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Towards the Photoreduction of CO₂ with Ni(bpy)_n²⁺ Complexes

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Abstract

When an acetonitrile solution containing Ni(bpy)₃²⁺, triethylamine and CO₂ is irradiated at 313 nm, CO is produced with a quantum yield ~ 0.1% (defined as CO produced/photons absorbed). Flash photolysis, electrochemistry, and pulse radiolysis experiments provide evidence for the formation of Ni^I(bpy)₂⁺, as an intermediate, in the photochemical Ni(bpy)₃²⁺/TEA/CO₂ system. Although Ni⁰(bpy)₂ does react with CO₂, Ni^I(bpy)₂⁺ seems unreactive toward CO₂ addition. The x-ray structure of [Ni₃(bpy)₆](ClO₄), which crystallize as blue-violet needles, reveals the existence of a dimer in the solid. UV-vis spectra also indicate that reduced Ni(bpy)₃²⁺ solutions contain Ni^I(bpy)₂⁺, Ni⁰(bpy)₂ and [Ni(bpy)₂]₂ complexes in equilibrium.

Introduction

The efficient reduction of CO₂ to fuels and organic chemicals is a fundamental chemical challenge. The activation of CO₂ by transition metal complexes continues to be the subject of considerable interest.³ Nickel(0) complexes have been previously used as catalysts for the C-C coupling reaction between alkenes and CO₂, and for CO₂ reduction to CO. Inoue et al. found that Ni(COD)₂

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(COD = 1, 5-cyclooctadiene) catalyzes the reaction of 1-hexyne and CO₂ into 4, 6-dibutyl-2-pyrone along with 1-hexyne oligomers.⁴ A similar reaction, studied by Hoberg et al.⁵, indicated that an oxanickela-5-membered ring complex is formed by condensation of CO₂ and alkyne with the Ni(0) complex. Addition of another alkyne yields a complex with the seven-membered ring structure suggested by Inoue. The 2-pyrone and the starting Ni(0) complex are formed upon heating this complex. Hoberg et al. further studied the C-C coupling reactions of CO₂ with alkynes, alkenes (including cycloalkenes) and 1, 2- or 1, 3-dienes.⁶⁻¹² Unfortunately most of these reactions produce stable five-membered metallacycle complexes and the catalytic reactions, involving insertion of activated alkynes (or other reagents) into the five-membered metallacycle followed by reductive elimination, have not been realized.

CO₂ copolymerization is another attractive approach to chemical utilization of CO₂. Recently Tsuda et al. reported¹³⁻¹⁷ the efficient copolymerization of CO₂ with diynes to produce poly-(2-pyrones) using Ni(COD)₂ as a catalyst.

Electrochemical methods offer an alternative for bringing about nickel-catalyzed CO₂ insertion into acetylenic derivatives under mild conditions (i.e. 1 atm CO₂ at 25 °C compared to 50 atm CO₂ at 90-120 °C in Tsuda's and Inoue's experiments). Duñach et al. successfully showed that the incorporation of carbon dioxide into alkynes catalyzed by electrogenerated nickel-bipyridine complexes gives α , β -unsaturated acids in moderate to good yields.¹⁸⁻²³ The electrocatalytic carboxylation reaction was undertaken on a preparative scale in the presence of a sacrificial magnesium anode; the cleavage of the 5-membered nickelacycle by magnesium ions is thought to be the important step in this catalytic system.

The electrochemistry of Ni(bpy)₃²⁺ (bpy = 2,2'-bipyridine) in acetonitrile (MeCN) or dimethylformamide (DMF) has been studied by several researchers.^{18,24-29} However there is no agreement on the identity of the redox

