A Metal-Metalloporphyrin Framework Featuring Lewis-acid Centers

for CO2 Chemical Transformation

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Abstract

The chemical transformation of inexpensive, abundant, and sustainable carbon dioxide (CO_2) into useful chemicals paves an avenue to reduce greenhouse gas emission. Herein, a porous metal-metalloporphyrin framework, MMPF-10, was utilized as a heterogeneous Lewis-acid catalyst for CO_2 cycloaddition reaction with aziridine. MMPF-10 was fabricated by a octatopic porphyrinic ligand and in situ generated $Cu_2(CO_2)_4$ paddlewheel clusters, which exhibits unsaturated Cu(II) centers in the accessible channels. The reactions between different substituted aziridines and CO_2 were performed to examine how the side chains influence the reaction yield. Through NMR spectroscopy, the yield of oxazolidinone was determined, and it was shown that 1-methyl-2-phenylaziridine had the highest yield of 57.5%, followed by 2-phenyl-1-propylziridine with a 33.0% yield and 1-benzyl-2-phenylaziridine with a 19.0% yield. The decreasing yield of these aziridine substrates may be attributed to size-selective catalysis.

Keywords: Lewis-acid catalysis, CO_2 chemical transformation, aziridine, 2-oxazolidinone

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The high levels of carbon dioxide in the atmosphere has become a major contributor to climate change in the past decade, and many pathways have been investigated to capture this carbon dioxide and store it elsewhere. One such possibility investigated is the chemical conversion of carbon dioxide, a C1 source and a readily available waste, with aziridine to produce oxazolidinone, an antibacterial compound used in pharmaceutical products. This CO2 cycloaddition reaction has already been investigated with different catalysts, but in this study, we explored a porous metal–metalloporphyrin framework, MMPF-10, as the catalyst and tetra-n-butylammonium bromide (TBAB) as the co-catalyst.

Metal–metalloporphyrin frameworks (MMPF) are a class of coordination networks composed of metal-containing secondary building units combined with metalloporphyrin ligands. The metal ion in the porphyrin core may be manipulated to generate different metalloporphyrin-based networks. The structure of a MMPF, then, is essentially a cavity in which the corners and edges are composed of metallic ions and ligands respectively. The cavity functions as a space for many possible applications such as selective gas capture and catalysis. The varying electron densities in the metal-containing secondary building units and metalloporphyrin ligands contribute to the specificity of each MMPF and what molecule it might capture.

MMPFs are a sub-class of Metal-Organic Frameworks (MOFs), which are highly porous materials with centers of metals ions or clusters connected by organic linkers. The MMPF-10 used in this study has copper paddlewheel cluster nodes connected with a octatopic porphyrin ligand. MMPF-10 has already been shown to be an effective catalyst in the coupling reaction of

carbon dioxide to aziridine, and in this study, we show the effect of the aziridine side chain (methyl-, propyl-, benzyl-) on the product yield of oxazolidinone.

It is hypothesized that as the size of the aziridine side chain increases, the product yield of oxazolidinone will decreases. This may be explained by size-selective catalysis, which has already been observed previously in the coupling reaction between epoxides and carbon dioxide. This phenomenon may be attributed to the limited diffusion of large-sized aziridine substrates into the catalyst MMPF-10, thus displaying size-selective catalysis that favors 1-methyl-2-phenylaziridine because of its smallest side chain.

Method and Materials

The procedure involves first synthesizing the MMPF-10 and the various aziridines (1-methyl-2-phenylaziridine, 2-phenyl-1-propylziridine, 1-benzyl-2-phenylaziridine) before performing the coupling reaction. The MMPF-10 was already synthesized and in stock prior to this experiment by Wenyang Gao.

Synthesis of Aziridine

Synthesis of Bromodimethyl sulfonium Bromide (S1). Dimethyl Sulfide (12.4 g) and bromine (32.0 g) were separately dissolved in 40 mL of dry dichloromethane each. The bromine solution was then added dropwise over an ice-cooled solution of dimethyl sulfide for one hour. During the addition, light orange crystals of bromodimethyl sulfonium bromide began to separate. The solution was stirred for two hours and the crystals of S1 were collected by filtration and washed with dry ether before dried under vacuum overnight.

Synthesis of Styrene sulphonium bromide (S2). Styrene (160 mmol) was added dropwise to a stirred 160 mL acetonitrile solution of compound S1 in an ice-water bath. During

the addition, a white solid began to separate. The solid was stirred for one hour before the

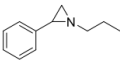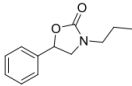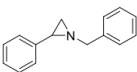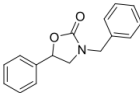crystals were collected by filtration and dried under vacuum overnight.

