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Photochemical CO_2 Reduction

Selective Generation of Formamides through Photocatalytic CO_2 Reduction Catalyzed by Ruthenium Carbonyl Compounds**

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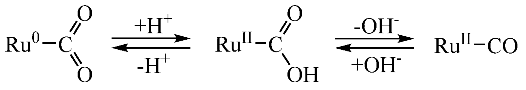
Abstract: *The selective formation of dialkyl formamides through photochemical CO_2 reduction was developed as a means of utilizing CO_2 as a C_1 building block. Photochemical CO_2 reduction catalyzed by a $[Ru(bpy)_2(CO)_2]^{2+}$ (bpy: 2,2′-bipyridyl)/$[Ru(bpy)_3]^{2+}$/Me_2NH/$Me_2NH_2^+$ system in CH_3CN selectively produced dimethylformamide. In this process a ruthenium carbamoyl complex ($[Ru(bpy)_2(CO)(CONMe_2)]^+$) formed by the nucleophilic attack of Me_2NH on $[Ru(bpy)_2(CO)_2]^{2+}$ worked as the precursor to DMF. Thus Me_2NH acted as both the sacrificial electron donor and the substrate, while $Me_2NH_2^+$ functioned as the proton source. Similar photochemical CO_2 reductions using R_2NH and $R_2NH_2^+$ (R = Et, nPr, or nBu) also afforded the corresponding dialkyl formamides (R_2NCHO) together with HCOOH as a by-product. The main product from the CO_2 reduction transitioned from R_2NCHO to HCOOH with increases in the alkyl chain length of the R_2NH. The selectivity between R_2NCHO and HCOOH was found to depend on the rate of $[Ru(bpy)_2(CO)(CONR_2)]^+$ formation.*

Increases in the concentration of atmospheric CO_2 are primarily associated with the consumption of fossil fuels. Responses to the associated greenhouse effect have included reductions in the consumption of fossil fuels by some nations as well as the recycling of CO_2 as a C_1 resource under mild reaction conditions. Photo- and electrochemical reactions are the most feasible pathways for the utilization of CO_2 in this respect. However, despite substantial efforts to develop effective electrode materials and solid and molecular catalysts for use in electro- and photochemical CO_2 reductions, with a few exceptions the reduction products remain limited to CO and/or HCOOH.[1] Thermal reactions between CO_2 and electron donating substrates, such as olefins, dienes, and epoxides, have been widely applied during the use of CO_2 as a C_1 building block in organic synthesis.[2] In contrast, the catalytic incorporation of CO_2 into organic moieties through the reductive activation of the CO_2 molecule rather than by reaction with a reactive organic functional group has rarely been achieved.

Metal complexes are widely used as molecular catalysts in photo- and electrochemical CO_2 reduction,[1d,3] and the reaction mechanisms associated with CO_2 reductions using Ru[4] and Re complexes[5] have been well-documented. When using Ru, a carbonyl group of the dicationic species $[Ru(bpy)_2(CO)_2]^{2+}$ (bpy = 2,2′-bipyridyl) successively reacts with OH^- to give $[Ru(bpy)_2(CO)(COOH)]^+$ and $[Ru(bpy)_2(CO)(CO_2)]^0$. In aqueous solution, these three complexes exist in equilibrium [Eq. (1)],[6,7] and act as precursors to CO and HCOOH production and as CO_2 carriers in electro-[7,8] and photochemical[9] CO_2 reductions.



$$\mathrm{Ru^{0}{-}C(O)O} \underset{-\mathrm{H}^+}{\overset{+\mathrm{H}^+}{\rightleftarrows}} \mathrm{Ru^{II}{-}C(O)OH} \underset{+\mathrm{OH}^-}{\overset{-\mathrm{OH}^-}{\rightleftarrows}} \mathrm{Ru^{II}{-}CO} \qquad (1)$$