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active species. The first reduction wave is assigned to a variety of reactions involving $\text{Ni}^0(\text{bpy})_2$, $\text{Ni}^0(\text{bpy})_3$, $\text{Ni}^{\text{I}}(\text{bpy})_2^+$, and $\text{Ni}^{\text{I}}(\text{bpy})_3^+$. The majority of the studies indicate that the first reduction at -1.25 V vs. SCE is a two-electron reduction followed by loss of a bpy ligand. The reasons are: (1) the current is twice that expected for a one-electron reduction; (2) the difference between E_{pc} and E_{pa} is ~40 mV, which is close to the theoretical value of 27 mV for a two-electron reduction process. Tanaka et al. have suggested that the first reduction is the result of two one-electron processes: $\text{Ni}^{\text{II}}(\text{bpy})_3^{2+}$ to $\text{Ni}^{\text{I}}(\text{bpy})_3^+$ followed by $\text{Ni}^{\text{I}}(\text{bpy})_3^+$ to $\text{Ni}^0(\text{bpy})_3$, based on the observation of an Ni(I) EPR signal that they assign to $\text{Ni}^{\text{I}}(\text{bpy})_3^+$. Prasad and Scaife have isolated a blue solid that they identify as $[\text{Ni}^{\text{I}}(\text{bpy})_2]\text{ClO}_4$, from bulk electrolysis of $\text{Ni}^{\text{II}}(\text{bpy})_3^{2+}$ (UV-vis of the solution: 400 nm (9000), 570 nm (6900)). They concluded that $\text{Ni}^{\text{II}}(\text{bpy})_3^{2+}$ is first reduced to $\text{Ni}^{\text{I}}(\text{bpy})_3^+$ followed by loss of a bpy ligand. However, the elemental analysis of their solid contains large errors for C, H, and Ni. Misono et al. reported³⁰ the spectrum of dark green $\text{Ni}^0(\text{bpy})_2$ (with an absorption at 680 nm), prepared by de-ethylation from $\text{NiEt}_2(\text{bpy})$ in the presence of bpy,³¹ in HMPT (hexamethylphosphoric triamide). This absorption maximum does not agree with that found by Prasad and Scaife. Dark violet crystals of $\text{Ni}^0(\text{bpy})_2$ have been prepared by metal-vapor synthesis and characterized by IR and NMR spectroscopies, however, UV-vis data were not reported.²⁷

Although electrochemical CO_2 incorporation into unsaturated hydrocarbons is a significant advancement, it is not economical to fix CO_2 in this manner. We are interested in using $\text{Ni}(\text{bpy})_3^{2+}$ to photochemically reduce CO_2 . We have found that when an MeCN solution containing $\text{Ni}(\text{bpy})_3^{2+}$, triethylamine (TEA) and CO_2 is irradiated at 313 nm, it produces CO with a quantum yield ~ 0.1% (defined as CO produced/photons absorbed). Here we present results on photochemical CO_2

reduction using $\text{Ni}(\text{bpy})_3^{2+}$ and discuss the nature of the various intermediates studied by electrochemistry, flash photolysis, and pulse radiolysis.

Experimental Section

Na-Hg Reduction. A solution of the reduced species in MeCN was prepared by successively reducing portions of $[\text{Ni}(\text{bpy})_3](\text{ClO}_4)_2$ (0.1 mM - 2.5mM) with 0.5 % Na-Hg under vacuum in sealed glassware. UV-vis spectra were monitored during the reduction, and when the absorption of the bands in the visible region maximized, the reduction was stopped.

Photoreactions. A sample solution containing 0.33 mM $[\text{Ni}(\text{bpy})_3](\text{ClO}_4)_2$ and 0.5 M triethylamine in MeCN (3.0 mL) was bubbled with CO_2 for 20 min and then irradiated at 313 nm (100 W Hg-Xe arc lamp with 1/4 m monochromator) in a 1-cm quartz cuvette under stirring. After photolysis, 0.1 mL air and 0.1 mL of water were added to decompose the CO adduct. The CO evolved was analyzed using a Varian gas chromatograph (Model 3700, He carrier gas, 5A molecular sieve column (4 m length, 1/8 inch diameter)) equipped with a thermal conductivity detector. Each run was carried out two or three times.

Laser Flash Photolysis. A sample solution was prepared by vacuum-transfer techniques just before the measurements. Transient-absorption spectra and lifetimes of various intermediates were measured using the previously described apparatus.³² Excitation was with the fourth harmonic of a Nd:YAG laser with a pulse width of ca. 30 ps. The solution was vigorously stirred for 10 s between laser shots.

