Integrated Electrochemical Processes for CO_2 Capture and Conversion to Commodity Chemicals

Project Number: DE-FE0004271

Dr. Jennifer A. Kozak,[1,2] Dr. Fritz Simeon,[2] Prof. T. Alan Hatton,*[,2] and Prof. Timothy F. Jamison*[,1]

[1]Department of Chemistry and [2]Department of Chemical Engineering

Massachusetts Institute of Technology

U.S. Department of Energy

National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the Infrastructure for CO_2 Storage

August 21-23, 2012

Presentation Outline

- Motivation, Goals, Objectives
- Background
- Cyclic Carbonate Synthesis via Catalytic Coupling of CO_2 and Epoxides
- New Catalysts and Reaction Scope
- Mechanism – A New Paradigm for Activating Epoxides
- Conclusions

Benefit to the Program

- Identify the Program goals being addressed.
  - Develop technologies to demonstrate that 99 percent of injected CO_2 remains in the injection zones.
- The research project is developing a novel approach to capturing and converting CO_2 into commodity chemicals, which may thus reduce the burden on CO_2 storage sites, in addition to providing a means to reduce anthropogenic CO_2 emissions and an inexpensive method for producing useful materials from CO_2.

Project Overview:
Goals and Objectives

- To develop and demonstrate a novel *chemical* sequestration technology that utilizes CO_2 from dilute gas streams generated at industrial carbon emitters as a raw material in order to produce useful commodity chemicals.
  - **Single** electrochemical system for CO_2 capture and chemical conversion
  - **Coupled** system for CO_2 capture and chemical conversion

Project Overview:
Goals and Objectives

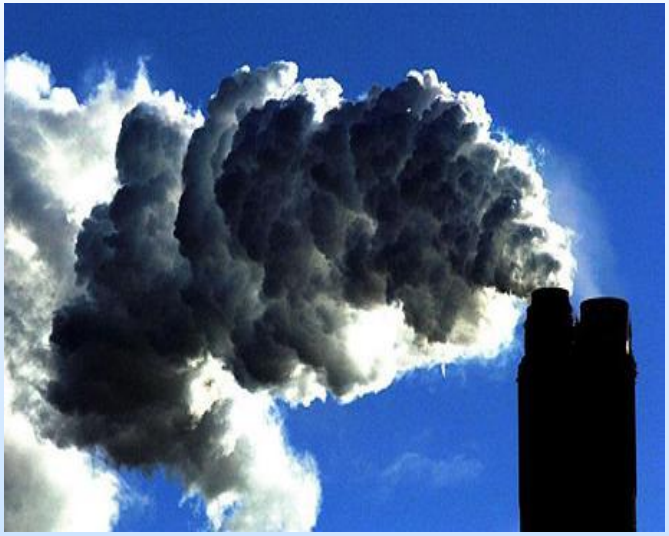
- To develop and demonstrate a novel *chemical* sequestration technology that utilizes CO_2 from dilute gas streams generated at industrial carbon emitters as a raw material in order to produce useful commodity chemicals.
  - **Single** electrochemical system for CO_2 capture and chemical conversion
  - **Coupled** system for CO_2 capture and chemical conversion

Accomplishments to Date

- A novel catalytic method for the continuous chemical conversion of CO_2 has been developed and thoroughly investigated mechanistically.
  - Several novel chemical features.
  - Several advantages over existing methods.
  - Springboard for development of several other classes of CO_2 conversion.
- We envision coupling this continuous chemical conversion with a newly developed electrochemical capture/separation system.
- We anticipate that this continuous chemical conversion can be coupled with a variety of other CO_2 capture methods.

Motivation for CO_2 Capture, Sequestration, and Conversion

- Anthropogenic carbon dioxide (CO_2)
  - considered a primary cause of global climate change
  - coal-fired power plants, and the petroleum and natural gas industries account for 86% of anthropogenic CO_2
  - we will continue to depend on *non-renewable* fossil fuels for the next several decades
- The CO_2 cycle is not balanced
  - 3.9% excess (caused by anthropogenic CO_2) with respect to the yearly CO_2-flow in the natural “carbon cycle”
  - Only 30-35% of the chemical energy content associated with anthropogenic CO_2 emissions is converted into various forms of energy.
  - 65-75% is lost as heat to the Earth’s atmosphere.



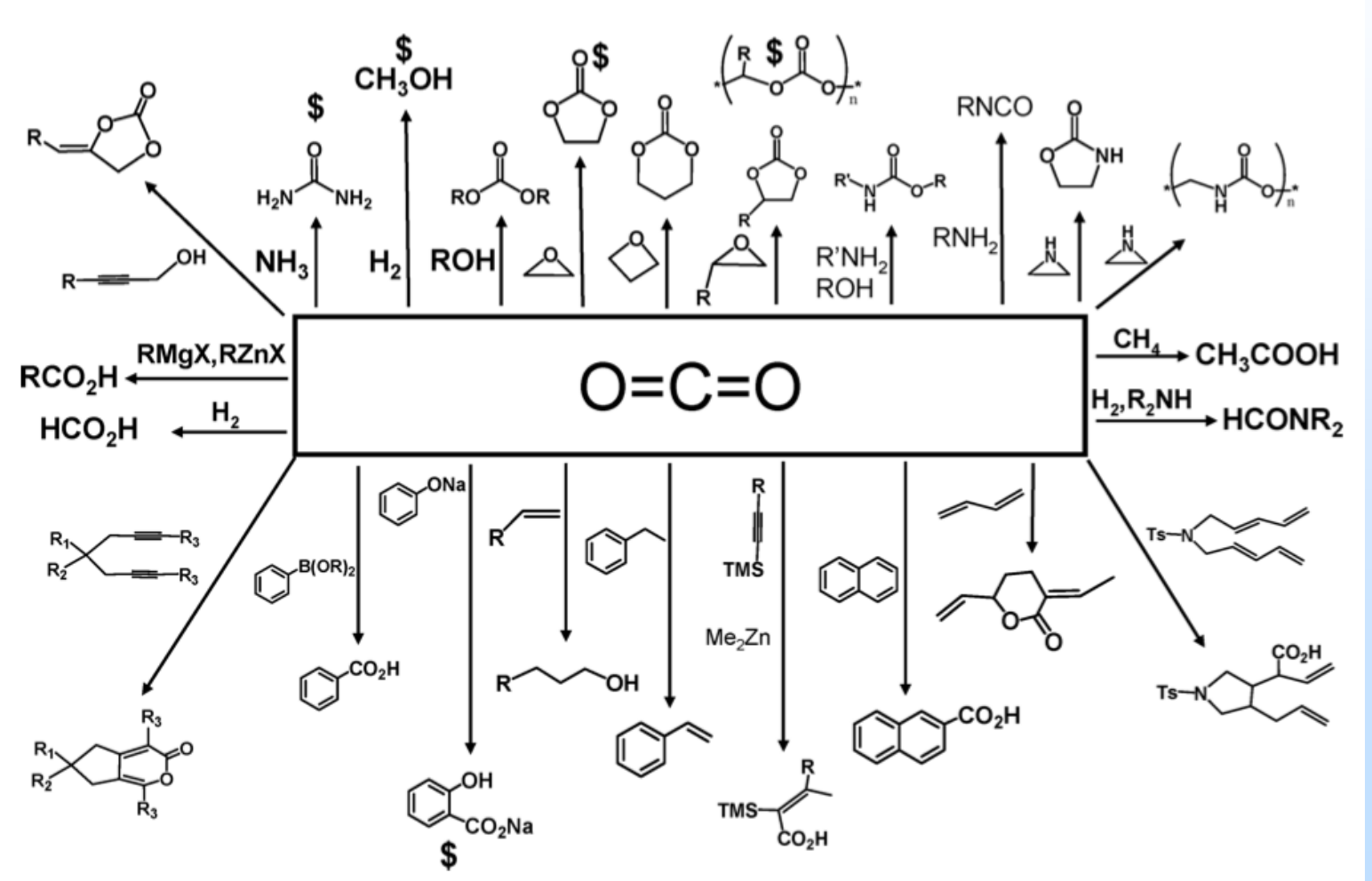
http://www.telegraph.co.uk/earth/earthnews/5257162/Power-plants-could-store-carbon-dioxide-under-North-Sea.html

