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ELECTROCHEMICAL APPROACHES TO THE REDUCTION OF CARBON
DIOXIDE(U) ROCHESTER UNIV NY DEPT OF CHEMISTRY
C O'CONNELL ET AL. 30 OCT 86 TR-12 N00014-83-K-0154

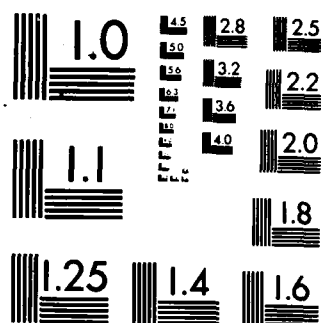
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Contract N00014-83-K-0154

Task No. NR 634-742

TECHNICAL REPORT NO. 12

Electrochemical Approaches to the Reduction of Carbon Dioxide

by

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Prepared for Publication

in

"Carbon Dioxide: Chemical and Biochemical Uses",
Proceedings of a NATO Advanced Study Institute

University of Rochester

Department of Chemistry

Rochester, NY 14627

October 30, 1986

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REPORT DOCUMENTATION PAGE									
1a REPORT SECURITY CLASSIFICATION Unclassified		1b RESTRICTIVE MARKINGS							
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2b DECLASSIFICATION/DOWNGRADING SCHEDULE		5 MONITORING ORGANIZATION REPORT NUMBER							
4 PERFORMING ORGANIZATION REPORT NUMBER Technical Report No. 12		7a NAME OF MONITORING ORGANIZATION							
6a NAME OF PERFORMING ORGANIZATION University of Rochester		7b ADDRESS (City, State, and Zip Code)							
6b ADDRESS (City, State, and Zip Code) Department of Chemistry Rochester, New York 14627		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER							
6c NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		6d OFFICE SYMBOL (If applicable)		10 SOURCE OF FUNDING NUMBERS		11 WORK UNIT ACCESSION NO			
6e ADDRESS (City, State, and Zip Code) Department of the Navy Arlington, VA 22217		6f PROJECT NO		6g TASK NO		6h PROGRAM ELEMENT NO NR 634-742			
11 TITLE (Include Security Classification) Electrochemical Approaches to the Reduction of Carbon Dioxide									
12 PERSONAL AUTHOR Catherine O'Connell, Sven I. Hommeltoft and Richard Eisenberg ^a									
13a TYPE OF REPORT Internal Technical Report		13b TIME COVERED TO		13c DATE OF REPORT (Year, Month, Day) 1986, October, 30		13d PAGE COUNT 23			
14 SUPPLEMENTARY NOTES									
15		16		17		18		19	
15a FIELD		15b GROUP		15c SUB-GROUP		18a SUBJECT TERMS (Continue on reverse if necessary and identify by block number)			
						19a ABSTRACT (Continue on reverse if necessary and identify by block number)			
Carbon dioxide reduction requires the input of energy or a high energy reductant to drive the reaction. Two possible energy sources which can be used in this capacity are electrochemical potential and light. Various ^{Various} paper approaches to CO₂ reduction by direct and indirect electrochemical methods are reviewed and analyzed. The indirect reductions involve the use of metal complexes in solution or on the electrode surface as electron transfer mediators and catalysts for reduction. The product distributions are sensitive to reaction media and conditions, but in many cases inadequate analyses are reported. A brief discussion of photochemical and photoelectrochemical reductions of CO₂ is also given.									
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED ☐ SAME AS RPT ☐ DTC USERS		21 ABSTRACT SECURITY CLASSIFICATION							
22a NAME OF RESPONSIBLE INDIVIDUAL Richard Eisenberg		22b TELEPHONE (Include Area Code) 716-275-5573		22c OFFICE SYMBOL					

DO FORM 1073, 8/84

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The reduction of carbon dioxide and its conversion into fuels and metabolic feedstocks represents an important challenge to chemists of all types. Many factors, both thermodynamic and kinetic, must be considered in analyzing this problem.¹⁻³ Of particular note are the energetics of CO_2 reduction, the binding and activation of CO_2 , and the disposition of oxygen released through C—O bond cleavage when reduction beyond the C^{+} oxidation state occurs.^{4,5} In this paper, we examine the problem of CO_2 reduction using both electrochemical and photochemical methods with an emphasis on the former.

Carbon dioxide is an extremely stable molecule, as evidenced by its ΔG_f° of -94.26 kcal/mole. Because of its stability, CO_2 serves along with H_2O as the major end product of metabolism and fossil fuel combustion. These two species thus function as the principal "redundancies" or "sinks" of fixed oxygen in the biosphere. An analysis of CO_2 production must therefore begin with thermodynamics.

Reduction by Hydrogen. For favorable reduction of CO_2 , either a high energy reductant or an external source of energy must be employed to drive the reaction. Of the possible chemical reductants, molecular hydrogen is clearly the most desirable since it is easily produced by electrolysis of H_2O , and it serves as an effective O atom acceptor via

the formation of H_2O . However, the simple reductions of CO_2 by H_2 as shown in eqs (1)-(4) reveal themselves to be thermodynamically unfavorable with small, positive ΔG° 's, although the reactions can be driven when H_2O is removed from the reaction system as it is formed. It is only when the reduction of CO_2 reaches methanol as the carbon product (eq (4)), becomes favorable. This analysis, however, does not take into account the intermediate oxidation states which a carbon atom of CO_2 must pass through before reaching the CH_3OH product.

(1)	$\text{CO}_2 + \text{H}_2$	$= \text{CO} + \text{H}_2\text{O} (l)$	$\Delta G^\circ, \text{ kcal/mole}$
(2)	$\text{CO}_2 + \text{H}_2$	$= \text{HCOOH} (l)$	4.79
(3)	$\text{CO}_2 + 2 \text{H}_2$	$= \text{HCHO} (g) + \text{H}_2\text{O} (l)$	7.86
(4)	$\text{CO}_2 + 3 \text{H}_2$	$= \text{CH}_3\text{OH} (aq) + \text{H}_2\text{O} (l)$	10.57
			-4.33

