Lawrence Berkeley National Laboratory
Recent Work

Title

Photochemical Reduction of Carbon Dioxide Using Nickel Tetraazamacrocycles

Permalink

https://escholarship.org/uc/item/84612832

Authors

Craig, C.A.
Spreer, L.O.
Otvos, J.W.
et al.

Publication Date

1990-02-01

eScholarship.org Powered by the California Digital Library
University of California

LBL-28561
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

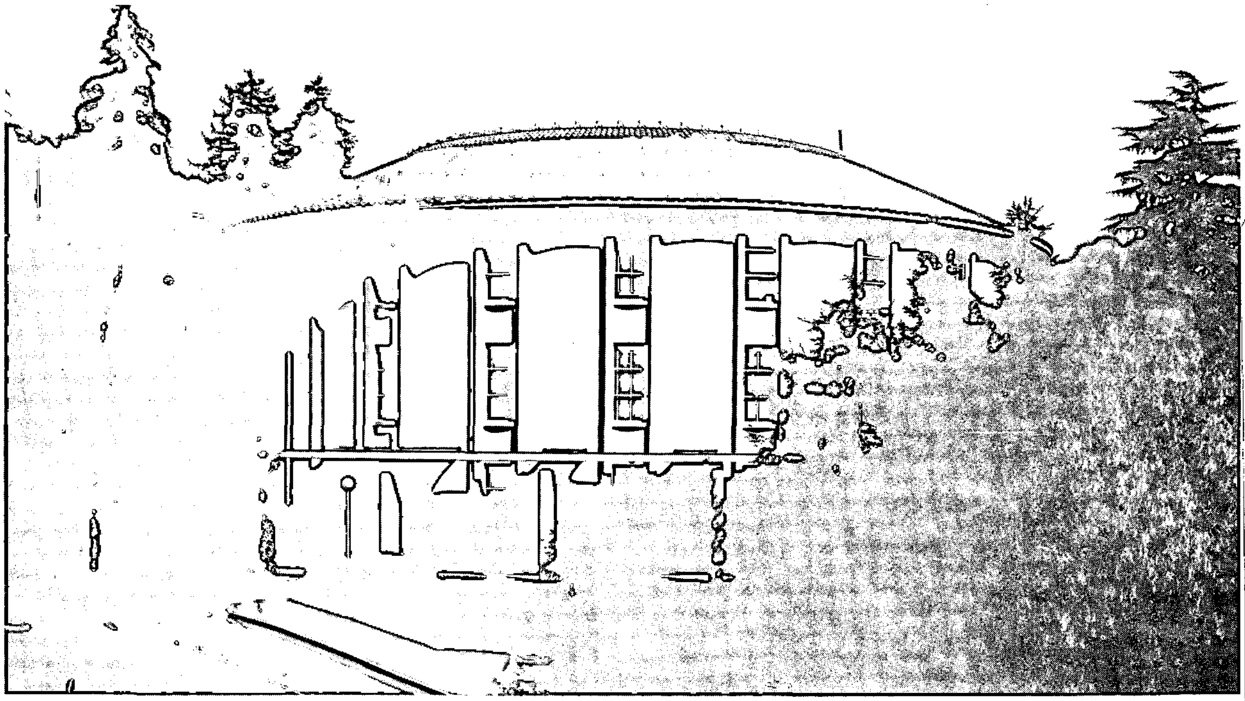
CHEMICAL BIODYNAMICS DIVISION

Submitted to Journal of Physical Chemistry

Photochemical Reduction of Carbon Dioxide Using Nickel Tetraazamacrocycles

C.A. Craig, L.O. Spreer,
J.W. Otvos, and M. Calvin

February 1990



| LOAN COPY |
|Circulates |
|for 2 weeks| Bldg. 50 Library.
Copy 2
LBL-28561

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

PHOTOCHEMICAL REDUCTION OF CARBON DIOXIDE USING NICKEL TETRAAZAMACROCYCLES

Carl A. Craig*, Larry O. Spreer**, John W. Otvos and
Melvin Calvin
Department of Chemistry and Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

* Present address: Terrapin Technologies, Inc., 165-8th St., San Francisco, CA 94103

** Department of Chemistry, University of the Pacific, Stockton, CA 95211

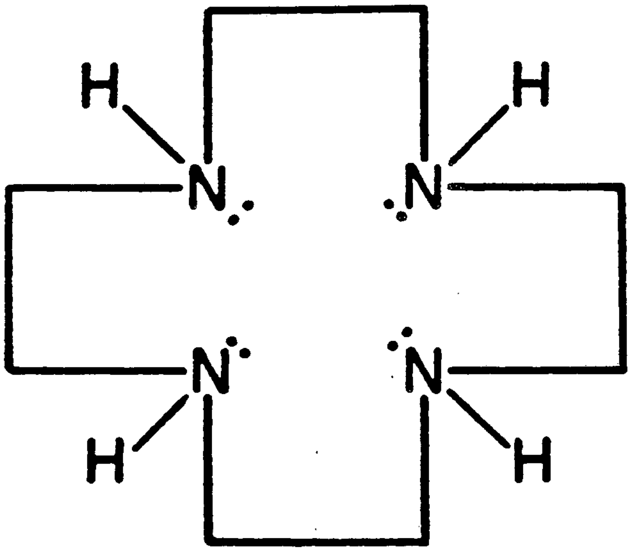
ABSTRACT

Irradiation at 440 nm of a photosensitizer, $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine), in an ascorbate buffered solution at room temperature under one atmosphere of carbon dioxide in the presence of either of the nickel(II) complexes, $[Ni(14\text{-aneN}_4)]^{2+}$ or $[Ni(12\text{-aneN}_4)]^{2+}$ (14-aneN_4 = 1,4,8,11-tetraazacyclotetradecane, 12-aneN_4 = 1,4,7,10-tetraazacyclododecane), results in the reduction of carbon dioxide. We have measured the quantum efficiency of CO_2 reduction, and we report that both of the Ni(II) macrocycles reduce carbon dioxide to carbon monoxide with similar quantum yields; $[Ni(12\text{-aneN}_4)]^{2+}$ produces formate in addition to carbon monoxide. By using ^{14}C-labeled carbon we were able to identify carbon dioxide as the only source of carbon in both carbon monoxide and formate.

