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Determination of the Rate Constant for Reaction of Ozone with 1-Hexene in Water

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Determination of the Rate Constant for Reaction of Ozone with 1-Hexene in Water

A Master's Project Presented by
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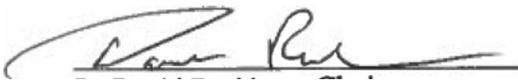
DETERMINATION OF THE RATE CONSTANT FOR REACTION OF OZONE WITH I-HEXENE IN WATER

A Masters Project Presented
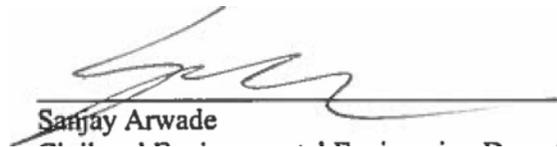
by

PRANAV ANANT MASHANKAR

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Dr David Reckhow, Chairperson

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ABSTRACT

Low molecular weight aldehydes such as formaldehyde may be formed as disinfection byproducts (DBPs) of ozonation when low molecular weight, aliphatic, alpha olefins are present as contaminants in water. Such alkenes form a small but significant part of crude oil, and would therefore be present in water contaminated with an oil spill. This project studied the kinetics of the reaction between ozone and 1-hexene in water as part of a study to predict the effects of an oil spill on the water quality in the Wachusett reservoir in Massachusetts. The data for the reaction rate constant for the aqueous ozonolysis of low molecular linear alpha olefins that are liquid under ambient conditions (such as 1-hexene) is sparse in existing literature, and such data would be essential to any attempt to model the formation of DBPs due to ozonation of water contaminated with crude oil. Two methods were used to measure the rate constant for the reaction between ozone and 1-hexene in water. The first method used direct spectrophotometry, and measured the concentration of ozone over time as it was reacted with an excess of 1-hexene. The data was then fit to a pseudo first order kinetic model and the reaction rate constant was calculated. The rate constant calculated using the above method was found to be many orders of magnitude smaller than those for ethene and propene calculated previously, and it was theorized that the decay of ozone here was limited by the rate of dissolution of 1-hexene in water instead of the reaction itself. Therefore, a second method, involving competition kinetics was employed where 1-hexene was made to react with ozone in competition with styrene (whose rate constant for aqueous ozonolysis has been calculated previously), and the yields of the products of each olefin were quantified using gas chromatography. These yields were then used to calculate the rate constant for the reaction between 1-hexene and ozone using equations derived through the course of this project. The rate

constant for 1-hexene calculated using this method was found to be of a similar order of magnitude to those for ethene and propene. Since the electron density around the double bond does not change significantly with small changes in alkene chain length, it was theorized that the rate constant of the reaction between ozone and other linear alpha olefins such as 1-pentene and 1-heptene would be very similar to that of 1-hexene. Finally, the formation of aldehydes due to ozonation of a 1 mg/L DOC aqueous solution of West Texas Intermediate crude oil was modeled.

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1. INTRODUCTION

1.1 Disinfection

The deactivation, removal, or killing of pathogens in water to avoid their potential infectivity is known as water disinfection. It is essential in order to prevent the spread of diseases like cholera, diarrhea, hepatitis and typhoid among others. Historically, disinfection was first used in the 1880s and 1890s, and was primarily accomplished using chlorine and ozone, while Jersey City Water Works in New Jersey was the first utility in the United States to use sodium hypochlorite as a primary disinfectant (Buchanan, 2011). Today, disinfection is achieved through use of several disinfectants such as chlorine, chloramines, ozone, etc.

Ozone as an oxidant in the treatment of drinking water and wastewater has been used since the 19th century. This chemical water treatment technique is based on the dissolution of gaseous ozone in water, and is used for disinfection, color removal, and oxidative decomposition of trace organic compounds and natural organic matter (NOM) (Gardoni, Vailati, & Canziani, 2012). The dissolved ozone is inherently unstable, with a half-life of just a few minutes (Staehelin & Hoigne, 1982), and it decomposes to form extremely reactive oxygen species that readily react with a variety of organic compounds and microorganisms. One of the other main uses of ozone, besides oxidative decomposition of NOM, is the decomposition of precursor compounds that ultimately form disinfection byproducts (DBPs) during final chlorination or chloramination. Such DBPs include classes of compounds like trihalomethanes (THMs) and haloacetic acids (HAAs).

Although ozone has been used to decrease the concentration of DBPs formed due to chlorination, ozone itself has been known to form DBPs such as aldehydes, ketones, mixed aldo and keto acids, and carboxylic acids among others.

1.2 Aldehydes as DBPs

Aldehydes may be formed as DBPs of ozonation if alkenes are present in the water as contaminants. These alkenes undergo oxidative cleavage by ozone to produce aldehydes or ketones. Though alkenes are not typically found in drinking water sources, they may be introduced into the water in the event of an oil spill, since crude oil typically contains low molecular weight straight chain alkenes that are liquid at ambient temperature. Despite the extensive use of ozone in water treatment, relatively little kinetic data exists for the reaction of ozone with alkenes in fresh water.

1.3 Research Objectives

The Wachusett Reservoir is a large (7 mi^2, 59.7 billion gallon) drinking water supply reservoir located in Central Massachusetts, and is currently used to provide drinking water to the Boston metropolitan area. Treatment processes for water from the Wachusett Reservoir include ozonation, ultraviolet (UV) disinfection, and chlorination and corrosion control. Petroleum products such as crude oil are prominent among the materials transported along the railroad adjacent to the Thomas basin and by vehicles across the Route 140 and Route 12 bridges. For the past few years, the Environmental and Water Resources Engineering (EWRE) Program at University of Massachusetts Amherst (UMass) has been studying the potential impacts of an oil spill at the Route 140 Bridge and other Thomas Basin locations on water quality in Wachusett Reservoir. The following study was conducted as part of this project.

Crude oil contains organic compounds not normally present in water, therefore disinfection of water results in formation of non-typical DBPs. Any strategy to mitigate the effects

of such an oil spill could be informed by modeling the processes of formation of DBPs in the reservoir. For example, simple alkenes are known constituents of crude oil. Most oxidants are known to react with simple alkenes forming products that are similarly known. In the case of ozonation, the byproducts are simple aldehydes and organic acids. However, the lack of kinetic data on these reactions renders the extent of reaction and DBP formation uncertain. The only kinetic ozone data for reaction with low molecular weight alkenes is for ethene and propene, both of which are gases at normal temperatures and pressures. This study focuses on developing rate expressions for ozonolysis of lower molecular weight straight chain alkenes that are liquid at ambient temperature- such alkenes would typically account for a small, but significant fraction of the components of an oil spill.

