

# Integrated Electrochemical Processes for CO<sub>2</sub> Capture and Conversion to Commodity Chemicals

Project Number: DE-FE0004271

**Dr. Jie Wu,<sup>1,2</sup> Dr. Jennifer A. Kozak,<sup>1,2</sup> Xiao Su,<sup>2</sup> Dr. Fritz Simeon,<sup>2</sup>  
Prof. Timothy F. Jamison\*,<sup>1</sup> and Prof. T. Alan Hatton\*,<sup>2</sup>**

<sup>1</sup>Department of Chemistry and <sup>2</sup>Department of Chemical Engineering  
Massachusetts Institute of Technology

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U.S. Department of Energy  
National Energy Technology Laboratory  
Carbon Storage R&D Project Review Meeting  
Developing the Technologies and  
Infrastructure for CCS  
August 20-22, 2013

# Presentation Outline

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- Motivation, Goals, Objectives
- Background
- Cyclic Carbonate Synthesis via Catalytic Coupling of CO<sub>2</sub> and Epoxides
- Cyclic Carbonate Synthesis via oxidative carboxylation using CO<sub>2</sub> and Olefins
- Conclusions

# Benefit to the Program

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- Identify the Program goals being addressed.
  - Develop technologies to demonstrate that 99 percent of injected CO<sub>2</sub> remains in the injection zones.
- The research project is developing a novel approach to capturing and converting CO<sub>2</sub> into commodity chemicals, which may thus reduce the burden on CO<sub>2</sub> storage sites, in addition to providing a means to reduce anthropogenic CO<sub>2</sub> emissions and an inexpensive method for producing useful materials from CO<sub>2</sub>.

# Project Overview: Goals and Objectives

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- To develop and demonstrate a novel *chemical* sequestration technology that utilizes CO<sub>2</sub> 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<sub>2</sub> capture and chemical conversion
  - **Coupled** system for CO<sub>2</sub> capture and chemical conversion

# Project Overview:

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# Technical Status

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# Accomplishments to Date

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- A novel catalytic method for the continuous chemical conversion of CO<sub>2</sub> has been developed and thoroughly investigated mechanistically.
- A mechanism-guided design of sequential continuous flow systems has been developed to achieve a variety of carbonates using CO<sub>2</sub> and olefins.
  - Detailed mechanistic exploration.
  - Several advantages over existing methods.
  - Springboard for development of several other classes of CO<sub>2</sub> conversion.

# Motivation for CO<sub>2</sub> Capture, Sequestration, and Conversion

- Anthropogenic carbon dioxide (CO<sub>2</sub>)
  - 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<sub>2</sub>
  - we will continue to depend on *non-renewable* fossil fuels for the next several decades
- The CO<sub>2</sub> cycle is not balanced
  - 3.9% excess (caused by anthropogenic CO<sub>2</sub>) with respect to the yearly CO<sub>2</sub>-flow in the natural “carbon cycle”
  - Only 30-35% of the chemical energy content associated with anthropogenic CO<sub>2</sub> 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<sub>2</sub>?
  - CO<sub>2</sub> 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<sub>2</sub> is a renewable resource, as compared to oil or coal; the future supply of fossil fuels is considered limited.
  - The use of CO<sub>2</sub> in new routes to existing chemical intermediates and products could be more efficient and economical than current technologies.
  - The production of chemicals from CO<sub>2</sub> could have a small but likely significant positive impact on the global carbon balance.
  - CO<sub>2</sub> 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).

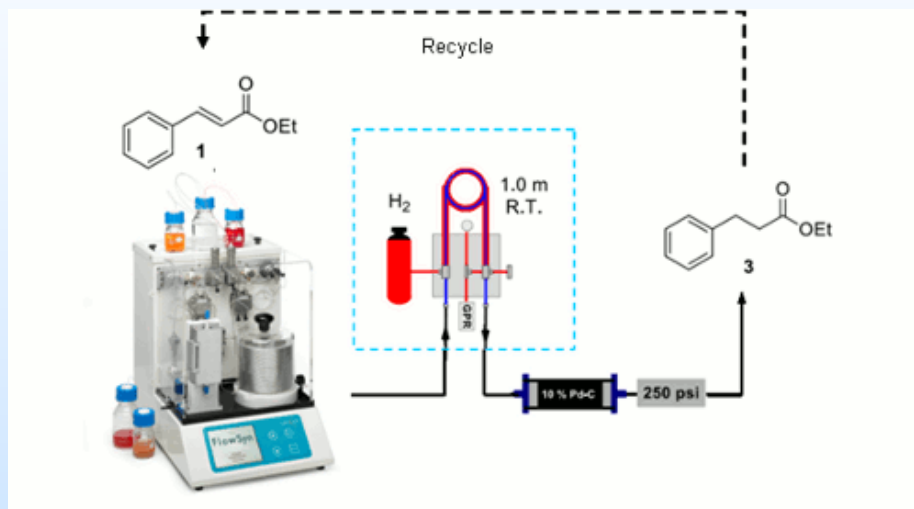
Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; 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.

# Gas/Liquid Continuous Flow Chemistry

## Traditional batch reactions:



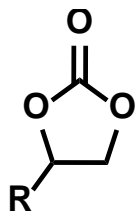
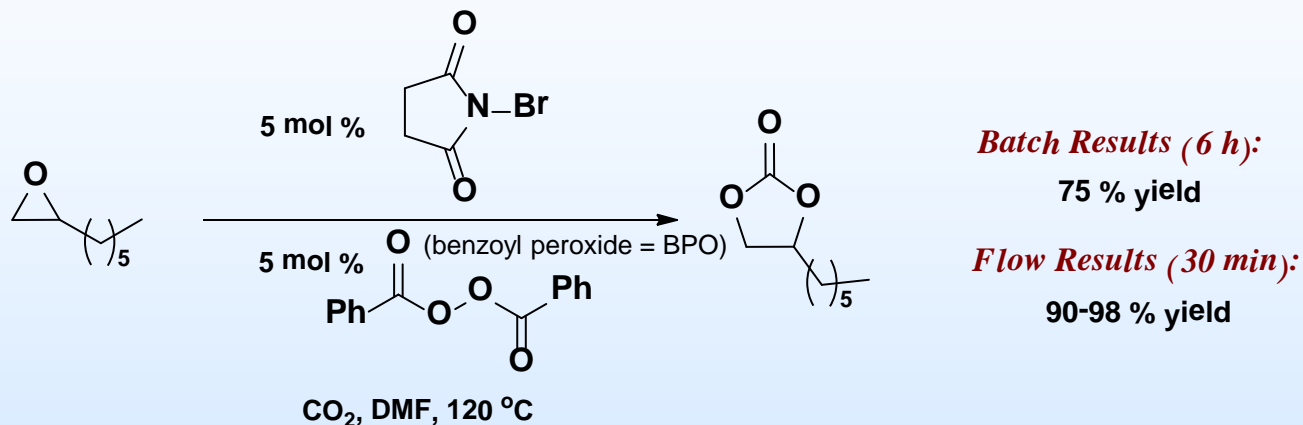
## Continuous flow synthesis:



- *Low interaction and mass transfer*
- *Interfacial area of ca. 100-300 m<sup>2</sup>/m<sup>3</sup><sub>liq</sub>*
- *High capital and infrastructure costs*
- *Associated safety factors*
- *Exceedingly high surface-to-volume ratio*
- *Efficient heterogeneous mass-transfer*
- *Excellent reproducibility*
- *Reduced equipment footprint and labor work*