Pulse Radiolysis. Pulse radiolysis was performed by using electrons from a 2-MeV van de Graaff accelerator.³³ The samples were thermostated, and optical path length was generally 6.1 cm. About 1×10^{-6} M Ni(I) per pulse was produced in most studies.

Results

Photochemical Reduction of CO₂. When a solution containing [Ni(bpy)₃](ClO₄)₂ in TEA-MeCN was irradiated with 313 nm light under a CO₂ atmosphere, the color of the solution changed from colorless to orange. After photolysis for 50 min no CO was detected in the gas phase. On addition of 0.1 mL air and 0.1 mL water to the solution, however, the orange color of the CO adduct disappeared and CO was observed. As shown in Table 1, no CO was detected without TEA or [Ni(bpy)₃](ClO₄)₂, and the reaction did not take place in the dark. These results indicate that the nickel complex, TEA, and light are necessary for the reduction of CO₂ to CO.

Figure 1 shows the variation of the optical spectrum of [Ni(bpy)₃](ClO₄)₂ observed during irradiation at 313 nm. A broad absorption band appeared around 450 nm and increased with irradiation for 20 minutes. Continued photolysis for 50 minutes yielded a decrease in the 450 nm band, an increased absorption to the blue with a shoulder at ~380 nm and an isosbestic point at 430 nm. When the photolyzed solution was kept in the dark, the optical spectrum changed slowly and a broad absorption band was observed around 480 nm. If the photolysis was continued longer than 50 min, the isosbestic point was lost, although the absorbance at 380 nm continued to increase.

The yield of CO is plotted vs irradiation time in Figure 2. The CO yield was not linearly correlated with irradiation time but showed an induction period. After irradiation for 20 min, when the absorbance at 450 nm maximized, only trace amounts of CO were detected. It is noteworthy that after the 50 min irradiation the CO yield significantly increased when the solution was stored in the dark before the addition of air. The CO yield reached 50 % of the amount of [Ni(bpy)₃](ClO₄)₂ used at 100 min. These results suggest that a two-step reaction takes place in the presence of CO₂.

In order to obtain information on the mechanism of this photochemical reaction, the effects of some additives were investigated. The results are summarized in Table 2. When the progress of the reaction was monitored in the visible region, addition of free bipyridine accelerated the reaction rate, while the presence of excess Ni(II) ion retarded it. However, no significant difference in the CO yield was observed. When water or water-MeCN mixture was used as a solvent instead of pure MeCN, neither a spectral change nor CO formation was detected.

Sodium-amalgam Reduction of $[\text{Ni}(\text{bpy})_3]^{2+}$. When a 0.1 - 2.5 mM $[\text{Ni}(\text{bpy})_3](\text{ClO}_4)_2$ acetonitrile solution was treated with 0.5 % Na-Hg under vacuum, the solution exhibited an intense olive-green color with absorption maxima at 422, 592, and 910 nm. As the reduction proceeded the color changed to blue-green, and the absorption intensity increased throughout the visible region, with the peak at 592 nm red-shifting to 610 nm (Figure 3). The intensity increase of the band at 422 nm depended on the concentration of $[\text{Ni}(\text{bpy})_3]^{2+}$. At low nickel concentration (< 0.2 mM) the increase is almost negligible with a final absorbance ratio of the bands at 422 and 610 nm of about 1:1. A new band at 1300 nm, whose intensity was also dependent on the concentration of $[\text{Ni}(\text{bpy})_3]^{2+}$, appeared as the band at 910 nm disappeared. The molar absorptivity of the 1300 nm band is $\sim 9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ with 2.5 mM Ni. At the end of the experiment, the two-electron reduction of $[\text{Ni}(\text{bpy})_3]^{2+}$ was confirmed by adding one equivalent mole of $\text{Co}^{\text{III}}\text{dimBr}_2\text{ClO}_4$ (dim = 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene) to the reduced solution. The intense blue-green color disappeared and a band at 428 nm appeared due to the absorption³⁴ of $\text{Co}^{\text{I}}\text{dim}^+$. Therefore the species with absorption bands at 422, 592 and 910 nm may be a mono-reduced Ni(I) species and the species with absorption bands at 422, 610 and 1300 nm may be a di-reduced Ni(0) species which partially dimerizes allowing π - π interaction of the bpy ligands. (See the results of the x-ray structure.) Further reduction by Na-Hg leads to the production of the relatively

unstable bpy radical anion³⁵ together with the loss of the bands at 422, 610 and 1300 nm, and eventually the solution loses its intense color almost completely.