2. BACKGROUND

2.1 Mechanism of Ozonolysis:

Ozonolysis of olefins takes place via the Criegee mechanism, as demonstrated in figure 1:
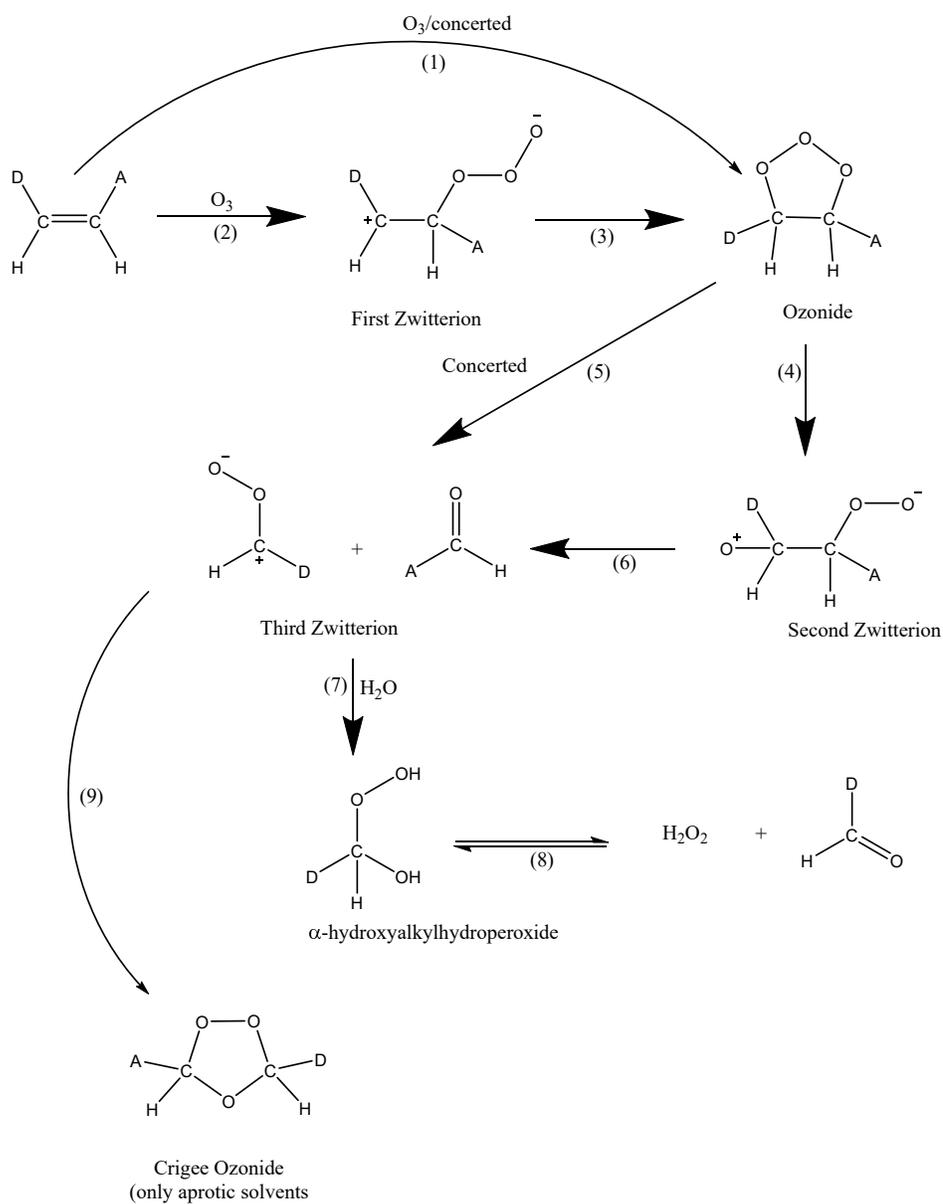
Figure 1: Ozonolysis via Criegee Mechanism (Sonntag & Gunten, 2012)

In an aqueous medium, the formation of an α-hydroxyalkylhydroperoxide [reaction (7)] is favored over the formation of a Criegee ozonide, which is only formed in aprotic solvents (Dowideit & Sonntag, 1998). Thus, ozonolysis of alkenes in an aqueous medium yields two molecules of aldehyde per molecule of alkene.

2.2 Kinetic Model:

The reaction of ozone with a solute M may be represented as:

$$M + \eta O_3 \xrightarrow{k_{O_3}} M_{oxid}$$
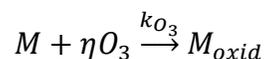
In case of straight-chain α-olefins, the stoichiometric coefficient, η, is unity. Thus, the reaction becomes

$$M + O_3 \xrightarrow{k_{O_3}} M_{oxid}$$
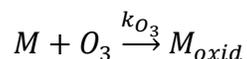
And the reaction is of 1st order with respect to each of the reactants, and of 2nd order overall. The rate law is expressed as follows.

$$\frac{d[O_3]}{dt} = k_{O_3}[O_3][M] \tag{1}$$

3. METHODS AND MATERIALS

3.1 Overview of experiments

One can observe from equation (1) that, should $[M]$ be far greater than the dissolved ozone concentration, it could be approximated to remain constant through the course of the reaction. This would make the reaction one of pseudo-first order in $[O_3]$. The rate expression will then reduce to

$$\frac{d[O_3]}{dt} = K_1[O_3] \tag{2}$$

where

$$K_1 = k_{O_3}[M] \tag{3}$$

The method of studying the ozonolysis reaction under pseudo-first order conditions has been favored in the past (Hoigne & Bader, 1981; Hoigne & Bader, 1981), since it is much easier to study and quantify a single component reaction.

Two methods were used in this study to determine k_{O_3}. The first method employed direct spectrophotometry to track the progress of the ozonolysis reaction over time, and the value of k_{O_3} was then calculated graphically. The second method employed the use of competitive kinetics, where the target alkene was made to react with ozone in competition with another olefin that has a known rate constant, and the yields of the product aldehydes of each olefin were quantified using gas chromatography. These yields were then used to calculate k_{O_3} for the target alkene using equations derived later in this report.

3.1.1 Determination of k_{O_3} from $[O_3]$ vs t curve using UV-vis spectrophotometry

When ozone reacts with an excess of alkene in an aqueous medium, the ozone concentration varies with time according to the expression

