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Electrochemical Reduction of Carbon Dioxide Using Ruthenium and Amines

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Honors Thesis

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Abstract:

With an increased concern for climate change in the recent years, a significant area of research has been devoted to the reduction of greenhouse gases. Carbon dioxide (CO_2) resides in the atmosphere between 300 – 1000 years, making the reduction of the molecule a substantial field of study.[1] Amines have been used as CO_2 scrubbing agents in literature historically, due to their ability to form bonds to carbon.[2] Although studies involving metal catalysts and amines have been reported numerous times, research involving chemical reduction of CO_2 using purely amines is scarce. In this paper, amines, in addition to hydride donors and other additives, were used to chemically reduce CO_2. Additionally, six ruthenium hydrides were synthesized and were used in combination with amines to electrochemically reduce CO_2.

Introduction:

Carbon dioxide (CO_2) buildup in the atmosphere and the associated increase in global temperatures has become a defining issue for the current generation. Since the industrial revolution, the CO_2 concentration in the atmosphere has increased significantly, with the leading source being fossil fuels.[3] The major air pollutant is a direct result of the combustion of fuels such as natural gas and oil. Anthropologic activity driving an amplified amount of CO_2 into the environment has led to the subtle heating of the globe, leading to devastating effects. The warming is caused by the double bonds between the carbon and the oxygens which trap infrared heat. CO_2 has an atmospheric time of between 300 to 1,000 years, compared to a reactive molecule such as methane which has an atmospheric time of 12 years.[4] The long atmospheric time results in a CO_2 buildup and associated negative effects. Scientists aim to reduce atmospheric CO_2 to offset the current and future environmental issues.

Current strategies for transforming CO_2 into liquid fuels involve the use of transition metal catalysts along with methods such as hydroboration, hydrogenation, and electrochemistry. Paired with amines, the most common transition metal hydride typically used in reduction experiments is ruthenium-based hydride catalysts, although rhenium catalysts have also been used in many reactions.[5] Many previous reductions recorded using these methods and reagents produce formate and CO, while reactions producing high-value fuels such as methanol are scarce in literature. Mechanistic studies suggest that the CO_2 coordinates to a Lewis base, typically an amine, while sequential hydride transfers reduce the molecule. Historically, amines have been used as carbon capture to break one of the carbon-oxygen bonds.[6] These notable reactions have been popular in scientific literature, but rarely mention control reactions with just the amines, despite being known to have CO_2 reduction effects by acting as proton shuttles, trapping agents, and electron donors.[2]

The main goal of this research is to understand how amines (phenylamines, isopropylamines, ethanolamines, and diamines) interact with CO_2 and how they affect the product selection via hydrogenation reactions. Using the results from these reactions, previously synthesized ruthenium hydrides were added to the amines with the goal of electrochemically reducing CO_2 and understanding product selectivity.

Experimental

Materials

Aniline, *N,N*-diisopropylethylamine (DIPEA), diethanolamine (DEA), diphenylamine, ethylene diamine (ED), sulfuric acid, and ethanolamine (EA) were purchased from Sigma-Aldrich. Triphenylamine, triethanolamine (TEA), N,N,N’,N’-tetramethylethylenediamine (TMEDA), and diisopropylamine (DIA) were purchased from Oakwood Chemical. B-nicotinamide adenine dinucleotide reduced form disodium salt (NADH) was purchased from CHEM-IMPEX INT'L INC.. Diphenylsilane (Ph_2SiH_2) was purchased from AmBeed. Isopropylamine (IA), zinc (II) trifluoromethanesulfonate ($Zn(OTf)_2$), and triethylsilane ($HSiEt_3$) were purchased from TCI Chemical. Triphenylborane (Ph_3B) was purchased from Alfa Aesar. Sodium bicarbonate, dimethyl sulfoxide-D6 (DMSO-d_6), acetonitrile-D3 (CD_3CN), and deuterium Oxide (D_2O) were purchased from Cambridge Isotope. Pyridin-4-ylboronic acid (py-4-$B(OH)_2$) was purchased from Ark Pharm. Triethanolamine (TEA) was purchased from Fluka Biochemika. Tetrabutylammonium bromide ($^NBu_4NBr$) source was not documented.

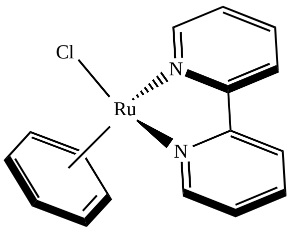
$[Ru(\eta^6\text{- }C_6H_6)(bpy)Cl]_2Cl_2$ and $[Ru(\eta^6\text{- }C_{10}H_{16})(bpy)Cl]_2Cl_2$ were synthesized by literature preparation.[7] 2,2'-bipyridine (bpy) and [2,2′-Bipyridine]-4,4′-dicarboxylic acid (bpy-cooh) were purchased from Combi-Blocks. 4,4'-dimethyl-2,2'-bipyridine (bpy-dm), 2,2' biquinoline (bql), and 1,10 phenanthroline (patl) were purchased by AmBeed. All other reagents were ACS grade and used without additional purification.

NMR experiments were performed using either a Bruker Advance 400 MHz or Bruker Advance 500 MHz spectrometer. Electrochemical experiments were performed using CH Instruments Electrochemical Analyzer. Microwave synthesizes were performed using the CEM Discovery machine.