When Na-Hg reduction of 2.5 mM $[\text{Ni}(\text{bpy})_3](\text{ClO}_4)_2$ was performed in the presence of 25 mM bipyridine the same spectrum was obtained. Addition of TEA to the solution of the reduced species also did not cause any significant differences to the absorption spectrum.

The reaction with CO and CO₂ were examined by adding each gas to the mono and di-reduced species. The addition of CO to the mono-reduced solution produced an unstable CO adduct (sh 350 nm and 470 nm), which decomposed in one hour. The addition of CO to the di-reduced solution produced a stable CO adduct (peaks at 382 nm and 466 nm). The addition of CO₂ to the mono-reduced solution caused the slow decay of the reduced nickel species in one hour without any indication of intermediates. The addition of CO₂ to the di-reduced solution resulted in peaks at 350 nm and 470 nm which indicates the formation of the "CO adduct". A study to identify the CO adduct by means of x-ray structure and IR is in progress.

Laser Flash Photolysis. A sample solution containing 1×10^{-4} M $[\text{Ni}(\text{bpy})_3](\text{ClO}_4)_2$ and 0.5 M TEA in MeCN under vacuum was excited with the fourth harmonic of a Nd:YAG laser pulse (266 nm) and the transient absorption spectrum was observed. Immediately after excitation (~15 ns) two absorption bands were observed around 420 and 590 nm, which are similar to those obtained for Na-Hg reduction of $[\text{Ni}(\text{bpy})_3](\text{ClO}_4)_2$. The observed spectrum remained unchanged for 100 μsec . This suggests that the photoproduct is rapidly formed and has a relatively long lifetime. While the transient spectrum measured under a CO₂ atmosphere was almost the same as that observed under vacuum, the transient spectrum measured under a CO atmosphere showed a peak at 470 nm, which indicates formation of CO adduct.

Pulse Radiolysis. Some of the transients produced by photolysis, electrolysis, and Na-Hg reduction could be conveniently studied in more detail in aqueous solution by pulse radiolysis. The Ni(I) species were produced by reaction of the Ni(II) complexes with the hydrated electron (with the $H^\cdot$ and $OH^\cdot$ removed by reaction with 2-methyl-2-propanol).

These reactions were found to be so rapid ($k = 4.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for $Ni^{II}(bpy)^{2+}$ and $Ni^{II}(bpy)_2^{2+}$, $5.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for $Ni^{II}(bpy)_3^{2+}$) that there is no chance of further reduction on the time scale of the experiment. $Ni^I(bpy)^+$ has absorption maxima at 390 nm ($\epsilon = 3100 \text{ M}^{-1} \text{ cm}^{-1}$) and 590 nm ($\epsilon = 1900$). Reduction of either $Ni^{II}(bpy)_2^{2+}$ or $Ni^{II}(bpy)_3^{2+}$ produced $Ni^I(bpy)_2^+$ within the time scale of the experiment (maxima at 415 nm, $\epsilon = 5300$, and 570 nm, $\epsilon = 3300$). These spectra are similar to those obtained in MeCN by Na-Hg reduction and by flash photolysis. Both Ni(I) species were found to react with CO with nearly the same rate constant ($2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and resulted in spectra similar to those observed in flash photolysis under a CO atmosphere and in Na-Hg reduction followed by the addition of CO.

The $CO_2^\cdot$ radical, produced in solutions of $Ni(bpy)_n^{2+}$ with formate and either N_2O or CO_2 present, also reduces the Ni(II) to Ni(I), but much more slowly than e_{aq}^- with rate constants of about $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. In this case it is difficult to avoid some further reduction of the Ni(I) to Ni(0), and there is strong indication of an interaction of one of these species with CO_2 .

