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# Higher Value Product from Corn Ethanol



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**November 2013**

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**Funded in part by:**

Minnesota Corn Research & Promotion Council

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### Project Goals:

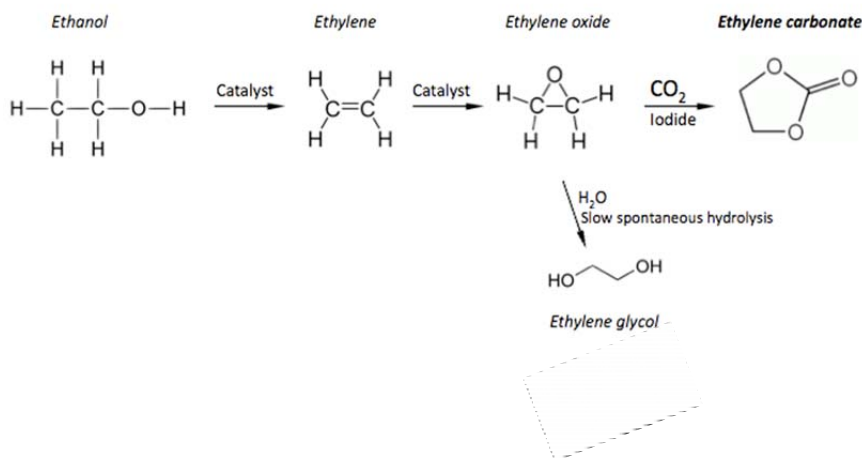
We investigated the chemical conversion of bioethanol to produce a more valuable commodity chemical, ethylene carbonate, and determine if this conversion is viable on an industrial scale. Ethylene carbonate is used as a solvent, as an electrolyte in advanced batteries, and the demand for this chemical has been increasing steadily over the last decade.

The process we studied is the conversion of ethanol through two increasingly valuable chemical intermediates, ethylene and ethylene oxide. Ethylene oxide is then reacted with carbon dioxide to produce ethylene carbonate and the carbon dioxide can be obtained from trapping that gas during the corn ethanol fermentation process. This chemical process, coupled with corn ethanol processes, is both economically and environmentally attractive. The final product incorporates one molecule of carbon dioxide for each molecule of bioethanol produced, so that all carbon atoms are retained and the process is completely carbon neutral. A key goal of the research was to demonstrate that ethylene carbonate can be efficiently and cleanly prepared from ethylene oxide.

### Experimental Tasks Accomplished:

*Clean and efficient synthesis of ethylene carbonate from ethylene oxide.*

Initial studies investigated a standard method for epoxide-carbon dioxide cyclization reactions using an iodide catalyst system.



While we found this reaction to proceed as shown at the top, the yields were never greater than 90% under any of the conditions tested, and there was a significant side reaction that led to the formation of ethylene glycol (bottom of figure), an undesired product.

We next investigated the potential to run the reaction enzymatically. While this reaction is not known in nature, we knew of enzymes that catalyze similar reactions that could potentially be co-opted to do this chemistry. In one example, we were aware of an iminase enzyme that runs the reaction backwards (1), and it would potentially run the reaction efficiently in the forward direction under high pressures and concentrations of the reactants. However, the lack of a known gene sequence for this enzyme precluded our producing the enzyme from a bacterial source such that it could be tested.

Halohydrin dehalogenase is an interesting enzyme that was considered for this application (2). The enzyme has a halide-binding pocket that accepts an array of linear or slightly bent anionic nucleophile (using epoxybutane as substrate in literature). It accepts bicarbonate and does an epoxide ring opening reaction, but the product does not cyclize and instead hydrolyzes to the diol. Cyanate attacks the epoxide ring with the nitrogen and then cyclizes to produce a compound much like ethylene carbonate except that it contains one nitrogen and one oxygen in the ring instead of two oxygen atoms, so this is not an acceptable reaction. In the end, we decided to not further pursue the enzyme approach but to develop more efficient chemical catalysts for driving the reaction of ethylene oxide with carbon dioxide.