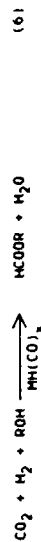
Also neglected in our consideration of eqns. (1)-(4) is the possible thermal stabilization which can be achieved by completion of the C product to the metal center of the catalyst. For example, eqn (1), which is the reverse of the well-studied water gas shift reaction, is favorable only at temperatures above -1000°C , but it can be driven to the right at far milder temperatures through coordination of CO. Specifically, when Wilkinson's catalyst, $\text{RhCl}(\text{PPh}_3)_3$, in HMPA is treated with $\text{CO}_2 + \text{H}_2$ (1:1, 40 atm), the carbonyl complex $\text{RhCl}(\text{CO})(\text{PPh}_3)_3$ forms in up to 70% yield.⁶ Similarly, the bicarbonate complex $\text{RhH}_2(\text{O}_2\text{CH}(\text{PPh}_3)_3)_2$ reacts at 298°K in pyridine with CO (1 atm) to give $\text{RhCl}(\text{CO})(\text{O}_2\text{CH}(\text{PPh}_3)_3)_2$ with CO coordination providing the driving force for the reaction.^{7,8}

While the hydrogenation of CO_2 to formic acid, (2), is thermodynamically unfavorable with ΔG° of -1.88 kcal/mole for HCOOH in the liquid state, an equivalent reaction, the hydrogenation of aqueous bicarbonate to formate, eqn (5), is essentially thermodynamically neutral at ambient conditions. This reaction has been studied by



Wrighton and co-workers who find that under 1 atm H_2 at room temperature nearly equal concentrations of HCO_3^- and $HCOO^-$ exist at equilibrium.^{6,9} The equilibrium was examined using as catalysts Pd on carbon and Pd with polymeric methylviologen on silica. This equilibrium has also been studied using the enzyme formate dehydrogenase.¹⁰ Through the use of D and ^{13}C isotope labelling, Wrighton and co-workers found that the exchange rate of (5) using Pd on C was nearly comparable to the rate of H/D exchange between H_2O and D_2 .

The direct hydrogenation of CO_2 to HCOOH can be drawn to the right by esterification. Thus CO_2 can be hydrogenated to alkyl formates in the presence of alcohols (MeOH , EtOH), eqn (b), the reaction being catalyzed by various transition metal carbonyl anions and hydrides such as $\text{HfRu}_5(\text{CO})_{11}^-$ and $\text{MH}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$).¹¹⁻¹³ The reaction has been studied



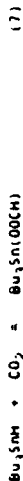
mechanistically by Darenbourg and Ovals using the group 6 carbonyl anions¹ and they propose that the catalysts produces formic acid which



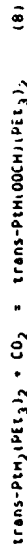
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subsequently undergoes esterification.¹³ A separate study published earlier shows that CO_2 reduction can also be driven by formamide formation from $\text{CO}_2 + \text{H}_2 + \text{R}_2\text{NH}$ at 800 psi using various group 8 complexes including $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Co}(\text{acac})_2$.¹⁴

Since catalyzed reductions of CO_2 by H_2 will invariably proceed via CO , interaction with M-M, the thermodynamics of this interaction are of importance. To date, only a few studies have dealt with this problem explicitly. Katsue and co-workers have examined the $\text{CO}_2/\text{Bu}_3\text{SnH}$ system and have found that at 200 °C under 2 atm of CO_2 , the equilibrium mixture contains roughly equal amounts of tin hydride and tin formate, eqn (7).¹⁵



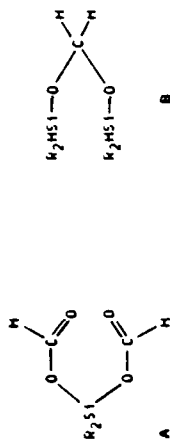
In the absence of a catalyst eqn (7) occurs fast enough at 115 °C - 175 °C to allow determination of $\Delta H = -18.3$ kcal/mole and $\Delta S = -20.2$ cal/mole-deg for this equilibrium. The negative entropy change is consistent with the reaction consuming one mole of gas. For the platinum hydride system $\text{trans-PtH}_2(\text{PEt}_3)_2$, Troglor finds that eqn (8) in toluene



has an equilibrium constant of 2 atm⁻¹ at 25 °C whereas in polar media, free formate and a cationic dimer, $\text{Pt}_2\text{H}_2(\text{PEt}_3)_4^+$, are observed to form.¹⁶

Other High Energy Reductants. In considering the use of other high energy reductants for reaction with CO_2 , we note that these reductants must also be capable of serving as σ atom acceptors. Possible reductants include oxophilic metals and their low oxidation-state compounds, phosphines, and silanes, but these systems can only be adapted for large-scale, catalytic reductions of CO_2 if they can be produced easily from a primary energy source such as by electrolysis or photosynthesis. Floriani's work using Cp complexes of the oxophilic metals Zr and Ti¹⁷ is noteworthy regarding the employment of other high energy reductants, and is discussed elsewhere in this volume.

Because of the strength of Si-O bonds and the reaction chemistry of R_3SiH with metal complexes which in some respects parallels that of H_2 , silanes are interesting candidates for reducing CO_2 . The hydrosilylation of CO_2 to silyl formates, eqn (8), has been reported using various Ru complexes including $\text{RuH}_3(\text{CO})_3$ ¹⁸ and $\text{RuCl}_2(\text{PPh}_3)_4$.^{18,19} and the reduction of CO_2 to CO has been found in the reaction of $\text{RhCl}(\text{PPh}_3)_3$ with R_3SiH and CO_2 .²⁰ In the latter reaction, the siloxane $\text{R}_3\text{SiOSiR}_3$ presumably forms as the oxygen sink. At Rochester, we have found that hydrosilylation using primary and secondary silanes proceeds readily at 298 °K using $\text{Ir}(\text{CH}_3\text{CO})\text{Cl}(\text{PPh}_3)_2$.²¹ In addition to the simple silyl formate produced, other products are observed which may correspond to A and B. Species B is attractive since it represents reduction to the C(0) oxidation state.