Carbon Dioxide as a Chemical Feedstock

- What is the motivation for producing chemicals from CO_2?
  - CO_2 is an inexpensive, non-flammable, non-toxic feedstock that is stable, easy to store, and readily available.
  - It can be used to replace toxic chemicals such as phosgene and isocyanates.
  - CO_2 is a renewable resource, as compared to oil or coal; the future supply of fossil fuels is considered limited.
  - The use of CO_2 in new routes to existing chemical intermediates and products could be more efficient and economical than current technologies.
  - The production of chemicals from CO_2 could have a small but likely significant positive impact on the global carbon balance.
  - CO_2 is an exceptionally inexpensive source of carbon, at ~0.1 ¢/mol.
  - For comparison: Ethylene, ~3 ¢/mol (1.5 ¢/mol of C atoms); propylene, (~5 ¢/mol, 1.5 ¢/mol of C atoms).

Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.*; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953.

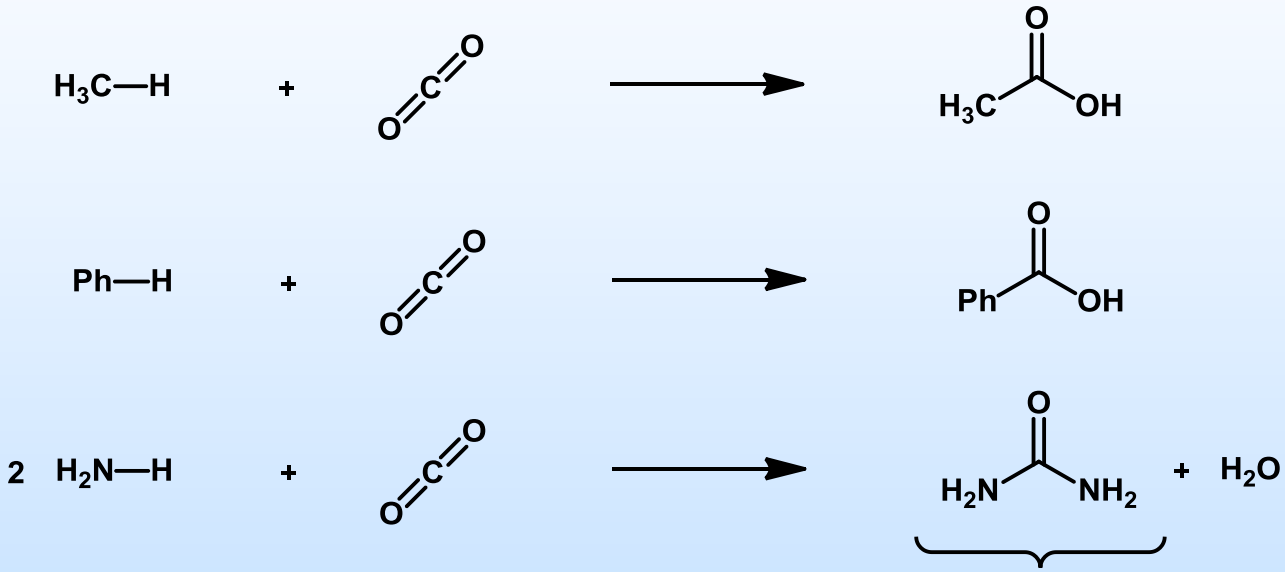
Known Reactions of CO_2



Riduan, S. N.; Zhang, Y. *Dalton Trans.* **2010**, *39*, 3347.

Why is CO_2 capture and conversion a difficult problem?

- reactions of CO_2 can be thermodynamically favorable!



ΔH = -16.6 kJ mol^{-1}

ΔH = -40.7 kJ mol^{-1}

ΔH = -101 kJ mol^{-1}

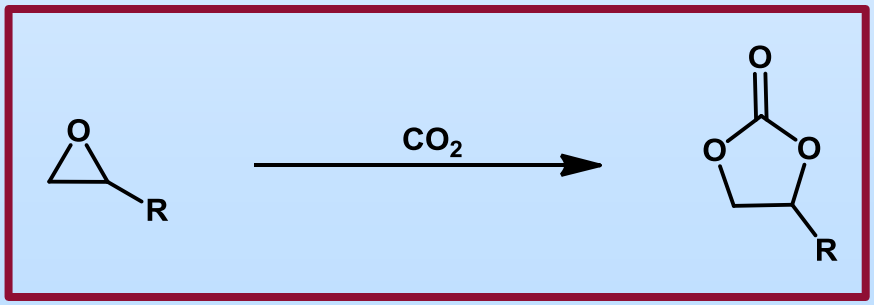
90 Mt/year industrially!

Primary problem is <u>kinetic stability</u> of CO_2.