Electrochemical CO_2 reduction catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ using $Me_2NH_2^+$ in place of H_2O as a proton source predominantly produces HCOOH in CH_3CN because the regeneration of $[Ru(bpy)_2(CO)_2]^{2+}$ is depressed owing to the reduced availability of protons in the catalytic cycle.[10] Furthermore, electrochemical CO_2 reduction in the presence of Me_2NH under otherwise similar reaction conditions generates both HCOOH and DMF in a molar ratio of 3:1.[11] One-step conversion from the dialkyl amine into the corresponding dialkyl formamide in this manner during CO_2 reduction represents an attractive utilization of CO_2 as a carbon source [Eq. (2)].

$$CO_2 + Me_2NH + 2\,H^+ + 2\,e^- \rightarrow Me_2NCHO + H_2O \qquad (2)$$

Herein we report the selective generation of either dialkyl formamide or HCOOH during photochemical CO_2 reduction, catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ in the presence of $[Ru(bpy)_3]^{2+}$, R_2NH, and $R_2NH_2^+$ acting as the photosensitizer, electron source, and proton source, respectively, in dry CH_3CN.

Photochemical CO_2 reduction catalyzed by $[Ru(bpy)_2(CO)_2](PF_6)_2$ (0.5 mM) was performed in CH_3CN (15 mL) in the presence of $[Ru(bpy)_3](ClO_4)_2$ (5 mM), Et_3NHPF_6 (0.2 M), Et_3N (0.5 M), and Na_2SO_4 (see the Experimental Section). The irradiation of this mixture with visible light (385 nm < λ < 740 nm) for 12 h readily generated H_2 (70 µmol) and HCOOH (75 µmol), accompanied by a small

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amount of CO (3.8 μmol). Thus Et_3NHPF_6 was found to work as a good proton source in photochemical CO_2 reduction. To our surprise, a similar CO_2 reduction process using Me_2NH_2Cl in place of Et_3NHPF_6 under otherwise the same reaction conditions completely depressed H_2 evolution, instead generating DMF (165 μmol) as the main product, together with small amounts of HCOOH and CO (Table 1). This result clearly indicates that Me_2NH_2Cl plays the role of the proton source in the photochemical CO_2 reduction, and the resultant Me_2NH reacts with $[Ru(bpy)_2(CO)_2]^{2+}$ to produce $[Ru(bpy)_2(CO)(CONMe_2)]^+$ as the precursor to DMF.[11] Indeed, DMF was selectively produced as the sole product from photochemical CO_2 reduction when Me_2NH was used as the electron source in place of NEt_3 (Table 1).

Table 1: Photochemical CO_2 reduction using $[Ru(bpy)_2(CO)_2]^{2+}$ under various conditions.

Amine	Ammonium	Li salt	Products [μmol][a]			
			H_2	CO	HCOOH	DMF
Et_3N	Et_3NHPF_6		70	3.8	75	N.D.
Et_3N	Me_2NH_2Cl		N.D.	6.4	14	165
Me_2NH	Me_2NH_2Cl		N.D.	N.D.	trace	131
Me_2NH	Me_2NH_2Cl	$LiBF_4$	N.D.	1.5	15	9.6

[a] N.D. = not detected.

The participation of Et_3NH^+ or $Me_2NH_2^+$ in the equilibrium between $[Ru(bpy)_2(CO)(CO_2)]^0$, $[Ru(bpy)_2(CO)(COOH)]^+$, and $[Ru(bpy)_2(CO)_2]^{2+}$ as the proton source in CH_3CN is the key factor in photochemical CO_2 reduction. In aqueous solutions, the $Ru{-}CO_2$ scaffold of $[Ru(bpy)_2(CO)(CO_2)]^0$ undergoes hydrogen bonding with H_2O, whereas the complex is stabilized by an acid–base interaction with Lewis acids in non-protic media. The Li^+ ion shows especially strong interaction with the oxygen of the $Ru{-}CO_2$ scaffold.[12] As such, photochemical CO_2 reduction in the presence of Li^+ ions was conducted to clarify the effects of a Lewis acid on the equilibrium shown in Equation (1) when assisted by $Me_2NH_2^+$ in CH_3CN. The substantial decrease in DMF production observed in the presence of Li^+ can be explained by the blocking effect of Li^+ on the interspecies conversions of Equation (1) owing to the stabilization of $[Ru(bpy)_2(CO)(CO_2)]^0$ in CH_3CN (Table 1).