Synthesis of aziridine. To a stirred solution of S2 in 20 mL of room temperature water, a

solution of amine (40mmol) in water was added dropwise. The procedure so far is repeated for

all three amines: methylamine, propylamine, and benzylamine. The mixture was stirred

overnight. The mixture was then poured into 20 mL of saturated brine and extracted with diethyl

ether three times with 20 mL each. The resulting solution was then dried with $MgSO_4$ and the

solvent evaporated under reduced pressure.

Coupling reaction between carbon dioxide and aziridine

To determine the yield of oxazolidinone from the fixation of carbon dioxide to

aziridine, 1.0 mmol of aziridine was placed in a pressurized chamber along with 0.0125 mmol of

catalyst MMPF-10 and 0.0125 mmol of co-catalyst TBAB. These compounds were then

dissolved in 0.5 mL of 2-proponal and carbon dioxide gas was pumped in at 2.5 MPa at room

temperature. After ten minutes, the chamber was sealed and placed in an oil bath at 50 ºC for two

hours while the mixture inside was kept stirring. Finally, the mixture was removed and cooled in

an ice bath. Through NMR spectroscopy, the yield of oxazolidinone was determined. This

procedure was repeated for all three aziridines: methylaziridine, propylaziridine, and

benzylaziridine.

Results

Table 1. CO_2 cycloaddition reactions with different substituted aziridines.

Entry	Substrate	Product	Yield (%)
1			57.5
2			33.0
3			19.0

All reactions were performed with 0.0125 mmol MMPF-10 catalyst, 0.0125 mmol TBAB as the coc-atalyst, and 0.5 mL 2-proponal as the solvent under CO2 pressure of 2.5 MPa at 50 °C for two hours.

The yield of oxazolidinone decreased as the size of the aziridine substrate increased from methyl- to propyl-, and then to benzyl-.

Discussion

MMPF-10 cooperated with TBAB and proved to be an efficient catalyst system for CO_2 chemical transformation with different substituted aziridines into 2-oxazolidinones. Furthermore, an impressive decrease in the yield of 2-oxazolidinone was observed with an increase of the molecular size of the aziridine substrate. For the large molecule of 1-benzyl-2-phenylaziridine, there was a yield of 19.0%. This value increased to 33.0% with the smaller molecule of 2-phenyl-1-propylaziridine, and even furthermore to 57.5% with the smallest molecule of 1-methyl-2-phenylaziridine. This supports the previous hypothesis that the product yield of oxazolidinone will decreases as the size of the aziridine side chain increases.

Initially, there was anomalous deviations from what was expected in the procedure. The coupling reaction of carbon dioxide to aziridine with just the catalyst of MMPF-10 was extremely low at 4-5%, and it was only after the addition of TBAB and 2-propoanl as a

cocatalyst and solvent respectively that a marked increase in product yield was observed (see

Jesse Hope). From our findings, a conclusion can be drawn that MMPF-10, combined with

TBAB and a solvent of 2-propoanl, is an efficient catalyst system.

The use of a MMPF as a catalyst is similar to a previous work in which MMCP-2,

another MOF, was used as a catalyst to fixate carbon dioxide to epoxide. In fact, there are many

similarities between this reaction and the cycloaddition of carbon dioxide to aziridine performed

in this study. For instance, both procedures employ a form of a MOF to serve as a catalyst. The

MOF is able to function as a catalyst by opening the epoxide or aziridine ring and inserting the

carbon dioxide into it. Both the MOFs have a Lewis-acid center and use TBAB as a cocatalyst,

and the coupling reaction of epoxide also shows a trend of decreasing yield as the side chain on

the epoxide increases in size. The study on epoxide ascribes this decrease in yield to size-

selective catalysis. This trend of decreasing yields parallels the one observed in the cycloaddition

of aziridine and carbon dioxide. From the findings of the study on epoxide and carbon dioxide,

we infer that a similar mechanism is responsible for the reaction observed between aziridine and

carbon dioxide. MMPF-10 likely opens the aziridine ring to insert the carbon dioxide, similar to

MMPC-2, and the lower yield of MMPF-10 as the substrate size increases may be attributed to

the limited diffusion of the large substrate into the narrow channels of MMPF-10, hence

displaying size-selective catalysis.

There are many possible practical implications of our findings, one being the production

of oxazolidinone in the industry as a way to remove carbon dioxide and generate a useful

product. The ability to take a waste from the air and turn it into an antibacterial substance used in

pharmaceutical products has great potential, especially since filtering out the MMPF-10 catalyst

is relatively easy as it is heterogeneous. However, further research on scale and effects of

moisture must be done before any real-world applications.

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