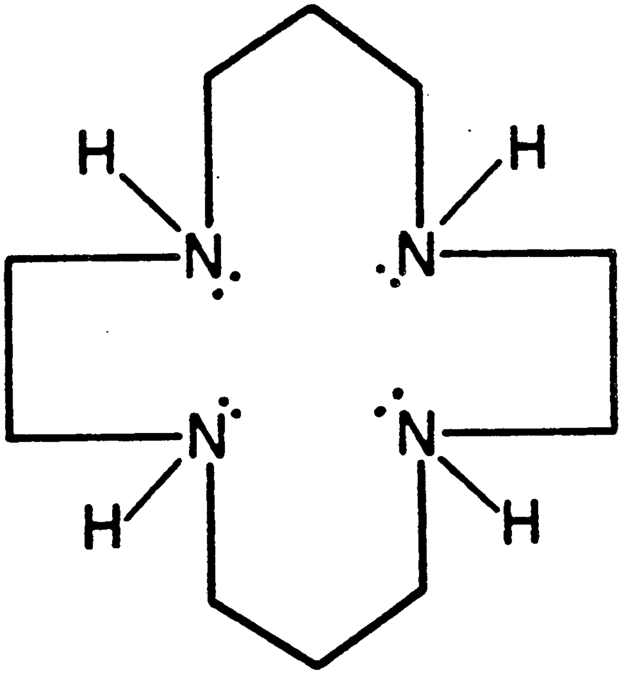
INTRODUCTION

Research dedicated to developing light harvesting solar conversion systems, particularly those intended to produce chemical fuels from inexpensive starting materials, has had significant and exciting advances.[1-5] The photochemical production of chemical fuels is important, when we keep in mind the necessity for the eventual replacement of our primary energy resource, fossil fuels. Like fossil fuels, synthetically produced chemical fuels are feasible for use as sources of energy only if the production and storage of the fuels meet criteria for economical synthesis as well as safe transportation and storage.[6] Simple organic compounds such as methane and methanol are quite well suited for use as fuels in those respects. The generation and use of alternative fuels deserves ecological consideration as well.[7] Current concerns regarding greenhouse gases and pollutants produced from combustion of fossil fuels have renewed interest in utilizing carbon dioxide as a feedstock in the production of organic fuels.[8]

The chemistry of CO_2 has been well studied.[9-11] The use of carbon dioxide in the electrochemical production of methanol and methane with semiconductors and metal electrodes has been demonstrated.[12-14] Furthermore, electrochemical reduction of carbon dioxide to carbon monoxide mediated by the nickel tetraaza macrocycle compound $[Ni(14\text{-}aneN_4)]^{2+}$ (1,4,8,11-tetraazacyclotetradecane) has been reported.[15] The importance of this particular Ni(II) complex was first described by Sauvage.[16] Further work by Sauvage[17] established that $[Ni(14\text{-}aneN_4)]^{2+}$ was unique among numerous complexes investigated in showing a high selectivity for the electroreduction of CO_2 over the electroreduction of water. In



12-aneN_4



14-aneN_4

addition, their reports indicated that the reduction of CO_2 was due to adsorbed species on the electrode surface and the contribution by reduced nickel species in the bulk solution was marginal.

We reported on a homogeneous aqueous system utilizing $[Ni(14\text{-ane-}N_4)]^{2+}$ that was capable of the photochemical reduction of CO_2 to CO.[18] In this report we describe further work on the photochemical reduction of CO_2 with $[Ni(14\text{-ane}N_4)]^{2+}$. We have also extended our study to include another nickel macrocycle $[Ni(12\text{-ane}N_4)]^{2+}$ (1,4,7,10-tetraazacyclododecane). In contrast to the electrochemical studies, $[Ni(12\text{-ane}N_4)]^{2+}$ is almost as effective as $[Ni(14\text{-ane}N_4)]^{2+}$ in mediating the photoreduction of CO_2 to CO. The $[Ni(12\text{-ane}N_4)]^{2+}$ complex also reduces CO_2 to formate while the $[Ni(14\text{-ane}N_4)]^{2+}$ does not. The two nickel complexes have very different conformational structures; this fact may play a role in the determination of product distribution.

EXPERIMENTAL

Synthesis. 1,4,8,11-tetraazacyclotetradecane nickel (II) triflate $[Ni(II)(CF_3SO_3)_2]$ was prepared via a metathesis reaction. HCF_3SO_3 was added dropwise to an acetonitrile solution of $Ni(NO_3)_2$. Upon addition of triflic acid, the acetonitrile solution shows a slight but noticeable color change from green to blue-green. Under a flush of N_2, the acetonitrile was evaporated until a blue-green slurry formed. A green solid was removed from the slurry by filtration. The green solid $[Ni(CF_3SO_3)_2]$ was washed repeatedly with ether and used without further purification. The $Ni(CF_3SO_3)_2$ (0.8 g) was dissolved in 50 ml of acetonitrile. An equimolar quantity of 1,4,8,11-tetraazacyclotetradecane (14-aneN_4) was added to the acetonitrile solution. The solution immediately began to darken. After 10 min, 5 ml of H_2O and 5 ml of ethanol were added to the brown solution. The reaction was stirred at ambient temperature for 2 hr. The acetonitrile was then removed by roto-evaporation. An oily yellow residue was formed. It was combined with several ml of H_2O and passed through a Sephadex G-25/H_2O column. The major fraction was collected and crystallized from H_2O in the presence of $LiCF_3SO_3$. The orange crystalline solid (0.41 g, 33% yield) gave good analysis. Anal. Calcd. for $NiC_{14}H_{24}F_6S_2O_6$ C, 25.90; H, 4.34; N, 10.06; Found C, 25.45; H, 4.34; N, 10.14.

