Photocatalytic Conversion of CO_2 to CO and its Study in the Production of Acrylic Acid

Eric Oweggi
Faculty: D. Paul Rillema

Department of Chemistry, Fairmount College of Liberal Arts and Sciences

Abstract. The synthesis of various Rhenium complexes is followed by an investigation of their capacity to reduce CO_2 photocatalytically. $Re(bpy)(CO)_3X$ (X=Cl, NCS) is irradiated in a CO_2 saturated DMF:TEOA solution in a Pyrex tube capped with a serum cap. The CO produced in the reaction is tracked using a gas chromatograph, and this is followed by examining the carboxylated $Re(dcbpy)(CO)_3X$ dye derivatives in the same manner. The objective is attaching the Rhenium dye to TiO_2 making it a photocathode and replacing the sacrificial reagent, TEOA, with a photoanode in a photo-electrochemical cell which would produce both electricity and carry out a catalytic reaction simultaneously. CO_2 Insertion into olefin-metal bonds is also studied for the production of acrylic acid

1. Introduction

Atmospheric carbon dioxide (CO_2) has been increasing at an alarming rate since the beginning of the industrial age [1]. The use of coal as the earth's main energy source through the burning of fossils has been the biggest contributor to this huge spike in CO_2 levels. Yet in spite of its abundance, few industrial processes actually utilize it as a raw material because of its thermodynamically and kinetically stable structure. At the same time, several of these industries continue to produce CO_2 as waste.

Since our fossil fuel reserves are getting depleted faster than new ones are forming, there has been a global movement toward the generation of renewable energy sources as well as methods of recycling CO_2 productively.

Our experiments involve the conversion of CO_2 into other products using solar cell molecules and attempt to create a cell that would both conduct electricity as a solar cell but also reduce CO_2. We also look into incorporation of CO_2 into alkenes on Molybdenum molecules to create acrylate, and then irradiate the molecule to isolate Acrylic acid.

2. Experiment, Results, Discussion, and Significance (Describe how you developed your idea)

$Re(CO)_5$ is reacted with the carboxylated ligand under reflux overnight, and finally with NaSCN to produce the final product (reaction scheme).All products are verified using NMR and IR techniques.
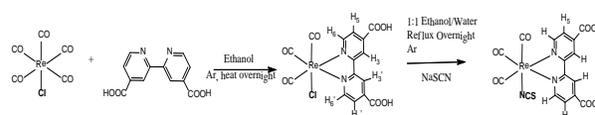
Reaction scheme 1. Synthesis of dicarboxylated Rhenium complexes.

0.5mM of the complex, a 4ml solution of 5:1 DMF:TEOA solution is added to a pyrex test tube capped with a serum cap, and bubbled with CO_2 for 20 minutes. The solution is then irradiated with a visible light source fitted with a cutoff filter. The CO_2 is converted to CO the rhenium complex regenerated according the cycle shown in Figure 1.
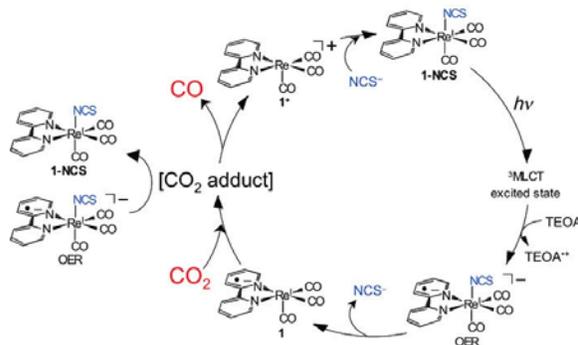

Fig. 1. Mechanism of CO_2 reduction (Ishitani et al [2])