Direct Electrochemical Reduction of CO_2

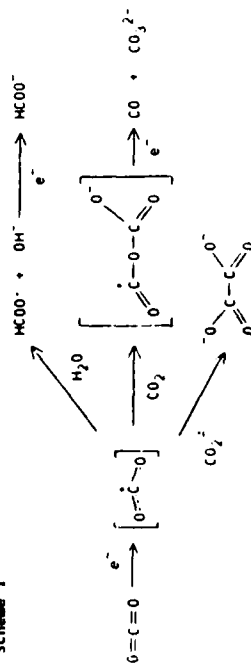
External energy sources which can be used to promote CO_2 reduction include both light and electrochemical potential. Both of these will be discussed in this paper with major emphasis given to electrochemical reductions of CO_2 . The simplest half-cell reactions for CO_2 reduction are shown as eqns (9)-(14) along with half-cell potentials adjusted to pH 7. In analyzing these half-cell reactions, it should be remembered that $2 e^- + 2 \text{H}^+$ is stoichiometrically equivalent to H_2 . The reduction to methanol shows itself to be least unfavorable but as with eqn (4), eqn (14) does not take into account intermediate oxidation states of C which must be traversed in the reduction process. In the $2 e^-$ reductions, the formation of oxalate is perhaps the most interesting process since it involves CO_2 coupling and C-C bond formation, but it is also the most unfavorable of the $2 e^-$ reductions thermodynamically. Which of the electrochemical reduction pathways is actually followed for a particular system depends more on numerous kinetic factors than on the reduction potentials of eqns (9)-(14).

	E° , VS MHE (pH 7)
$\text{CO}_2 + 2 e^- + 2 \text{H}^+ = \text{C} + \text{H}_2\text{O}$	-0.52 (9)
$\text{CO}_2 + 2 e^- + 2 \text{H}^+ = \text{HCOOH}$	-0.61 (10)
$2 \text{CO}_2 + 2 e^- = \text{C} + \text{CO}_2$	-0.55 (11)
$2 \text{CO}_2 + 2 e^- = \text{C}_2\text{O}_4^{2-}$	-0.90 (12)
$\text{CO}_2 + 4 e^- + 4 \text{H}^+ = \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.48 (13)
$\text{CO}_2 + 6 e^- + 6 \text{H}^+ = \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38 (14)

Kinetic Considerations. CO_2 reduction electrochemically may be carried out directly at an electrode surface or indirectly using a complex in solution as an electron transfer mediator and catalyst. In direct electrochemical reduction, large differences exist between the thermodynamic potentials of eqns (9)-(14) and the actual potentials which must be applied to the electrodes to achieve CO_2 reduction. These differences correspond to overpotential and represent a measure of the kinetic barrier for the particular reduction reaction. The large overpotential for CO_2 reduction at an electrode surface arises because of the relative instability of the initial reduction product, CO_2^- , and the energy needed to generate it.

In the direct electrochemical reduction of CO_2 , the particular pathway followed depends on the conditions of the electrolysis including

Scheme 1



Analysis of gaseous products (CO , H_2) can be done routinely by gas chromatography, although a carrier gas other than He will be needed for accurate H_2 determination if a t.c. detector is used. Qualitatively, the presence of CO can also be indicated by FTIR spectroscopy²⁵ and by IGC-MS spectroscopy.²⁶ The identification and quantification of formate and oxalate are best done by esterification followed by GC analysis.^{25,27-30} However, because of differences in the reaction conditions, and in particular the solvent systems used, the esterification procedures vary widely and for the most part have not been optimized. In this regard the work by Savent on electrochemical reduction in DMF deserves mention since the gas chromatographic analysis of oxalate was compared with a precipitation method based on CaC_2O_4 and conditions for the

oxalate to glyoxalate was seen in aqueous DMF. Relatively little difference was seen between Hg and Pb as cathode materials in these studies.

A survey of voltammetric reduction waves for CO_2 in water, DMSO, MeCN, and propylene carbonate using mercury, platinum, gold, lead, and glassy carbon electrodes has been carried out by Eggers.⁴¹ In general the potentials are quite negative (-2.2 v vs SCE), although in MeD peak potentials as positive as -1.12 v are seen for indium. The possible use of indium may therefore represent a significant lowering of the overpotential for CO_2 electroreduction. A study by Kapusta and Macerum⁴² shows that tin and indium electrodes are active to CO_2 reduction at applied potentials more negative than -1.3 v, giving formate as the major product. The high reactivity of these electrodes relative to Hg is ascribed to the possibility of adsorption of radical intermediates to the electrode surface, but the overall power efficiency of the reduction process is low because high overpotentials are needed to obtain reasonable current levels. Subsequent studies by others indicate that indium does not display the catalytic properties suggested by the earlier c.v. data.⁴³

The reduction of CO_2 to MeOH on semiconductor electrodes has been reported by several different groups.⁴⁴⁻⁴⁸ In the first of these communications, Monnier, et al., used TiO_2 and TiO_2 -Ru electrodes in aqueous solution at -0.9 v vs SCE but neither the method of product analysis nor quantitation of the product is given in the report.⁴⁷ Frese and co-workers in a series of studies have described reduction of CO_2 to MeOH over GaAs at -1.2 to -1.4 v vs SCE in aqueous solutions with current efficiencies of up to 100%.⁴⁴⁻⁴⁶ Increasing the current density, however, resulted in a lowering of the faradaic yield. In general, the current efficiencies were highly variable, and with one set of conditions including high electrolyte purity, no MeOH was obtained.⁴⁵ In another study, Frese reports electrochemical reduction of CO_2 at Ru electrodes. The products included MeOH, CH_4 , and CO obtained in variable but generally low yields at potentials in the range -0.55 to -0.65 v vs SCE. No details of analysis were given.⁴⁶

While these recent results using indium, tin, ruthenium and semiconductor electrodes at low applied potentials are tantalizing, they must be substantiated by more quantitative studies involving detailed and unambiguous product analyses. In general, most of the direct electrochemical reductions occur at very negative potentials owing to the instability of the $\text{CO}_2^{\cdot -}$ radical anion. Numerous mechanistic proposals have been made including adsorbed species, surface hydrides, and competitive pathways for H^+ and CO_2 reduction. However, there is little direct evidence at this point to support these proposals, and many of the questions regarding the intimate mechanism of CO_2 reduction remain unanswered.

Indirect Electrochemical Reduction of CO_2

Efforts to circumvent the principal difficulties in direct electroreduction of CO_2 , namely the high overpotentials required and the low current efficiencies observed, have centered on the use of homogeneous transition metal complexes as catalysts to mediate the reduction. These

complexes function by activating CO_2 and/or stabilizing its $1e^-$ reduction product through coordination. The electrocatalysts may also store the necessary reducing equivalents to convert CO_2 to specific and desired products without forming higher energy intermediates.