1,4,7,10-tetraazacyclododecane nickel(II) triflate [$Ni(CF_3SO_3)_2$] (1.75 g) was dissolved in 80 ml of acetonitrile. Fifteen ml of distilled water was added to the blue-green solution followed by a twofold excess of free base ligand (12-aneN_4). The solution became purple in color within 5 min of stirring at ambient temperature. The solution was stirred for 12 hr and the solvent volume reduced under a flow of N_2 to approximately 10 ml. This dark purple solution was chromatographed on Sephadex G-25/H_2O column where the most concentrated fraction was collected. Excess $LiCF_3SO_3$ was added to the solution and the water was evaporated under a flow of N_2. The residual solid was dissolved in 80 ml ethanol and 10 ml of H_2O, and [Ni(12-aneN_4)]$(CF_3SO_3)_2$ was crystallized by slow evaporation. The product yield was 1.56 g (59%). The purple solid was recrystallized from aqueous solution with a slow vapor infusion of acetonitrile. Anal. Calcd. for $NiC_{12}H_4H_20^F6^S2^06$ C, 22.73; H, 3.81; N, 10.60. Found C, 22.23; H, 4.01; N, 11.04.

Photochemistry: $Ru(bpy)_3Cl_3 \cdot 6H_2O$ (GFS Chemicals) was found to be suitable for use without further purification. Photolysis was carried out with a 1000 W lamp. The source beam was passed through a 20 cm water filter, focused, and passed through a 440 nm band pass filter into the aqueous photolysis solution. Light intensities for quantum yield measurements were determined with a Scientific Model 36-20002 power and energy indicator. Gas chromatographic analyses for CO and H_2 were made with a Varian Model 3700 gas chromatograph. Radio-gas chromatography was completed on a Varian Model 3700 gas chromatograph which had been configured for counting beta particle emission.[19] Liquid scintillation counting of aqueous ^{14}C samples was carried out in Aquasure scintillator cocktail with a Packard Model 1900 liquid scintillation counter.

Solutions for photolysis were all prepared using deionized water (Millipore). $Ru(bpy)_3^{2+}$ concentration was $1x10^{-4}$ M, Ni(II) macrocycle concentration was $2x10^{-3}$ M, ascorbic acid concentration was 0.1 M and the pH was adjusted to 5±0.1. Photolysis solutions were deoxygenated in the photolysis cell through a glass frit for 30 min with CO_2 at a flow rate of 4 ml/min immediately prior to the photolysis.

RESULTS AND DISCUSSION

Carbon dioxide was reduced photochemically by the nickel macrocycles $[Ni(14\text{-}aneN_4)]^{2+}$ and $[Ni(12\text{-}aneN_4)]^{2+}$ in the presence of $Ru(bpy)_3^{2+}$ as photosensitizer. The photolysis, using monochromatic 440 nm radiation, was carried out in an aqueous solution buffered at pH 5 by ascorbate which also acted as a sacrificial reductive quencher. In view of the unique nature of the $[Ni(14\text{-}aneN_4)]^{2+}$ as an efficient and selective catalyst for the electroreduction of CO_2,[17] we were interested in comparing and contrasting its behavior with its $[Ni(12\text{-}aneN_4)]^{2+}$ analogue in our homogeneous photochemical system. We found that the $Ni(II)L^{2+}$ complexes were very selective for CO_2 reduction versus hydrogen production. The structures of the two nickel complexes are quite different. Quantum yields for photoreduction of CO_2 were determined for each Ni(II)L^{2+} complex. Formate was found to be a product of CO_2 reduction when [Ni(12-aneN$_4$)]$^{2+}$ was used but no formate was identified when [Ni(14-aneN$_4$)]$^{2+}$ was used. These matters are discussed below.

Carbon Dioxide Reduction

Carbon monoxide was a product of the photoreduction of CO_2 in all experiments. The reduction of CO_2 does not occur in the absence of the photosensitizer Ru(bpy)$_3^{2+}$. Similarly, the photoreduction does not take place if the Ni(II) macrocycles or the reductive quencher (ascorbate) are omitted from the reaction solution.

Figure 1 illustrates CO formation over the course of a typical experiment. Initially, the rate of carbon monoxide formation is constant with either of the Ni(II) macrocycles. Then after approximately five hours of photolysis the rate of CO production decreases. Absorbance measurements of the reaction solution before and after irradiation establish that the Ru(bpy)$_3^{2+}$ sensitizer is undergoing decomposition. Under our conditions only 75 percent of the Ru(bpy)$_3^{2+}$ remains after four hours of photolysis. In several runs, additional photosensitizer was added after four hours of reaction and the photolysis was continued. The rate of CO production after five hours during these runs was above the normal rate but did not reach the rate observed at the beginning of the photolysis. This suggests that some degradation of the nickel complexes may be occurring although this is difficult to confirm spectrophotometrically since the absorbance measurements are dominated by the Ru(bpy)$_3^{2+}$ chromophore.

One important point that is apparent from Figure 1 is that both [Ni(12-aneN$_4$]$^{2+}$ and [Ni(14-aneN$_4$]$^{2+}$ mediate the reduction of CO_2. The [Ni(14-aneN$_4$)]$^{2+}$ complex is more efficient than the [Ni(12-aneN$_4$)]$^{2+}$

species. The differences, however, are not nearly as dramatic as those noted in the electrochemical reduction studies[17] where the $[Ni(14\text{-}aneN_4)]^{2+}$ complex was unique in its ability to catalyze the reduction of CO_2.