Metal carbamoyl complexes have been isolated following the reactions of $[(C_5H_5)W(CO)_4]PF_6$ and $[(C_5H_5)Mo(CO)_4]PF_6$ with primary amines.[13] In the present study, a colorless CH_3CN solution of $[Ru(bpy)_2(CO)_2]^{2+}$ turned yellow upon the addition of excess Me_2NH, which is due to the formation of $[Ru(bpy)_2(CO)(CONMe_2)]^+$. However, concentration of this solution under a N_2 stream caused the Me_2N^- to dissociate from the carbamoyl group, leading to recovery of the original $[Ru(bpy)_2(CO)_2]^{2+}$. Similarly, a yellow CH_3CN solution containing $[Ru(bpy)_2(CO)_2]^{2+}$ and an excess of Me_2NH and $Me_2NH_2^+$ did not give any reaction products following concentration of the solution in the dark. Although pure $[Ru(bpy)_2(CO)(CONMe_2)]^+$ has not been successfully isolated,[11] cyclic voltammograms (CVs) acquired in this study did show strong interactions between $[Ru(bpy)_2(CO)_2]^{2+}$ and Me_2NH [Eq. (3)]. As has been

$$[Ru(bpy)_2(CO)_2]^{2+} + 2\,Me_2NH \rightleftharpoons [Ru(bpy)_2(CO)(CONMe_2)]^+ + Me_2NH_2^+ \qquad (3)$$

reported, $[Ru(bpy)_2(CO)_2]^{2+}$ in CH_3CN exhibits an irreversible cathodic peak at −1.03 V vs. SCE and anodic peaks at −0.45 and −0.14 V under Ar (Figure 1 a).[9b] The addition of excess Me_2NH to this solution results in the complete disappearance of the original redox peaks of $[Ru(bpy)_2(CO)_2]^{2+}$, and these are replaced by two pseudo reversible redox couples at −1.39 and −1.63 V (Figure 1 b). The large negative shift of the redox wave is attributed to bond formation between Me_2N^- and the $Ru{-}CO$ scaffold, which acts as a strong donor group. Indeed, the ESI-MS spectrum of a CH_3CN solution of $[Ru(bpy)_2(CO)_2]^{2+}$ containing 0.5 M Me_2NH indicates the generation of $[Ru(bpy)_2(CO)(CONMe_2)]^+$ (*m*/*z* 514.11) and also contains small peaks owing to $[Ru(bpy)_2(CO)(COOH)]^+$ (*m*/*z* 487.11) (Figure 2 a). The appearance of $[Ru(bpy)_2(CO)$-

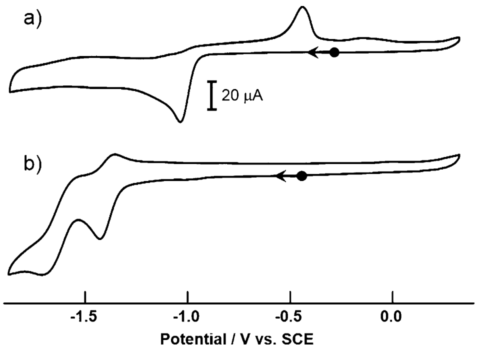


Figure 1. Cyclic voltammograms of $[Ru(bpy)_2(CO)_2]^{2+}$ (1.0 mM) in a) the absence and b) the presence of 0.5 M Me_2NH in CH_3CN containing 0.1 M nBu_4NPF_6 under argon. The sweep rate of both voltammograms was 0.1 $V\,s^{-1}$.