The complexes which can function as electrocatalysts are electrochemically active in the range between the E° values for CO_2 reduction and that needed for reduction directly at an electrode surface. Ideally, these complexes should show clean, reversible electrochemical behavior, and should possess long-term stability. The extent of catalysis can be readily determined from the observed decrease in required overpotential, the level of catalytic current generated, and the current efficiency for the formation of each product. While indications of interaction between CO_2 and the reduced metal complex can be easily ascertained by current enhancements in cyclic voltammetry and in electrolysis, the detailed nature of these interactions remains for the most part unclear.

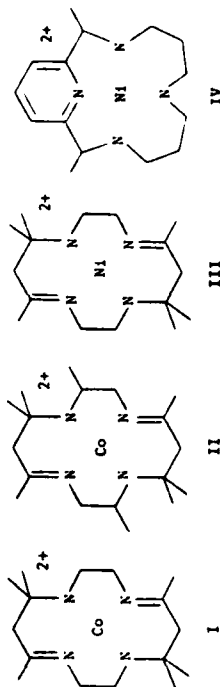
Indirect Reductions Using Ni and Co Complexes. To date, work in this field has concentrated on complexes of tetraaza macrocycles including phthalocyanines and porphyrins. Most of the complexes studied have been of Ni and Co. The earliest report involved phthalocyanine complexes of Ni and Co adsorbed onto a graphite electrode for CO_2 electroreduction in aqueous media at -1.5 v vs SCE.³⁴ Qualitative analytical tests showed positive for oxalic and glycolic acids but confirmatory tests were not applied and the gas phase above the electrolyte was not analyzed. When tetrasulfonated phthalocyanine complexes of these same metals were used in a second study,³⁵ current enhancement at -1.2 v vs SCE was observed at an amalgamated Pt electrode in aqueous solution but no product analyses were performed. Similar activity was found using solubilized Co tetraphenylporphyrin derivatives at -1.1 to -1.5 v vs SCE over Hg in aqueous solution.³⁶ Only qualitative tests were done, showing positive for formic acid, but small amounts of MeOH were noted in the absence of catalyst as well.

A more recent study using Ni and Co phthalocyanines showed that the electrode material was important in the electrocatalysis of CO_2 reduction, indicating that the complexes bind in some way to the electrode surface.³⁰ In particular, graphite and glassy carbon seem specific in their ability to utilize the phthalocyanines as catalysts with an overpotential ~ 200 mV lower than the best metals. Some electrocatalytic behavior was observed on high overpotential metals (Hg and Pb) but none was detected on Pt or Au. With graphite or glassy carbon electrodes, Co and Ni phthalocyanines catalyzed the electroreduction of CO_2 to formate in neutral aqueous solutions with a current efficiency of $\sim 60\%$ between -1.2 and -1.4 v vs SCE. Deactivation of the catalyst occurs, however, on cycling to more negative potentials, and no analysis of the gas phase above the solution was given. Interestingly, small amounts of MeOH ($< 5\%$ current efficiency) were reported on electrolysis at pH less than 4.

In contrast to these results, Lewis and Lieber have recently studied the cobalt phthalocyanine (CoPC) system on carbon electrodes and have found that the only C-containing product is CO .³⁹ Controlled potential electrolysis at -0.95 to -1.2 v vs SCE of CoPC deposited on pyrolytic graphite or carbon cloth in aqueous solution at pH 5 under 1

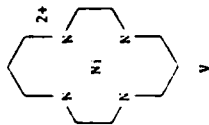
atm of CO_2 yielded CO and H_2 (2:1) with an overall current efficiency for more than 10^5 turnovers of 90-95%. Only trace amounts of oxalate and formate were detected by spot tests. The pH dependence of the CO₂ reduction waves and the lack of current enhancement under CO_2 relative to Ar led the authors to propose that reduction occurs by protonation of CoPC⁺ followed by a second reduction and subsequent reaction with CO_2 . Use of CoPC dissolved in aqueous 1M solution rather than adsorbed onto the C electrode resulted in poor stability and low catalytic efficiency for CO_2 reduction.

The first report of synthetic macrocycle complexes of Ni and Co for CO_2 electroreduction was made in 1980 from our laboratory.²⁷ This work which employed complexes such as I-IV was also the first to provide quantitative analysis of the gas phase products and their respective current efficiencies. CPC of I-IV in aqueous acetonitrile at a Hg pool electrode (-1.3 to -1.6 v vs SCE) under CO_2 yielded CO and H_2 with high overall current efficiencies (>90%). A protic source appeared to be necessary for CO_2 reduction as no CO was detected upon electrolysis in dry DMSO. It was suggested that both CO and H_2 may arise from a common intermediate, possibly a metal-hydride formed by protonation of the reduced macrocycle.



Two subsequent studies have used the same and closely related macrocycle complexes for promoting CO_2 reduction, and presumably they involve the same catalytic chemistry as that of Fisher and Eisenberg. The first study, by Bradley and coworkers, employed p-Si as the cathode. Instead of Hg which allowed the applied potential to be up to 0.6 v less negative than that required at a metal electrode.³¹ The additional energy needed to promote reduction was provided by irradiation at 352 nm. The second study was by Finnemann, et al., who studied CO_2 reduction promoted by these macrocycles under conditions of electrochemical reduction at Hg in aqueous DMF or MeCN, and photochemical reduction using Ru(bpy)₃²⁺ as sensitizer, ascorbic acid as sacrificial electron donor, and the macrocycle complex as electron transfer mediator and catalyst in aqueous solution.³² Both CO and H_2 were obtained in each case with CO/H_2 selectivity generally low although in one instance a ratio of 26 was obtained. Positive qualitative tests for formate and oxalate after electrolyses were also observed. Thus while these macrocycle complexes of Ni and Co serve as electrocatalysts for CO_2 reduction, their selectivity is not great because of competitive H_2O reduction.

The most promising results to date using tetraaza macrocycle complexes for catalytic electroreduction of CO_2 are those of Sauvage and coworkers with micacyclams,^{33, 34} V.3.35 The most remarkable aspect of this wire is the extremely high selectivity (>10⁶) to CO formation from CO_2 relative to H_2 production from water. Catalysts by V over a Hg pool electrode was fast (10³ moles of CO produced per mole of complex per hour) and selective (the faradaic yield was >95%) at potentials of -1.25 v vs SCE or greater. Almost no H_2 was detected even in pure aqueous media. Through variation of pH, MeCO_2^- and CO_3^{2-} were ruled out as precursors for CO formation; the reduction was thus shown proceed from CO_2 .