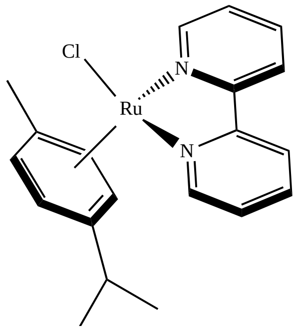
Methods

Four general types of amines (phenylamines, isopropylamines, ethanolamines, and diamines) were selected in each a primary, secondary, and tertiary form. For this survey, we evaluated various combinations of these general types of amines with three different solvents and various reducing agents and additives. The specific combinations are shown in Tables 1-4. HBPin, $HSiEt_3$, and H_2SiPh_2 were tested as the reducing agent for CD_3CN and for each reducing agent there was either no additive, $Zn(OTf)_2$, $^nBu_4NBr$, or Ph_3B. NADH, $HSiEt_3$, and H_2SiPh_2 were tested as the reducing agent for DMSO-d_6 and for each reducing agent there was either no additive or py-4-$B(OH)_2$. For D_2O, the procedure was the same as DMSO-d_6.

For each reaction, 0.5 mL of solvent was pipetted into a 3 mL test tube followed by roughly 10 mg of the reducing agent (if solid), 10 mL or 10 mg of the amine, and 10 mg of the additive. Then, the mixture was added to an NMR tube and sealed with a white rubber septum and electrical tape. To create a super-saturated solution, ^{13}C labelled sodium bicarbonate was placed into a Schlenk flask and was sealed with a rubber septum. A tube connected to a needle was place on the Schlenk flask and the needle was inserted into the NMR tube. A solution containing sulfuric acid and water was dripped into the sodium bicarbonate from the septum; the gas (CO_2) from the reaction was bubbled into the NMR tube for two minutes. The liquid reducing agent (0.20 mL) was added into the tube if it wasn't added before the bubbling of CO_2. ^{13}C and ^1H NMRs were taken both 2-6 hours and 48 hours after the bubbling.



Ru-1



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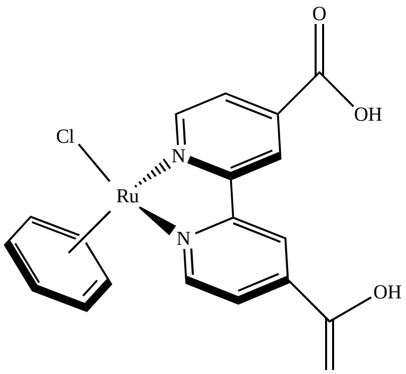

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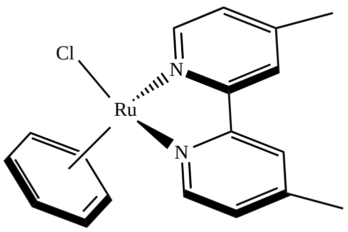
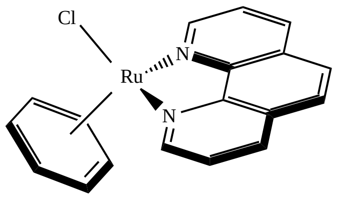


Ru-4



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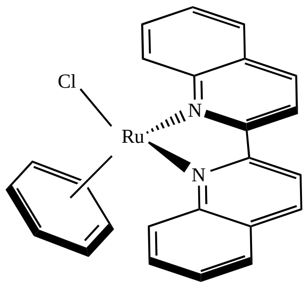

Ru-6

[Ru(η^6- C_6H_6)(bpy)Cl]Cl (Ru-1) was synthesized by modification of a literature preparation.[7] 2,2'-bipyridine (312 mg, 2.00 mmol) and [Ru(η^6- C_6H_6)(bpy)Cl]$_2$Cl$_2$ (500 mg, 1.00 mmol) were suspended in methanol (20 mL). The reaction was heated at reflux under nitrogen overnight. The solvent was then removed on a rotary evaporator. A green solid resulted that was collected under diethyl ether and filtered. Yield: 794 mg (97%)

[Ru(η^6- $C_{10}H_{16}$)(bpy)Cl]Cl (Ru-2) was synthesized by modification of a literature preparation.[7] 2,2'-bipyridine (161 mg, 1.00 mmol) and [Ru(η^6- $C_{10}H_{16}$)(bpy)Cl]$_2$Cl$_2$ (318 mg, 0.50 mmol) were suspended in methanol (20 mL). The reaction was heated at reflux under nitrogen overnight. The solvent was then removed on a rotary evaporator. An orange solid resulted that was collected under diethyl ether and filtered. Yield: 452 mg (94%)

[Ru(η^6- C_6H_6)(bpy-cooh)Cl]Cl (Ru-3) was synthesized by modification of a literature preparation.[7] [2,2′-Bipyridine]-4,4′-dicarboxylic acid (175 mg, 0.72 mmol) and [Ru(η^6--C_6H_6)(bpy)Cl]$_2$Cl$_2$ (180 mg, 0.36 mmol) were suspended in methanol (4 mL) in a microwave flask. The reaction was heated to 100°C for 20 minutes. The solvent was then removed on a rotary evaporator. A green solid resulted that was collected under diethyl ether and filtered. Yield: 308 mg (87%)

[Ru(η^6- C_6H_6)(bpy-dm)Cl]Cl (Ru-4) was synthesized by modification of a literature preparation.[7] 4,4'-dimethyl-2,2'-bipyridine (132 mg, 0.72 mmol) and [Ru(η^6- C_6H_6)(bpy)Cl]$_2$Cl$_2$ (180 mg, 0.36 mmol) were suspended in methanol (10 mL). The reaction was heated at reflux under nitrogen overnight. The solvent was then removed on a rotary evaporator. A black solid resulted that was collected under diethyl ether and filtered. Yield: 254 mg (81%)

[Ru(η^6- C_6H_6)(patl)Cl]Cl (Ru-5) was synthesized by modification of a literature preparation.[7] 1,10 phenanthroline (129 mg, 0.75 mmol) and [Ru(η^6- C_6H_6)(bpy)Cl]$_2$Cl$_2$ (180 mg, 0.36 mmol) were suspended in methanol (10 mL). The reaction was heated at reflux under nitrogen overnight. The solvent was then removed on a rotary evaporator. A green solid resulted that was collected under diethyl ether and filtered. Yield: 275 mg (89%)