Nickel Macrocycles

The two nickel macrocycles differ in both their solid state and solution properties. The 14-member macrocyclic ligand is sufficiently large to produce a Ni(II)L structure with a planar arrangement of the Ni(II) and the four coordinating N atoms. The yellow square-planar complex is diamagnetic as the d^8 Ni(II) adopts a low spin electron configuration.[20] This structure is maintained in solution as shown by the single visible absorption peak which is characteristic of low spin D_{4h} nickel complexes (Figure 2).[20] In contrast, the 12-member macrocyclic ligand is too small to form a planar structure with Ni(II) and the $[Ni(12\text{-}aneN_4)]^{2+}$ adopts a folded or cis geometry. The crystal structure of $[Ni(12\text{-}aneN_4)(OH_2)_2](ClO_4)_2 \cdot H_2O$ was recently determined.[21] This structure is also maintained in solution as the electronic spectrum resembles that of high-spin octahedral nickel complexes.[22]

Source of Carbon Monoxide

Carbon monoxide was observed as a product in the photochemical studies when all the components, ie, $Ru(bpy)_3^{2+}$ as sensitizer, ascorbate as reductive quencher, nickel complex, and CO_2 substrate were present. We also observed that photolysis of solutions containing $Ru(bpy)_3^{2+}$, ascorbate, and nickel complex that were deoxygenated by helium instead of CO_2 produced small amounts of CO_2. The source of this CO_2 is unknown but could involve the oxidation of ligand or ascorbate. Furthermore, continued photolysis (over 2 hr) of the helium-purged solution leads to CO production, presumably from the reduction of the CO_2 that is formed.

Radiolabeling measurements were performed in order to determine unequivocally the carbon source for CO in the photoredox reaction. A photochemical run was set up with CO_2 used to deoxygenate a solution containing ascorbate, $Ru(bpy)_3{}^{2+}$, and Ni(II) macrocycle complex. Then a volume of CO_2 gas from the headspace of the photolysis cell was removed and replaced with an equal volume of $^{14}CO_2$ of known specific activity. The solution was stirred for one hour in the dark to equilibrate $14CO_2/CO_2$. The system was then photolyzed for 24 hr. Following photolysis, a 1 ml sample of the headspace gas of the cell was injected into a gas chromatograph equipped to measure both mass and radioactivity.[19] Retention times together with integrated areas of the mass peaks and the radioactivity peaks provide quantitative information regarding the products. In this way the specific activities of both CO_2 and CO in dpm/μl of gas injected were measured. Table 1 lists the specific activities for CO_2 and CO for separate experiments using $[Ni(14\text{-}aneN_4)]^{2+}$ and $[Ni(12\text{-}aneN_4)]^{2+}$. The specific activities of CO_2 and CO are the same within experimental error. This provides conclusive evidence that carbon dioxide is being reduced in these photoredox systems and that carbon dioxide is the only source of carbon in CO.

Formate Production

Carbon monoxide is, of course, only one of a number of possible CO_2 reduction products.[18] Many of the other possible products such as formate, formaldehyde or methanol are soluble in aqueous solution. In our system we have a large amount of ascorbate which acts as a sacrificial electron donor. The organic products from this process make it difficult to analyze for solution-soluble CO_2 reduction products. Radiolabeling studies were again utilized to overcome this difficulty.

Carbon dioxide labeled with ^{14}C was added to the photolysis cell containing photosensitizer, ascorbate and nickel complex. After irradiation, the remaining radioactive CO_2 was removed from the solution by purging with normal CO_2. Figure 3 shows the solution ^{14}C activity versus purging time. After prolonged irradiation of solutions containing $[Ni(14\text{-}aneN_4)]^{2+}$, the solution radioactivity could be reduced to near background levels. Under similar conditions, the photoredox system with $[Ni(12\text{-}aneN_4)]^{2+}$ yielded considerably higher levels of residual radioactivity after purging to remove $^{14}CO_2$. The reaction solution was distilled in order to identify and measure the radioactive compounds. The distillate was found to contain the same amount of radioactivity as the reaction solution following CO_2 purging. In other words, no activity was lost during distillation. When the distillate was made basic with sodium hydroxide, and the basic solution redistilled, the radioactivity could be concentrated in the residue. The concentrated sample which contained all the radioactivity was acidified with HCl and an aliquot was injected into the radio-gas chromatograph. The radioactive compound was found to be formic acid and was quantitated by standard gas chromatographic response factors.

Hydrogen Production

Remarkably in this aqueous solution, the photochemistry is very selective for the reduction of carbon dioxide versus the reduction of water. In the presence of either of the nickel complexes the photoredox reaction produces almost exclusively reduction products of CO_2 with little H_2. In contrast, photolysis of an aqueous solution of $Ru(bpy)_3^{2+}$

and ascorbate in the absence of nickel complex results in formation of appreciable amounts of hydrogen. This occurs in CO_2-saturated solution and in helium-deoxygenated solution. Figure 4 illustrates the quantitative results of hydrogen production in the presence and absence of the nickel macrocycles. How the nickel complexes inhibit the production of hydrogen is unclear especially since decomposition of the $Ru(bpy)_3 2+$ sensitizer occurs both in the presence and absence of the nickel species.

Quantum Yield

The homogeneous photochemical reduction of CO_2 in the presence of $[Ni(14\text{-}aneN_4)]^{2+}$ and $[Ni(12\text{-}aneN_4)]^{2+}$ proceeds with low quantum efficiency which is not surprising given the multi-step nature of the photoredox reaction. Quantum Yields: $[Ni(14\text{-}ane\text{-}N_4)]^{2+}$ CO, 6.0×10^{-4}, formate 5×10^{-5}; $[Ni(12\text{-}aneN_4)]^{2+}$ CO, 4.5×10^{-4}, formate 1.9×10^{-4}. The initial step following photon absorption by the sensitizer is reductive quenching of the ruthenium excited state by ascorbate ion. Quenching does not occur at lower pH values where only ascorbic acid is present. The rate constant for reductive quenching by ascorbate[23] is $2x10^7 s^{-1}$, which was confirmed in our laboratory. Creutz and Sutin have established the cage escape yield for the ruthenium-ascorbate complex. The cage escape efficiency is approximately 50%.[23] The free ruthenium mono-cation must then undergo a bimolecular electron transfer with the Ni(II) macrocycle. The efficiency of this electron transfer reaction is currently under investigation in our laboratory. Our previous discussion[18] of the mechanism for the photoreduction of CO_2 in this aqueous system involved nickel hydride species. If these are present, there must be a multiple-step sequence in which the nickel hydride is formed and then undergoes reaction with CO_2. In spite of numerous studies involving CO_2 reaction with transition metal complexes there is not yet a clear understanding of the intermediates or mechanistic steps.