• Excellent candidate for catalysis

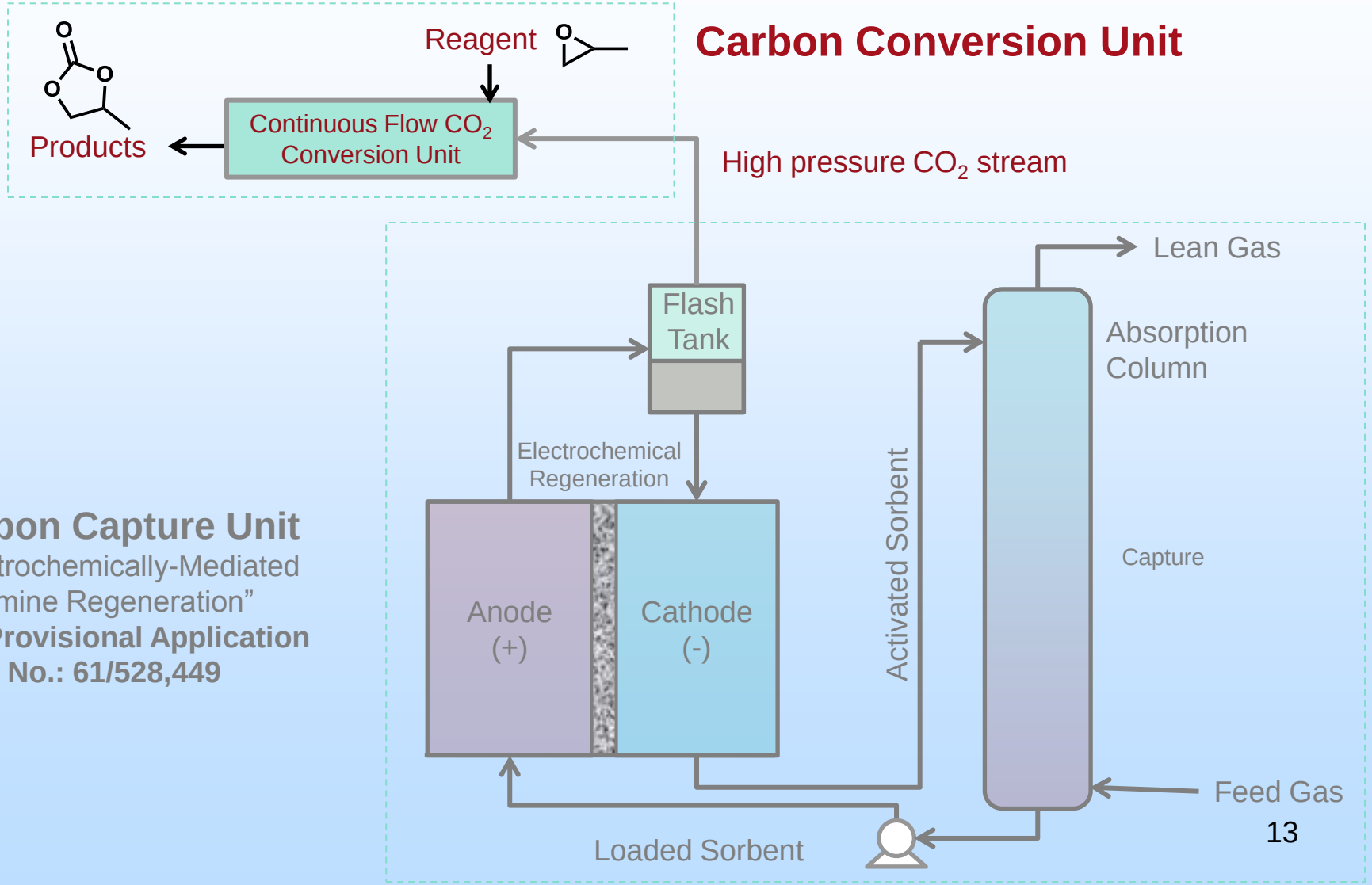
Cyclic Carbonate is The Target Commodity Chemical

- Most common reaction of CO_2 in the recent literature
- On an industrial scale, cyclic carbonates are synthesized using Lewis acid or base catalysts involving high temperature and pressures
- Uses of cyclic carbonates
  - polar aprotic solvents, electrolytes in lithium-ion batteries, constituents of oils and paints, raw materials in the synthesis of polycarbonates and polyurethanes

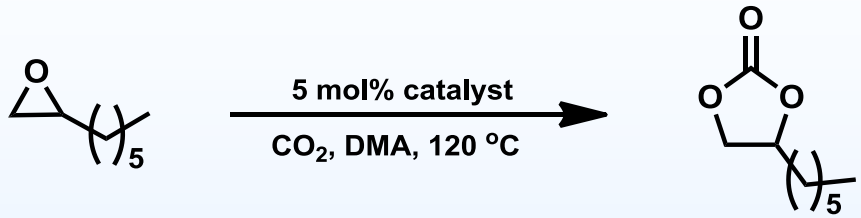


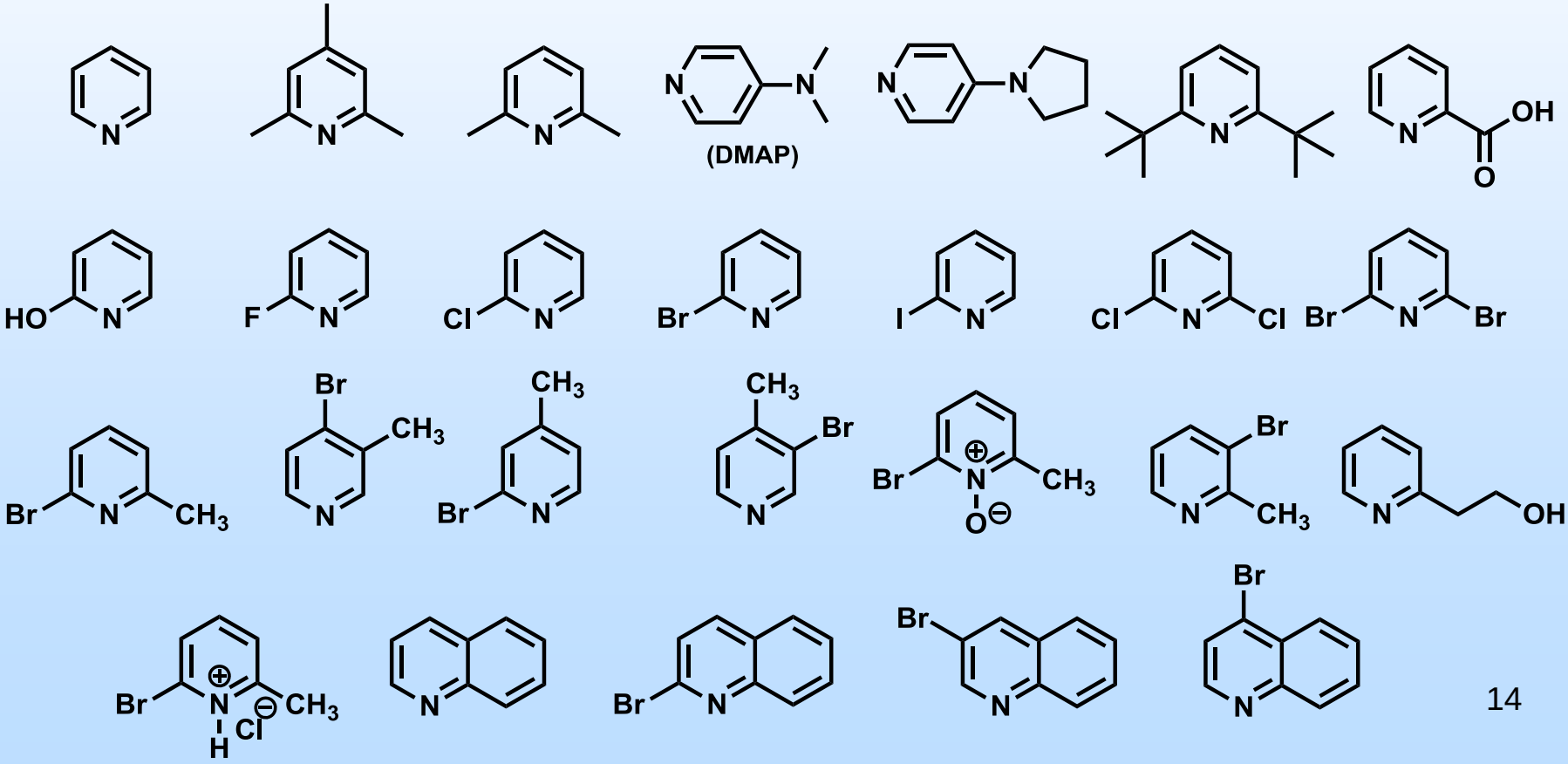
North, M.; Pasquale, R.; Young, C. *Green Chem*. **2010**, *12*, 1514-1539.