$[Ru(\eta^6\text{- }C_6H_6)(bql)Cl]Cl$ (Ru-6) was synthesized by modification of a literature preparation.[7] 2,2’ biquinoline (192 mg, 0.72 mmol) and $[Ru(\eta^6\text{- }C_6H_6)(bpy)Cl]_2Cl_2$ (180 mg, 0.36 mmol) were suspended in methanol (10 mL). The reaction was heated at reflux under nitrogen overnight. The solvent was then removed on a rotary evaporator. A green solid resulted that was collected under diethyl ether and filtered. Yield: 352 mg (95%)

Each of the six ruthenium complexes was paired with each eight amines (IPA, DIPA, DIPEA, EA, DEA, TEA, ED, and TMEDA) in all acetonitrile, acetonitrile + 5% DIH_2O, acetonitrile + 10% DIH_2O, pH 7, pH 8, pH 8.5, and pH 9 solutions for the electrochemical studies. For the solvents containing acetonitrile, $TBAPF_6$ (186 mg for 5 mL of solvent) was added to the electrochemical vial. For each experiment, 10 mg of ruthenium complex was added to the electrochemical vial and 10 mg (or 10 mL) of amine. 5 mL of solvent was added as well as any additional reagent to the flask.

A working glassy carbon electrode, platinum counter electrode, and either an $Ag/AgNO_3$ or Ag/AgCl reference electrode were added to the electrochemical vial along with a cap. Argon was then bubbled through the vial for two minutes. Potentials of 300 mV, 100 mV, or 50 mV were used to promote the electrochemical reactions. Then, unlabeled CO_2 (dry ice) was bubbled through the electrochemical vial for five minutes. The same electrochemistry was performed at the same voltages following CO_2 exposure.

Results and Discussion:

NMR Studies

Several studies have shown that CO_2 reduction in the presence of amines can result in product selectivity for 6 and 8-electron reduced products.[8] This selectivity is different from the hydrogenation or electrochemical reduction of CO_2 using transition metal catalysts where mainly 2-electron reduced species, formate and CO, are produced.[9] Additionally, chemical reductions of CO_2 using a variety of hydride donors has been shown to result in the production of methanol, only in the presence of amines. To further evaluate amines in CO_2 reduction, several classes of amines were monitored for their ability to affect the chemical reduction of CO_2 via hydride transfer. Results of peaks other than those associated with the starting material are shown after 48 hours.

The solubility of some of the amines and additives may have produced less than favorable results. The phenylamines were not soluble in D_2O, so there were no data to analyze. Some reactions did not show CO_2 on the NMR after ample bubbling, but had precipitate, so other experiments would need to be conducted to conclude the product formed for reactions with solids. The ethanolamines regularly produced precipitate, which could be due to the carbamate/carbonyl equilibrium.

Table 1. Three phenylamines (aniline, diphenylamine, and triphenylamine) CO_2 reduction NMR product peaks.

Amine	Solvent	Reducing Agent	Additive	Observations	
				^1H	^{13}C
Aniline	CD_3CN	H_2SiPh_2	$^nBu_4NBr$	δ (ppm): 8.33, $J_{H\text{-}C}$ = 213 Hz	δ (ppm): 162.78
Aniline	DMSO-d_6	H_2SiPh_2	Ph_3B	δ (ppm): 8.56, $J_{H\text{-}C}$ = 44.3 Hz	δ (ppm): 163.83, 167.01
Aniline	DMSO-d_6	H_2SiPh_2	None	δ (ppm): 8.16, $J_{H\text{-}C}$ = 214.7Hz	δ (ppm): 163.51, 160.03, 149.08, 72.59, 53.06

Aniline	DMSO-d_6	H_2SiPh_2	py-4-$B(OH)_2$	δ (ppm): 7.93, J_{H-C} = 209.7Hz	δ (ppm): 163.79, 53.05
Diphenylamine	CD_3CN	H_2SiPh_2	$^nBu_4NBr$	δ (ppm): 8.32, J_{H-C} = 214.3 Hz	δ (ppm): 162.54
Diphenylamine	DMSO-d_6	H_2SiPh_2	py-4-$B(OH)_2$	δ (ppm): 8.15, J_{H-C} = 212.8 Hz, 4.98, J_{H-C} = 296.9 Hz , 2.5	δ (ppm): 163.84
Triphenylamine	CD_3CN	H_2SiPh_2	$^nBu_4NBr$	δ (ppm): 8.33, J_{H-C} = 209.5 Hz	δ (ppm): 163.35
Triphenylamine	DMSO-d_6	H_2SiPh_2	py-4-$B(OH)_2$	δ (ppm): 8.18, J_{H-C} = 213.3 Hz	δ (ppm): 163.67

Table 2. Isopropylamine and diisopropylamine CO_2 reduction NMR product peaks.