# Conversion of CO<sub>2</sub> Using Epoxides

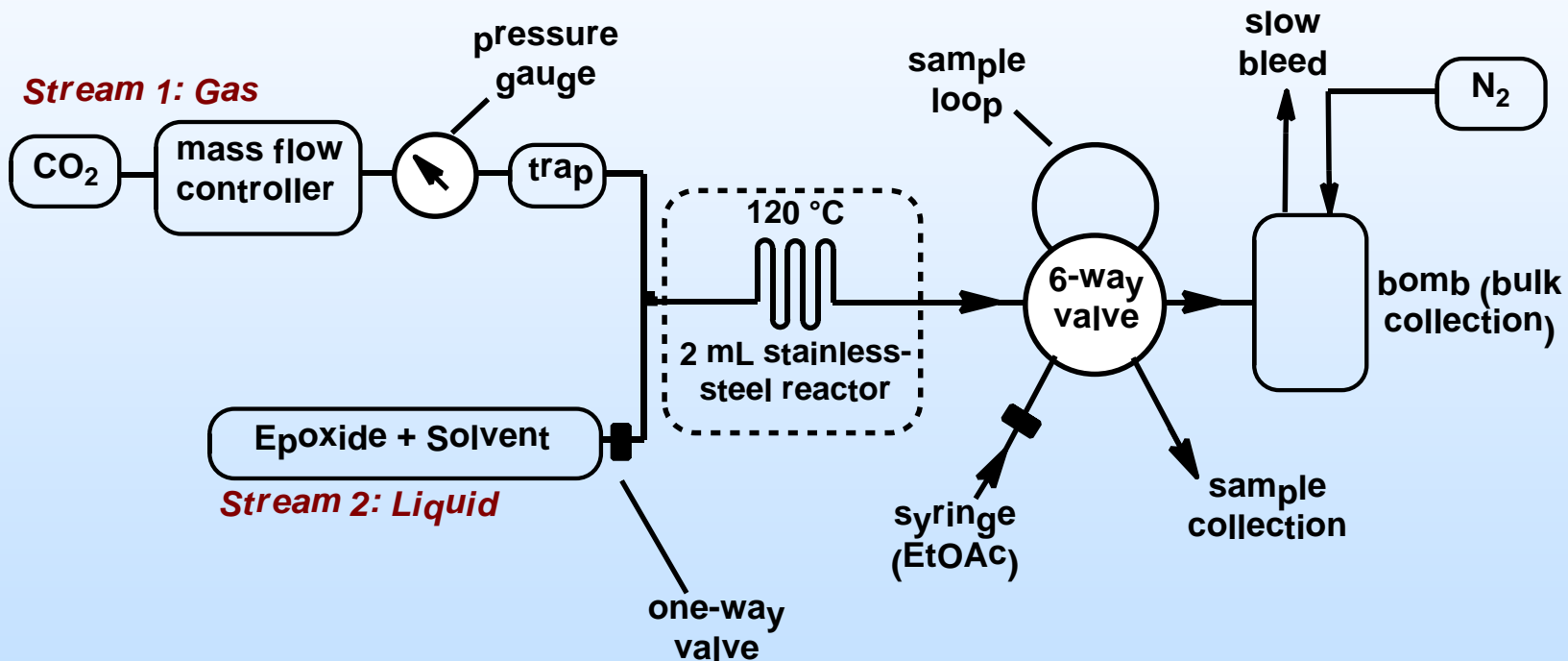
Bromine-catalyzed conversion of CO<sub>2</sub> and epoxides to cyclic carbonates:



- *polar aprotic solvents*
- *electrolytes in lithium ion batteries*
- *constituents in oils and paints*
- *antifoam agents for antifreeze and plasticizers*
- *raw materials for the synthesis of polycarbonates and polyurethanes*

Kozak, J. A.; Wu, J.; Su, X.; Simeon, F.; Hatton, T. A.; Jamison, T. F., "Bromine-Catalyzed Conversion of CO<sub>2</sub> and Epoxides to Cyclic Carbonates under Continuous Flow Conditions," **2013** (*submitted for publication*).

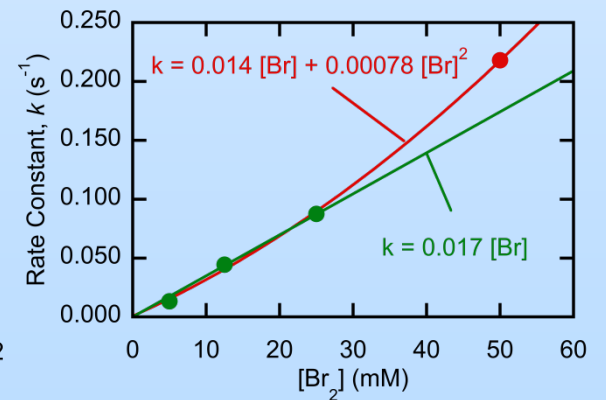
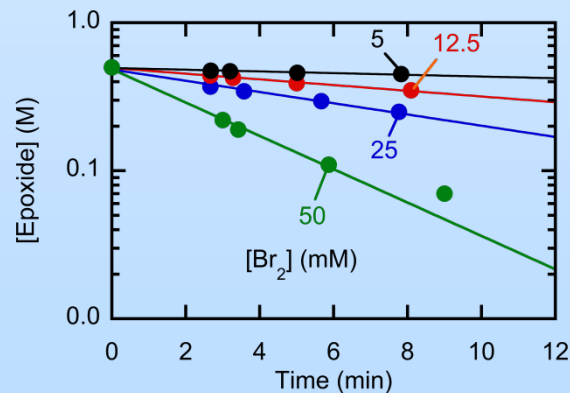
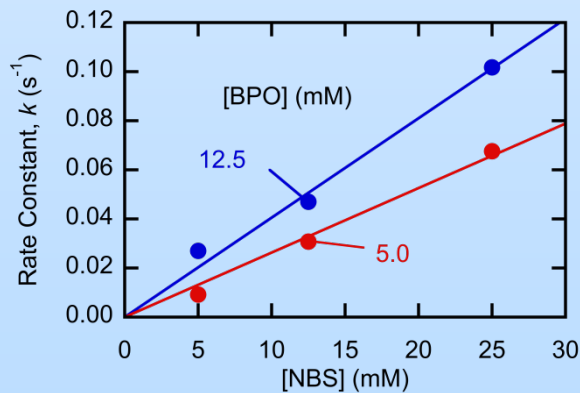
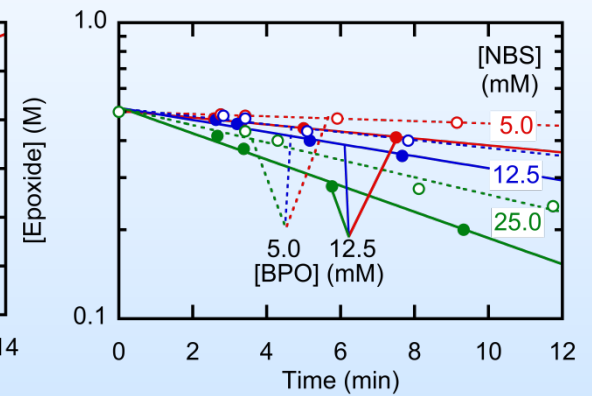
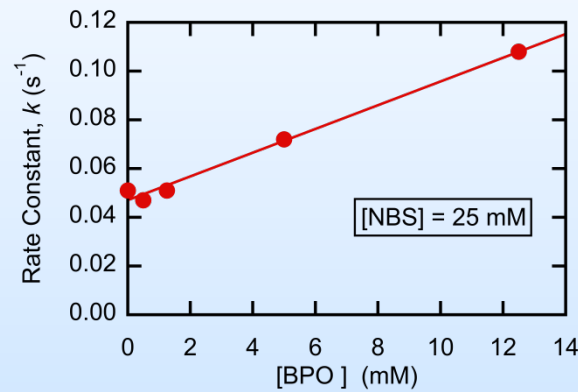
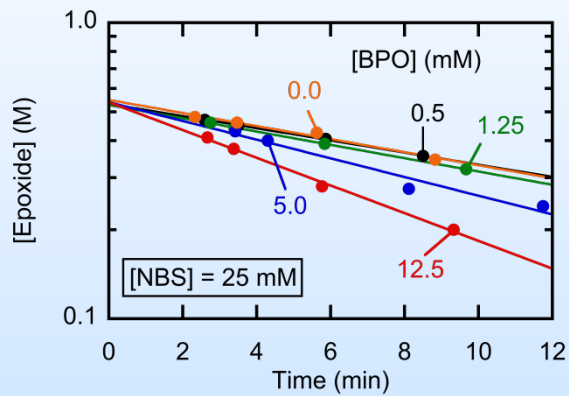
# Schematic of the Continuous Reactor



