 1982b. *Int. J. Solar Energy* **1**: 213.
- Yao, C.C.D., M. Su, and T. Mill. 1995. Preprint Extend. Abstract, Div. Environ. Chem., Amer Chem. Soc. Meet, Chicago, IL, August 20-24.
- Yoneyama, H. 1997. *Catal. Today* **39**:169.