SUMMARY

Carbon dioxide is reduced photochemically by Ni(II) macrocyclic complexes in aqueous solution in the presence of a photosensitizer. The quantum yields for CO_2 reduction are low but this may be explained by consideration of the multi-step nature of the reaction.

As previously noted, the $[Ni(14\text{-aneN}_4)]^{2+}$ complex is a remarkably efficient catalyst for the electroreduction of CO_2. The electrochemical results are best explained by adsorbed species on the electrode surface. The fact that $[Ni(14\text{-aneN}_4)]^{2+}$ is a much better electrocatalyst than any other Ni(II) complex has been attributed to its planar nature which presumably facilitates adsorption and subsequent access of the CO_2 substrate to the nickel center. In contrast, the 14- and 12-member macrocyclic nickel complexes are quite similar in their ability to reduce CO_2 in our homogeneous system. The $[Ni(14\text{-aneN}_4)]^{2+}$ species is very selective in the electrochemical system in favoring CO_2 reduction over water reduction. Similarly, in our photoredox system the 14-member as well as the 12-member macrocyclic nickel complexes reduce CO_2 with H_2 only a very minor product. We are currently doing laser flash photolytic studies to obtain more information about the role of reduced nickel species in our photoredox system.

One interesting difference in the action of the two nickel macrocycles is that $[Ni(12\text{-aneN}_4)]^{2+}$ produces both CO and formate while the $[Ni(14\text{-aneN}_4)]^{2+}$ yields only CO. The two nickel complexes have very different structures and properties. The $[Ni(14\text{-aneN}_4)]^{2+}$ is a low-spin square-planar complex while $[Ni(12\text{-}aneN_4)]^{2+}$ is six-coordinate with two cis water molecules. A detailed explanation for the difference in product distribution for the 12- and 14-member nickel complexes is not possible at this time but the structural differences most probably play a significant role. In the planar 14-complex, CO_2 can only coordinate to one site and probably only through one atom, ie, an oxygen or less favorably the carbon. In the 12-member macrocycle with two cis positions available for possible coordination, the carbon dioxide could conceivably act as a bidentate ligand and occupy both sites through a carbon and an oxygen. Adjacent coordination sites might favor attack at carbon which must occur in order to produce formate.

Acknowledgement.We would like to thank Mr. B. E. Gordon for his assistance in the radiolabeling experiments. One of us (L.O.S.) is funded partially by the Associated Western Universities, Inc. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Fundamental Interactions Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

REFERENCES

1. Fugita, E.; Szalda, D.J.; Creutz, C.; Sutin, M. J. Am.Chem. Soc. 1988, 110, 4870 and references therein.
2. Lehn, J.-M.; Zeissel, R. Proc. Natl. Acad. Sci. 1982, 79, 701.
3. Kutal, C.; Corbin, J.A.; Ferraudi, G. Organometallics'1987, 6, 553.
4. Mandler, D.; Willner, I. J. Am. Chem. Soc.. 1987, 109, 7884.
5. Blajeni, B.A.; Halmann, M.; Manassen, J. Solar Energy Materials 1983, 8, 425.
6. Bolton, J.R.; Haught, A.F.; Ross, R.T. Photochemical Conversion and Storage of Solar Energy; Connolly, J.S., Ed.; Academic Press: New York, 1981, 297-339.
7. Calvin, M. Solar Energy: Chemical Conversion and Storage; Hautala, R.R.; King, B.R.; Kutal, C., Eds.; Humana Press, Clifton, New Jersey, 1979, 31-50.
8. Macdonald, G. J., Ed. The Long-Term Impacts of Increasing Carbon Dioxide Levels; Ballinger Publishing Co.: Cambridge, Mass. 1982.
9. Sneeden, R.P.A. Comprehensive Organometallic Chemistry, Wilkinson, G., Ed.; Pergamon: New York, 1982, 1153-1154.
10. Palmer, D.A.; Van Eldik, R. Chem. Rev. 1983, 83, 651.
11. Halmann, M. Energy Resources Through Photochemistry and Catalysis; Gratzel, M., Ed.; Academic Press: New York, 1983, 507-531.
12. Ulman, M.; Tinnemans, A.H.A., Mackor, A.; Blajeni, B.A.; Halmann, M. Int. J. Solar Energy, 1982, 1, 213.
13. Summers, D.P.; Frese, K.W., Jr. Langmuir, 1988, 4, 51.
14. Willner, I.; Maidan, R.; Mandler, D.; Durr, H.; Dorr, G.; Zengerle, K. J. Am. Chem. Soc. 1987, 109, 6080.
15. Fisher, B.; Eisenberg, R. J. Am. Chem. Soc. 1980, 102, 7361.

16. Baley, M.; Collin, J.P.; Ruppert, R.; Sauvage, J.P. J. Chem. Soc. Chem. Commun. 1984, 1315.

17. Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.P. J. Am. Chem. Soc. 1986, 108, 7461.