Amine	Solvent	Reducing Agent	Additive	Observations	
				^{1}H	^{13}C
Isopropylamine	CD_3CN	H_2SiPh_2	Ph_3B	δ (ppm): 8.59, J_{H-C} = 188.9 Hz	δ (ppm): 168.61, 157.78
Diisopropylamine	CD_3CN	H_2SiPh_2	None	δ (ppm): 1.97	δ (ppm): 30.79, 161.96 (tiny)
Diisopropylamine	CD_3CN	H_2SiPh_2	$Zn(OTf)_2$	δ (ppm): 8.25, J_{H-C} = 204.1 Hz	δ (ppm): 31.84, 169.74
Diisopropylamine	CD_3CN	H_2SiPh_2	$^nBu_4NBr$	δ (ppm): 1.97	δ (ppm): 30.79
Diisopropylamine	CD_3CN	H_2SiPh_2	Ph_3B	δ (ppm): 8.58, J_{H-C} = 189.9 Hz	δ (ppm): 157.60, 167.91
Diisopropylamine	D_2O	NADH	None	δ (ppm): 8.23, J_{H-C} = 108.4 Hz	δ (ppm): 167.99
Diisopropylamine	D_2O	NADH	py-4-$B(OH)_2$	δ (ppm): 7.74, J_{H-C} = 301.2 Hz	δ (ppm): 160.54, 45.64
Diisopropylamine	D_2O	$HsiEt_3$	py-4-$B(OH)_2$	δ (ppm): 7.78, J_{H-C} = 310.2 Hz	δ (ppm): 163.59
Diisopropylamine	D_2O	H_2SiPh_2	None	δ (ppm): 7.46, J_{H-C} = 96.3 Hz	δ (ppm): 164.20
Diisopropylamine	D_2O	H_2SiPh_2	py-4-$B(OH)_2$	δ (ppm): 7.87, J_{H-C} = 306.3 Hz	δ (ppm): 164.87
Diisopropylamine	DMSO-d_6	NADH	None	δ (ppm): 8.31, J_{H-C} = 131.5 Hz	δ (ppm): 154.62
Diisopropylamine	DMSO-d_6	NADH	py-4-$B(OH)_2$	δ (ppm): 8.87, J_{H-C} = 127.8 Hz	δ (ppm): 160.25, 156.17
Diisopropylamine	DMSO-d_6	$HsiEt_3$	None	δ (ppm): 8.50, J_{H-C} = 167.7 Hz	δ (ppm): 165.83
Diisopropylamine	DMSO-d_6	$HsiEt_3$	py-4-$B(OH)_2$	δ (ppm): 7.83, J_{H-C} = 355.8 Hz	δ (ppm): 156.01
Diisopropylamine	DMSO-d_6	H_2SiPh_2	None	δ (ppm): 8.51, J_{H-C} = 188.5	δ (ppm): 165.87
Diisopropylamine	DMSO-d_6	H_2SiPh_2	py-4-$B(OH)_2$	δ (ppm): 8.41, J_{H-C} = 157.9	δ (ppm): 166.42, 165.32

Table 3. Diisopropylethylamine CO_2 reduction NMR product peaks.

Amine	Solvent	Reducing Agent	Additive	Observations	
				^{1}H	^{13}C
Diisopropylethylamine	CD_3CN	HBPin	None	δ (ppm): 8.45, $J_{H\text{-}C}$ = 206.5 Hz δ (ppm): 8.36, $J_{H\text{-}C}$ = 207.1 Hz	δ (ppm): 164.72, 165.26, 83.49, 24.46, 39.06 (s), 48.74 (s)
Diisopropylethylamine	CD_3CN	H_2SiPh_2	None	δ (ppm): 3.71, $J_{H\text{-}C}$ = 142.4 Hz	δ (ppm): 52.39
Diisopropylethylamine	CD_3CN	H_2SiPh_2	$^nBu_4NBr$	δ (ppm): 3.50, $J_{H\text{-}C}$ = 143.3 Hz	δ (ppm): 51.00, 162.29*
Diisopropylethylamine	CD_3CN	H_2SiPh_2	Ph_3B	δ (ppm): 8.62, $J_{H\text{-}C}$ = 189.2 Hz	δ (ppm): 157.0, 50.64, 40.29, 19.82
Diisopropylethylamine	D_2O	NADH	None	δ (ppm): 8.21, $J_{H\text{-}C}$ = 99.0 Hz, δ (ppm): 3.34, $J_{H\text{-}C}$ = 207.3 Hz	δ (ppm): 160.26, 54.36
Diisopropylethylamine	D_2O	NADH	py-4-$B(OH)_2$	δ (ppm): 7.99, $J_{H\text{-}C}$ = 207.3 Hz, 3.31, $J_{H\text{-}C}$ = 188.5 Hz	δ (ppm): 160.20, 54.35
Diisopropylethylamine	D_2O	$HsiEt_3$	None	δ (ppm): 3.20, $J_{H\text{-}C}$ = 212.1 Hz	δ (ppm): 160.16, 54.36
Diisopropylethylamine	D_2O	$HsiEt_3$	py-4-$B(OH)_2$	δ (ppm): 8.03, $J_{H\text{-}C}$ = 207.4 Hz, 3.37, $J_{H\text{-}C}$ = 207.3 Hz	δ (ppm): 160.20, 54.37
Diisopropylethylamine	D_2O	H_2SiPh_2	None	δ (ppm): 4.69, 3.35 $J_{H\text{-}C}$ = 216.8 Hz	δ (ppm): 160.25, 54.38, 42.57
Diisoproypethylamine	D_2O	H_2SiPh_2	py-4-$B(OH)_2$	δ (ppm): 4.69, 8.07, $J_{H\text{-}C}$ = 213.0 Hz, 3.27, $J_{H\text{-}C}$ = 207.3 Hz	δ (ppm): 160.21, 42.55, 4.37
Diisoproypethylamine	DMSO-d_6	H_2SiPh_2	None	δ (ppm): 8.85, $J_{H\text{-}C}$ = 194.9 Hz	δ (ppm): 165.05, 49.08, 20.60

Table 4. Ethanolamine and diethanolamine CO_2 reduction NMR product peaks.