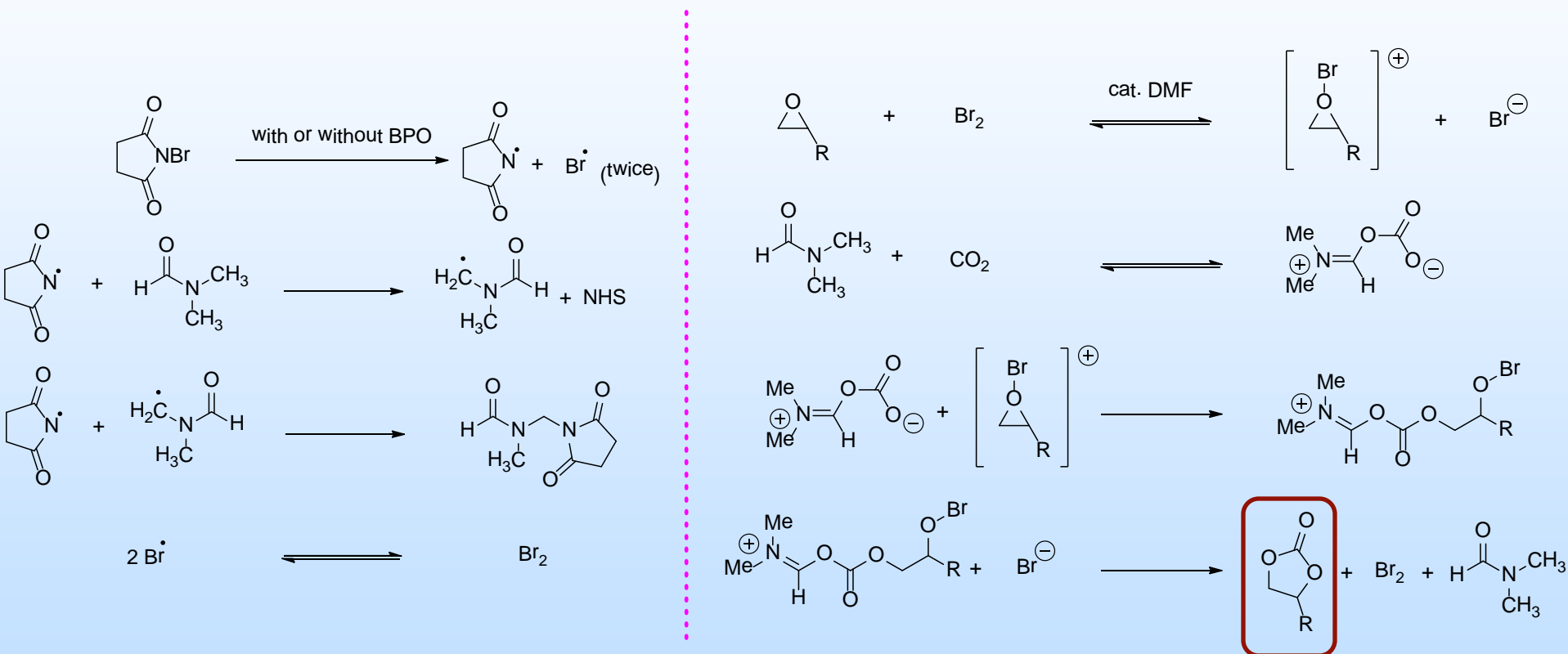
Slug flow reduces dispersion; provides efficient mass transfer contact  
Well-controlled conditions for evaluation of reaction kinetics and mechanisms

# Kinetic Study

$$\frac{d[\text{Epoxide}]}{dt} = -(k_{10}^{\text{exp}} + k_1^{\text{exp}} [\text{BPO}]_0) [\text{NBS}]_0 [\text{Epoxide}]$$



# Proposed Mechanism Based on Kinetics Investigations

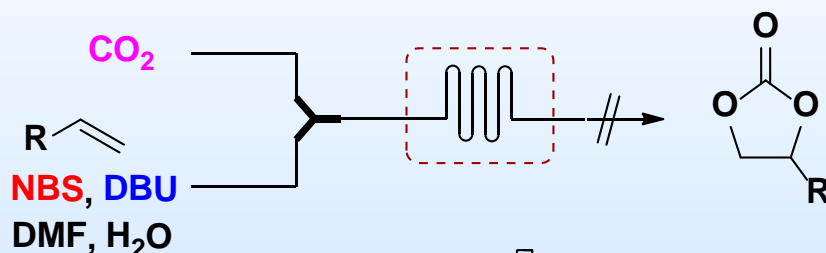


$$r_{\text{overall}} = \frac{k_4 k_{r4} [k_{10} + k_1 [\text{BPO}]] [\text{NBS}] [\text{Epoxide}]}{2(k_4^2 - k_{r4}^2)}$$

# Capture of CO<sub>2</sub> Using Simple Olefins

## Mechanism-guided flow design to avoid reagent incompatibility:

### Originally designed multi-stream flow

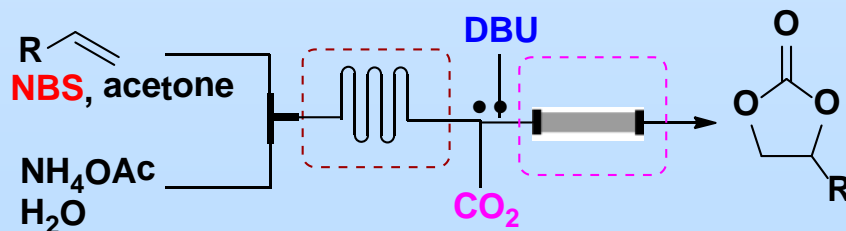


- *Low reaction rate*  
(especially for aliphatic olefins)
- *Reagent incompatibility*  
(such as DBU and NBS)

