The Rate of Reaction of the Ozonation of Prozac

Max Edelstein, max@familyedelstein.com
Professor Daniel McCurry
Grover Cleveland High School, Class of 2021
USC Viterbi Department of Environmental Engineering, SHINE 2019

USC Viterbi School of Engineering

SHINE Summer High School Intensive in Next-Generation Engineering

Introduction

The increased scarcity of freshwater resources has required scientists to study the implications of wastewater reuse. In order for wastewater to become potable, it must go through additional levels of treatment to purge the effluent of contaminants such as pharmaceuticals. Two of these processes that can disinfect treated wastewater are ozonation and chlorination, in which the respective molecules are passed through influent water and bound to pharmaceuticals, rendering them harmless. However when these two processes are done in series, the ozone and chlorine bond to contaminants, creating toxic byproducts that are unsafe for human consumption. An example of this process is the chemical formation pathway of the toxic byproduct chloropicrin from prozac, a common antidepressant, in which prozac is ozonated to form nitromethane before nitromethane is chlorinated to form chloropicrin. In order to better understand the formation of chloropicrin, this project focuses on the rate of reaction at which prozac ozonates to form nitromethane. Ozone is both a disinfectant and oxidant are well used in potable reuse processes. By quenching the reaction of ozone with prozac at different intervals and measuring the amount of prozac and nitromethane, it is possible to determine the rate constant at which the nitromethane is created. By understanding how quickly prozac reacts with ozone to form nitromethane, scientists can determine the reaction mechanism that results in the creation of nitromethane from prozac.

Methods

Nitromethane was measured via gas chromatography/triple quadrupole mass spectrometry (GC/MS) (Agilent 7890B/7010, Santa Clara, CA). 5 mL aqueous samples in 20 mL headspace vials with 2-3 gram of sodium sulfate were introduced with a static headspace sampler (Agilent 7697A). Samples were first equilibrated with moderate shaking for 20 minutes at 85 ºC, then pressured with helium into a 1 mL headspace sample loop and injected onto a DB-1701 column (60 m ´ 0.25 mm ´ 0.25 µm) at 150 ºC. The inlet was operated in split mode with a split ratio of 10:1 at 120 °C. Helium was used as the carrier gas with a constant flow of 1.2 mL/min. The GC oven temperature was held at 40 ºC for 1 min and then increased to 150 ºC at a rate of 10 ºC/min and finally raised to 250 ºC at a rate of 100 ºC/min with a holding time of 1 min. The mass spectrometry interface temperature was set at 250 ºC. Ions were generated with an Agilent high efficiency electron ionization (EI) source. The EI source was kept at 230 ºC and both quadrupoles at 150 ºC. Mass spectra of nitromethane is acquired in multiple reaction mode with m/z transitions of 61 to 46 with the collision energies at 5 eV.

Prozac was measured on an Agilent 6560 ion mobility quadrupole time-of-flight mass spectrometer. Separation was achieved on an Agilent 1290 HPLC with Eclipse Plus C18 column (1.8µm, 2.1 mm ´ 50 mm). The mobile phase was 55% formic acid (1 mL/L) and 45% methanol. The QTOF was operated in positive ion scan mode (m/z 100 – 1700)

Results

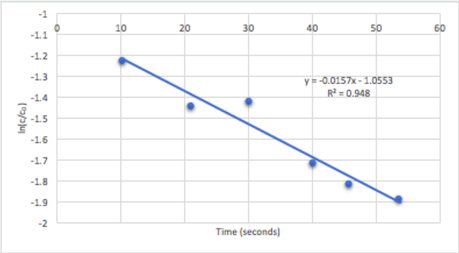


Figure 1: Pseudo-first order rate constant expression

$K_{obs} = 0.0157\ (s^{-1})$

$t_{1/2} = \ln 2/K_{obs} = 44.15\ (s)$

$o_3 = 0.84215\ (mM)$

$\alpha = Ka/([H^+]+Ka) = 1.38038 \times 10^{-8}$

$K_{app} = K_{obs}/([o_3]\alpha) = 1.35 \times 10^{9}\ (s^{-1}M^{-1})$

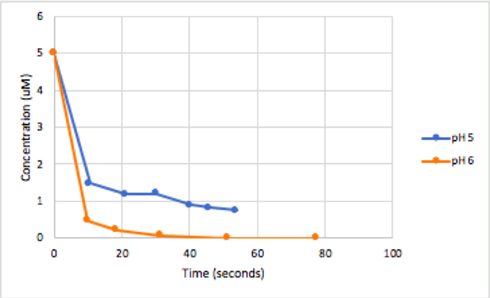


Figure 2: Displays how lower pH slows the reaction
Original concentration is 5 uM of prozac

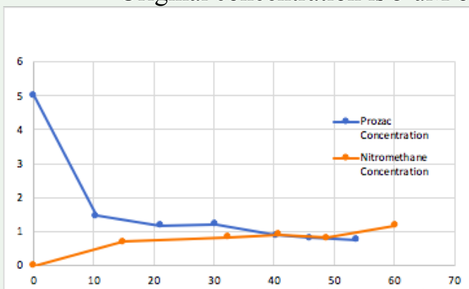
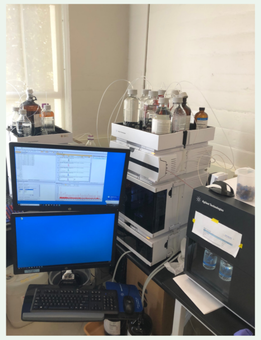


Figure 3: Prozac Concentration and Nitromethane Concentration as a function of time. The mass balance between prozac and nitromethane doesn't close due to possible side product formation.

Skills Acquired

-Dilution Equations
-Stoichiometry
-Titration
-Buffers
-Standard Curves
-Use of analytical instruments such as LCMS, GCMS, and UV-Spectrometer
-Lab Skills
-Microsoft Excel



Discussion

This experiment determined that at pH7, the standard pH at which ozonation occurs, prozac is ozonated very quickly, making the process an effective way to remove prozac. The GCMS proved that nitromethane is the disinfection-byproduct created from the ozonation of prozac. This experiment also concluded that lower pHs will slow down the reaction of prozac into nitromethane. This is because the part of prozac that interacts with ozone, the second amine group, can only be ozonated in its neutral form and not in its protonated form, which is found in higher concentrations at lower pH levels. The lower the pH, the higher the concentration of the nonreactive prozac, and therefore the slower the reaction.

Acknowledgement

A special thanks to Professor McCurry, as well as PHD students Lily Shi and Zakiyyah Brown. Thank you to Graduate student Grace Yao. Thank you to Dr. Katie Mills, Dr. Megan Herrold, and the rest of the SHINE team. Thank you to my fellow SHINE students Andrew Sung, Pearson Mewbourne, and Sarah Burke.