Amine	Solvent	Reducing Agent	Additive	Observations	
				^{1}H	^{13}C
Ethanolamine	CD_3CN	H_2SiPh_2	$^nBu_4NBr$	δ (ppm): 8.49, $J_{H\text{-}C}$ = 186.6 Hz	δ (ppm): 164.55, 169.81
Ethanolamine	D_2O	NADH	None	δ (ppm): 8.22, $J_{H\text{-}C}$ = 101.6 Hz	δ (ppm): 164.79, 162.81
Ethanolamine	D_2O	NADH	py-4-$B(OH)_2$	δ (ppm):7.96, $J_{H\text{-}C}$ = 129.6 Hz	δ (ppm): 160.52, 164.77
Ethanolamine	D_2O	$HsiEt_3$	py-4-$B(OH)_2$	δ (ppm):7.65, $J_{H\text{-}C}$ = 117.8 Hz, 3.21, $J_{H\text{-}C}$ = 49.5	δ (ppm): 164.75, 162.81, 48.84

Diethanolamine	CD_3CN	$HsiEt_3$	$^nBu_4NBr$	δ (ppm): 7.39, J_{H-C} = 487.3 Hz	δ (ppm): 165.70, 19.92
Diethanolamine	CD_3CN	H_2SiPh_2	$Zn(Otf)_2$	δ (ppm): 8.39, J_{H-C} = 198.2 Hz	δ (ppm): 170.06, 164.99, 61.71, 51.19
Diethanolamine	CD_3CN	H_2SiPh_2	$^nBu_4NBr$	δ (ppm): 8.47, J_{H-C} = 188.5 Hz	δ (ppm): 168.95, 165.61, 59.92, 51.57
Diethanolamine	D_2O	NADH	None	δ (ppm): 3.15, J_{H-C} = 356.7 Hz, 8.22, J_{H-C} = 108.4 Hz	δ (ppm): 164.29, 162.08
Diethanolamine	D_2O	NADH	py-4-$B(OH)_2$	δ (ppm): 7.81, J_{H-C} = 315.7 Hz	δ (ppm): 164.29, 161.80
Diethanolamine	D_2O	H_2SiPh_2	py-4-$B(OH)_2$	δ (ppm): 7.60, J_{H-C} = 306.3 Hz	δ (ppm): 164.24, 161.31, 49.40

Any peak, besides the known starting material, observed in sample was determined to be a product of CO_2 reduction or degradation of the starting material. Since the most common literature reduction products are formate, carbamate, and methanol, peaks within the ^{13}C 150-170 ppm or the 45-50 ppm region were recorded in the tables above. The reactions that produced products within those regions are recorded in Tables 1-4.

Specific products observed include the production of formate, methanol, carbamate, and methylamine. Formate is observed in the ^{13}C NMR as a single peak in the 160 ppm region and in the ^{1}H NMR 8 ppm region as a doublet. Methanol is observed in the ^{13}C NMR as a single peak in the 50 ppm region and in the ^{1}H NMR 3 ppm region as a doublet. Carbamate is observed in the ^{13}C NMR as a single peak in the 170 ppm region and methylamine is observed around 30 ppm in the ^{13}C NMR.

Diphenylsilane was the reducing agent that demonstrated the most reactivity of the reduction of CO_2 regardless of the amine. The most common peaks produced with diphenylsilane as the reducing agent suggest the production of formate. However, several experiments with diphenylsilane produced a peak around 50 ppm for the ^{13}C NMR and around 3 ppm regions in the ^{1}H NMR. A possible explanation for the observation of Si-OMe formation in the case of diphenylsilane may be related to the steric bulk around the hydride donor, however, further evaluation of the specific mechanism is necessary to better understand these results.

Diisopropylamine produced ^{13}C NMR peaks around 30 ppm with diphenylsilane as the reducing agent in all solvents. This was consistent with ^{1}H NMR peaks around 2.22 ppm. Literature sources have reported the methylation of amines in CO_2 reduction experiments with diphenylsilane.[10] Upon further experimentation, the product was suggested to be N-Methyl-N-(1-methylethyl)-2-propanamine.

Electrochemical Studies

The chemical reduction of CO_2 to value-added products with hydride donors and amine additives supports the claim that the additive affects the product selectivity. However, the use of sacrificial reducing agents does not provide a pathway for sustainable reduction of CO_2 to fuels. In order to remove the sacrificial hydride donor, a series of Ru complexes, which are known to produce metal hydrides, were investigated *via* electrochemical reduction.[5] Altering the ligand on the Ru complex changes the hydricity of the complex, so ligands differing in bulk and electronics were assessed. The amine, solvent environment, and Ru complex work together to reduce CO_2. A series of Ru complexes were synthesized and tested in an electrochemical system with amine additives to tune the product selectivity of CO_2 reduction.

Six previously mentioned Ru complexes were evaluated alongside different solvents and amines to fully examine the extent of product selectivity of CO_2 reduction. The ruthenium complexes tended to outperform the complexes alongside the amines in both current and potential. However, the ethanolamines added to the complexes increased the current of the reduction and positively shifted the potential.

The cyclic voltammetry result that had the biggest change in potential or current from the ruthenium complex alone in comparison to each ruthenium complex plus amine is shown below. Most products that positively shifted the potential and increased the current included ethanolamines, specifically diethanolamine, which is the amine shown in the results in addition to isopropylamine. Additionally, upon experimentation, the results with increased current and shifted potential occurred with 10% added water into the solvent, most likely due to the amplified concentration of hydrogens in the environment.

The main peak is shown in the cyclic voltammetry around -0.8 V and is the popping off the chlorine on the ruthenium complex if the peak is irreversible. However, only [Ru(η^6- C_6H_6)(bpy)Cl]Cl and [Ru(η^6- C_6H_6)(bql)Cl]Cl produced reversible ruthenium peaks, while the other four complexes had irreversible ruthenium reduction peaks. The second irreversible reduction peak visible in all six cyclic voltammetry is conducive to the formation of the ruthenium hydride, which then reduces CO_2. The results below are shown at 100 mV; however, the determination of catalysis is possible by stacking the potential speeds.