$$[O_3] = [O_3]_0 e^{-K_1 t} \tag{4}$$

Graphically, this may be expressed as a straight line on a $\ln([O_3])$ vs t plot.
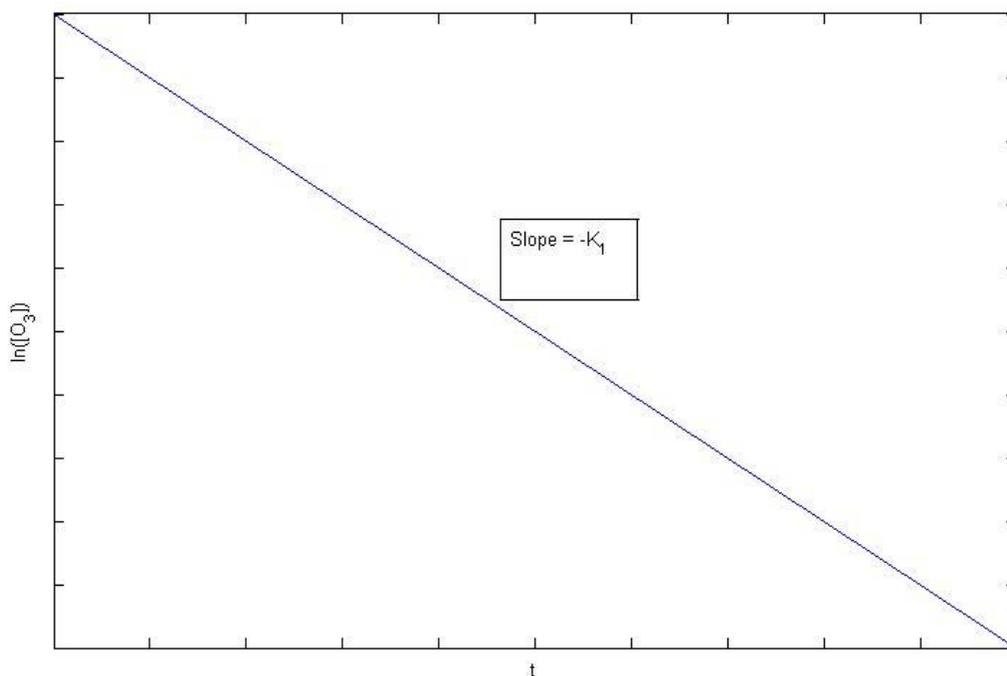
Figure 2: $\ln([O_3])$ vs t plot

The negative of the slope of the straight line is the pseudo-first order rate constant, K_1. In this study, the ozonolysis of a target alkene was performed under a known excess concentration of the said alkene, and the concentration of ozone was measured spectrophotometrically over time. K_1 for the reaction was then calculated, from which the second order rate constant of ozonolysis was calculated.

This technique was used in the past to calculate the reaction rate constants of ozonolysis of certain olefins (Hoigne & Bader, 1981). One major drawback of this method is that in case of extremely fast reactions, measurement of ozone concentration over time becomes extremely challenging.

3.1.2 Determination of k_{O_3} through competition kinetics

This method of calculating k_{O_3} is useful for olefins whose rate constant of ozonolysis is potentially very large. Consider two olefins with terminal double bonds, A_1 and A_2, where the second order ozonolysis rate constant of A_1 is to be determined, and A_2 has a known second order ozonolysis rate constant. A_1 reacts with ozone to give two product aldehydes, P_1 and P_2, and A_2 reacts with ozone to give two product aldehydes, P_1 and P_3; A_1 and A_2 share a common ozonolysis product, P_1.

$$A_1 + O_3 \xrightarrow{k_1} P_1 + P_2$$

$$A_2 + O_3 \xrightarrow{k_2} P_1 + P_3$$
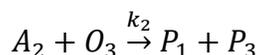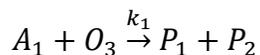
According to the rate law,

$$\frac{d[O_3]}{dt} = -[O_3](k_1[A_1] + k_2[A_2]) \tag{5}$$

Or

$$\frac{d[O_3]}{dt} = -[O_3](K_1 + K_2) \tag{6}$$

Where

$$K_1 = k_1[A_1] \text{ and } K_2 = k_2[A_2]$$

Similarly,

$$\frac{d[P_1]}{dt} = [O_3](K_1 + K_2) = -\frac{d[O_3]}{dt} \tag{7}$$

$$\therefore [P_1]_f = [O_3]_0 \tag{8}$$

Where $[P_1]_f$ is the final P_1 concentration and $[O_3]_0$ is the intial ozone concentration.

Finally,

$$\frac{d[P_2]}{dt} = K_1[O_3] = -\frac{K_1}{(K_1 + K_2)}\frac{d[O_3]}{dt} \tag{9}$$

$$\therefore [P_2]_f = \frac{K_1}{(K_1 + K_2)}[O_3]_0 \tag{10}$$

Dividing (8) by (10),

$$\frac{[P_1]_f}{[P_2]_f} = \frac{k_1[A_1] + k_2[A_2]}{k_1[A_1]} \tag{11}$$

Solving for k_1 gives us

$$k_1 = \frac{k_2[A_2]}{[A_1](\frac{[P_1]_f}{[P_2]_f} - 1)} \tag{12}$$

Equation (12) gives us k_{O_3} for the target olefin if the initial concentrations of both olefins

(A_1 and A_2) and the final concentrations of P_1 and P_2 are known. As mentioned before, this method

is suitable for calculating the ozonolysis rate constant of olefins that react very rapidly with ozone

because here only initial and final concentrations of reactants and products are required.

In this study, $[A_1]$ and $[A_2]$ were calculated by reacting aqueous solutions of A_1 and A_2

with a moderate molar excess of ozone in water and measuring the decrease in ozone concentration

spectrophotometrically. Measurement of $[P_1]_f$ and $[P_2]_f$ was a more elaborate process that employed gas chromatography.

3.2 Experimental Procedure

3.2.1 Determination of k_{O_3} using direct spectrophotometry

Calculation of k_{O_3} using direct spectrophotometry was carried out for 1-hexene. The ozonolysis reaction was carried out at different concentrations of 1-hexene.

Stock solutions of 1-hexene were prepared in methanol, and they were usually stored in the refrigerator for up to a week. Ozone generated in a Welsbach Ozonator (Type T-408, Welshbach Ozonator Systems Corp., Philadelphia, PA, USA) was bubbled into a borosilicate glass vessel containing acidified Milli-Q water of pH 3 (acidified using HCl) for the preparation of the initial ozone stock solution. The exact concentration of ozone in this stock was determined using an Agilent 8453 UV-visible diodearray spectrophotometer and published values for ozone molar absorptivity.

The concentration of the initial ozone stock solution varied between 10 mg/L and 20 mg/L. The solution was acidified to improve the stability of the aqueous ozone concentration, as has been noted in the past (Hoigne & Bader, The role of hydroxyl radical reactions in ozonation processes in aqueous solutions, 1976; Sotelo, Beltran, Benitez, & Beltran-Heredia, 1987).

Three mL of an HCl solution (pH 3) was added to a cuvette of path length 1cm. Concentrated ozone stock solution was then pipetted into the cuvette such that the ozone concentration in it was 1 mg/L. Following this, a measured volume of 1-hexene stock solution in methanol was added to the cuvette using a syringe, such that the molar concentration of 1-hexene was at least ten times that of the ozone, and spectrophotometric measurement of ozone

concentration vs time was immediately started. The first 5 seconds of data was ignored to allow for effects due to mixing of 1-hexene, and ozone concentration was recorded for up to 3 minutes. The data were then fitted to a first order decay model, and the pseudo-first order decay rate constant was calculated.

3.2.2 Determination of k_{O_3} through competition kinetics

Calculation of k_{O_3} using competition kinetics was carried out for 1-hexene. Here, an aqueous mixture of 1-hexene and styrene (an olefin with a known rate constant) was reacted with ozone, and the products were quantified using gas chromatography to calculate the ozonolysis rate constant for 1-hexene.