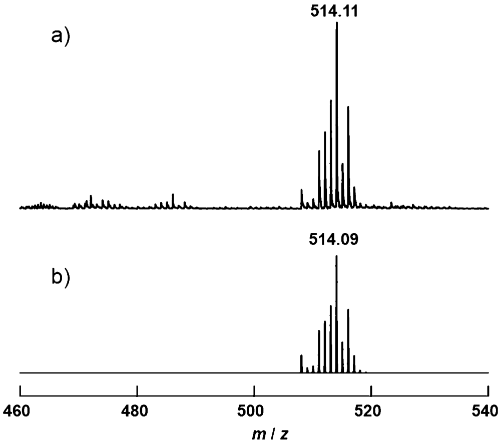


Figure 2. a) ESI-MS spectrum of $[Ru(bpy)_2(CO)_2]^{2+}$ (1.0 μM) in CH_3CN containing 0.5 M Me_2NH and b) the simulated spectrum of $[Ru(bpy)_2(CO)(CONMe_2)]^+$.

$(\mathrm{COOH})]^+$ in the ESI-MS spectrum of a mixture of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ and $\mathrm{Me_2NH}$ suggests another pathway to the formation of a carbamoyl complex through the displacement of the OH group on the Ru−COOH scaffold by $\mathrm{Me_2NH}$ [Eq. (4)] in the present DMF generation reaction. However,

$$[\mathrm{Ru(bpy)_2(CO)(COOH)}]^{2+} + \mathrm{Me_2NH} \rightleftharpoons [\mathrm{Ru(bpy)_2(CO)(CONMe_2)}]^+ + \mathrm{H_2O} \quad (4)$$

the ESI-MS spectra of $[\mathrm{Ru(bpy)_2(CO)(COOH)}]^+$ and $[\mathrm{Ru(bpy)_2(CO)(COOMe)}]^+$ in $\mathrm{CH_3CN}$ exhibited no changes at all following the addition of 0.5 M $\mathrm{Me_2NH}$ to their solutions. This result clearly rules out the occurrence of the reaction in Equation (4). It is therefore concluded that $[\mathrm{Ru(bpy)_2(CO)(CONMe_2)}]^+$ is formed through the reaction of $\mathrm{Me_2NH}$ with $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$, as in Equation (3), rather than with $[\mathrm{Ru(bpy)_2(CO)(COOH)}]^+$ [Eq. (4)].