Low solubility of olefins in DMF/H<sub>2</sub>O  
Interaction between NBS and DBU  
(DBU = 1,8-diazabicycloundec-7-ene)  
Dibromide formation promoted by DBU;  
form bromohydrins before addition of DBU

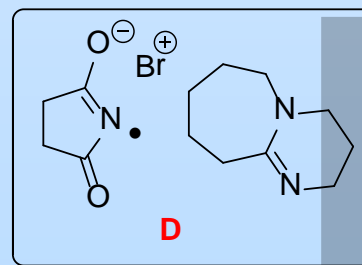
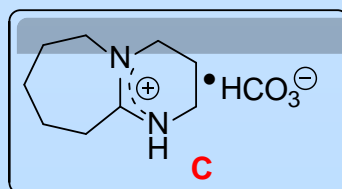
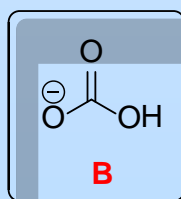
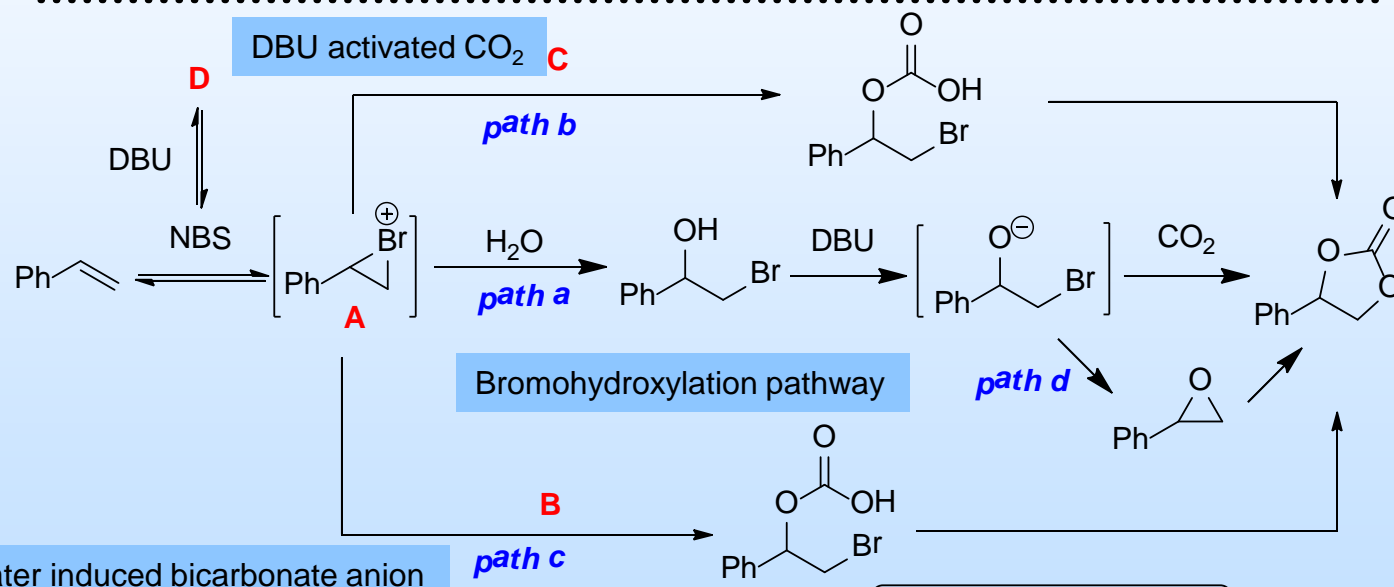
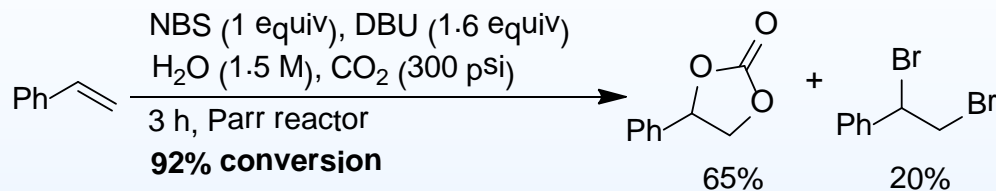
mechanistic investigation

### Mechanism-guided design of flow



- *Significantly enhanced rate*
- *Minimized by-products*
- *High yield*
- *Wide substrate scope*

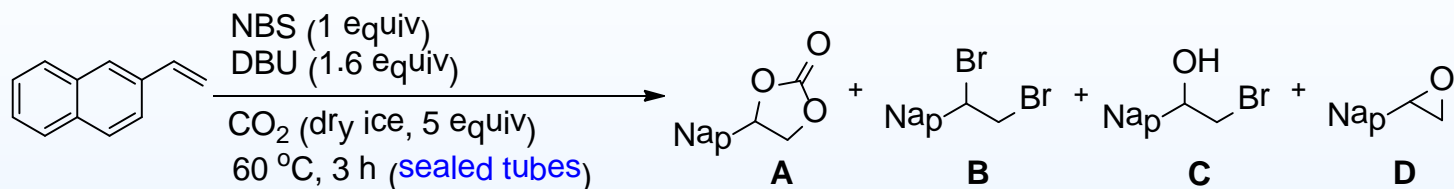
# Possible Reaction Pathways



Bromohydrin generated from olefins and NBS in water.