Discussion

Nature of the Reduced Species. While the electrochemistry of $Ni(bpy)_3^{2+}$ species is not well established we believe that the pulse radiolysis results give a

clear indication that $\text{Ni}(\text{bpy})_3^{2+}$ can be reduced in single electron step and that bpy is rapidly lost from the mono-reduced species.

In our pulse radiolysis study we avoid the second step of the reduction by using a very small dose to the solution. The spectra of $\text{Ni}^{\text{I}}(\text{bpy})_2^+$ and the product of reaction in eq 1 ($n = 3$) are identical, with bands at 415 nm and 570 nm indicating loss of a bpy ligand from $\text{Ni}^{\text{I}}(\text{bpy})_3^+$ in H_2O . Therefore the following reactions need to be considered to explain the electrochemistry of $\text{Ni}(\text{bpy})_3^{2+}$ species in MeCN.

When a Na-Hg reduction of $\text{Ni}^{\text{II}}(\text{bpy})_3^{2+}$ was performed in MeCN, bands at 422 and 592 nm increased in intensity. The spectrum is very similar to that of $\text{Ni}^{\text{I}}(\text{bpy})_2^+$ in H_2O except for a small red shift. When the Ni concentration is low ($< 0.15 \text{ mM}$), a clear change to a second reduction step is observed. While the absorption at 422 nm remains constant, the absorption at 592 nm shifts to 610 nm and a new absorption at 1300 nm appears. When the Ni concentration is higher, the change from the first to the second reduction step is not as clear, probably due to the increased rate of Ni(I) disproportionation shown in eq 4. The intensity of the absorption at 1300 nm shows a dependence on concentration. Certain reduced nickel complexes have a tendency to dimerize.³⁶ The dimers have a near IR absorption due to the stacking interaction between ligands.³⁷

The equilibrium constants of eqs. 4 and 5 are currently being investigated.

The above results indicate that the first reduction peak in the electrochemistry is the result of two single electron reduction steps (eq 2 and 3) involving

the loss of a bpy ligand from $\text{Ni}^{\text{I}}(\text{bpy})_3^+$. The two steps appear as one peak in the voltammetry because E_1 ($\text{Ni}^{\text{II}}(\text{bpy})_3^{2+}/\text{Ni}^{\text{I}}(\text{bpy})_3^+$) is very close to E_2 ($\text{Ni}^{\text{I}}(\text{bpy})_2^+/\text{Ni}^0(\text{bpy})_2$). The net equation is shown as

The x-ray structure of $[\text{Ni}_3(\text{bpy})_6](\text{ClO}_4)$ reveals the existence of a dimer in the solid as shown in Figure 4. It crystallized as blue-violet needles from the blue-green MeCN solution at room temperature, suggesting the existence of such a dimer in the solution. The crystal consists of three $\text{Ni}(\text{bpy})_2$ units with one perchlorate anion, indicating one $\text{Ni}(\text{I})$ and two $\text{Ni}(\text{0})$. One $\text{Ni}(\text{bpy})_2$ complex is a monomer, while the other two $\text{Ni}(\text{bpy})_2$ units form a dimer with a Ni-Ni distance of 3.440 ± 0.004 Å. The bpy's of one unit are parallel to the bpy's of the other unit with a bpy-bpy distance of ~ 3.5 Å. The coordination geometries of the three $\text{Ni}(\text{bpy})_2$ units are almost identical: each nickel atom is coordinated to the four nitrogen atoms of two bpy ligands (Ni-N 1.911 Å in the monomer, 1.931 and 1.997 Å in the dimer), and the dihedral angle between the two bpy's is about 40° in each unit.