Similar to $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$, $[\mathrm{Ru(tpy)(bpy)(CO)}]^{2+}$ (tpy = 2,2′:2″,6′-terpyridine) also catalyzes electrochemical $\mathrm{CO_2}$ reduction.[14] $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ and $[\mathrm{Ru(tpy)(bpy)(CO)}]^{2+}$ exhibit catalytic abilities for $\mathrm{CO_2}$ reduction under electrolysis at potentials more negative than −1.20 and −1.30 V, respectively, as the former undergoes irreversible two-electron reduction at −1.03 V and the latter exhibits one reversible and one irreversible reduction at −1.03 and −1.37 V in $\mathrm{CH_3CN}$. However, photochemical $\mathrm{CO_2}$ reduction using $[\mathrm{Ru(tpy)(bpy)(CO)}]^{2+}$ in place of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ under otherwise the same reaction conditions produced a relatively small yield of DMF (3.3 μmol), and no other products were detected. The absorption spectrum of $[\mathrm{Ru(tpy)(bpy)(CO)}]^{2+}$ changed upon the addition of 0.5 M $\mathrm{Me_2NH}$ in $\mathrm{CH_3CN}$ such that a new band emerged at 509 nm, implying the formation of an adduct between $[\mathrm{Ru(tpy)(bpy)(CO)}]^{2+}$ and $\mathrm{Me_2NH}$. The ESI-MS spectrum of $[\mathrm{Ru(tpy)(bpy)(CO)}]^{2+}$ in the presence of 0.5 M $\mathrm{Me_2NH}$ demonstrated the formation of the amine adduct rather than the carbamoyl complex (Supporting Information, Figure S1). In contrast, there was very little change in the (2+/+) and (+/0) redox waves in the CV of $[\mathrm{Ru(tpy)(bpy)(CO)}]^{2+}$ upon the addition of $\mathrm{Me_2NH}$ in $\mathrm{CH_3CN}$. These observations indicate that the redox potential of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ undergoes a substantial negative shift upon the formation of an adduct with $\mathrm{Me_2NH}$, while the one- and two-electron reduced forms of $[\mathrm{Ru(tpy)(bpy)(CO)}]^{2+}$ do not interact with $\mathrm{Me_2NH}$ at all. In contrast to the reaction with Equation (3), the amine adduct formation [Eq. (5)] in the presence of excess amounts of $\mathrm{Me_2NH}$ reflects the weak Lewis acidity of the CO ligand of $[\mathrm{Ru(tpy)(bpy)(CO)}]^{2+}$ ($\nu(\mathrm{CO}) = 2004\ \mathrm{cm^{-1}}$) compared with that of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ ($\nu(\mathrm{CO}) = 2039, 2091\ \mathrm{cm^{-1}}$).[14,15]

$$[\mathrm{Ru(tpy)(bpy)_2(CO)}]^{2+} + \mathrm{Me_2NH} \rightleftharpoons [\mathrm{Ru(tpy)(bpy)(COHNMe_2)}]^{2+} \quad (5)$$

The coexistence of $\mathrm{R_2NH}$ and $\mathrm{R_2NH_2}^+$ (R = Et, *n*Pr, and *n*Bu) in the photochemical $\mathrm{CO_2}$ reduction means that these species also work as the electron and proton sources for the formation of $\mathrm{R_2NCHO}$ (Table 2). Each CV of the mixture of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ and $\mathrm{Et_2NH}$, $n\mathrm{Pr_2NH}$, or $n\mathrm{Bu_2NH}$ in $\mathrm{CH_3CN}$ closely resembles that of $[\mathrm{Ru(bpy)_2(CO)(CONMe_2)}]^+$ (Table 3; Supporting Information, Figure S2). Furthermore, the ESI-MS spectra of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ in the presence of 0.5 M dialkyl amine ($\mathrm{Et_2NH}$, $n\mathrm{Pr_2NH}$, or $n\mathrm{Bu_2NH}$) in $\mathrm{CH_3CN}$ demonstrate the formation of $[\mathrm{Ru(bpy)_2(CO)(CONR_2)}]^+$ (Supporting Information, Figure S3). The tendency of the main product to transition from $\mathrm{R_2NCHO}$ to HCOOH with an increase in the carbon chain length of the *n*-alkyl group is correlated with the increasing difficulty of the nucleophilic attack of the increasingly bulky $n\mathrm{R_2NH}$ on the Ru−CO scaffold. Furthermore, photochemical $\mathrm{CO_2}$ reduction in the presence of both $i\mathrm{Pr_2NH}$ and $i\mathrm{Pr_2NH_2}^+$ produced only a small amount of HCOOH without any accompanying $i\mathrm{Pr_2NCHO}$. Such a drastic change in the reduction product is associated with the steric hindrance of the two *i*Pr groups of $i\mathrm{Pr_2NH}$ on the nucleophilic attack at the carbonyl carbon of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$, as neither $[\mathrm{Ru(bpy)_2(CO)(CON(}i\mathrm{Pr)_2)}]^+$ nor $[\mathrm{Ru(bpy)_2(CO)(CONH(}i\mathrm{Pr)_2)}]^{2+}$ was detected in the ESI-MS spectrum of a mixture of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ and a large excess of $i\mathrm{Pr_2NH}$ in $\mathrm{CH_3CN}$. Taking into account the $\mathrm{p}K_\mathrm{a}$ values of $i\mathrm{Pr_2NH_2}^+$ (11.9) and $[\mathrm{Ru(bpy)_2(CO)(COOH)}]^+$ (9.6), $i\mathrm{Pr_2NH}$ will exclusively remove protons from traces of water in the $\mathrm{CH_3CN}$, and the resulting $\mathrm{OH^-}$ will shift the equilibrium shown in Equation (1) to $[\mathrm{Ru(bpy)_2(CO)(CO_2)}]^0$ that is more labile and slowly decomposes in dry $\mathrm{CH_3CN}$. Indeed, the CV of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ in the presence of 0.5 M $i\mathrm{Pr_2NH}$ did not show any clear redox couples (Supporting Information, Figure S5).