The fact that catalyst concentration had only a small effect on peak currents in c.v.s of V under CO_2 and on the rate of CO production led Sauvage to suggest that adsorbed species are relatively more important than those in the bulk, i.e., reduction of CO_2 takes place at the electrode surface. It was proposed that adsorption of Micacyclam⁺ on Hg is followed by attack of CO_2 to give a Ni(III)-CO species which is protonated and reduced to yield a Ni(II)-CO complex. Dissociation of CO then regenerates the starting Micacyclam²⁺ catalyst. Once the concentration of CO increases, several of the species in the proposed cycle may form carbonyl adducts which could be reduced more easily than the original species, helping to explain the relatively high activity of V as an electrocatalyst. The species Ni(CO)(Micacyclam)⁺ was detected in the electrolysis cell by UV/vis, infra-red and ESR spectroscopies, thus lending support to the mechanistic proposal.³²

In contrast to Micacyclams,³⁴ which exhibited high CO/H_2 selectivity, excellent current efficiencies, and long-term stability, other macrocycle complexes proved disappointing. Nickel complexes of saturated 14-membered rings related to I-IV did show catalytic activity but were not selective to reduction for CO_2 relative to H_2O . In these systems, the methyl groups at the periphery of the macrocycles may render the Ni center less accessible to attack by CO_2 relative to attack by H^+ . In addition, the Micacyclam⁺ system appears better suited to provide a stabilizing interaction for binding CO_2 , shown as Figure 1, than the other macrocycle complexes. Complexes of unsaturated macrocycles and open chain ligands were found to be less active and showed poorer long-term stability.³²

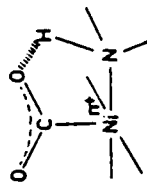
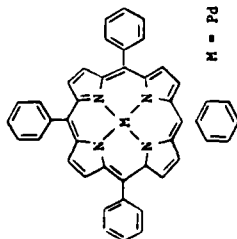
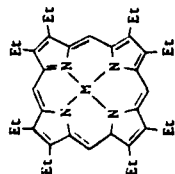


Figure 1. Proposed binding of CO₂ to nickelacyl²⁰. 32

Indirect Reductions Using Complexes of Other Metals. In earlier reports dealing with phthalocyanine and porphyrin complexes, the inactivity of Cu and Fe systems as electrocatalysts was mentioned.^{34,36,49} Recently, Becker and co-workers²⁵ have examined the electroreduction of CO₂ in anhydrous CH₂Cl₂ using various porphyrin complexes, VI and VII. Electrocatalysis was seen with Ag and Pd



VI



VII

systems at platinum and glassy carbon electrodes and applied potentials of -1.3 to -1.4 v vs SCE. A very significant aspect of this work was the observation of oxalic acid as the major CO₂ reduction product. Oxalate formation requires CO₂ coupling with C-C bond formation, and is probably the most interesting reduction channel for CO₂ utilization in the long run. In Becker's study, however, no current efficiencies were reported, H₂ (but no CO) was detected in the gas phase, and the metalloporphyrin catalysts exhibited decomposition. The particular combination of metal and ligand appears important since Ag(OEP), Pd(OEP) and Pd(TPP) showed catalytic activity whereas Ag(TPP), Cu(TPP), and Ni(TPP) did not (OEP = octaethylporphyrin; TPP = meso-tetraphenylporphyrin).²⁵

A number of bipy (2,2'-bipyridine) complexes have come under scrutiny as electrocatalysts for CO₂ reduction. Lehn, et al., have reported that ReCl(CO)₂(bpy) functions as an electrocatalyst at -1.5 v vs SCE in aqueous DMF with CO produced in >90% faradaic yield.²⁶ The

reaction was much slower in the absence of H₂O indicating the need for a protic source. Meyer and co-workers have examined the same complex in MeCN at -1.5 v vs SCE, and find only CO and CO₂⁻ with current efficiencies of ~98%.²⁹ Electrolyses at more negative potentials showed small amounts of H₂ indicative of Hofmann degradation of the supporting NBu₄PF₆ electrolyte, and no evidence for CO₂⁻. The Re complex undergoes a reversible bipy-based reduction at -1.35 v and an irreversible metal-based reduction at -1.7 v. While the mechanism of reduction is uncertain and may follow potential-dependent 1 e⁻ and 2 e⁻ paths, it appears that the reduced complex ReCl(CO)₂(bpy) or its MeCN solvate reacts readily with CO₂.

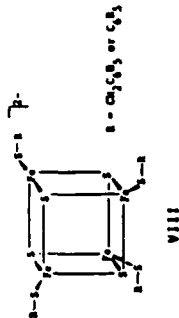
Meyer and co-workers have examined other polypyridyl complexes as electrocatalysts including Rh(bpy)₂(OTf)₂⁺ (OTf = triflate) and RuCl(terpy)(Ph₂PCH=CHPh)₂⁺ (terpy = 2,2',2''-terpyridine).³⁰ The Rh system in dry MeCN gives formate production upon cpc with 64% current efficiency. Other products include H₂ (12% c.e.) and NBu₃ from the NBu₄PF₆ electrolyte by a route which appears to involve generation of a strong base and Hofmann degradation, eqn (15). It is interesting that



H₂ only forms in the presence of CO₂. In contrast, the RuCl(terpy)-(Ph₂PCH=CHPh)₂⁺ yields CO as the only CO₂-derived product with no evidence for H₂ and a surprisingly positive test for NBu₃.

Another Rh complex examined as an electrocatalyst for CO₂ reduction is Rh(dpp)₂⁺, the electrochemistry of which has been studied independently by several groups. Sja. O. Wagenecht and Slater find that Rh(dpp)₂⁺ promotes formate formation in dry MeCN at -1.2 to -1.3 v vs SCE over Hg.²⁸ Cyanacetate was also detected, indicating generation of CH₃CN, which had been proposed earlier, followed by CO₂ trapping. No analysis of the gas phase is described. In a separate study of the reaction chemistry of Rh(dpp)₂⁺ and Rh(dpp)₂⁺ produced by Na naphthalenide reduction in benzene, we have found that both species react with CO₂ to produce CO as the only CO₂-derived product by gc and NMR spectroscopy.^{33c}

Indirect electroreduction of CO₂ using the iron-sulfur cubane-like clusters Fe₄S₄(SP)₂²⁺, VIII, (R = Ph, CH₂Ph) has been described recently by Tezuka.³³ The electrolysis is done in dry DMF at -1.7 to -2.0 v vs



SCE over Hg and yields predominantly formate, some CO and small and variable amounts of oxalate. In the absence of the Fe-S cluster, cpc at -2.4 v vs SCE gave primarily oxalate although addition of H₂O or

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surfactant led to formate and CO at the expense of oxalate. With the Fe-5 clusters, current efficiencies of up to 93 % for formate formation were observed, even in strictly anhydrous media. It was therefore proposed that CO_2^- is generated through electron transfer in the bulk solution rather than at the electrode surface, leading to protonation and HCOO^- formation rather than self-coupling and oxalate. The formate H atom may arise from R_4N^+ present as the cation of the cluster and the electrolyte.