The initial stock solutions of 1-hexene and styrene were prepared in water. For this, 5 to 10 mL of each compound was added to separate amber jars containing 250 mL of Milli-Q water. The jars were sealed, placed on a stir plate, and stirred using magnetic stir-bars for a day. After this, the contents of each jar were transferred to individual sealed conical separatory funnels and allowed to stand for another day. Finally, the aqueous phase in each funnel was decanted into a separate amber bottle. Additionally, an equal volume of each olefin solution was drawn into a third amber bottle to create a 1:1 (vol/vol) aqueous mixture. The shelf life of these olefin solutions was found to be about 2 days, after which a significant decrease in aqueous olefin concentration was observed, possibly due to degradation.

Acidified ozone stock solution was prepared as described previously. The concentration of this stock solution was measured by direct UV absorbance. Each of the olefin solutions was then reacted individually with an excess of ozone, and the amount of ozone consumed was measured. The value of the excess ozone concentration required was estimated after looking at the maximum

aqueous solubilities of 1-hexene (Leinonen & Mackay, 1973; McAulife, 1966) and styrene (Yalkowsky, Ye, & Jain, 2010) listed in literature. It must be noted that while for 1-hexene the decrease in ozone concentration was measured using direct UV absorbance, in case of styrene a different method was required. This is because the absorbance spectrum for styrene substantially overlaps with the absorbance spectrum for ozone, and the characteristic peak of styrene tends to obscure that of ozone. Therefore, the final ozone concentration in case of styrene was measured using the indigo method, which is a widely used method of measuring ozone concentration in water when UV absorbing compounds are present in the medium. Since both 1-hexene and styrene react with ozone in equimolar amounts, the moles of ozone consumed correspond to the moles of olefin in aqueous solution for each of the two compounds. Thus, the concentrations of 1-hexene and styrene in their respective aqueous solutions was calculated.

Two mL of acidified Milli-Q water (pH 3) was added to a cuvette of path length 1 cm. Concentrated ozone stock solution was then pipetted into the cuvette such that the ozone concentration in it was 1 mg/l. Next, a reading of the ozone concentration in the cuvette was taken, following which 1 mL of the aqueous mixture of the two olefins was added to the cuvette. After a period of about a minute, the contents of the cuvette were transferred to a vial to be analyzed using gas chromatography (GC-ECD).

Let us revisit the following equations first described in the previous section.

$$A_1 + O_3 \xrightarrow{k_1} P_1 + P_2$$

$$A_2 + O_3 \xrightarrow{k_2} P_1 + P_3$$
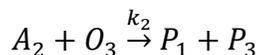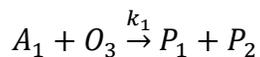
It is clear that A_1 and A_2 here are 1-hexene and styrene respectively. In order to calculate the second order rate constant of ozonolysis of 1-hexene, the concentrations of P_1 and P_2 are required as per equation (12), with the common product, P_1, being formaldehyde, and P_2 being

valeraldehyde. Therefore, formaldehyde and valeraldehyde concentrations in the sample were measured through GC-ECD using normalized concentration curves as described in the following section. Finally, the measured concentrations of formaldehyde and valeraldehyde, along with the ozonolysis rate constant of styrene (Hoigne & Bader, 1981) were used to calculate the second order rate constant for the ozonolysis of 1-hexene.

3.3 Methods

3.3.1 Direct UV-Vis Spectrophotometry

Aqueous ozone concentrations in pure water can be determined by direct spectrophotometric measurement at 260 nm.

$$C_{O_3}\left(\frac{mg}{L}\,as\,O_3\right) = 14.59 * (Abs@260nm) \tag{13}$$

The above equation is based on a molar absorptivity of 3290 $M^{-1}cm^{-1}$ (Hart, Sehested, & Holeman, 1983). This method works well when working with aliphatic olefins, as they do not absorb light at at 260 nm.

3.3.2 Indigo Method

The indigo method is a colorimetric procedure that employs the use of indigo trisulfonate solution (Bader & Hoigne, 1981). Ozone reacts with indigo trisulfonate with 1:1 stoichiometry, and in the process, bleaches this intense blue dye. Therefore, a loss in absorbance at 600 nm is directly related to a decrease in ozone concentration in aqueous solution. The reaction product is relatively unreactive to further ozonation. The reaction is best carried out at low pH to minimize ozone decomposition, and preserve the 1:1 stoichiometry. A sensitivity factor or apparent absorptivity for indigo trisulfonate of 20,000 $M^{-1}cm^{-1}$ based on previous literature (Bader &

Hoigne, 1981) was used here. This is based on an aqueous ozone molar absorptivity of 2900 M^{-1}cm^{-1}.

Though this method is fairly selective, it is still susceptible to interferences from certain species, namely chlorine and oxidized manganese species. However, this was not a problem in the present study.

Reagents: Two reagents were used in this method. The first, a standard indigo stock solution, was prepared by diluting 1.36 mL of concentrated phosphoric acid to 1 liter using Milli-Q water and adding 0.6 g of indigo trisulfonate to it. This solution was stored in a brown glass bottle. The second reagent used was a phosphate buffer prepared by dissolving 28 g NaH$_2$PO$_4$.H$_2$O and 20.6 mL concentrated sulfuric acid in 1 liter of Milli-Q water.

Procedure: An indigo blank was prepared by adding 1 mL of standard indigo stock solution to a 25 mL volumetric flask and filling up to the mark with phosphate buffer. Absorbance was measured at 600 nm. When the standard indigo stock is new the absorbance is expected to be about 0.650, and once it has dipped to 80% of this value, new indigo stock must be prepared. A series of 25 mL volumetric flasks were assembled and filled with 1mL standard indigo stock, followed by about 10 mL phosphate buffer. After this, the samples were transferred to their designated volumetric flasks, and finally the flasks were filled up to the mark with phosphate buffer.

Absorbance at 600 nm was measured for each sample using a 1cm cuvette. The ozone concentration was calculated as follows.

$$Ozone\ concentration \left(\frac{mg}{L} as\ O_3\right) = \frac{V_t(Abs_i - Abs_f)}{fV_sL} \tag{14}$$

Abs_i: Absorbance of indigo blank solution

Abs_f: Absorbance of sample

V_t: Volume of sample in flask

V_t: Total volume in flask (25 mL)

L: Path length of cuvette (1 cm)

f: Calibration factor determined by calibration against direct UV method.

The calibration factor was calculated as follows. Acidified ozone stock was prepared as described earlier and diluted into standards of different concentrations. Absorbance for each of these standards was first measured by the direct UV method, then by the indigo method. The sample volume for each of the standards was kept constant for the indigo method. Finally, absorbance by indigo method vs ozone concentration by direct UV method was plotted as a straight line, and the slope of this line multiplied by V_t/V_s gave us f. This calibration factor is usually found to be about 0.42 when the standard indigo stock is fresh, and progressively decreases as the stock gets older.

3.3.3 Determination of aldehyde concentration using gas chromatography

This study used O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) as a derivatizing agent in the extraction and measurement of aldehydes in samples using the procedure described in Standard Methods 6252. Disinfection By-Products: Aldehydes (Proposed) (American Public Health Association; American Water Works Association; Water Environmnent Federation, 2005). PFBHA reacts with low molecular weight carbonyl compounds, such as aldehydes, to produce

oximes. These oximes, which can be easily extracted using organic solvents, are highly sensitive to analysis by gas chromatography with electron capture detection.