# Mechanistic Study

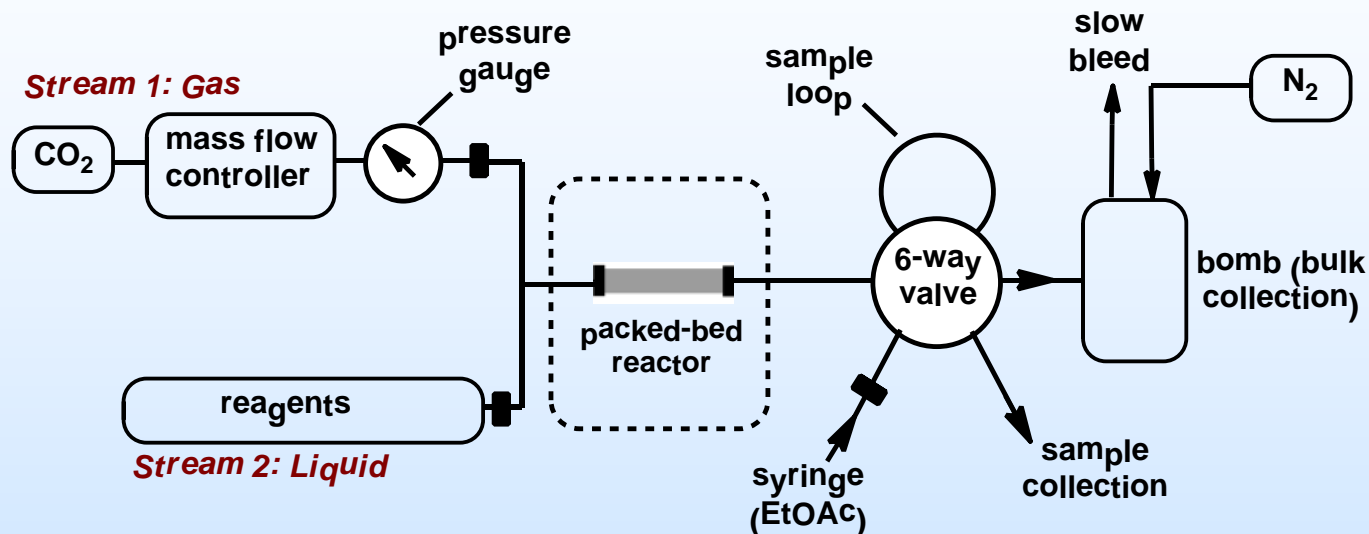


entry	condition	conversion <sup>a</sup>	yield of <b>A</b> <sup>a</sup>	other products <sup>a</sup>
1	NBS + H <sub>2</sub> O	100%	0%	87% <b>C</b>
2	NBS + H <sub>2</sub> O + DBU	26%	0%	15% <b>D</b>
3	NBS + H <sub>2</sub> O + DBU + CO <sub>2</sub>	84%	55%	8% <b>D</b>
4	NBS + DMF + DBU + CO <sub>2</sub>	50%	0%	45% <b>B</b>

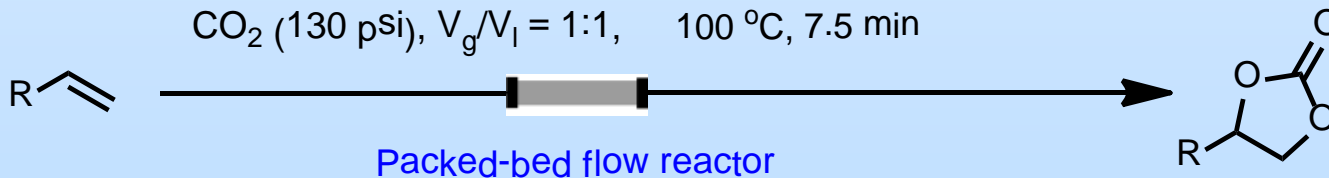
<sup>a</sup> Conversion and yield are based on analysis of crude <sup>1</sup>H NMR spectra using trichloroethylene as the external standard.

- Water was necessary
- **DBU significantly decreased the rxn rate** (indicated formation of DBU-NBS complex)
- CO<sub>2</sub> increased the reaction rate (indicated DBU-CO<sub>2</sub> complex formation)
- DMF helped formation of epoxide.

# Initial Two-Stream Gas/Liquid Flow Setup



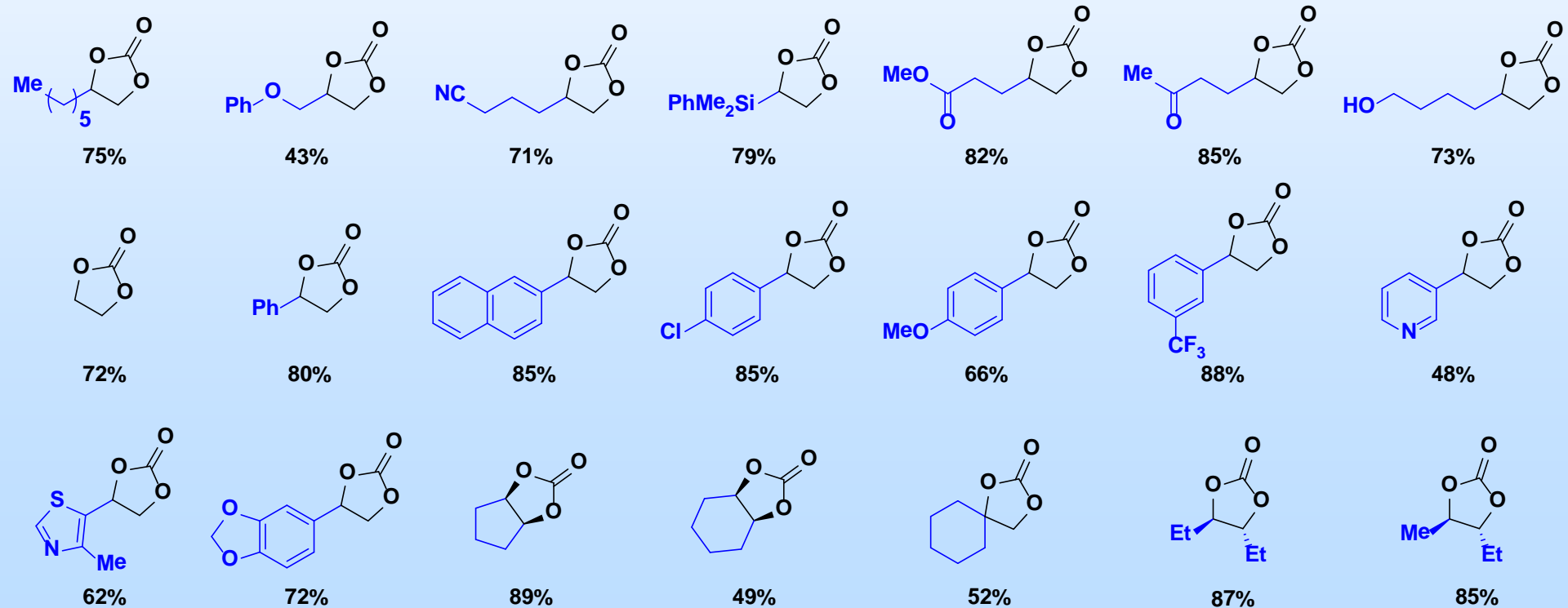
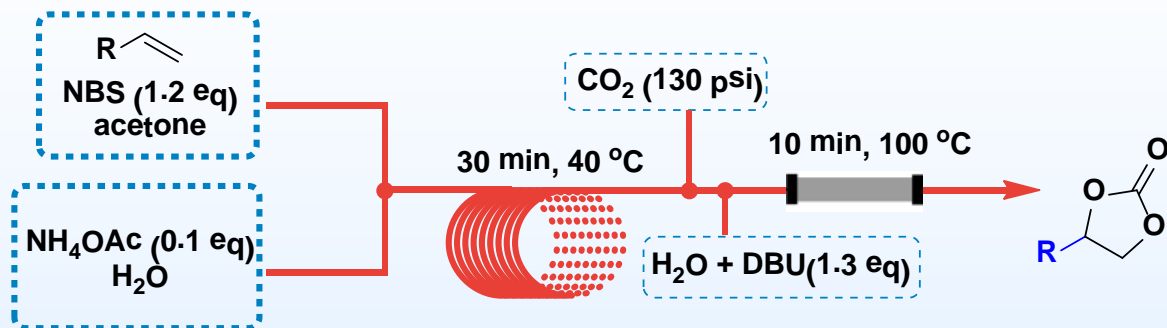
NBS (1.2 equiv), DBU (1 equiv), DMF/H<sub>2</sub>O (2:1, 0.4 M)  
CO<sub>2</sub> (130 psi), V<sub>g</sub>/V<sub>l</sub> = 1:1, 100 °C, 7.5 min