18. Grant, J.L.; Goswami, K.; Spreer, L.O.; Otvos, J .W.; Calvin, M. J. Chem. Soc. Dalton Trans. 1987, 2105.

19. Gordon, B.E.; Erwin, W.R.; Press, M.; Lemmon, R.M. Anal. Chem. 1978, 50, 179.

20. Vigee, G.S.; Watkins, C.L.; Bowen, J.F. Inorg. Chim. Acta 1979, 35, 255.

21. Scott, B.; Brewer, K.J.; Spreer, L.O.; Craig, C.A.; Otvos, J.W.; Calvin, M.; Taylor, S.E. J. Coord. Chem. in press.

22. Martin, L.Y.; Sperati, C.R.; Busch, D.H. J. Am. Chem. Soc. 1977, 99, 2968.

23. Creutz, C.; Sutin, N.; Brunschwig, B.S.; J. Am.Chem. Soc. 1979, 101, 1297.

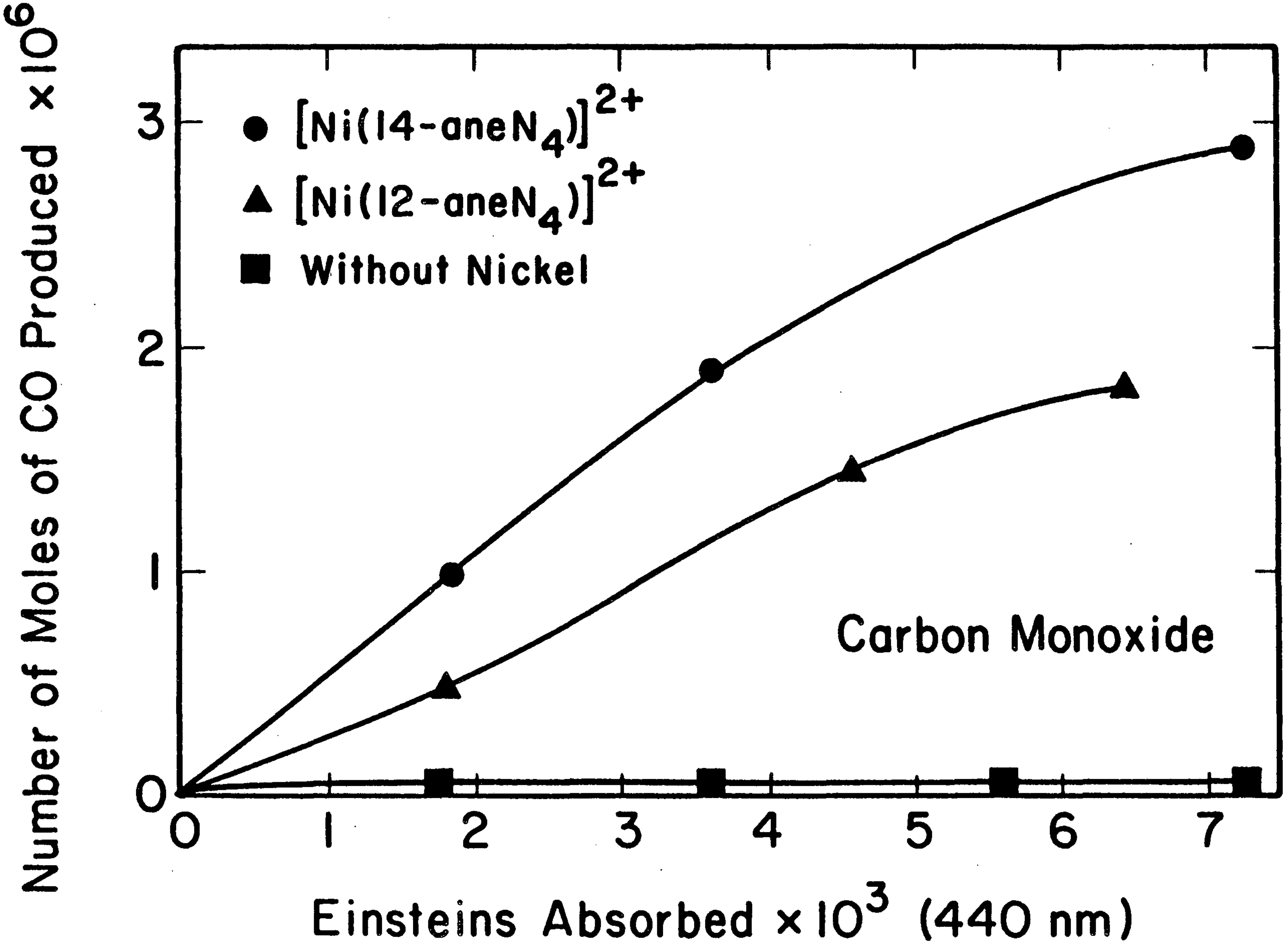
FIGURE CAPTIONS

Figure 1 Number of moles of CO produced versus Einsteins absorbed (440 nm) for solutions containing 2 x 10^{-3} M ● $[Ni(14\text{-}aneN_4)]^{2+}$, ▲ $[Ni(14\text{-}aneN_4)]^{2+}$ or ■ no nickel complex; solutions also contain 1 x 10^{-4} M $[Ru(bpy)_3]^{2+}$. 0.1 M ascorbate (pH = 5), T = 301 K.

Figure 2 Electronic absorption spectra in aqueous solutions of square planar $[Ni(14\text{-}aneN_4)]^{2+}$ —— and cis octahedral $[Ni(12\text{-}aneN_4)(OH_2)_2]^{2+}$ ⋯⋯ .