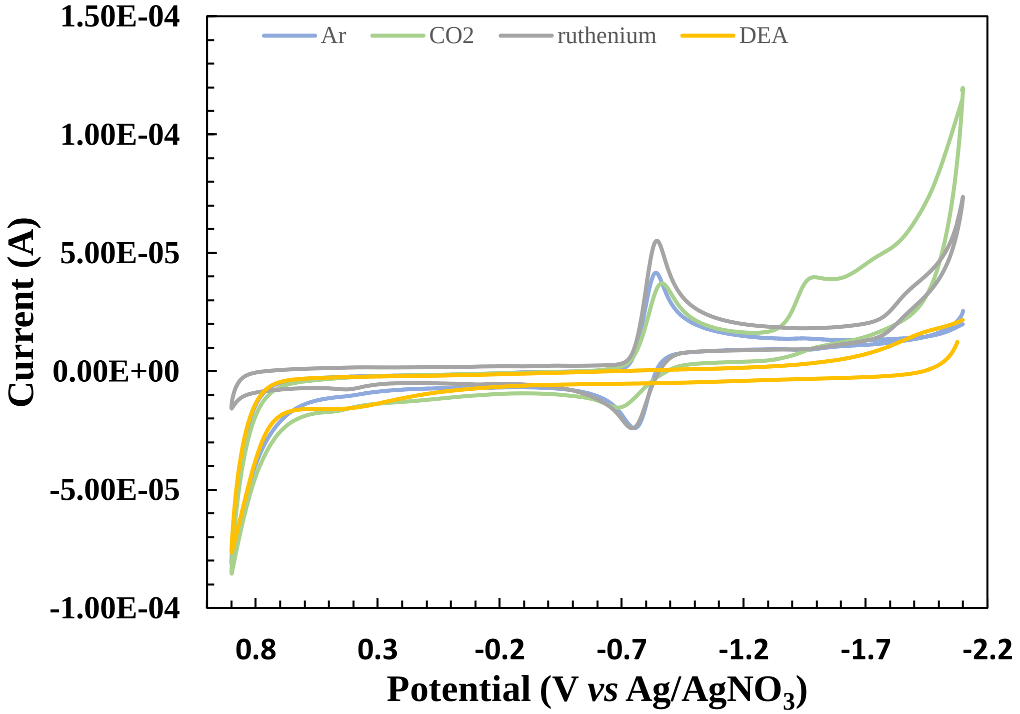

Figure 1: [Ru(η^6- C$_6$H$_6$)(bpy)Cl]Cl 100 mV in CH$_3$CN with 0.1 M TBAPF$_6$. GC, Ag/AgNO$_3$ ref, and Pt counter electrode.

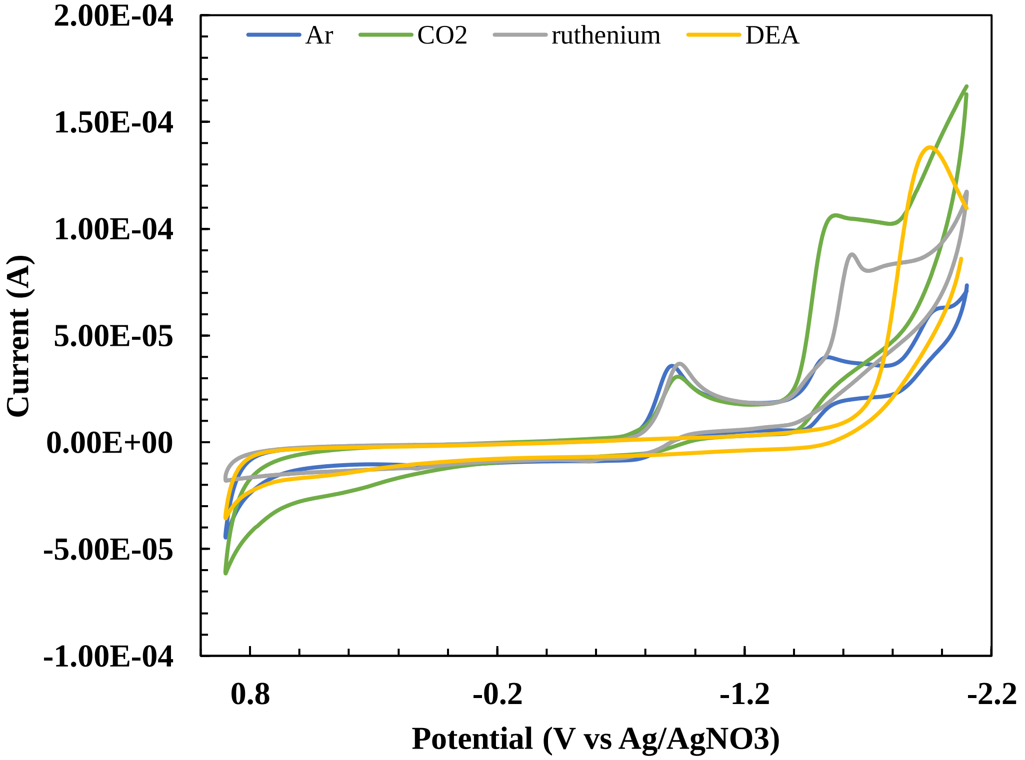

Figure 1: [Ru(η^6- C$_{10}$H$_{16}$)(bpy)Cl]Cl 100 mV in CH$_3$CN + 10% DIH$_2$O with 0.1 M TBAPF$_6$. GC, Ag/AgNO$_3$ ref, and Pt counter electrode.