It is attractive to assign the monomer as $\text{Ni}(\text{I})$ because: (1) the monomer has a shorter Ni-N distance than the dimer; (2) the UV-vis spectrum of the dimer in solution only appears after the one-electron reduction is complete. However, it is difficult to distinguish $\text{Ni}(\text{I})$ from $\text{Ni}(\text{0})$ species using the x-ray structures. There are some reported nickel structures containing bpy: $\text{CpNi}^{\text{I}}(\text{bpy})$ (Cp = cyclopentadienyl)³⁸ Ni-N 1.957 Å; $\text{Ni}^0(\text{COD})(\text{bpy})$ Ni-N 1.940 Å³⁹; $\text{Ni}^0(\text{phosphaalkene})(\text{bpy})$ ⁴⁰ 1.946 Å. The Ni-N distance in these compounds may differ from those of $\text{Ni}(\text{bpy})_2^+$ and $\text{Ni}(\text{bpy})_2$ because of the different coordination environment. The bridging C-C bond distance in most known tris(bipyridine) complexes is very close to the 1.490 (3) Å found in free bpy.⁴¹ By contrast, the structure of $\text{Ni}(\text{bpy})_2^+$ monomer reveals an extremely short C-C bond distance (avg. 1.42 Å), indicating a substantial transfer of electron density from nickel to the π^*

orbital of bpy, as found in the structures of $\text{Co}^{\text{I}}(\text{bpy})_3^+$ (1.42 (2) Å),⁴¹ $\text{Mo}^{\text{II}}(\text{O-i-Pr})_2(\text{bpy})_2$ (1.425 (4) Å),⁴² and $\text{Fe}^0(\eta^6\text{-tol})(\text{bpy})$ (tol = $\text{C}_6\text{H}_5\text{CH}_3$) (1.417 (3) Å)⁴³. The distances in $[\text{Ni}(\text{bpy})_2]_2$ (avg. 1.45 Å) are longer than that of $\text{Ni}(\text{bpy})_2^+$ (probably due to the stacking interaction of bpy), but is as short as found in other low valent nickel complexes: 1.455 Å in $\text{CpNi}^{\text{I}}(\text{bpy})$, 1.459 (6) Å in $\text{Ni}^0(\text{COD})(\text{bpy})$, and 1.480 Å in $\text{Ni}^0(\text{phosphaalkene})(\text{bpy})$.

Flash Photolysis. The flash photolysis results show that the $\text{Ni}(\text{bpy})_2^+$ is rapidly formed and stable for > 100 μsec. This indicates that the rate of reaction 4 is slow under flash photolysis conditions, where the $\text{Ni}(\text{bpy})_2^+$ concentration is low. The addition of CO to the flash photolysis solution resulted in the immediate formation of the CO adduct of the $\text{Ni}(\text{bpy})_2^+$. However the addition of CO_2 did not affect the formation or stability of $\text{Ni}(\text{bpy})_2^+$, indicating that the reaction does not occur under these conditions.

Photochemical Reaction with CO_2 . $\text{Ni}(\text{bpy})_3^{2+}$ - TEA system produces CO from CO_2 by irradiation at 313 nm with quantum yield ~0.1 %. Since $\text{Ni}(\text{bpy})_3^{2+}$ has an absorption band at 309 nm ($\epsilon = 41,700 \text{ M}^{-1} \text{ cm}^{-1}$), over 95 % of light was absorbed by $\text{Ni}(\text{bpy})_3^{2+}$. The CO produced reacts with the reduced $\text{Ni}^{\text{I}}(\text{bpy})_2^+$ and $\text{Ni}^0(\text{bpy})_2$ to form CO adducts, therefore photochemical reaction is stoichiometric and the CO production is 0.5 mole from 1.0 mole of $\text{Ni}^{\text{II}}(\text{bpy})_3^{2+}$. The addition of excess bpy (3 times that of $\text{Ni}(\text{bpy})_3^{2+}$) accelerated the reaction rate, however, no significant difference was observed for CO yield. Emission from $\text{Ni}(\text{bpy})_3^{2+}$ in MeCN was not observed at room temperature or at 77 K. However flash photolysis, electrochemistry, and pulse radiolysis experiments provide evidence of the intermediate, $\text{Ni}^{\text{I}}(\text{bpy})_2^+$, in the photochemical $\text{Ni}(\text{bpy})_3^{2+}$ - TEA system. The mechanism of the photochemical formation of $\text{Ni}^{\text{I}}(\text{bpy})_2^+$ has not yet been identified. The formation of $\text{Ni}^{\text{I}}(\text{bpy})_2^+$ could involve the direct excitation of an electron from a donor (TEA) to the solvent.^{32,44,45} This electron would be expected