The time-dependent electronic absorption spectra of a $\mathrm{CH_3CN}$ solution of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ (0.50 mM) upon the addition of excess amounts of $\mathrm{R_2NH}$ (R = Me and Et) were monitored by rapid scanning spectroscopy (Figure 3 a,b). The spectral changes in the presence of $\mathrm{Me_2NH}$ and $\mathrm{Et_2NH}$ exhibited first-order kinetics and ceased within 50 ms and 1 s, respectively, and the final spectra of both solutions were

Table 2: Products of photochemical $\mathrm{CO_2}$ reduction catalyzed by $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ (0.5 mM) in the presence of various dialkyl amines and their ammonium salts.

Amine	Ammonium	Products [μmol]		
		CO	HCOOH	$\mathrm{R_2NCHO}$
$\mathrm{Me_2NH}$	$\mathrm{Me_2NH_2Cl}$	N.D.	trace	131
$\mathrm{Et_2NH}$	$\mathrm{Et_2NH_2PF_6}$	4.6	14	29
$n\mathrm{Pr_2NH}$	$n\mathrm{Pr_2NH_2PF_6}$	2.6	45	14
$i\mathrm{Pr_2NH}$	$i\mathrm{Pr_2NH_2PF_6}$	N.D.	21	N.D.
$n\mathrm{Bu_2NH}$	$n\mathrm{Bu_2NH_2PF_6}$	2.9	73	25

Table 3: Redox potentials of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ in the presence of various amines and the reaction rate constants between $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ (0.5 mM) and various alkyl amines (0.5 M).

Amine	E [V]	k_obs [$\mathrm{s^{-1}}$]
$\mathrm{Me_2NH}$	−1.39, −1.63	165
$\mathrm{Et_2NH}$	−1.43, −1.64	4.4
$n\mathrm{Pr_2NH}$	−1.40, −1.62	2.7
$n\mathrm{Bu_2NH}$	−1.42, −1.63	4.2

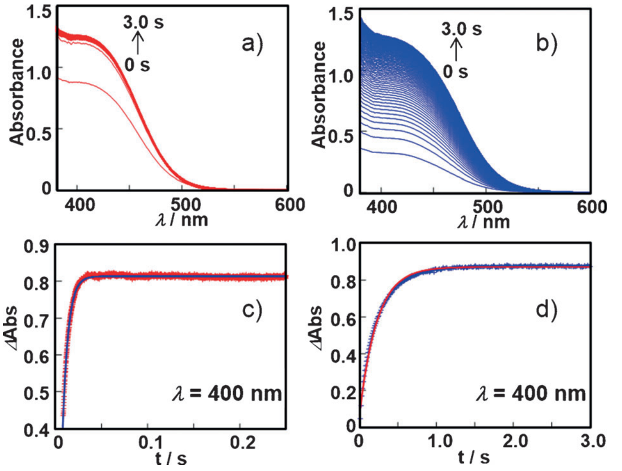
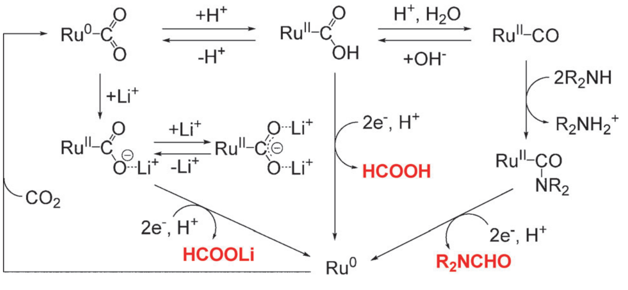