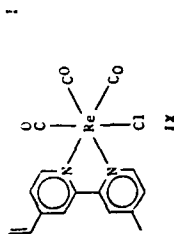
In assessing the different studies of indirect electrochemical reduction of CO_2 , we note that the success of any system (decrease in overpotential), product selectivity and current efficiency, level of catalytic current, and electrocatalyst stability) depend on many factors including the reaction medium, the supporting electrolyte, the electrode, and the applied potential in addition to the nature of the electrocatalyst itself. Most of the studies have not been able to examine all of these variables in any systematic way. Unfortunately, the care with which the electrode reactions have been done and the methods of product analysis also factor in any analysis of the results discussed above.

In most cases the formation of product is consistent with Saveant's original scheme for direct electrochemical reduction of CO_2 with CO and HCOO^- as the major products seen to date.²³ In terms of catalytic efficiency, the most encouraging result remains that of Sauvage using the macrocycle H_2Cyclam to promote reduction to CO.^{31,32} The formation of oxalate as the major CO_2 -derived product is observed in but one instance, in dry CH_2Cl_2 using Ag and Pd porphyrins.²⁵ It is surprising that in several studies using anhydrous media, the R_4N^+ electrolyte appears to enter as a reagent, giving up a proton and undergoing Hofmann degradation.^{29,30,37}

Modified Electrodes. The lack of long-term stability of certain complexes as electrocatalysts, and the apparent differences when the complexes are physically adsorbed on the electrode surface relative to being in solution suggests that immobilization of the electrocatalysts using modified electrodes will be a fruitful avenue of inquiry for further indirect reductions of CO_2 . To date, immobilization has been achieved by adsorption, electropolymerization, and incorporation into a polymer film by chemical coating methods. Through modified electrodes, local concentration of catalyst might channel CO_2 reduction selectively such as to oxalate formation via the dimerization of CO_2^- . The use of polymer modified electrodes for CO_2 reduction will require the synthesis of large modified electrodes for coulometry as well as more easily prepared smaller ones for voltammetry.

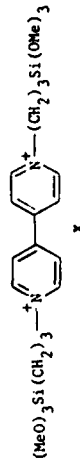
To date, Meyer and coworkers have studied a polymeric analog of the known CO_2 reduction catalyst $\text{ReCl}(\text{CO})_3(\text{bpy})$. Thus $\text{ReCl}(\text{CO})_3(\text{vbpy})$ (vbpy = 4-methyl-4'-vinyl-2,2'-bipyridyl), IX, was electropolymerized onto a platinum gauze electrode.³⁴ Experiments using modified rotating disc electrodes showed that currents were independent of rotation rate, suggesting that CO_2 penetrates the film rapidly and that its mass-transport is not rate limiting in catalysis. In dry MeCN at -1.55 V vs SCE, this electrode exhibited current efficiency for CO_2 reduction of 92 % which corresponded to 387 turnovers h^{-1} as compared to 15-23

turnovers h^{-1} by the monomer complex in solution under analogous conditions.²⁹ Whereas equal quantities of CO and CO_2^- were generated in



the solution experiment, no CO_2^- was detected using electropolymerized $\text{ReCl}(\text{CO})_3(\text{vbpy})$. It is possible, however, that carbonate remains trapped in the polymer film thus avoiding detection. Unfortunately, long-term stability remains a problem with this system. After 80 min of electrolysis, the electroactive material had been lost from the electrode surface.

Wrighton has followed up his studies of the $\text{HCO}_3^- + \text{H}_2 = \text{HCOO}^-$ system discussed above with polymer modified electrodes which can carry out the reduction of bicarbonate to HCOO^- at potentials close to the thermodynamic limit for this couple.³⁶ The chemically derivatized electrodes consist of organosilane viologens, X, which are electropolymerized onto tungsten or platinum and then impregnated with Pd metal, as shown in Figure 2. These electrodes effect the reduction of



HCO_3^- to HCOO^- in aqueous solution at -0.7 to -0.8 V vs SCE. Formate was the only reduced C-containing product detected by ^{13}C NMR spectroscopy after using $\text{H}^{13}\text{CO}_3^-$, and current efficiencies of up to 85 % were reported. However, significantly lower current efficiencies were also

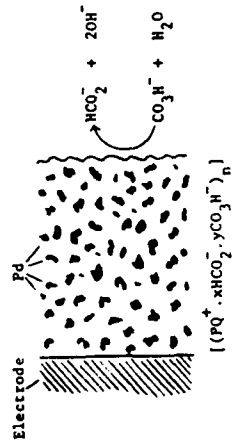


Figure 2. Modified electrode based on $\text{MW}^{2+}/\text{PQ}^+/ \text{Pd}$ for HCO_3^- reduction.³⁸

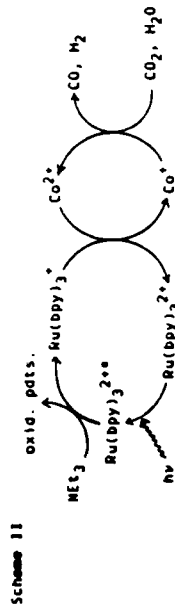
observed, and these were attributed to Pd hydride formation, reduction of the viologen polymer, and competing H₂ evolution. Degradation of activity occurred with time due to reduction of the viologen polymer.

Photo- and Photoelectrochemical Approaches

The development of artificial photosynthesis in which CO₂ is selectively reduced to a fuel or chemical feedstock material is an essential goal of present day chemistry. The use of light to drive CO₂ reduction involves the creation of an electron-hole pair. Its separation into isolated charges, and the channeling of the energetic electron to a catalyst site at which the reduction can occur. Two different but related approaches will be discussed in this section.