Coupled system for CO_2 capture and chemical conversion

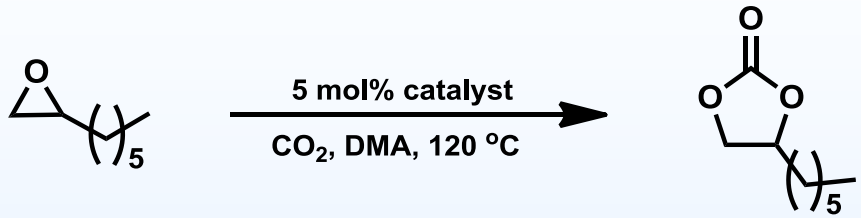


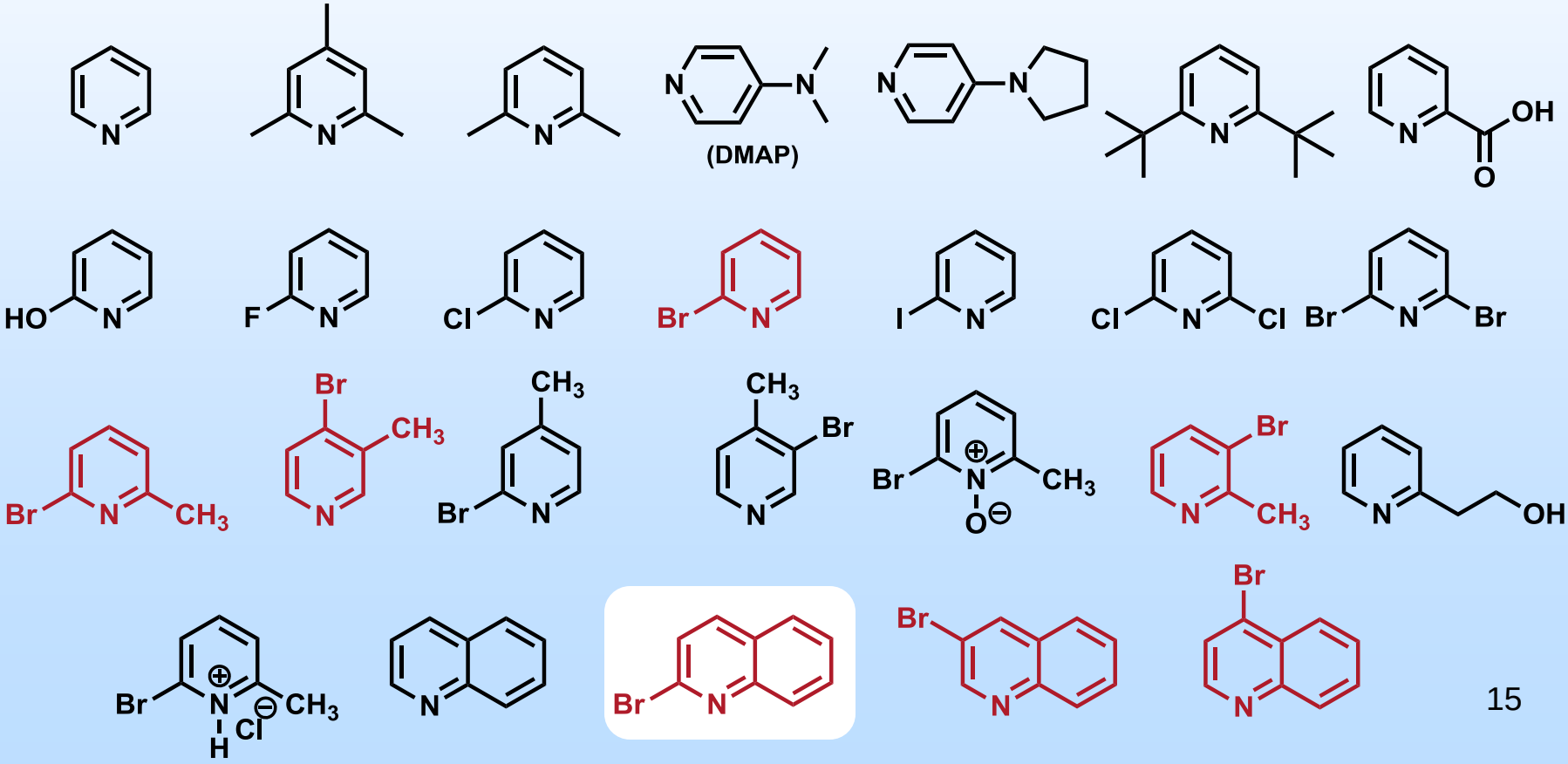
Catalyst Evaluation (Partial List)



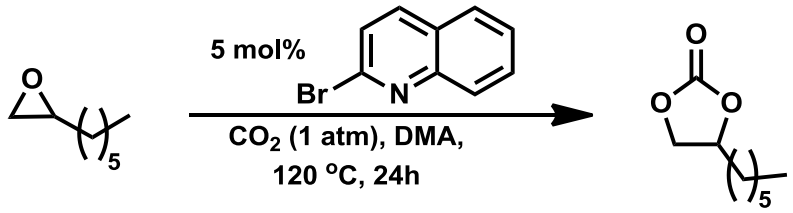


Catalyst Evaluation (Partial List)