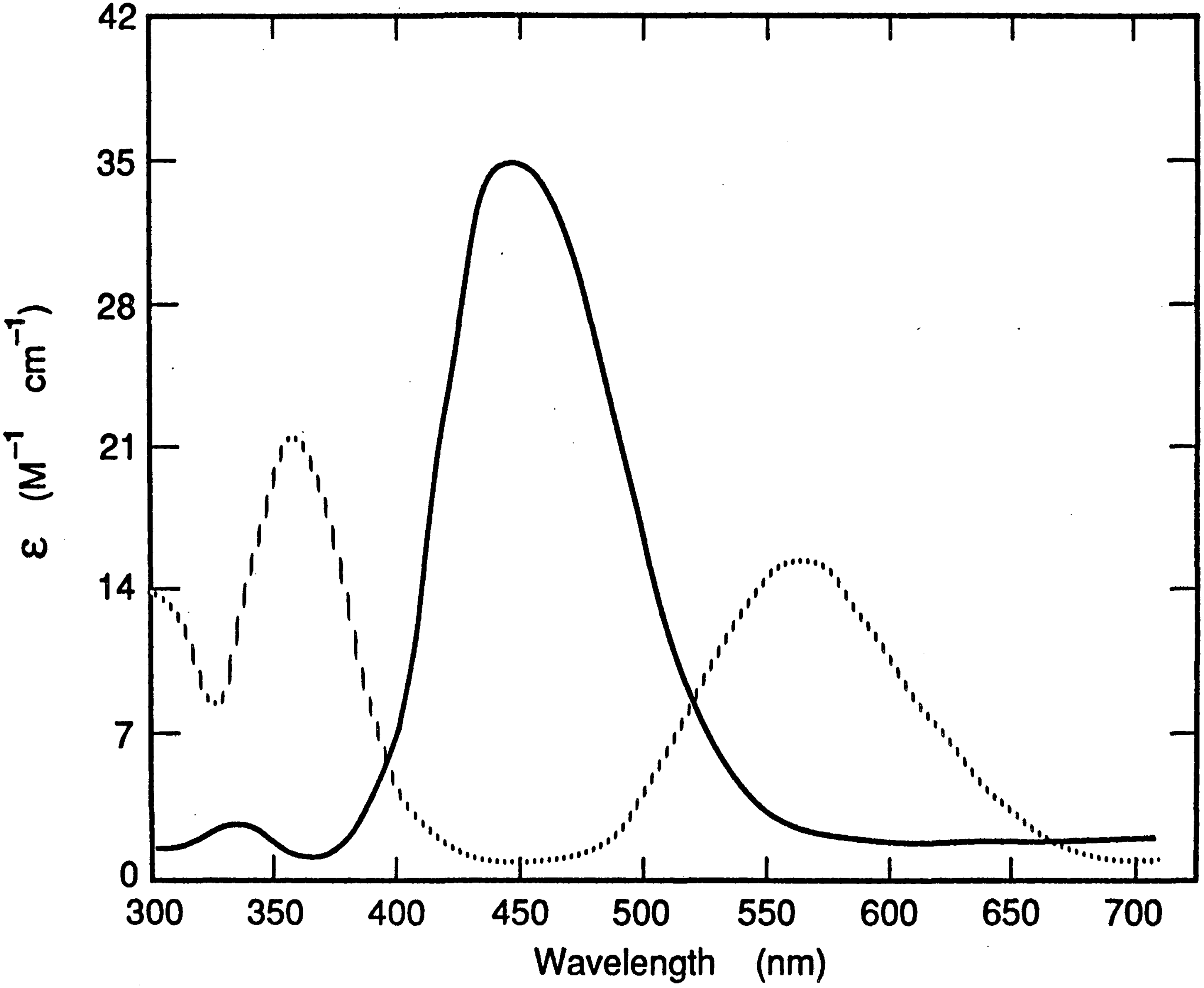
Figure 3 Solution ^{14}C activity as a function of purging time with unlabeled CO_2.

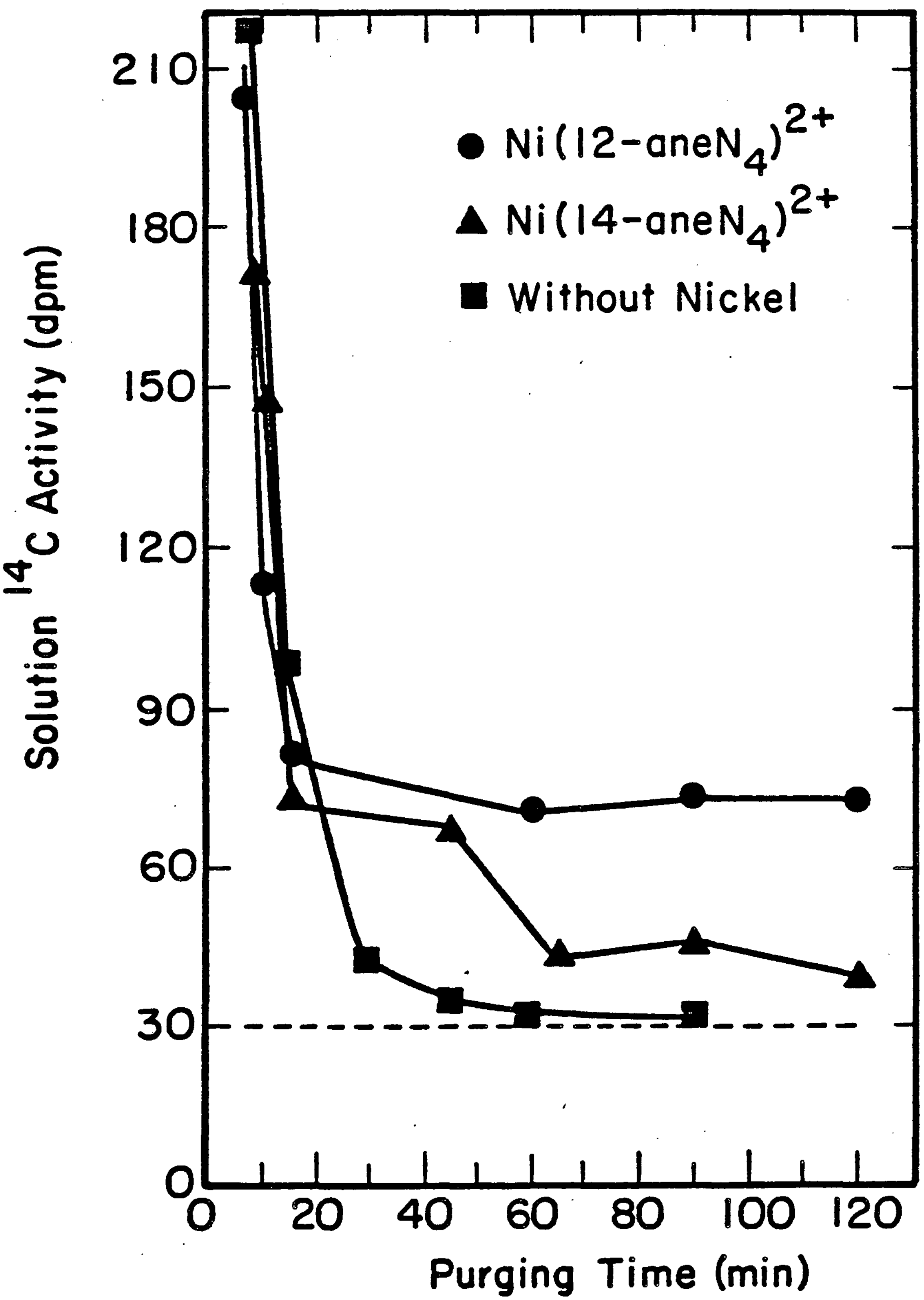
Figure 4 Moles of hydrogen produced versus Einsteins absorbed (440 nm), ● $[Ni(14\text{-}aneN_4)]^{2+}$, ▲ $[Ni(12\text{-}aneN_4)]^{2+}$, ■ no nickel complex present. All solutions contain $[Ru(bpy)_3]^{2+}$, ascorbate and CO_2.