Ph-CH=CH<sub>2</sub> : 100% conversion  
85% yield

PhO-CH<sub>2</sub>-CH=CH<sub>2</sub> : 15% conversion  
10% yield

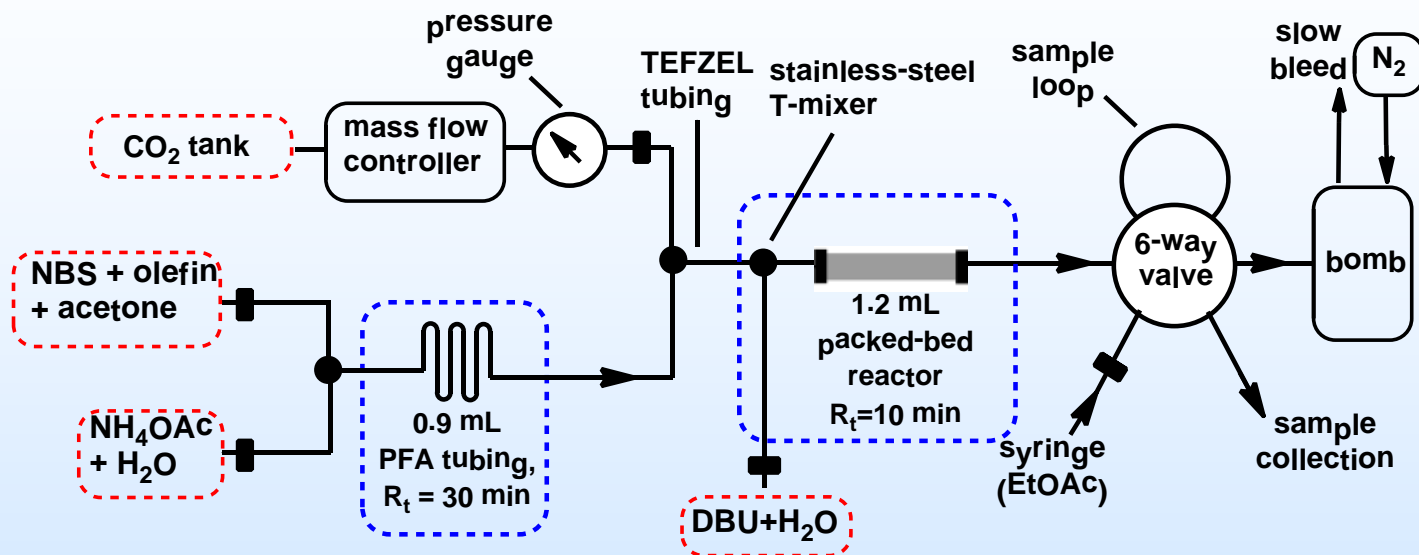
# Sequential Transformations in Flow







# Sequential Transformation in Flow



## feature

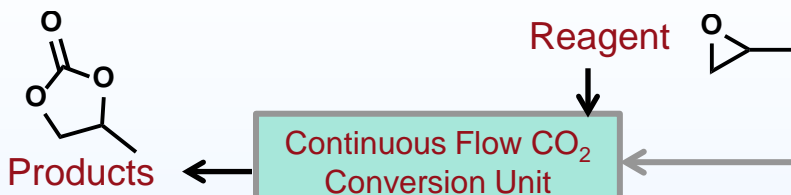
- sequential reactions
- excellent surface-to-volume ratio
- packed-bed reactor
- acetone as co-solvent
- elevated temperature and pressure
- no headspace

## function

- significantly enhances the reaction rate; avoids reagent incompatibility
- increases the reaction rate; suppresses byproduct formation
- increases the reaction rate; more steady flow
- avoids phase-transfer-reagents
- provides rate enhancement
- reduced equipment footprint (safety)



# An Integrated Capture and Conversion System

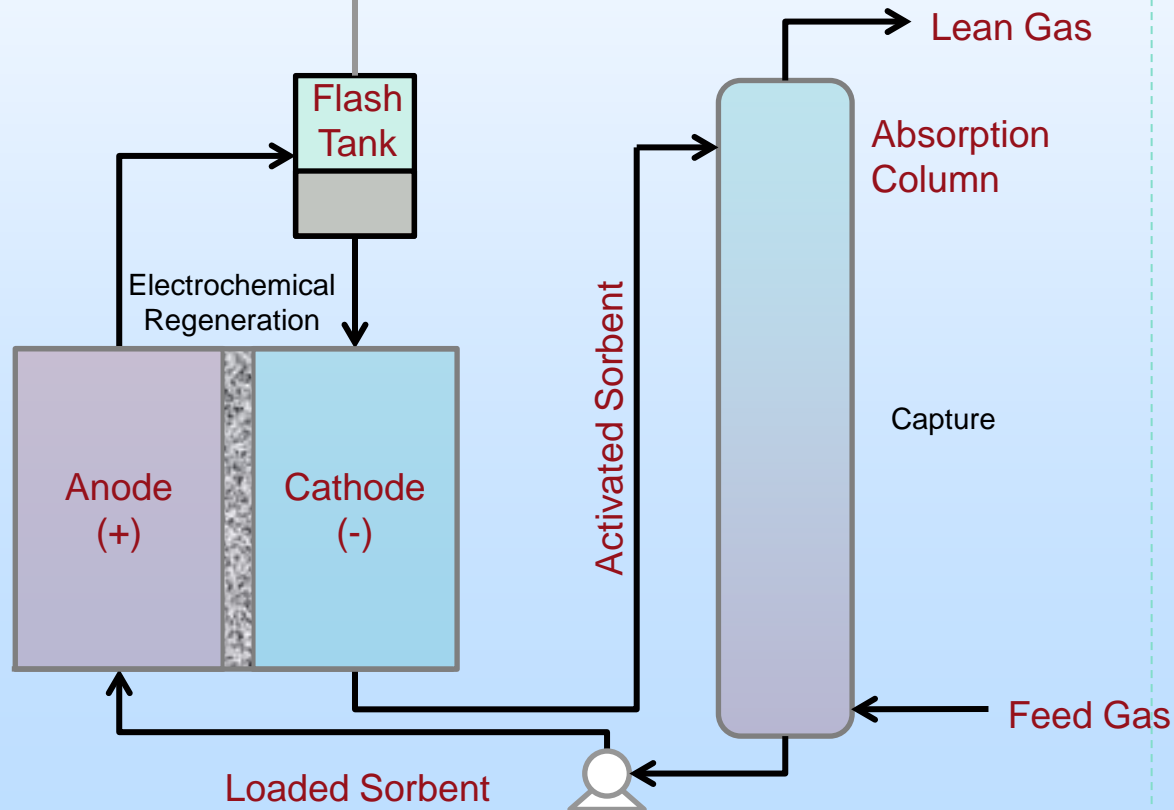
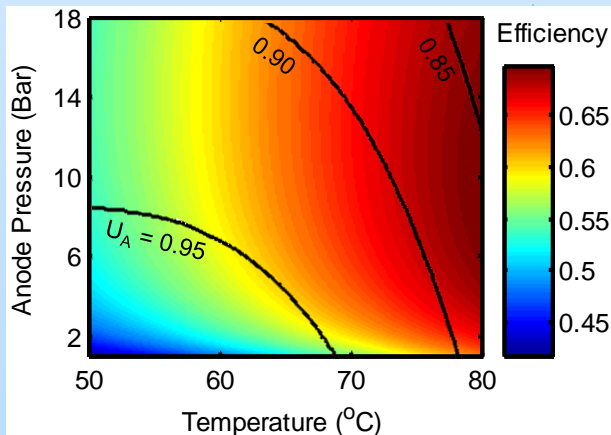