Initial stock standards for the target aldehydes (formaldehyde and valeraldehyde) were prepared using methanol. An internal standard stock solution was prepared by mixing 1,2-dibromopropane in hexane. According to Standard Methods 6252, these stock aldehyde standards could be stored in the fridge for 1-3 months, while the internal standard solution could be stored for up to 6 months. However, when analyzing 1-hexene samples that had been ozonated, it was found that the two products of ozonolysis, formaldehyde and valeraldehyde, were detected in molar ratios of 1:10 or more, instead of the expected 1:1. Upon investigating it was theorized that the concentration of the valeraldehyde standard used was far less than what it was supposed to be (possibly due to decomposition of the valeraldehyde in the standard), thus skewing the calibration curve. Therefore, it was decided that the initial stock solution for valeraldehyde be prepared freshly for each experiment. From these initial stock standards, an additive mixture in methanol containing both the aldehydes was prepared. Five calibration standards in Milli-Q water were then prepared using the additive mixture. The aldehyde concentrations in the standards ranged from 0 µg/L to 80 µg/L.

20 mL of each of the five standards was added to a 40 mL vial and buffered using 200 mg potassium hydrogen phthalate (KPH, $C_8H_5KO_4$). Similarly, each of the samples was diluted to 20 mL and added to 40 mL vials along with 200 mg KPH. The buffered standards and samples were then derivatized with 1 mL of 15 mg/L of PFBHA aqueous solution. The vials were incubated in a water bath at 35°C for 2 hours. The vials were then cooled and excess PFBHA was quenched using concentrated sulfuric acid. 4 mL of internal standard stock solution containing 100 µg/L 1,2-dibromopropane in hexane was then added to the vials, and the vials were agitated. After allowing

the aqueous and organic layers in the vials to separate, the organic layer was drawn into 20 mL vials containing 3 mL of 0.2 N sulfuric acid. These vials were then agitated for 30 seconds and made to stand for about 5 minutes till distinct phase separation was observed. Finally, the organic layer was drawn into GC autosampler vials and analyzed. These vials could be stored in the dark at 4°C for up to 2 weeks.

The machine used for this analysis was an Agilent 6890N GC with electron capture detector. The gas chromatograph injector was set to 180°C with the split valve open at 0.5 min and the split flow at 50 mL/min. A fused silica DB-5 capillary column (30 m long, 0.25 mm internal diameter, 0.25 μm film thickness) was used with helium carrier gas (flow of 1.5 mL/min at 100°C) and the following temperature program: 50°C for 1 minute, rising at 4°C/min to 220°C, and finally rising at 20°C/min to 250°C. The detector was set to 300°C with a nitrogen make-up gas flow of 27 mL/min.

The GC peak area response and concentration for each analyte and the internal standard were tabulated. Formaldehyde and the internal standard each displayed a single characteristic peak on the gas chromatogram, whereas valeraldehyde displayed two characteristic peaks of roughly equal areas which corresponded to its E and Z geometric isomers. The two peak areas of valeraldehyde for each concentration were then added to calculate the total peak area. Formaldehyde, being a symmetrical carbonyl compound, does not have E and Z isomers. Calibration curves for each analyte were generated by plotting the normalized areas (A_a/A_{is}) against the concentrations of the calibration standards, where A_a is the peak area of the analyte and A_{is} is the peak area of the internal standard. The calibration curves were fitted as straight lines. Finally, the normalized peak areas for each analyte in the samples were converted to concentrations using the calibration curves.

4. RESULTS AND DISCUSSION

4.1 Determination of k_{O_3} using direct spectrophotometry

Different known initial concentrations of 1-hexene were reacted with a known concentration of ozone in aqueous medium using the procedure described previously. The concentration of 1-hexene was always significantly greater than that of ozone, therefore the reaction followed pseudo-first order kinetics and was independent of the 1-hexene concentration. The absorbance of ozone vs time was recorded and plotted. An example of the ozone absorbance vs time graph is shown below.
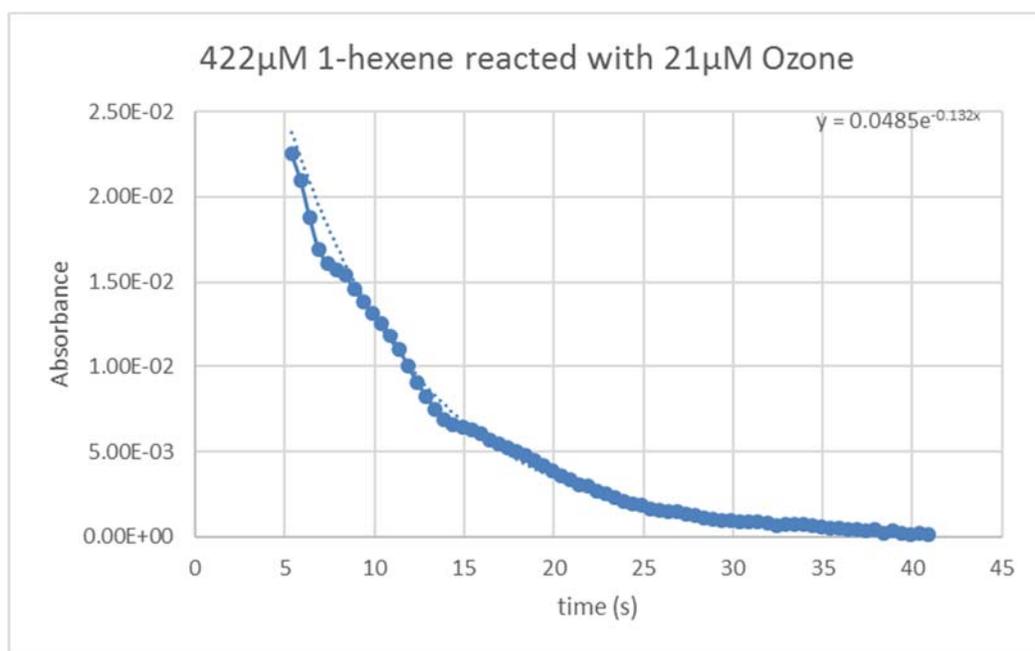

Figure 3: Sample ozone absorbance vs time plot

The data was then fitted to an exponential curve of the type $[O_3] = [O_3]_0 e^{-K_1 t}$, and K_1, the pseudo-first order rate constant of ozonolysis for 1-hexene, was calculated. In the above example, K_1 was calculated to be 0.132 s^{-1}. Also, as described previously,

$$K_1 = k_{O_3}[M]$$

Where k_{O_3} is the second order rate constant for ozonolysis and $[M]$ is the 1-hexene concentration in solution, which is assumed to be constant. For the example above, k_{O_3} was calculated to be 312.8 $M^{-1}s^{-1}$. Similarly, the experiment was carried out for different concentrations of 1-hexene.

Plots for ozone decay in presence of excess 1-hexene are presented in the Appendix. The table below shows the calculated values for the second order rate constant of ozonolysis for the data shown above.