Figure 3. Spectral changes of a $[Ru(bpy)_2(CO)_2]^{2+}$ solution upon addition of a) 0.5 M Me_2NH and b) Et_2NH, and variations in the absorption at 400 nm over time after the mixing of $[Ru(bpy)_2(CO)_2]^{2+}$ and c) Me_2NH or d) Et_2NH.

essentially the same. The rate constants, k_{obs}, determined by analysis of the time course data at 400 nm were 165 and 4.4 s^{-1} for the reactions of $[Ru(bpy)_2(CO)_2]^{2+}$ with Me_2NH and Et_2NH, respectively (Figure 3c and d). Similarly, the pseudo-first-order rate constants for the reaction of $[Ru(bpy)_2(CO)_2]^{2+}$ with $n Pr_2NH$ and $n Bu_2NH$ were also determined, and the results are summarized in Table 3. The rate constant of the reaction of $[Ru(bpy)_2(CO)_2]^{2+}$ with Me_2NH is close to two orders of magnitude larger than those obtained with Et_2NH, $n Pr_2NH$, and $n Bu_2NH$, and comparison of Tables 2 and 3 clearly indicates that the selectivity for dialkyl formamide formation is regulated by the reaction rate of the nucleophilic attack of the dialkyl amine on $[Ru(bpy)_2(CO)_2]^{2+}$.

The most plausible mechanism for photochemical CO_2 reduction affording dialkyl formamides is presented in Scheme 1. The reaction rate of the adduct formation between $[Ru(bpy)_2(CO)_2]^{2+}$ and R_2NH has a crucial effect on the selectivity for dialkyl formamide formation, and selective production of DMF in the presence of Me_2NH and $Me_2NH_2^+$ is ascribed to the rapid formation of $[Ru(bpy)_2(CO)(CONMe_2)]^+$.

In conclusion, we have succeeded in the selective formation of DMF from CO_2 and Me_2NH by photochemical reduction. The selectivity for the dialkyl formamide has been shown to increase with an increase in the reaction rate of the nucleophilic attack on the carbonyl ligand of $[Ru(bpy)_2(CO)_2]^{2+}$. Furthermore, it is evident that Li^+ blocks the formation of Ru−CO due to its stabilization of the Ru−CO_2 scaffold, and thus completely inhibits formamide formation.



Scheme 1. Proposed reaction mechanism for dialkyl formamide and HCOOH generation by CO_2 reduction.

Experimental Section

Photochemical formamide generation was conducted in CH_3CN (15 mL) containing $[Ru(bpy)_2(CO)_2](PF_6)_2$ (0.5 mM), $[Ru(bpy)_3](ClO_4)_2$ (5 mM), dialkyl amine (0.5 M), dialkyl ammonium salt (0.2 M), and Na_2SO_4 (3.0 g). After bubbling CO_2 into the CH_3CN solution for several minutes, photoirradiation was carried out using a 300 W Xe lamp filtered by a mirror module (385–740 nm) with stirring. The reaction was continued for 12 h. The concentrations of H_2 and CO in the product gas phase were determined by gas chromatography (GC) and the quantity of HCOOH in the solution phase was measured by capillary electrophoresis. The identities of formamide derivatives were assessed by GC–mass spectrometry (GC-MS), and their quantities were determined by GC.

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