to react rapidly with $\text{Ni}(\text{bpy})_3^{2+}$ to produce $\text{Ni}^{\text{I}}(\text{bpy})_2^+$. It should also be pointed out that $\text{Ni}^{\text{I}}(\text{bpy})_2^+$ seems unreactive toward CO_2 addition. However, $\text{Ni}^0(\text{bpy})_2$ does react with CO_2 . The reduced $\text{Ni}(\text{bpy})_3^{2+}$ solution contains various species such as $\text{Ni}^{\text{I}}(\text{bpy})_2^+$, $\text{Ni}^0(\text{bpy})_2$ and $[\text{Ni}(\text{bpy})_2]_2$. Studies to determine the equilibrium constants between these species is in progress.

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Figure Captions

Figure 1. Variation of optical spectrum during photolysis of a solution containing 3.3×10^{-4} M $[\text{Ni}(\text{bpy})_3](\text{ClO}_4)_2$ and 0.5 M TEA in CO_2 saturated MeCN at 313 nm. Numbers indicate irradiation time (min).

Figure 2. Relationship between CO yield and irradiation time on photolysis of a solution containing 3.3×10^{-4} M $[\text{Ni}(\text{bpy})_3](\text{ClO}_4)_2$ and 0.5 M TEA in CO_2 saturated MeCN at 313 nm. o: Analyzed immediately after photolysis. □: Analyzed after the photolyzed solution was kept in the dark for 2h.

Figure 3. Absorption spectra recorded during the Na-Hg reduction of 1.24 mM $\text{Ni}(\text{bpy})_3(\text{ClO}_4)_2$ in MeCN with 0.1 cm cell.

Figure 4. Structure of $[\text{Ni}(\text{bpy})_2]_3(\text{ClO}_4)_4(\text{CH}_3\text{CN})$. Only the $\text{Ni}(\text{bpy})_2$ units are shown.

Figure 1.

Figure 2.

Figure 3.

Fig. 1

Table 1. Photochemical CO formation with $[\text{Ni}(\text{bpy})_3](\text{ClO}_4)_2$.^a

$[\text{Ni}(\text{bpy})_3^{2+}]$ [*] mM	$[\text{TEA}]$ M	added $[\text{bpy}]$ M	solvent	Atmosphere	CO
0.33	0.5	—	MeCN	CO_2	+
0.33	0.5	—	MeCN	CO_2 (dark)	—
0.33	—	—	MeCN	CO_2	—
—	0.5	—	MeCN	CO_2	—
0.33	0.5	—	MeCN	Ar	—
0.33	0.5	—	water	CO_2	—
—	0.5	1.0	MeCN	CO_2	—

^a Each solution (3.0 mL) was irradiated with 313 nm light under stirring, kept in the dark for 2h, and then air and water (0.1 mL ea.) were added just before GC analysis. H_2 was not detected in any run.

Table 2. CO yield from photochemical reaction of $[\text{Ni}(\text{bpy})_3](\text{ClO}_4)_2$ under various conditions.^a

$[\text{Ni}(\text{bpy})_3]$ mM	$[\text{TEA}]$ M	solvent	additive	time min	CO produced μmol
0.33	0.5	MeCN	none	50	0.38
0.33	0.5	MeCN	none	100	0.49
1.0	0.5	MeCN	none	100	0.51
0.33	0.5	MeCN-EtOH (1:1)	none	40	0.34
0.33	0.5	MeCN-H ₂ O (1:1)	none	50	0
0.33	0.5	MeCN	1 mM bpy	100	0.46
0.33	0.5	MeCN	none	120	0.30
0.33	0.5	MeCN	3.3 mM bpy	120	0.30
0.33	0.5	MeCN	0.33 mM $\text{Ni}(\text{ClO}_4)_2$	220	0.28
0.33	5.0	MeCN	none	120	0.19
0.33	0.05	MeCN	none	240	0

^a Each solution (3.0 mL) was irradiated under 1 atm CO₂ with 313 nm light under stirring, kept in the dark for 2 h, and then air and water (0.1 mL ea.) were added just before GC analysis.

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