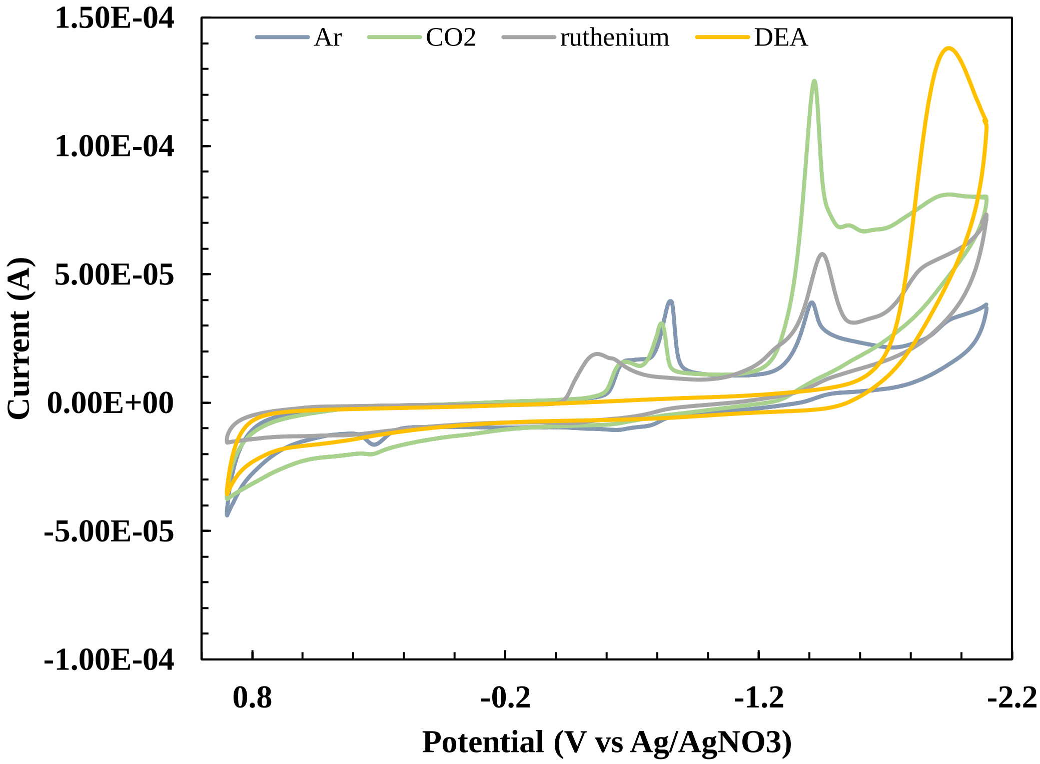

Figure 2: [Ru(η^6- C_6H_6)(bpy-cooh)Cl]Cl 100 mV in CH_3CN + 10% DIH_20 with 0.1 M $TBAPF_6$. GC, Ag/$AgNO_3$ ref, and Pt counter electrode.

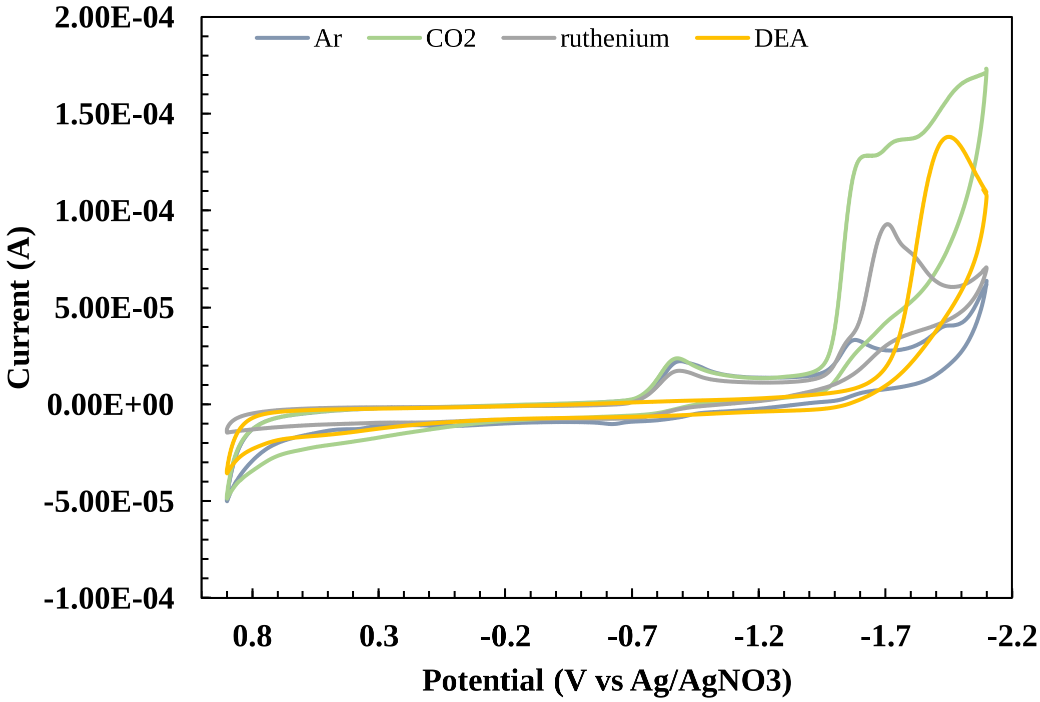

Figure 3: [Ru(η^6- C_6H_6)(bpy-dm)Cl]Cl 100 mV in CH_3CN + 10% DIH_20 with 0.1 M $TBAPF_6$. GC, Ag/$AgNO_3$ ref, and Pt counter electrode.

