Ozonolysis Reactions in Dense Phase CO_2

Andrew M. Danby*, Bala Subramaniam and Daryle H. Busch
Center for Environmentally Beneficial Catalysis (CEBC), University of Kansas, Lawrence, Kansas 66047 USA
* amdanby@ku.edu

Introduction

Due to its high oxidation potential (E^0 = 2.075V in acid, 1.246V in base), ozone has been investigated as a powerful oxidant [1]. Since it ultimately decomposes to form O_2 it can be considered a green oxidant. While waste water treatment utilizes ozone as an oxidant, where its indiscriminate nature as an oxidant is beneficial, ozonolysis in process chemistry using conventional solvents has yet to realize its full potential. Reasons for this include; (i) low solubility at the low temperatures necessitated by ozone's reactivity and destruction at higher temperatures, and (ii) reactivity of ozone with many organic solvents. This work demonstrates a novel approach to overcoming these problems by utilising dense phase carbon dioxide as a solvent for ozonolysis reactions. We exploit the compressiblity of O_3 (T_c = -12.1 °C; P_c = 54.9 atm) at moderate temperatures to significantly enhance its solubility in liquid CO_2. Given that liquid CO_2 is in an inert solvent, selective ozonolysis of substrates may be achieved without the ozone loss that occurs with most conventional solvents. For substrates that are insoluble in liquid CO_2 we have utilized ultrasonic mixing to overcome interphase mass transfer limitations.

Materials and Methods

Ozonolysis studies were performed by batch in a CEBC designed, 15 mL titanium reactor fitted with an ultrasonic horn (Sonics and Materials, Inc.) [Figure 1]. Substrates were obtained commercially and ozone was generated from oxygen using a Praxair-Trailgaz Unizone™ Lo corona discharge ozone generator. Products were analyzed by GC, GC/MS or HPLC.

Results and Discussion

In liquid CO_2 we have observed that ozone demonstrates an interesting solubility behavior with pressure changes. As pressure is isothermally increased through the critical pressure of ozone (54.9 atm), the solubility of ozone in liquid carbon dioxide increases dramatically [Figure 2]. Hence, it is highly compressible at near critical pressure, resulting in enhanced dissolution into the CO_2 phase. The ozone concentrations in the liquid CO_2 phase may be adjusted over approximately one order of magnitude with relatively small changes in pressure [2]. Utilising this pressure tunability of the system, we have investigated the ozonolysis of a variety of olefin substrates. *cis* and *trans*-Stilbene are substrates that are soluble in liquid CO_2 and underwent facile ozonolysis, with 85% and 95% conversions, respectively, to form predominantly benzaldehyde and benzoic acid. For substrates that are insoluble in liquid CO_2, a high pressure titanium reaction cell equipped with an ultrasonic horn (see picture in Figure 1) was used to form emulsions of the substrate in liquid CO_2 in order to enhance the interfacial mass transfer area. For the ozonolysis of methyl oleate, mechanical mixing alone gave conversions of *ca*. 24%. However, performing ozonolysis after using powered ultrasound to form emulsions of methyl oleate in dense phase CO_2, conversions of 100% were obtained. Product distributions were determined for a variety of conditions and several catalysts were used to direct the reactions towards higher yields of desirable products. With tunability, improved safety, low toxicity and more facile product separation, the use of CO_2 as a medium for ozonolysis allows the full potential of ozone as a green oxidant in the arena of sustainable chemistry to be realized.

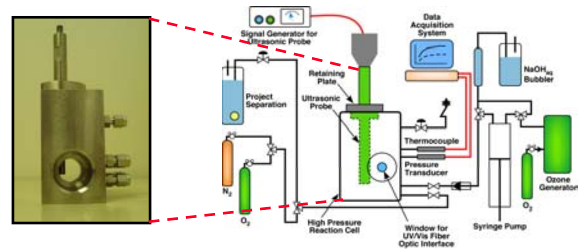
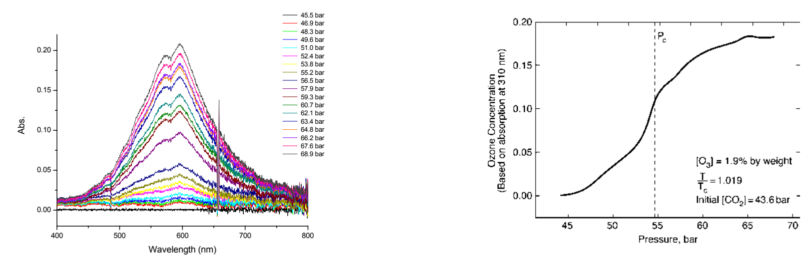


Figure 1. Experimental apparatus for performing ozonolysis in high pressure CO_2 with ultrasonic mixing.



(a) (b)

Figure 2. Ozone solubility in liquid CO_2 as a function of pressure under isothermal conditions; (a) UV-Vis Spectra showing the increase of O_3 peak with pressure-tuning;
(b) Pressure tunability of O_3 solubility in liquid CO_2, increasing exponentially in the vicinity of the critical point.

Significance

Ozone is an attractive, green oxidant. By using (a) liquid CO_2 as an inert solvent medium, (b) pressure-tuned enhanced solubility of O_3 in the liquid phase, and (c) ultrasonic mixing and appropriate catalysts, we demonstrate for the first time that the ozonolysis of many organic substrates, including those of relevance in biomass processing, may be performed at high reaction rates and selectivity.

References

1. Oyama, S. T., *Catalysis Reviews - Science and Engineering* 42, 279 (2000)
2. Danby, A.M., Subramaniam, B., Busch, D.H., Binder, T.P., *Provisional Patent Application, Docket No. 16994.3* Filed November 5th, 2007.