Table 1: Rate constants for aqueous ozonolysis of 1-hexene determined through direct spectrophotometry

Sample	Concentration of 1-Hexene (μM)	Pseudo 1st order rate constant from graph (s^{-1})	2nd order rate constant of ozonolysis ($M^{-1}s^{-1}$)
1	211	0.10	473.93
2	211	0.07	331.75
3	422	0.13	312.80
4	422	0.18	417.06

4.2 Determination of k_{O_3} through competition kinetics

The concentration on styrene in the aqueous stock solution was calculated using the indigo method as described previously. The following table lists the calculated aqueous styrene solution concentration using the indigo method.

Table 2: Styrene stock solution concentration measured using the indigo method

Abs_i	Abs_f	V_t (mL)	V_t (mL)	f	Dilution factor	$C_{O_3,stock}$ (mg/l)	$C_{O_3,initial}$ (mg/l)	$C_{O_3,final}$ (mg/l)	ΔC_{O_3} (mg/l)	$C_{styrene}$ (mM)
0.68	0.47	25	2	0.42	10	19.05	17.32	6.36	10.95	2.28

The final ozone concentration was calculated using equation 14. The initial ozone concentration in sample differed slightly from the ozone stock solution concentration because the sample contained 10mL of ozone stock and 1mL of styrene solution. Therefore, the initial ozone concentration in the sample was $10/11^{th}$ of the ozone stock solution concentration. This is also where the sample dilution factor of 10 comes from.

The concentration of 1-hexene in its aqueous stock solution was calculated be reacting it with an excess of ozone and measuring the decrease in ozone concentration. The following table lists the calculated 1-hexene stock solution concentration.

Table 3: 1-hexene stock solution concentration

$C_{O_3,initial}$ (mg/l)	$C_{O_3,final}$ (mg/l)	dilution factor	$C_{1-hexene}$ (mM)
19.05	16.54	12	0.63

Using calibration curves such as the one shown in Appendix, the concentrations of formaldehyde and valeraldehyde in the ozonated olefin mixtures were measured. Then, using equation 12, the second order rate constant for ozonolysis of 1-hexene was calculated. The results are tabulated in the following table.

Table 4: Rate constants for aqueous ozonolysis of 1-hexene calculated using competition kinetics

Sample no.	1-Hexene concentration (mM)	Styrene concentration (mM)	$k_{styrene}$ ($M^{-1}s^{-1}$)	Formaldehyde concentration (mM)	Valeraldehyde concentration (mM)	$k_{1-hexene}$ ($M^{-1}s^{-1}$)
1	0.105	0.38	3×10^5	3.23×10^{-3}	1.29×10^{-3}	7.27×10^5
2	0.105	0.38	3×10^5	2.57×10^{-3}	1.28×10^{-3}	10.83×10^5
3	0.105	0.38	3×10^5	2.34×10^{-3}	9.88×10^{-4}	7.82×10^5

5. ANALYSIS AND CONCLUSION

The table below lists previously calculated aqueous ozonolysis rate constants for ethene and propene along with the mean values of ozonolysis rate constants for 1-hexene calculated in this study through two different methods.

Table 5: Rate constants for aqueous ozonolysis of 1-hexene

Substrate	Ozonolysis rate constant ($M^{-1}s^{-1}$)	Source
Ethene	1.80×10^5	(Dowideit & Sonntag, 1998)
Propene	8.00×10^5	(Dowideit & Sonntag, 1998)
1-Hexene	383.89	This study (direct spectrophotometry)
1-Hexene	8.64×10^5	This study (competition kinetics)

Looking at Table 5, the first order rate constant of ozonolysis for ethene and propene (both low molecular, aliphatic alkenes) is found to be of the order 10^5 $M^{-1}s^{-1}$, but the $k_{1-hexene}$ calculated in this study through direct spectrophotometry is significantly less than that value. It has been theorized that an increase in chain length of the alkene would not have a drastic effect on its ozonolysis rate constant (Dowideit & Sonntag, 1998). This is because in the case of 1-alkenes, an increase in chain length does not significantly change the electron density around the double bond. It is more likely that the consumption of ozone in solution here was limited by the rate of transfer of 1-hexene from the methanol phase to the aqueous phase, rather than the rate of ozonolysis itself, and therefore the $k_{1-hexene}$ calculated through direct spectrophotometry was not the true rate constant of ozonolysis of 1-hexene.

Table 2 gives the $k_{1-hexene}$ values calculated using competition kinetics. The mean value of the calculated rate constant is 8.64×10^5 $M^{-1}s^{-1}$. Previously, the ozonolysis rate constants for ethene and propene were calculated to be 1.8×10^5 $M^{-1}s^{-1}$ and 8×10^5 $M^{-1}s^{-1}$ respectively, and the

value calculated through competition kinetics in this study appears to fit this trend. As mentioned earlier, chain length does not have a significant effect on the rate of ozonolysis of the alkene in water, and this is borne out to a significant extent by the results in Table 2. Thus, it can be theorized that other low molecular aliphatic alkenes that are liquid at ambient temperature will have rate constants of ozonolysis which are roughly the same as that of 1-hexene. Such alkenes would typically form a small fraction of the components of an oil spill, and knowledge of the kinetic data for their reaction with ozone would be essential to any effort to model the formation of DBPs as part of the Wachusett Reservoir study carried out at the University of Massachusetts, Amherst. Finally, the mechanism of ozonolysis of olefins in water has been long established through the Criegee mechanism. Therefore, the nature and quantity of the products of aqueous phase ozonolysis of alkenes of interest can easily be predicted without experimental verification.

When looking at ozonation of water contaminated with alkenes, the ozonolysis reactions can be considered of pseudo first order. This is because the ozonation is a continuous process, and consequently the ozone concentration in the reactor is held constant. Therefore, the integrated rate law for an individual ozonolysis reaction can be described as follows.

$$[M] = [M]_0 e^{-[O_3]_0 k_{O_3} t} \tag{15}$$

Where M is the target alkene. The product of $[O_3]_0$ and t represents the 'CT' value for ozone. Therefore, equation 15 can be modified to the following form.