The CO formed is tracked using a gow mac gas chromatograph fitted with a molecular sieves column (Figure 2). The first two peaks are the oxygen and nitrogen peaks respectively which serve as standard reference points.
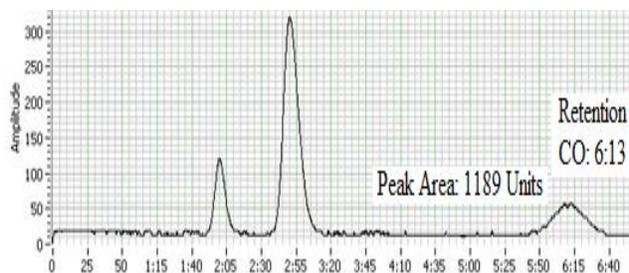
Fig. 2. Gas chromatograph tracking CO production

These rhenium complexes are carboxylated because they are also used in solar cells. Attempts to create a cell that would simultaneously conduct electricity and convert CO_2 failed. When the complex was attached to TiO_2, the complex did convert CO_2 to CO but only after detaching which made the cell model impractical. We do however report the quantum efficiencies or various complexes and their ability to reduce CO_2.

Table 1. Quantum efficiencies of Rhenium complexes

Complex (10μmol)	CO Ret. Time	CO μmol	Quantum yields
Re(CO)₃ (bpy)Cl	4.43	49.93	0.104
Re(CO)₃ (bpy)SCN	4.48	64.96	0.135
Re(CO)₃ (dcbpy)Br	4.44	29.6	0.0615
Re(CO)₃ (dcbpy)Cl	4.56	39.04	0.0811
Re(CO)₃ (dcbpy)NCS	5.06	32.53	0.0676
Re(CO)₃ (phen)(bpy)	4.56	4.61	0.0096
Re(CO)₃ (phen)Cl	4.58	24.09	0.05
Re(CO)₃ (dcbpy)I	4.59	47.08	0.0978

Chemical actinometry and equations (1) and (2) were used to determine the quantum efficiencies of the molecules.

$$\phi_{CO} = \frac{\#\ of\ molecules\ of\ CO\ formed}{\#\ of\ quanta\ absorbed} \quad (1)$$

$$I_0 = \frac{6.022 \times 10^{20} \times V_1 \times V_3 \times \Delta A}{V_2 l \varepsilon \phi t} \quad (2)$$

Also studied is the insertion of CO_2 into olefinic molybdenum complexes such as the one shown in Figure 3 in order to isolate acrylic acid from the coordination sphere photocatalytically.

The barrier to isolating acrylic acid from the coordination sphere may be circumvented by photochemical excitation where the population of the d-d excited state may weaken the bonding between the metal center and the ligand resulting in ligand lability [3]. This work is still in progress.
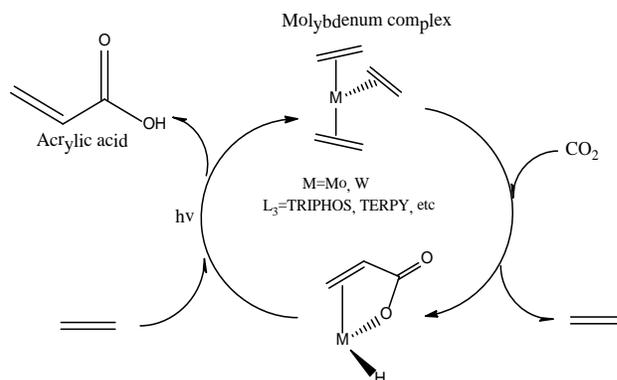

Figure 3. CO_2 insertion into an olefin and isolation of acrylic acid photocatalytically

3. Conclusions

Several of our Rhenium complexes successfully reduced CO_2 to CO as reported, but did not do so when their dicarboxylated derivatives were attached to TiO_2.

Many of the current methods of production of Acrylic acid have been abandoned because they are expensive and have environmentally consequences. Successful catalytic production of Acrylic acid would represent a significant achievement.

4. Acknowledgements

References
[1] http://climate.NASA.gov
[2] J. AM. CHEM. SOC. 2008, 130, 2023-2031
[3] Ollino, M; Cherry, W.R. *Inorg. Chem.* 1985, 24, 1417