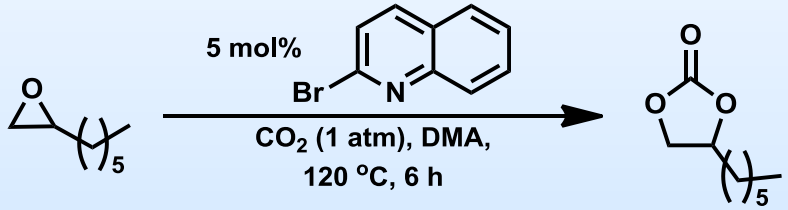




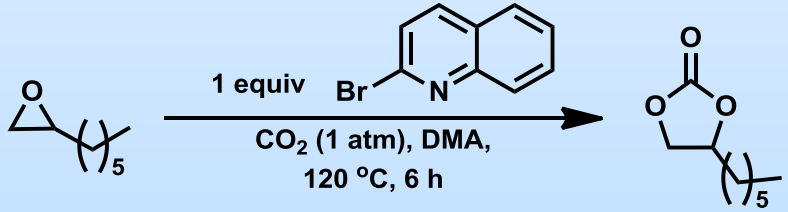
2-Bromoquinoline: A Challenge and A Clue



>95% yield



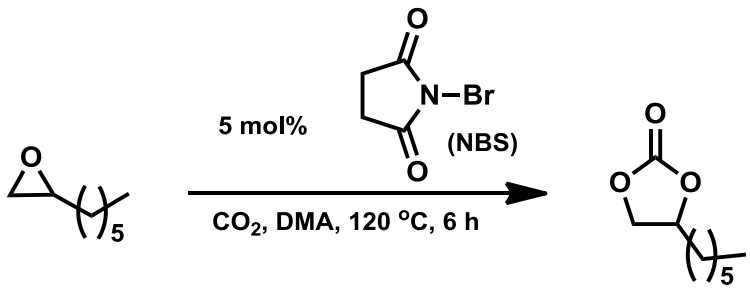
no conversion of epoxide observed



no conversion of epoxide observed even at 20x catalyst concentration

- ***long induction period and long reaction time (24 h)***
- ***not suitable for continuous production***
- ***mechanistic understanding and a new catalyst is required***

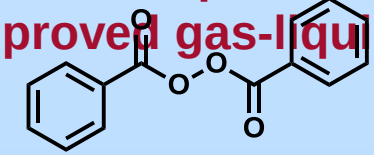
Radical Pathways Are Involved



Batch Reactions:

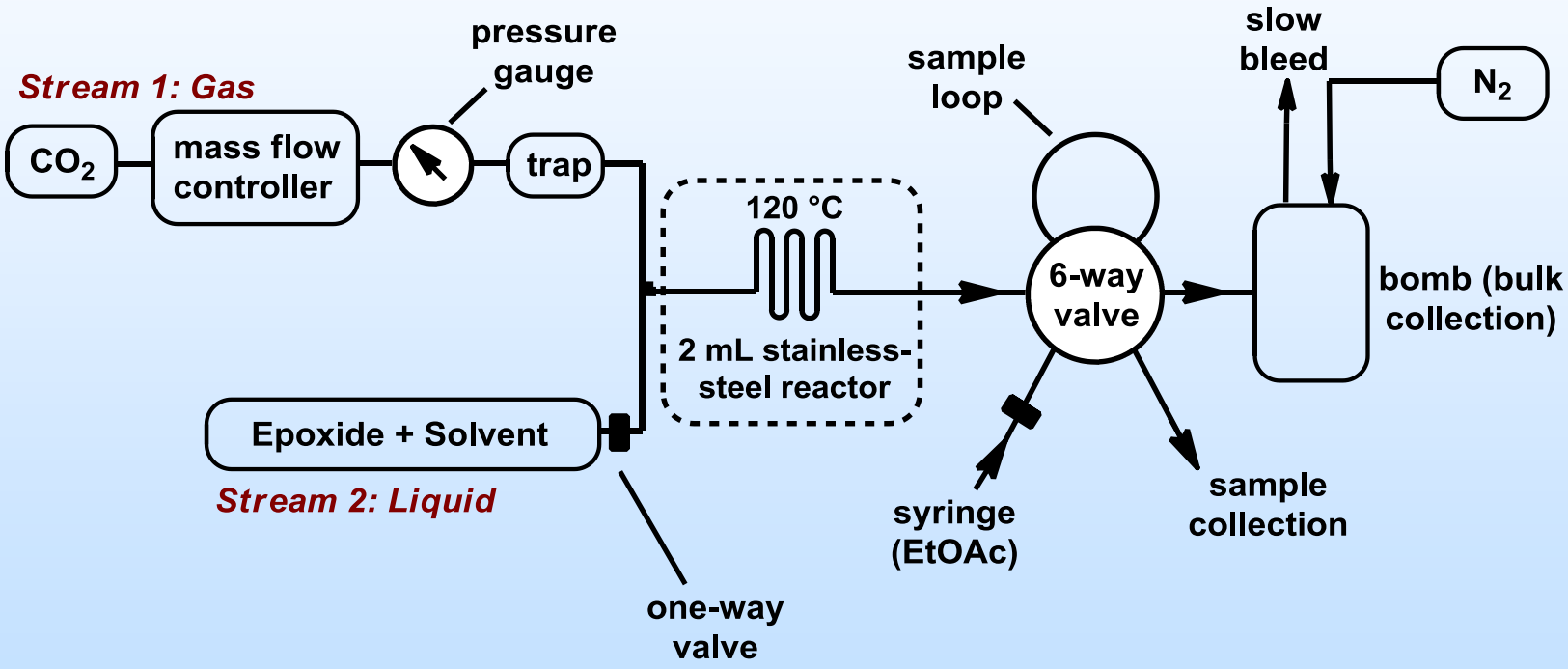
entry	catalyst	additive	conversion (%)	yield (%)
1	5% NBS	-	74	81
2	5% NBS	***dark***	31	33
3	5% NBS	1 equiv GALVINOXYL	-	0
4	5% NBS	5% benzoyl peroxide	80	75

Will a related continuous process enjoy improvements over batch due to improved gas-liquid mixing (slug flow)?