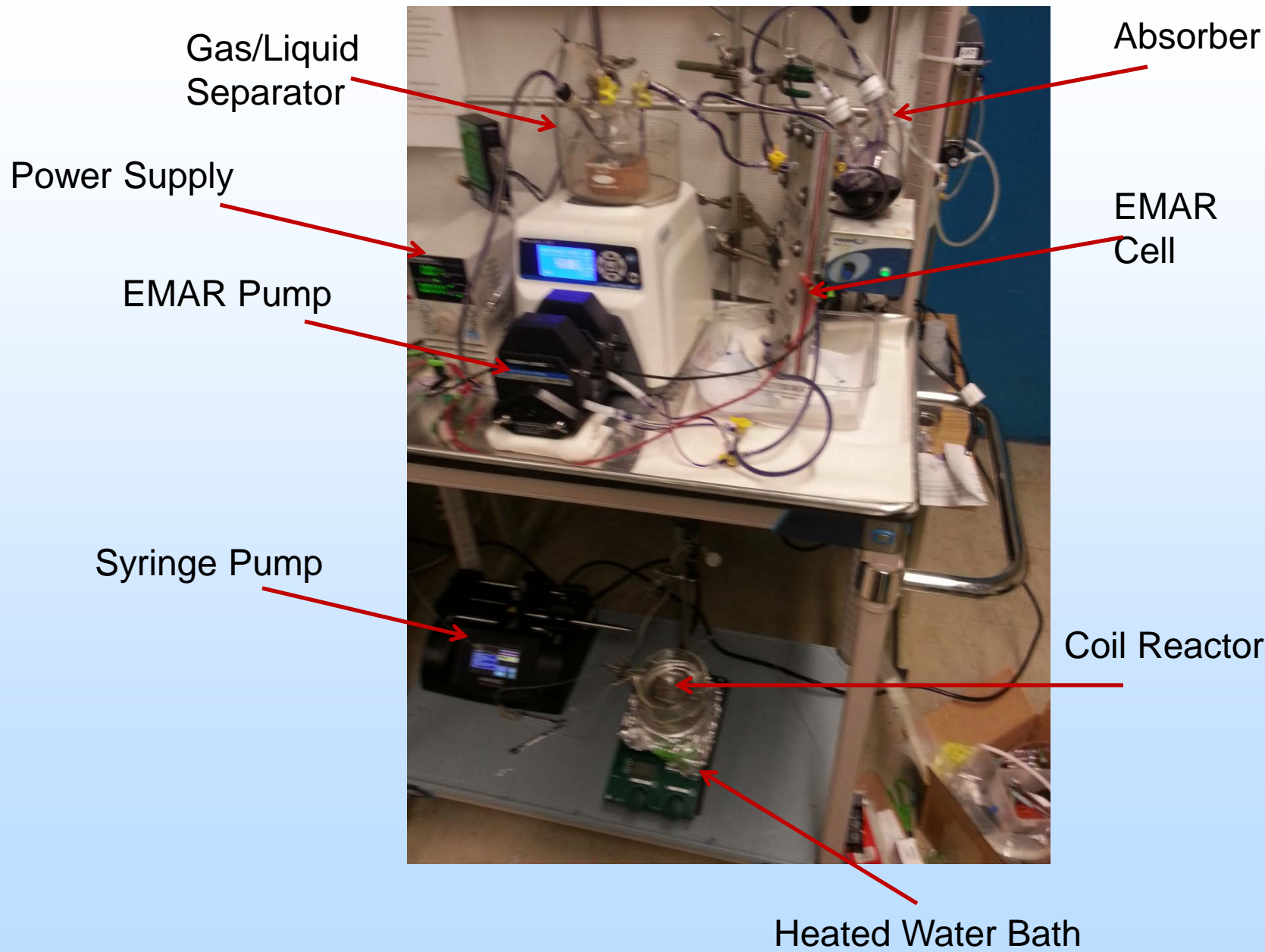
Organocatalytic Route -  
with decoupled capture and conversion units

## Carbon Conversion Unit

High pressure  
CO<sub>2</sub> stream

## Carbon Capture Unit “Electrochemically-Mediated Amine Regeneration”







# Summary

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## – Key Findings

- A novel mechanism of epoxide activation was discovered, and its impact may be very broad.
- A sequential flow system works best for the conversion of CO<sub>2</sub> using olefins due to the incompatibility between DBU and NBS.

## – Lessons Learned

- Continuous processing is superior to batch for elucidation of conversion mechanisms and kinetics

# Acknowledgments

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- MIT
  - Dr. Jie Wu
  - Dr. Jennifer A. Kozak
  - Xiao Su
  - Dr. Fritz Simeon
  - Prof. Timothy F. Jamison
  - Prof. T. Alan Hatton
- Siemens (Life Cycle Analyses)
  - Dr. Elena Arvinitis
  - Dr. Noorie Rajvanshi
  - Dr. Amit Kapur
- DOE-NETL
  - Dr. Bill O'Dowd

# Appendix

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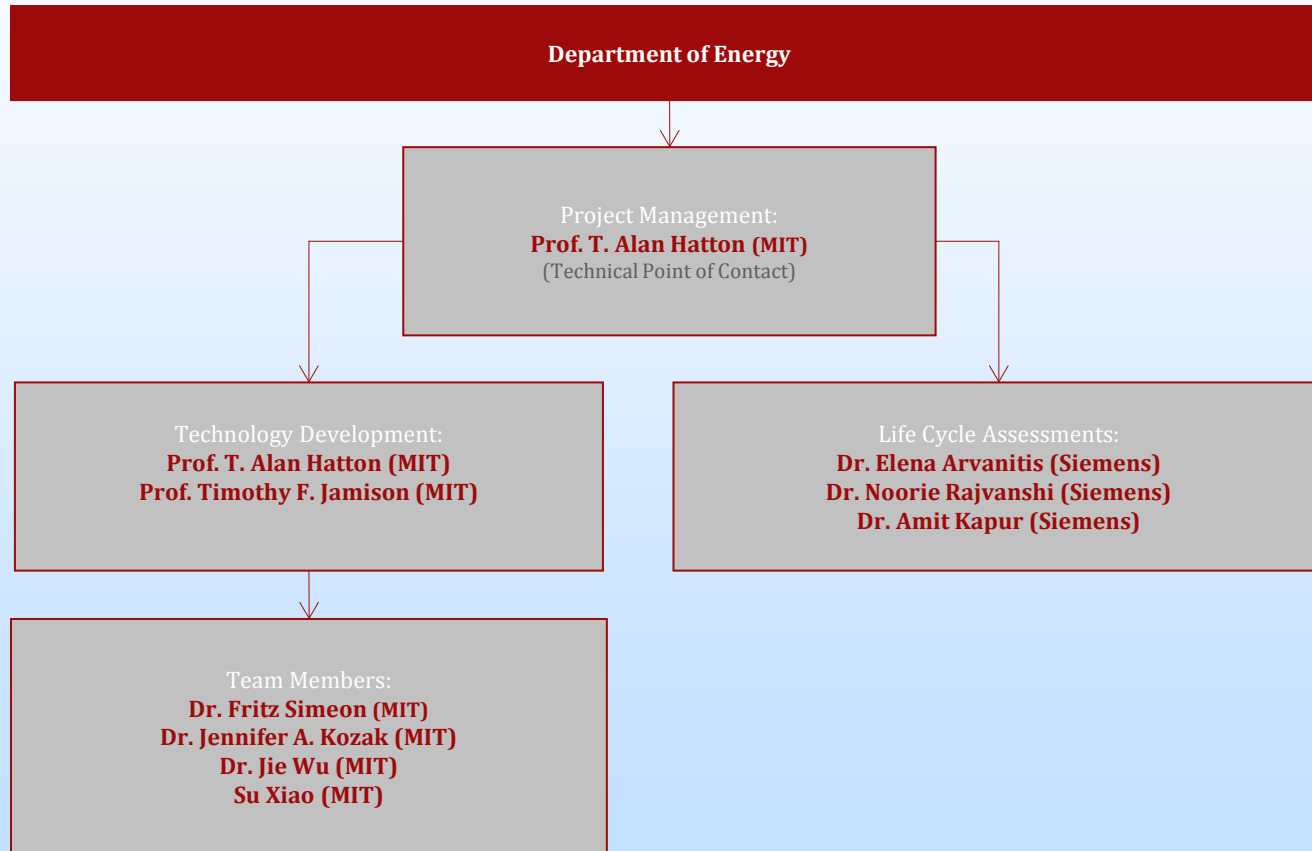
- These slides will not be discussed during the presentation, **but are mandatory**