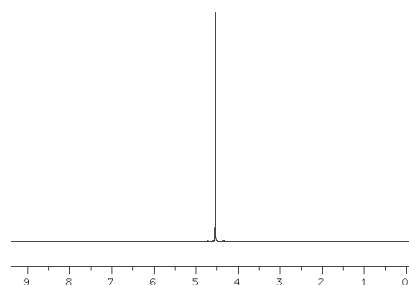
We subsequently studied the reaction of carbon dioxide with ethylene oxide in a neat ethylene carbonate solvent system in the presence of a second generation catalyst under a reasonably modest pressure of carbon dioxide. Note that a low-boiling co-solvent like methyl-*t*-butyl ether might be helpful in lowering the freezing point of the solvent. Using ethylene carbonate (EC) as the reaction solvent presents the experimental challenge of differentiating the product EC from a large excess of solvent EC. To do this, we designed a labeling experiment using 99% labeled  $^{13}\text{CO}_2$  as the reactant with unlabeled ethylene oxide in unlabeled (1.08% natural abundance at carbonyl carbon) EC as solvent in the presence of bis-tetrabutylammonium tetrachlorozincate, an inexpensive catalyst that is readily prepared.

The experiments were conducted as follows. To a heavy-walled-glass sealed tube of 7.5 mL capacity was added 2.49 g of ethylene carbonate (98% pure) and 35 mg of low melting solids of bis-tetrabutylammonium tetrachlorozincate. The contents were melted and stirred together. This tube was chilled ( $-78^\circ\text{C}$ ) and evacuated (30 mmHg) and then 25 mL ( $25^\circ\text{C}$ ) of ethylene oxide gas was condensed into this tube. Finally, this tube was frozen in liquid nitrogen and fully evacuated (0.1 mmHg) and 50 mL ( $25^\circ\text{C}$ ) of 99-atom %  $^{13}\text{CO}_2$  gas was condensed into the tube, which was then sealed by annealing the top of the glass vessel to make a gas tight system. Under cooling by dry ice, this tube was loaded into a 50 ml Parr reactor pressured to 200-250 psig with  $\text{CO}_2$  (Note: this  $\text{CO}_2$  did not enter into the reaction) and then heated to  $115\text{-}120^\circ\text{C}$ , holding for 1 hr before cooling ( $-78^\circ\text{C}$ ) and opening the sealed tube. The clear colorless melted contents of the reaction tube were charged 1:1 with  $\text{CDCl}_3$  into a 5 mm NMR tube for analysis by  $^{13}\text{C}$  and  $^1\text{H}$  NMR at 100 and 400 MHz, respectively. Integration of the signal for the carbonyl carbon (relative to unlabeled ethylene carbons for ethylene carbonate, which is expected to be accurate only to within +/- 5%), showed that the ratio of these integrals for the labeled versus unlabeled product increased by 5.86 fold, within experimental error of the 5.85 fold increase predicted for a 100% yield of 99% carbonyl-carbon-labeled EC from reaction of  $^{13}\text{CO}_2$  with the ethylene oxide.

### $^{13}\text{C}$ NMR of EC

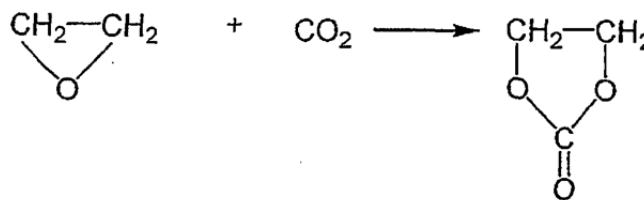


### $^1\text{H}$ NMR of EC



Analysis of the  $^1\text{H}$  NMR spectrum of this sample indicated that ethylene glycol was present at a level consistent with only about 2 % of the charged ethylene oxide having reacted with adventitious water present in the reaction mixture. Since as much as 2% of the charged ethylene carbonate (not anhydrous) could have been water, the low yield of glycol observed shows that selectively of the catalyst promoted the reaction of ethylene oxide with carbon dioxide rather than with water under these reaction conditions (<10 atm pressure of excess  $^{13}\text{C}\text{O}_2$ ). The yield of 2-( $^{13}\text{C}$ )-EC was > 95%.