Number of Moles of CO Produced ×10^6
3
2
1
0
● [Ni(14-aneN$_4$)]$^{2+}$
▲ [Ni(12-aneN$_4$)]$^{2+}$
■ Without Nickel
Carbon Monoxide
0
1
2
3
4
5
6
7
Einsteins Absorbed ×10^3 (440 nm)

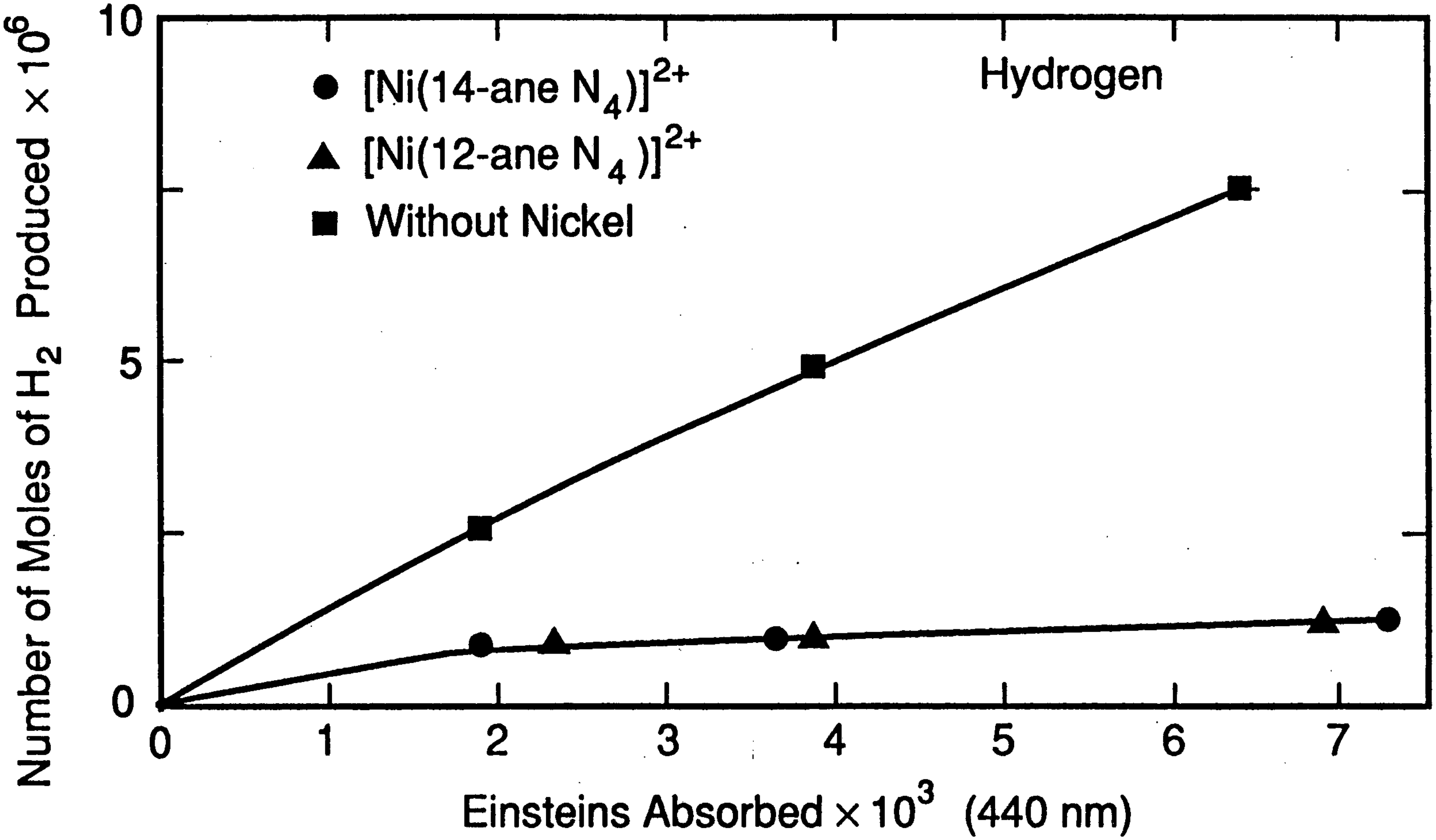
-- XBL 889-3272 --

Absorption Spectra of Ni(14–ane N_4)$^{2+}$ (——) and Ni(12–ane N_4)$^{2+}$ (⋯⋯)





● Ni(12-aneN4)2+
▲ Ni(14-aneN4)2+
■ Without Nickel
Solution 14C Activity (dpm)
0
30
60
90
120
150
180
210
0
20
40
60
80
100
120
Purging Time (min)



Craig/Calvin-1

RADIOLABELING EXPERIMENTS CONFIRM THAT THE ONLY ORIGIN OF CO IS CO_2

Ni(II) Macrocycle	Specific Activity ^{14}CO	Specific Activity $^{14}CO_2$
$[Ni(14\text{-}aneN_4)]^{2+}$	182±18 dpm/μl	171±8 dpm/μl
$[Ni(12\text{-}aneN_4)]^{2+}$	400±43 dpm/μl	440±5 dpm/μl

Photolysis Conditions:

$[Ni(II)\ macrocycle]^{2+} = 2 \times 10^{-3}$ M

$[Ru(bpy)_3]^{2+} = 1 \times 10^{-4}$ M

[Ascorbic Acid] = 0.1 M

pH = 5.0 ± 0.1

T = 301 K

XBL 889-3280

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720