$$\% \ Alkene \ remaining = 100 e^{-k_{O_3} CT} \tag{16}$$

Using equation 16, the graph below shows the '% alkene remaining' vs 'CT' curve for 1-hexene.
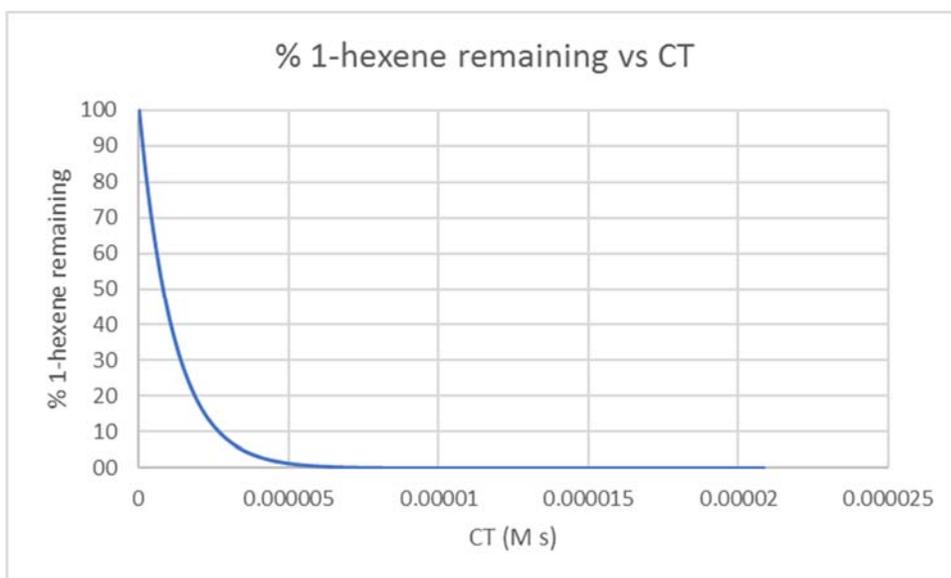
Figure 4: % 1-hexene remaining vs CT plot.

As part of the Wachusett Reservoir study, Aarthi Mohan studied the dissolution of West Texas Intermediate (WTI) crude oil in water (Mohan, Reckhow, & Tobiason, 2017). This was done by dissolving a fixed amount of crude in water (.28% v/v) with a contact time of 24hrs, after which the concentrations of various organic compounds typically found in crude oil were measured using prepared alkene standards. The following table summarizes the alkene concentrations detected in the samples.

Table 6: Aqueous concentrations of alkenes in WTI/water mixture as measured by Mohan et al.

Alkene	Concentration (µg/L)
1-octene	38
Trans-2-octene	40
1-nonene	155
Trans-3-nonene	20
Trans-2-nonene	170

The concentrations listed in table 6 are for 0.28% (v/v) O:W mixture. The components of crude oil are very sparingly soluble in water, and their aqueous concentrations are governed by their

partition coefficients. The partition coefficient for a compound is described by the following equation.

$$P_{O/W} = \frac{C_O}{C_W} \tag{17}$$

Where C_O is the concentration of the compound in the crude oil phase and C_W is the aqueous concentration of the compound. Since such compounds are very sparingly water soluble, one can assume that C_O is almost equal to the concentration of the compound in pure crude oil, C_T. Therefore,

$$P_{O/W} \approx \frac{C_T}{C_W} \tag{18}$$

Or,

$$C_W = \frac{C_T}{P_{O/W}} \tag{19}$$

If C_{W_i} represents the aqueous concentration of the ith component of WTI crude, the total crude oil concentration in the aqueous phase is given by the equation

$$C_{WTI,aq} = \sum_{i=1}^{n} C_{W_i} = \sum_{i=1}^{n} \frac{C_{T_i}}{P_{O/W_i}} \tag{20}$$

This can be further simplified to

$$C_{WTI,aq} = \frac{1}{P_{O/W_{avg}}} \sum_{i=1}^{n} C_{T_i} \tag{21}$$

where $P_{O/W_{avg}}$ is the average partition coefficient for n components of WTI crude oil. On observation it is apparent that $\sum_{i=1}^{n} C_{T_i}$ is in fact the density of WTI crude, ρ_{WTI}. Thus,

$$C_{WTI,aq} = \frac{\rho_{WTI}}{P_{O/W_{avg}}} \qquad (22)$$

Mohan et al. assumed that 80% by weight of WTI crude oil consisted of carbon. Thus,

$$DOC = 0.8C_{WTI,aq} = \frac{0.8\rho_{WTI}}{P_{O/W_{avg}}} \qquad (23)$$

$P_{O/W_{avg}}$ was calculated using data for n-alkane concentrations in pure WTI crude reported in literature (Wang, et al., 2003) and data for aqueous n-alkane concentrations reported by Mohan et al. This $P_{O/W_{avg}}$ was assumed to represent the average partition coefficient for the entire spectrum of WTI components. The density of WTI crude oil, ρ_{WTI}, was assumed to be 0.845 g/mL. Finally, using the calculated value of $P_{O/W_{avg}}$, aqueous alkene concentrations reported in table 6, and the equations derived above, the concentrations of alkenes in 1 mg/L DOC solution of WTI were calculated. These concentrations are listed in table 7.

Table 7: Estimated alkene concentrations in 1 mg/L DOC aqueous solution of WTI crude oil based on report by Mohan et al.

Alkene	Concentration (µg/L)
1-octene	7.90
Trans-2-octene	8.31
1-nonene	32.21
Trans-3-nonene	4.16
Trans-2-nonene	35.32

As explained earlier in this section, it is reasonable to assume that low molecular aliphatic alkenes that are liquid at ambient temperature will have rate constants of ozonolysis which are roughly the same as that of 1-hexene. Furthermore, assuming that the WTI-water mixture is ozononated at CT values high enough to ensure complete ozonolysis of its constituent alkenes,

Table 8 below shows the nature and concentrations of the products of ozonation for 1 mg/L DOC solution of WTI.

Table 8: Nature and concentration of ozonation products for 1 mg/L DOC aqueous solution of WTI based on alkene concentrations reported in table 7

Alkene	Concentration of alkene (µg/L)	Ozonolysis product 1	Concentration of product 1 (µg/L)	Ozonolysis product 2	Concentration of product 2 (µg/L)
1-octene	7.90	formaldehyde	2.12	Heptanal	8.04
Trans-2-octene	8.31	acetaldehyde	3.26	Hexanal	7.42
1-nonene	32.21	formaldehyde	7.67	Octanal	32.72
Trans-3-nonene	4.16	propionaldehyde	1.91	Hexanal	3.30
Trans-2-nonene	35.32	acetaldehyde	12.33	Heptanal	31.96

The chart below summarizes the predicted concentrations of the products formed due to ozonation of 1 mg/L DOC WTI solution using data from table 8.
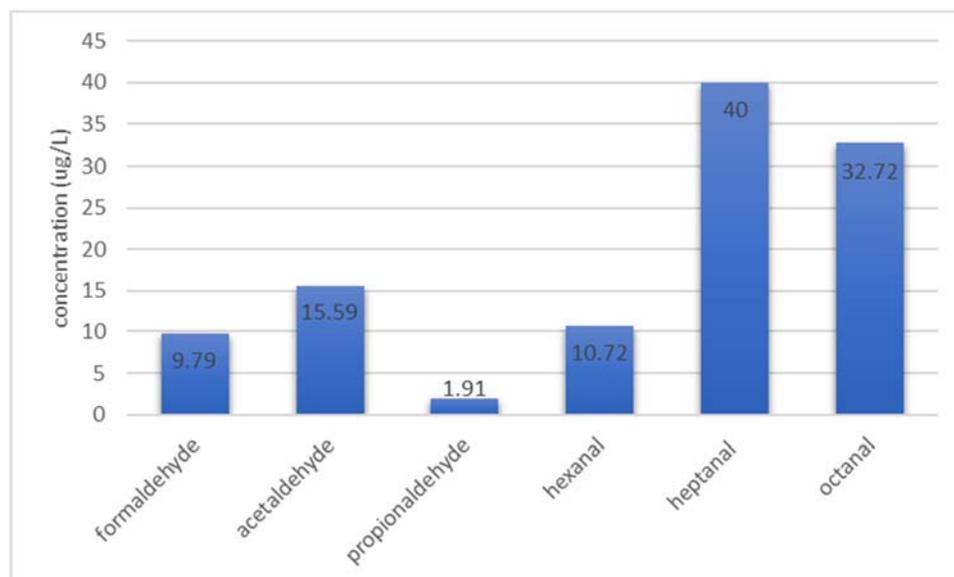