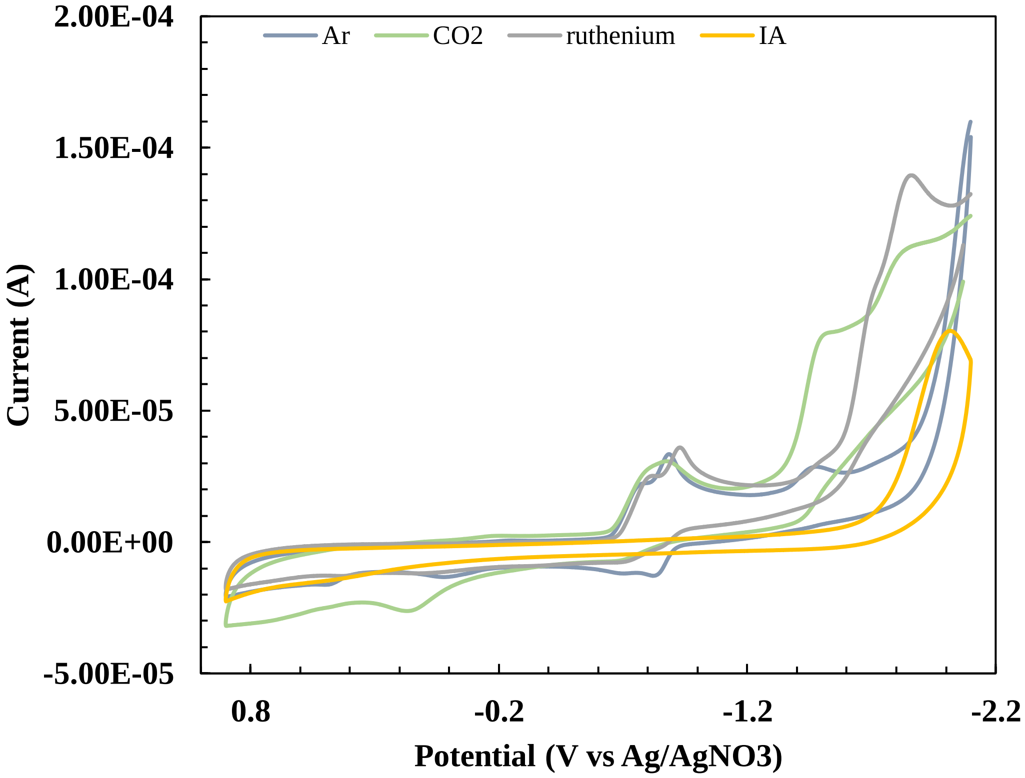

Figure 4: [Ru(η^6- C_6H_6)(patl)Cl]Cl 100 mV in CH_3CN + 10% DI$H_2$0 with 0.1 M $TBAPF_6$. GC, Ag/$AgNO_3$ ref, and Pt counter electrode.

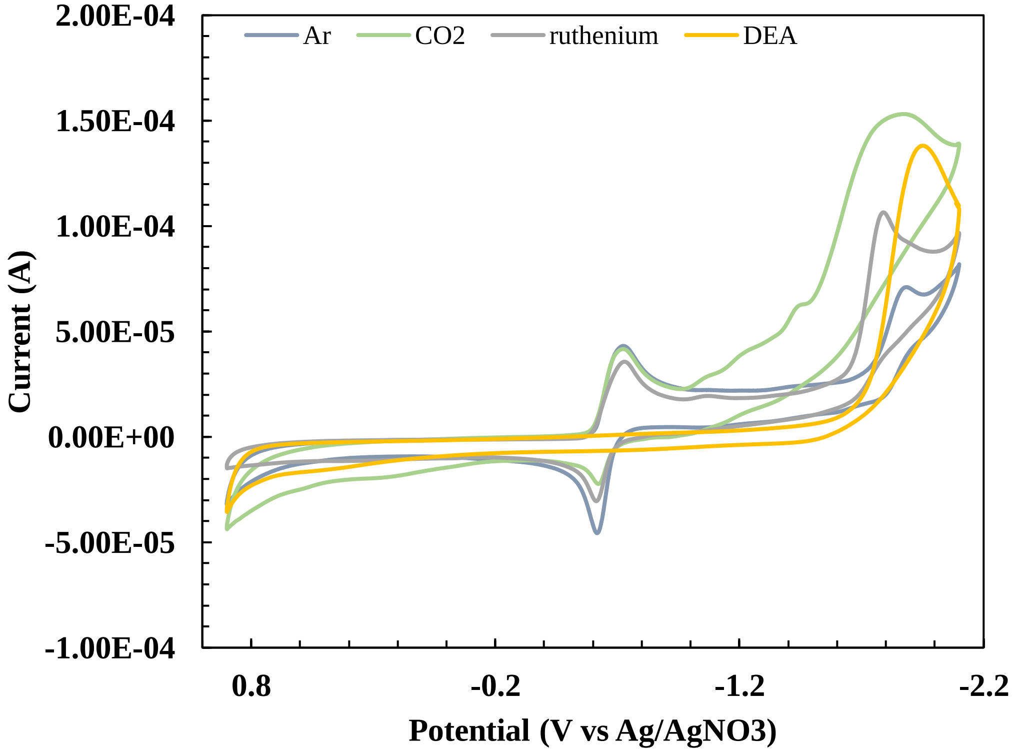

Figure 5: [Ru(η^6- C_6H_6)(bql)Cl]Cl 100 mV in CH_3CN + 10% DI$H_2$0 with 0.1 M $TBAPF_6$. GC, Ag/$AgNO_3$ ref, and Pt counter electrode.

Conclusion:

Chemically reducing CO_2 using amine resulted in a selective product formation of formate. More than 60% of the chemical reduction experiments using only amines and reducing agents/additives reduced CO_2. In the electrochemical study, altering the ligand of the ruthenium complex changed the hydricity of the compound and led to changes in potentials and currents of the reduction. More research needs to be completed to understand the changes in the hydricity and how the changes relate to the electrochemical differences observed. However, in the electrochemical experiments, the added amine with the ruthenium complex increased the current and shifted the potential positively. The investigation of both the chemical and electrochemical reduction of CO_2 using ruthenium and amines ultimately suggests that both chemicals work together to reduce the greenhouse gas.

Analyzing the gas products formed *via* headspace gas chromatography would be beneficial in the future to understand product selection. Bulk electrolysis would also be valuable to quantify the electrochemical reduction products.

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