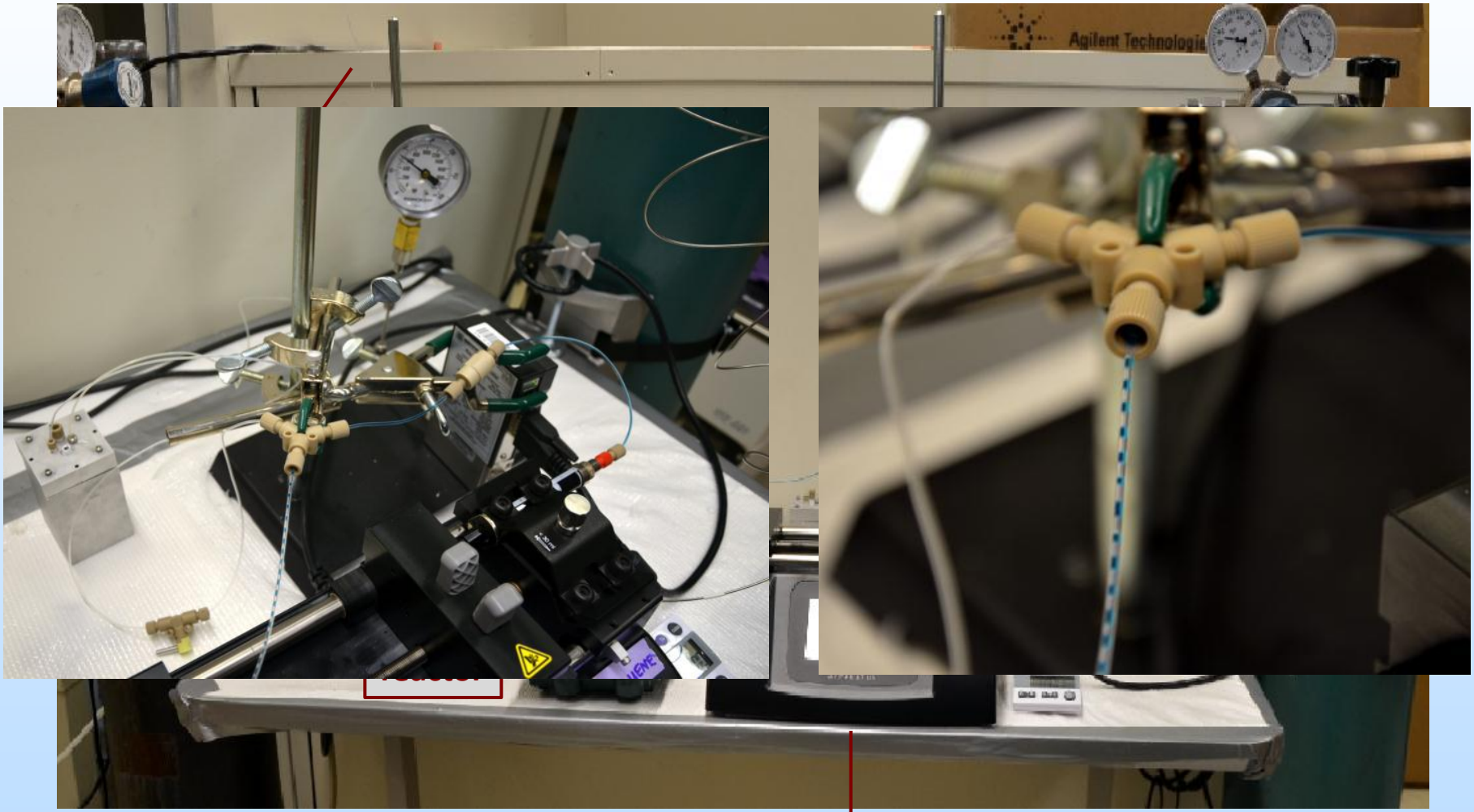


benzoyl peroxide – free radical initiator

Schematic of the Continuous Reactor

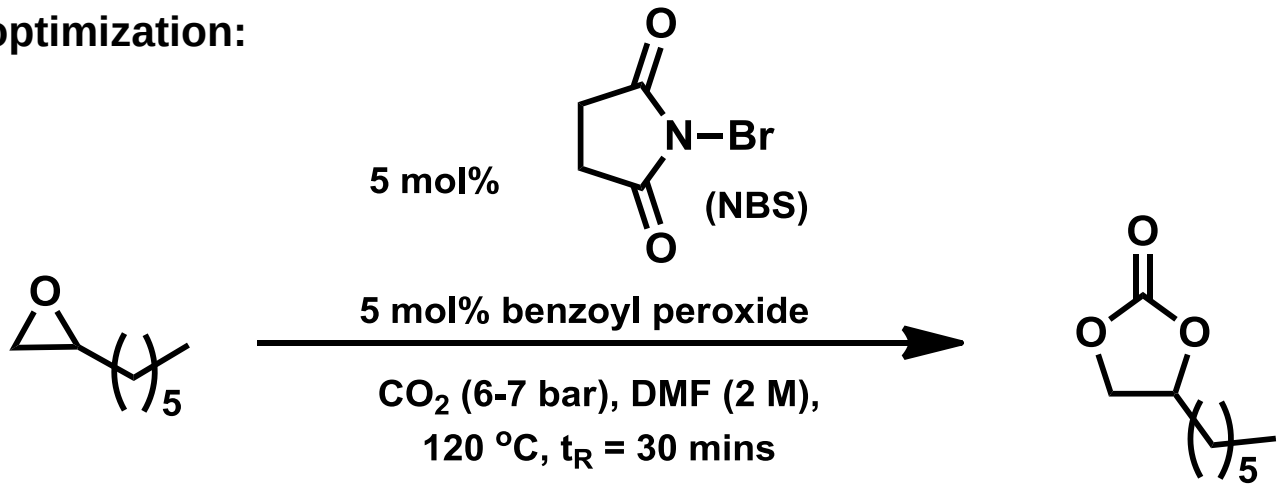


Continuous Conversion Reactor



Current State of the Art

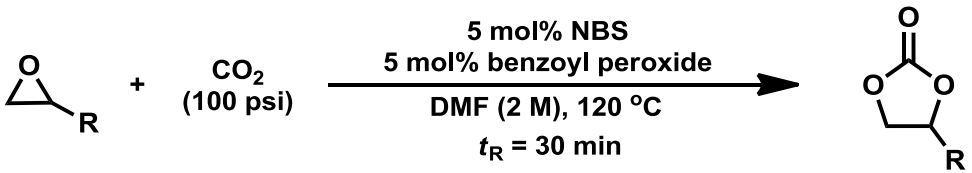
After optimization:

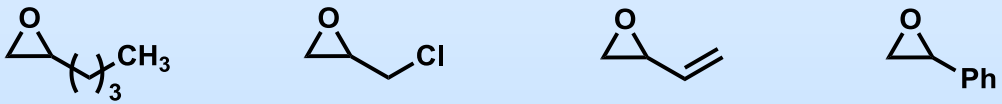


- **novel organocatalyst**
- **first demonstration of catalysis of epoxide opening by electrophilic bromine**
- **reaction complete in 30 min at 5 mol% catalyst loading**
- **superior performance under continuous slug flow conditions**
- **well-behaved reaction kinetics (no detectable induction period)**

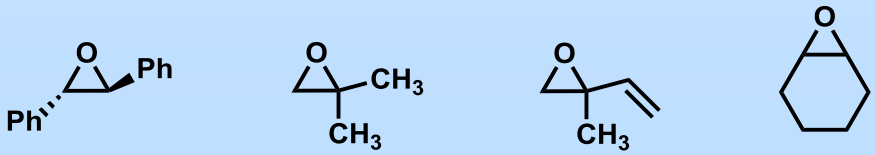
Kozak, J. A.; Simeon, F.; Hatton, T. A.; Jamison, T. F., “Bromine-Catalyzed Conversion of Carbon Dioxide and Epoxides to Cyclic Carbonates under Continuous Flow Conditions,” **2012** (*submitted for publication August 17, 2012*).