*Desired reaction occurring in high yield*



### *Step from ethanol to ethylene*

An efficient process for ethanol dehydration to ethylene has been developed by our colleagues in the Department of Chemical Engineering and Materials Science at the University of Minnesota (3). In this process, ethanol dehydration was accomplished in a stratified reactor comprised of an upstream oxidation zone that contained platinum-coated  $\text{Al}_2\text{O}_3$  beads and a downstream dehydration zone consisting of zeolite films. Reaction efficiency was achieved by investigating a range of fuel:oxygen ratios and reactor configurations. The majority of the product was ethylene, where the ethanol carbon-carbon bonds stayed intact while the oxygen was removed. Over 90% yield of ethylene was achieved by using methane as a sacrificial fuel. A patent for this process has been filed.

### *Step from ethylene to ethylene oxide*

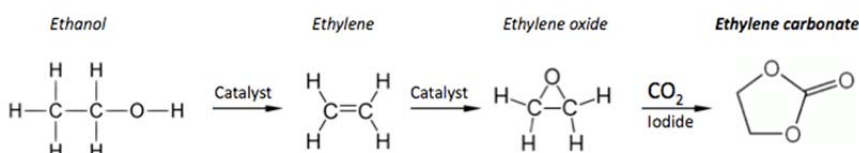
Currently, a number of processes are known to catalyze the conversion of ethylene to ethylene oxide. Some are commercial and others are in the public domain (4-7).

In the well-studied, direct oxidation process, ethylene and oxygen are mixed under pressure into a catalytic reactor. The catalyst is typically silver oxide supported on a porous carrier. The reaction, run at 200–300°C and 10–30 bar, is highly exothermic and the heat that is liberated can be used to generate steam for other operations in the plant. After a suitable reaction period, the gases from the reactor are typically cooled and passed through a scrubber where the ethylene oxide is absorbed as a dilute aqueous solution. This process of reactor gas stream clean up includes the removal of the CO<sub>2</sub> using physical sorbents. The resulting high purity CO<sub>2</sub> stream is typically vented.

### **Overall prospects:**

The conversion of ethanol to ethylene and ethylene oxide are industrial processes and there is new technology that can enhance the usefulness and implementation of these reactions. There is also local expertise at the University of Minnesota regarding these chemical transformations as practiced on industrial scale (3).

The conversion of ethanol to ethylene or ethylene oxide provides only modest value enhancement and thus little, if any, corn-based ethanol is fed into this chemical pipeline. Moreover, since ethylene oxide is fairly toxic to humans, it requires special conditions to store and transport. In light of these points, the current research was designed to explore methods for converting ethylene oxide, produced from corn ethanol, immediately to ethylene carbonate, using carbon dioxide derived from the process for fermenting corn sugar into ethanol. The critical step for this overall process was the chemical conversion of ethylene oxide to ethylene carbonate and that became the major focus of the research project.



A major problem that had to be solved was that ethylene glycol could arise from an alternative pathway, oxirane ring opening from water. Any significant production of ethylene glycol would then require extensive purification of the final product that would add great expense to the process. The research conducted demonstrated a solution to this problem.

### **Summary Conclusion:**

In conclusion, the research project showed the feasibility of converting ethylene oxide to ethylene carbonate, cleanly and in high yield. The conditions are not extreme and thus the reaction could be carried out on industrial scale and not use expensive equipment. The major issues relevant to corn ethanol are the reactions converting ethanol to ethylene and ethylene oxide. These are carried out by several companies and the patent landscape is large and complex. It is unclear if the best chemical conversion methods are currently patent protected or whether they are open to competition. Additionally, it needs to be determined how the reactions can best be linked in a single industrial

process. The intermediates between ethanol and ethylene carbonate, ethylene and ethylene oxide are both gases and so would need to be handled with the appropriate equipment. Thus, further studies are needed into process engineering to determine the efficiency and cost-effectiveness of an overall process.

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