The first involves systems based solely on photochemistry with solution electron transfer reactions serving to provide the means for electron-hole separation. The second involves systems which are photochemical and electrochemical hybrids and use irradiated semiconductor electrodes. The electron-hole separation is achieved in these systems in the semiconductor near the solution interface in the so-called space charge region. With these systems, the semiconductor electrode may be subject to an applied potential in addition to irradiation. A third type of photochemical system for CO₂ reduction, discussed elsewhere in this volume, employs irradiated suspensions of semiconductor particles in aqueous solution. These suspensions lead to a variety of CO₂ reduction products including CO, HCOOH, CH₃OH, and CH₃OH.

During the past decade, intense interest in solar energy storage and water splitting led to the development of a number of redox relay systems for H₂ production in which the well studied complex Ru(bpy)₃²⁺ served as the photoactive agent.⁵⁵ In these systems the excited state of Ru(bpy)₃²⁺ is quenched by methylviologen or paraquat (MV²⁺) via electron transfer, with the resultant Ru(III) complex reacting rapidly with a so-called sacrificial donor while the highly reducing MV^{•+} transfers its electron to a catalyst center for H⁺ reduction. A similar approach has been adopted by Lenn and Ziesler for CO₂ reduction.⁵⁶ They describe a relay system shown in Scheme II composed of Ru(bpy)₃²⁺/Co²⁺ in MeCN/H₂O/Et₃N under CO₂ which generates CO and H₂ in almost equal amounts upon irradiation. The reaction proceeds with electron transfer quenching of Ru(bpy)₃²⁺ by Co²⁺, giving a reactive Co(I) species capable of reducing both H⁺ and CO₂. Addition of bpy effects the relative product distribution, presumably by complexation to the Co catalyst.



Another Ru(bpy)₃²⁺-based system has been reported by Tazuke,⁵⁷ but the quantum yields for CO₂ reduction are very low (0.01), and the report raises an interesting mechanistic question. The system is composed of Ru(bpy)₃²⁺, MV²⁺, and triethanolamine. The major CO₂ reduction product is formic acid as determined by isotachopheresis. What is puzzling is that the catalyst usually provided in H₂O reduction systems⁵⁵ is not present; the species MV^{•+} is proposed to reduce CO₂ directly. This reaction is however prohibitively uphill (E⁰_{MV²⁺/MV^{•+}} is -0.44 v vs NHE while the reduction of CO₂ to CO₂^{•-} requires at least -2.0 v), suggesting that an unidentified component of the reaction system adopts the catalyst role of charge accumulation and substrate activation.

Recent work by Lenn and co-workers may shed light on this question.⁵⁸ They find that ¹³CO₂ is photochemically reduced to H¹³COO⁻ in DMF or MeCN solutions containing triethanolamine (TEOA) and catalytic amounts of Ru(bpy)₃²⁺ with H₂ and ¹³CO formed as by-products. They proposed formation of a bis(bpy) complex of Ru as the active catalyst based on the observations that: a) mixtures of electrolytically generated Ru(bpy)₃²⁺ and Ru(bpy)₂·H(CO)⁺ were found to reduce CO₂ to HCOO⁻ in the dark whereas Ru(bpy)₃²⁺ alone failed to produce formate; b) Ru(bpy)₂·H(CO)⁺ did not photochemically reduce CO₂ to HCOO⁻ in the absence of sensitizer but upon addition of Ru(phen)₃²⁺ and triethanolamine, the reaction took place; and c) Ru(phen)₃²⁺ and triethanolamine alone did not catalyze CO₂ reduction.

Lenn has also found that reduction of CO₂ can be promoted by Re(CO)₃(bpy) which functions as both the photosensitizer and the reduction catalyst. The photolysis is done in triethanolamine-DMF with the system showing very high selectivity to CO formation. The mechanism of the reduction using Re(CO)₃(bpy) has been studied by Lenn, et al.,⁵⁹ and by Katal, et al.,⁶⁰ who report quantum yields for CO formation using the x-Br complex of 0.15 at 436 nm. There is agreement that the initial reaction of the excited state of Re(CO)₃(bpy) involves reductive quenching, eqn (1b), and that the reduced species then rapidly reacts with CO₂ while the cation TEOA^{•+} undergoes oxidative decomposition.



Subsequent electrocatalytic studies by Meyer using Re(CO)₃(bpy) support the intermediacy of the 19 e⁻ species Re(CO)₃(bpy)^{•-} and its rapid reaction with CO₂.⁶¹ A related hydride complex, ReH(CO)₃(bpy), has been examined by Sullivan and Meyer⁶² who find that the complex reacts rapidly with CO₂ on photolysis leading to the corresponding formate species, Re(HCOO)(CO)₃(bpy). In contrast, the same CO₂ insertion reaction occurs only slowly upon heating.

One of the first examples of photoelectrochemical reduction of CO₂ was made by Helmann using a p-gap photocathode in aqueous buffer (pH 6.8) under CO₂.⁶³ A cathodic bias of -1.0 v vs SCE under illumination gave reasonable current levels, and products including formic acid, formaldehyde, and methanol. It is perhaps significant that reduction beyond the C(2x) state of HCOOH occurred in this system. Analysis of energy conversion vs applied potential showed that maximal energy conversion efficiencies were achieved at -0.8 to -0.9 v. Use of a

photoanode, n-Si, in to addition the p-Gap photocathode removed the necessity for the external bias to achieve CO_2 reduction. A mechanism similar to that proposed for CO_2 reduction at metal electrodes involving surface adsorbed CO_2^* was invoked without supporting evidence.

The p-Gap photocathode for CO_2 reduction was also studied by Yoneyama and co-workers with Li_2CO_3 electrolyte.⁶⁴ The applied potential for significant current under CO_2 must be more negative than -0.6 v vs SCE with HCOOH , CH_3OH , and MeOH obtained as the products. Current efficiencies for these products, which were rather low, improved greatly upon the addition of a crown ether to the system and led to the suggestion that the reduction proceeds by initial deposit of Li at the cathode which then reacts with CO_2 generating CO_2^* . However with the introduction of 0.1 M concentrations of crown ether into the system, confirmation of CO_2 reduction products using $^{13}\text{C}\text{CO}_2$ as substrate seems advisable.