Scope of the Reaction

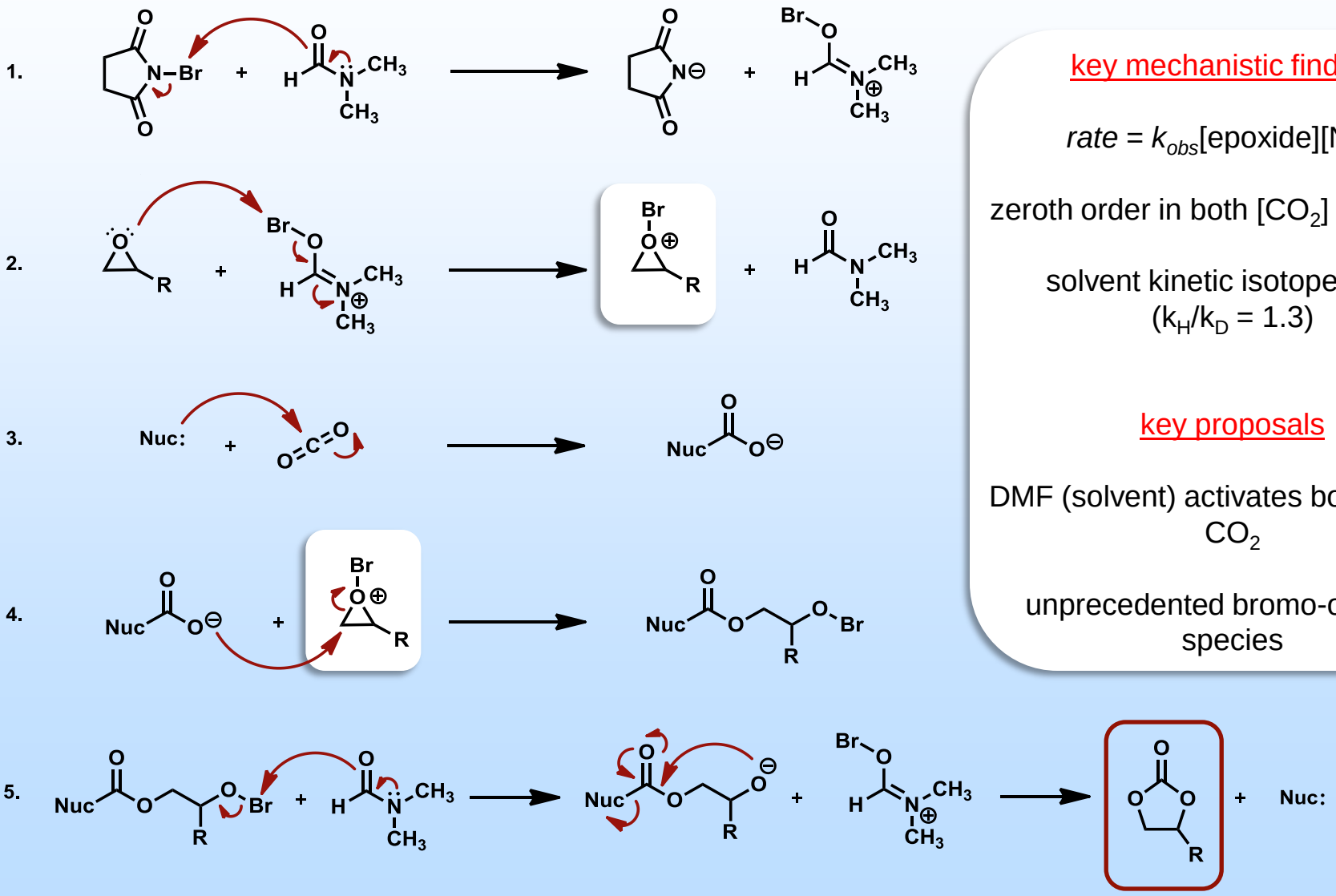




- ***currently limited to mono-substituted epoxides***
- ***no reaction was observed with the following epoxides***



Proposed Mechanism Based on Kinetics Investigations



key mechanistic findings

$rate = k_{obs}$[epoxide][NBS]

zeroth order in both [CO_2] and [BPO]

solvent kinetic isotope effect (k_H/k_D = 1.3)

key proposals

DMF (solvent) activates both Br^+ and CO_2

unprecedented bromo-oxonium species

Summary

- Key Findings
  - Electrophilic bromine sources are effective catalysts for conversion of CO_2 and epoxides into cyclic carbonates, which are valuable commodity chemicals.
  - A novel mechanism of epoxide activation was discovered, and its impact may be very broad.
- Lessons Learned
  - Continuous processing is superior to batch and is likely to be the preferred approach in the majority of CO_2 conversion methods.

Summary

– Future Plans

- Integration with electrochemical capture systems
- Development of related reactions using electrophilic bromine catalysts
- Development of superior catalysts (amides, polypeptides) designed based on mechanistic findings.
- Engineering implementation strategy for chemical conversion of CO_2 in continuous flow reactor
- Investigation of the effect of the impact of the quality of gas streams upon the conversion