# Gantt Chart

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Sub-  
Task

# Organization Chart



# Gantt Chart

Sub-Task	Project Milestone Description	Project Duration:10/01/2010-09/30/2013												Planned Start Date:	Planned End Date:	Actual Start Date:	Actual End Date:	Comments
		Project Year 1				Project Year 2				Project Year 3								
		1	2	3	4	5	6	7	8	9	10	11	12					
1.1	Project management plan	✓												10/01/10	12/31/12	10/01/10		
1.2	Project management	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓			10/01/10	12/31/12	10/01/10	12/31/12	Submission of Q1 progress report
2.1	Chemical reaction between bis(carbonates) and electrophiles	✓	✓											10/01/10	03/31/11	10/01/10	03/31/11	
2.2	Molecular characterization of "intermediate" complex	✓	✓											10/01/10	03/31/11	10/01/10	03/31/11	
2.3	Reaction kinetic analysis of "intermediate" complex formation			✓	✓									04/01/11	09/30/11	04/01/11	09/30/11	
2.4	Electrochemistry of "intermediate" complex formation			✓	✓									04/01/11	09/30/11	04/01/11	09/30/11	
2.5	Chemical sequestration with various redox-active molecules			✓	✓									04/01/11	09/30/11	04/01/11	09/30/11	
2.6	Organocatalytic chemical sequestration of CO <sub>2</sub>					✓	✓	✓	✓					10/01/11	09/30/12	10/01/11	09/30/12	Investigation of organocatalyst (NBS system) for production of cyclic carbonate from cyclic oxide and CO <sub>2</sub>
2.7	Reaction kinetic analysis of organocatalytic route for CO <sub>2</sub> conversion					✓	✓	✓	✓					10/01/11	09/30/12	10/01/11	09/30/12	Reaction kinetic of organocatalytic process (NBS system) for cyclic carbonate production from cyclic oxide and CO <sub>2</sub>
2.8	Organocatalyst for continuous chemical sequestration of CO <sub>2</sub>					✓	✓	✓	✓					10/01/11	12/31/12	10/01/11	12/31/12	Investigation of organocatalyst (NBS system) for production of cyclic carbonate from cyclic oxide and CO <sub>2</sub> with continuous flow reactor
3.1	Chemical analysis of integrated chemical sequestration				✓	✓	✓	✓	✓					01/01/11	09/30/12	01/01/11	09/30/12	Investigation of "active" catalyst in organocatalytic process for cyclic carbonate production from cyclic oxide and CO <sub>2</sub>
3.2	Chemical sequestration prototype unit							✓	✓					04/01/12	09/30/12	04/01/12	09/30/12	Development of continuous flow reactor.
4.1	Life cycle environmental analysis	✓	✓	✓	✓	✓	✓	✓	✓					10/01/11	09/30/12	03/01/11	09/30/12	Completion of LCA analysis
4.2	Life cycle cost analysis							✓	✓					10/01/11	03/31/12	05/01/12	09/30/12	Completion of LCC analysis
5.1	Investigate the impact of quality of CO <sub>2</sub> gas stream on the chemical conversion process													10/01/12	09/30/13			
5.2	Investigate and identify the required down-stream processing to isolate products and the catalyst													10/01/12	09/30/13			
5.3	Evaluate the activity of recycled catalyst in flow micro-reactor													10/01/12	09/30/13			
6.1	Immobilize the active organocatalysts in the porous MOFs								✓	✓	✓			10/01/12	09/30/13	10/01/12		Synthesis of various MOFs
6.2	Evaluate the activity of chemical conversion using the heterogeneous organocatalytic system in the flow micro-reactor								✓	✓	✓			10/01/12	09/30/13	10/01/12		Modification of MOFs with phosphorous ligands
7.1	Evaluate the direct synthesis of cyclic carbonates from olefins in the flow microreactor								✓	✓	✓			10/01/12	09/30/13	10/01/12		Investigation of sequential process for cyclic carbonate from olefins and CO <sub>2</sub> with continuous flow reactor
7.2	Investigate the reaction kinetics and mechanisms for the direct synthesis of cyclic carbonate from olefins								✓	✓	✓			10/01/12	09/30/13	10/01/12		Reaction kinetic for cyclic carbonate production from olefins and CO <sub>2</sub>

# Bibliography

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## Publication:

Kozak, J. A.; Wu, J.; Su, X.; Simeon, F.; Hatton, T. A.; Jamison, T. F., 2013, Bromine-Catalyzed Conversion of CO<sub>2</sub> and Epoxides to Cyclic Carbonates under Continuous Flow Conditions, *submitted for publication*.

Wu, J.; Simeon, F.; Hatton, T. A.; Jamison, T. F., 2013, Mechanism-Guided Design of Flow System for Multicomponent Reactions: Conversion of CO<sub>2</sub> and Olefins to Cyclic Carbonates, *in preparation*.

## 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 CO<sub>2</sub> Capture and Utilization Routes, LCA XII, Tacoma, Washington.

Wu, J.; Simeon, F.; Hatton, T. A.; Jamison, T. F. 2013, Mechanism-Guided Design of Flow Systems for Multicomponent Reactions: Conversion of CO<sub>2</sub> and Olefins to Cyclic Carbonates, Gordon Conference: Heterocyclic Compounds, Newport, RI.

# Gantt Chart (continued)

Sub-Task	Project Milestone Description	Project Duration:10/01/2010-09/30/2011								Planned Start Date:	Planned End Date:	Actual Start Date:	Actual End Date:	Comments
		Project Year 1				Project Year 2								
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8					
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

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## Publication:

Kozak, J. A.; Wu, J.; Su, X.; Simeon, F.; Hatton, T. A.; Jamison, T. F., 2013, Bromine-Catalyzed Conversion of CO<sub>2</sub> and Epoxides to Cyclic Carbonates under Continuous Flow Conditions, *submitted for publication*.

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