Another photoelectrochemical system based on p-CdTe has been reported which yields CO upon irradiation.⁶⁵ The solvent system is wet DMF with TBAP as the supporting electrolyte. The external bias required for CO_2 reduction was at least 0.7 v less negative than at metal electrodes, and the current efficiency for CO formation was as high as 70 %.

In a more recent study, Halmann and co-workers have examined a cell based on p-GaAs as the photocathode, and have found that the addition of a solution redox couple, in this case $\text{V}^{3+}/\text{V}^{2+}$, causes a marked shift in the current/voltage curve with much higher cathodic currents at an external bias of only -0.5 v vs SCE.⁶⁶ The CO_2 reduction products are as above HCOOH , CH_3OH , and MeOH . The optical to chemical energy conversion increased by more than an order of magnitude with the $\text{V}^{3+}/\text{V}^{2+}$ couple present relative to that in its absence. The presumed formation of H_2 as a by-product of the photoelectroreduction was not confirmed or quantified, and the role of the $\text{V}^{3+}/\text{V}^{2+}$ couple in the system remains unclear.

One of the more interesting reports of the photoelectrochemical reduction of CO_2 involves a system that employs components with clearly identifiable roles. The system contains p-InP as the photocathode, Mn^{2+} as an electrontransfer mediator, and the enzyme formate dehydrogenase as a catalyst to promote CO_2 reduction.⁶⁷ The system is illustrated in Figure 3. With an external bias of +0.05 v vs NHE and a solution pH of 6.8, formate was produced with a current efficiency in the range of 80-93 %. Again a labelling study using $^{13}\text{C}\text{CO}_2$ seems advisable to confirm unambiguously that the formate comes from CO_2 and not from the enzyme preparation added to the system. A leveling off of the formate concentration upon electrolysis using a carbon electrode in place of the photocathode was attributed to enzyme decomposition but Wrighton's previous work¹⁸ shows that an equilibrium is being established.

Final Comments and Conclusions

It is evident that significant progress has been made in direct and indirect electroreductions of CO_2 and in photo- and photoelectrochemical reductions during the past five years. A number of compounds have been found to act as electrocatalysts, and new systems have been devised

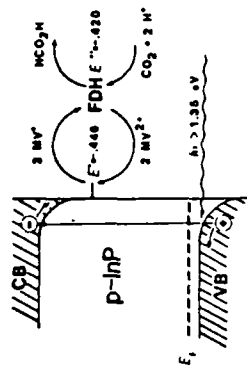


Figure 3. The semiconductor/enzyme system for photoelectrochemical reduction of CO_2 to formate.⁶⁷

which in a few instances show high selectivity to a particular product. The study by Sauvage^{31,32} using Mn^{2+} is probably the most complete and informative one done to date on the indirect electroreduction of CO_2 .

While Scheme 1, a generalized scheme for direct electrochemical reduction of CO_2 , suggests what conditions are needed for channeling to specific products, the detailed mechanism of direct electroreduction including the importance of surface adsorbed species is for the most part unknown. The situation is even more uncertain for the indirect electroreduction of CO_2 since the stabilization which makes indirect reduction possible by lowering the overpotential, requires that free CO_2^* radical anion not be involved in the mechanism. An understanding of the types of bonding and/or stabilizing interactions which can occur between CO_2 , CO_2^* , and the electrocatalyst in oxidized and reduced forms is essential to the rational development of new electrocatalysts.

Of the possible products of CO_2 reduction, formate and CO are by far the most common. While formate formation is thought to occur in aqueous systems, the reduction using Mn^{2+} in aqueous media yields primarily CO with only very small amounts of HCOOH . The possible intermediacy of metal hydrides has been invoked in a few cases which lead selectively to CO. However, M-H intermediates should channel the system to formate rather than CO based on the well documented insertion of CO_2 into M-H bonds.

We have stated that oxalate formation is the most interesting and potentially most useful of the CO_2 reduction channels because it would provide a path for converting an abundant C_1 material into a C_2 precursor. From a catalysis standpoint, the controlled formation of a C-C bond by CO_2 coupling represents a real challenge. The selective channeling to oxalate must be kinetically controlled since head-to-tail coupling of CO_2 leading to CO is thermodynamically more favorable and occurs more readily. The key to oxalate formation is the development of a radical character at the carbon atom of CO_2 . However, all stabilization of CO_2 by coordination to a transition metal complex is envisioned to occur between the CO_2 carbon atom and the metal by either an η^1 or η^2 interaction. It appears that the degree of stabilization

needed for oxalate formation must be great enough to reduce the overpotential for CO_2 formation significantly but weak enough to allow any M-C bond that is formed to be homolyzed easily. In this context, it is interesting to note that Co-C bonds found in alkyl cobalamins, cobaloximes, and Schiff base complexes are relatively weak and react primarily by homolytic bond scission.⁶⁸ Closely related to this is the observation by Floriani and co-workers⁶⁹ of coupling of CO_2 -like molecules such as methyl pyruvate promoted by $(\text{MnCoSalen})_2$.

If one key to oxalate formation is to have an electrocatalyst capable of forming a weak M-C bond, a second key is to have metal centers in close proximity. This can be accomplished in solution using dinuclear and polynuclear complexes, but a more attractive and flexible approach would be to use modified electrodes containing high concentrations of the electrocatalyst. Moreover, through such assemblies, the necessary charge could be stored for reduction beyond the Cl^- oxidation state. The development of modified electrodes containing electrocatalysts thus represents an important direction to be followed in CO_2 reduction chemistry.

With regard to photo- and photoelectrochemical reduction of CO_2 , the field is in its infancy. The attention given to the problem of light-to-chemical energy storage has focussed mainly on H^+ or H_2O reduction with only a few studies examining CO_2 as a substrate. Yet the progress has been significant with quantum yields of 0.15 at 436 nm for reduction to CO using $\text{ReBr}(\text{CO})_2(\text{bpy})$.⁶⁰ In future studies, examination of all components and steps is necessary, although those that are specific to CO_2 deal mainly with active site charge accumulation, substrate binding and activation, and selective product channeling. Questions regarding the photo-sensitizer, the electron transfer mediator, the quenching mechanism, and electron-hole separation will in most cases be the same as those posed in the development of water splitting systems. With proper catalyst development, use of photocathodes for photoelectroreduction of CO_2 appears promising, and significant progress along this line should be anticipated.

Acknowledgements

The support of the Office of Naval Research is gratefully acknowledged.

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