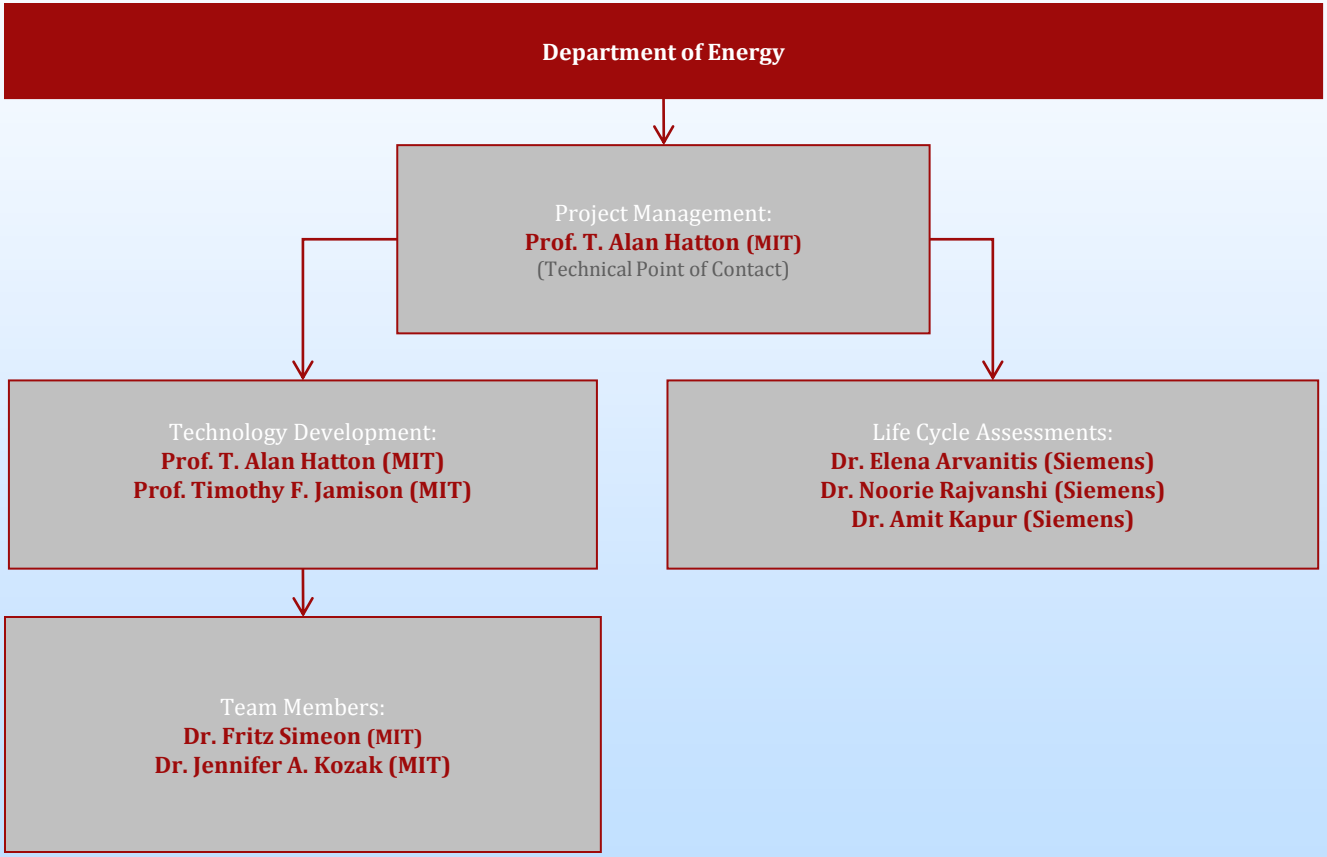
Acknowledgments

- MIT
  - Dr. Jennifer A. Kozak
  - Dr. Fritz Simeon
  - Prof. T. Alan Hatton
- Siemens (Life Cycle Analyses)
  - Dr. Elena Arvinitis
  - Dr. Noorie Rajvanshi
  - Dr. Amit Kapur
- DOE-NETL
  - Dr. Bill O’Dowd

Appendix

– These slides will not be discussed during the presentation, but are mandatory

Organization Chart



Gantt Chart

Sub-Task	Project Milestone Description	Project Duration:10/01/2010-09/30/2011 Project Year 1 Q1	Q2	Q3	Q4	Project Year 2 Q5	Q6	Q7	Q8	Planned Start Date:	Planned End Date:	Actual Start Date:	Actual End Date:	Comments
1.1	Project management plan	✔								10/01/10	09/30/12	10/01/10		
1.2	Project management	✔	✔	✔	✔	✔	✔	✔		10/01/10	09/30/12	10/01/10		Submission of Q7progress report on July 30, 2012
2.1	Chemical reaction between bis(carbonate)s and electrophiles	✔	✔	✔	✔	✔	✔	✔		10/01/10	03/31/11	10/01/10		Investigation of organocatalyst (NBS system) for production of cyclic carbonate from cyclic oxide and CO_2
2.2	Molecular characterization of “intermediate” complex	✔	✔	✔	✔	✔	✔	✔		10/01/10	03/31/11	10/01/10		Investigation of organocatalyst (NBS system) for production of cyclic carbonate from cyclic oxide and CO_2
2.3	Reaction kinetic analysis of “intermediate” complex formation			✔	✔	✔	✔	✔		04/01/11	09/30/11	07/01/11		Reaction kinetic of organocatalytic process (NBS system) for cyclic carbonate production from cyclic oxide and CO_2
2.4	Electrochemistry of “intermediate” complex formation			✔	✔					04/01/11	09/30/11	04/01/11		Investigation of intermediate and “active” catalyst in organocatalytic process for cyclic carbonate production from cyclic oxide and CO_2
2.5	Chemical sequestration with various redox-active molecules									10/01/11	03/31/12			
2.6	Computational modeling of “intermediate” complex formation									10/01/11	03/31/12			
3.1	Conceptual reactor design of integrated chemical sequestration process				✔	✔	✔	✔		01/01/11	09/30/11			Complete assemble and assessment of flow chemical reactor design for organocatalytic process. Pending electrochemical cell until the finalization of the synthetic route.
3.2	Impedance analysis of cell design and kinetics									04/01/11	09/30/11			Pending electrochemical cell until the finalization of the synthetic route.
3.3	Analysis of cell components for									10/01/11	03/31/12			

Gantt Chart (continued)

Sub-Task	Project Milestone Description	Project Duration:10/01/2010-09/30/2011 Project Year 1 Q1	Q2	Q3	Q4	Project Year 2 Q5	Q6	Q7	Q8	Planned Start Date:	Planned End Date:	Actual Start Date:	Actual End Date:	Comments
3.3	Analysis of cell components for integrated chemical sequestration process									10/01/11	03/31/12			
3.4	Computer simulation of dynamic analysis									10/01/11	03/31/12			
4.1	Chemical analysis of integrated chemical sequestration									04/01/12	09/30/12			
4.2	Optimization key components of integrated chemical sequestration									04/01/12	09/30/12			
4.3	Chemical sequestration prototype unit									04/01/12	09/30/12			
5.1	Life cycle environmental analysis		✔	✔	✔	✔	✔	✔		10/01/11	09/30/12	03/01/11		Life cycle assessment of different scenarios.
5.2	Life cycle cost analysis							✔		10/01/11	03/31/12	05/01/12		

Bibliography

Publication:

Kozak, J. A.; Simeon, F.; Hatton, T. A.; Jamison, T. F., 2012, Bromine-Catalyzed Conversion of Carbon Dioxide and Epoxides to Cyclic Carbonates under Continuous Flow Conditions, *submitted for publication*.

Conference Presentation:

Rajvanshi, N.; Arvanitis, E.; Kapur, A.; Hatton, T. A.; Jamison, T. F.; Simeon, F.; Kozak, J. A., 2012, Environmental Life Cycle Assessment of Novel CO2 Capture and Utilization Routes, LCA XII, Tacoma, Washington.