Figure 5: Concentrations of products of ozonation of 1mg/L DOC solution of WTI crude oil

The analysis summarized in Table 8 and Figure 5 is limited by the alkene standards chosen by Mohan et al. It is possible that the oil and water mixture contained C-10 and higher alkenes in significant amounts. Comparing the concentrations of alkenes to those of alkanes as reported by

Mohan et al., on average the concentration of a particular alkene was found to be 8 times that of the corresponding alkane of equal chain length. Thus, assuming that the concentrations of alkenes in pure WTI crude oil are 8 times those of n-alkanes of equal carbon chain length, Table 9 lists the expected aqueous concentrations of C-10 to C-20 alkenes. Each alkene was assumed to consist of two isomers of equal concentrations, the α-olefin and the β-olefin. The partition coefficient for these alkenes was assumed to be the same and equal to the value of $P_{O/W_{avg}}$ calculated previously.

Table 9: Estimated aqueous concentrations of C-10 to C-20 alkenes based on concentrations of n-alkanes in pure WTI crude as reported by Wang et al.

Alkene	Concentration (µg/L)
1-decene	10.35
2-decene	10.35
1-undecene	79.65
2-undecene	79.65
1-dodecene	149.44
2-dodecene	149.44
1-tridecene	197.33
2-tridecene	197.33
1-tetradecene	194.92
2-tetradecene	194.92
1-pentadecene	191.07
2-pentadecene	191.07
1-hexadecene	173.02
2-hexadecene	173.02
1-heptadecene	162.91
2-heptadecene	162.91
1-octadecene	114.55
2-octadecene	114.55
1-nonadecene	114.06
2-nonadecene	114.06
1-eicosene	93.13
2-eicosene	93.13

Assuming that the WTI-water mixture is ozononated at CT values high enough to ensure complete ozonolysis of its constituent alkenes, Table 10 below shows the nature and concentrations of the products of ozonation for 1 mg/L DOC solution of WTI.

Table 10: Concentrations of alkenes and their ozonation products for 1 mg/L DOC aqueous solution of WTI based on alkene concentrations reported in table 9.

Alkene	Concentration of alkene (µg/L)	Ozonolysis product 1	Concentration of product 1 (µg/L)	Ozonolysis product 2	Concentration of product 2 (µg/L)
1-decene	2.47	Formaldehyde	0.53	Nonanal	2.51
2-decene	2.47	Acetaldehyde	0.78	Octanal	2.26
1-undecene	19.04	Formaldehyde	3.71	Decanal	19.29
2-undecene	19.04	Acetaldehyde	5.44	Nonanal	17.56
1-dodecene	35.73	Formaldehyde	6.38	Undecanal	36.15
2-dodecene	35.73	Acetaldehyde	9.36	Decanal	33.17
1-tridecene	47.17	Formaldehyde	7.78	Dodecanal	47.69
2-tridecene	47.17	Acetaldehyde	11.40	Undecanal	44.06
1-tetradecene	46.60	Formaldehyde	7.13	Tridecanal	47.07
2-tetradecene	46.60	Acetaldehyde	10.46	Dodecanal	43.75
1-pentadecene	45.68	Formaldehyde	6.53	Tetradecanal	46.11
2-pentadecene	45.68	Acetaldehyde	9.57	Tridecanal	43.07
1-hexadecene	41.36	Formaldehyde	5.54	Pentadecanal	41.73
2-hexadecene	41.36	Acetaldehyde	8.12	Tetradecanal	39.15
1-heptadecene	38.95	Formaldehyde	4.91	Hexadecanal	39.27
2-heptadecene	38.95	Acetaldehyde	7.20	Pentadecanal	36.98
1-octadecene	27.38	Formaldehyde	3.26	Heptadecanal	27.60
2-octadecene	27.38	Acetaldehyde	4.78	Hexadecanal	26.08
1-nonadecene	27.27	Formaldehyde	3.08	Octadecanal	27.47
2-nonadecene	27.27	Acetaldehyde	4.51	Heptadecanal	26.04
1-eicosene	22.26	Formaldehyde	2.39	Nonadecanal	22.42
2-eicosene	22.26	Acetaldehyde	3.50	Octadecanal	21.31

Figure 6 below summarizes the predicted concentrations of the products formed due to ozonation of C-10 to C-20 alkenes in 1 mg/L DOC WTI solution using data from Table 10.
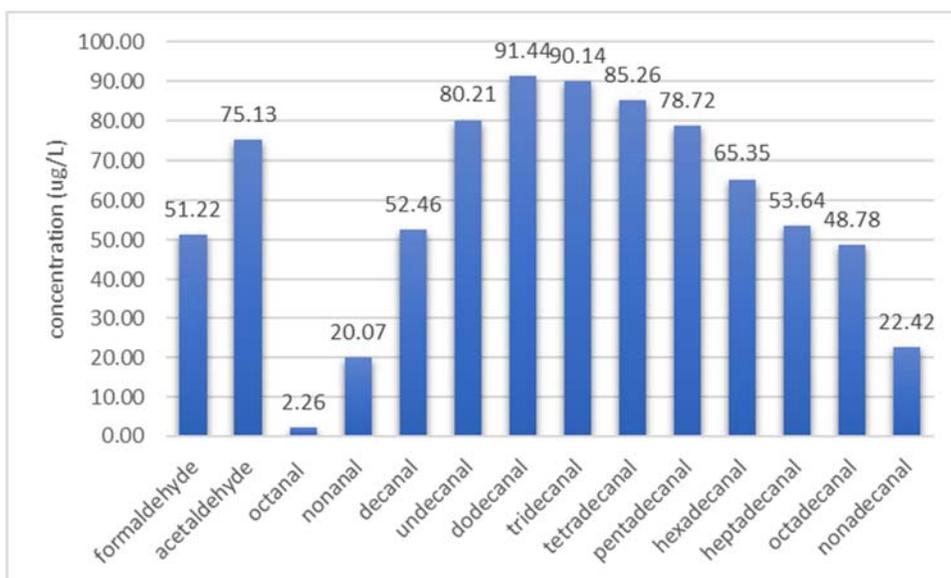
Figure 6: Concentrations of products of ozonation of C-10 to C-20 alkenes in 1mg/L DOC solution of WTI crude oil

Finally, combining data from Figures 5 and 6 we get the following plot showing the total concentration of products due to ozonation of C-8 to C-20 alkenes in 1mg/L DOC solution of dissolved WTI crude oil.
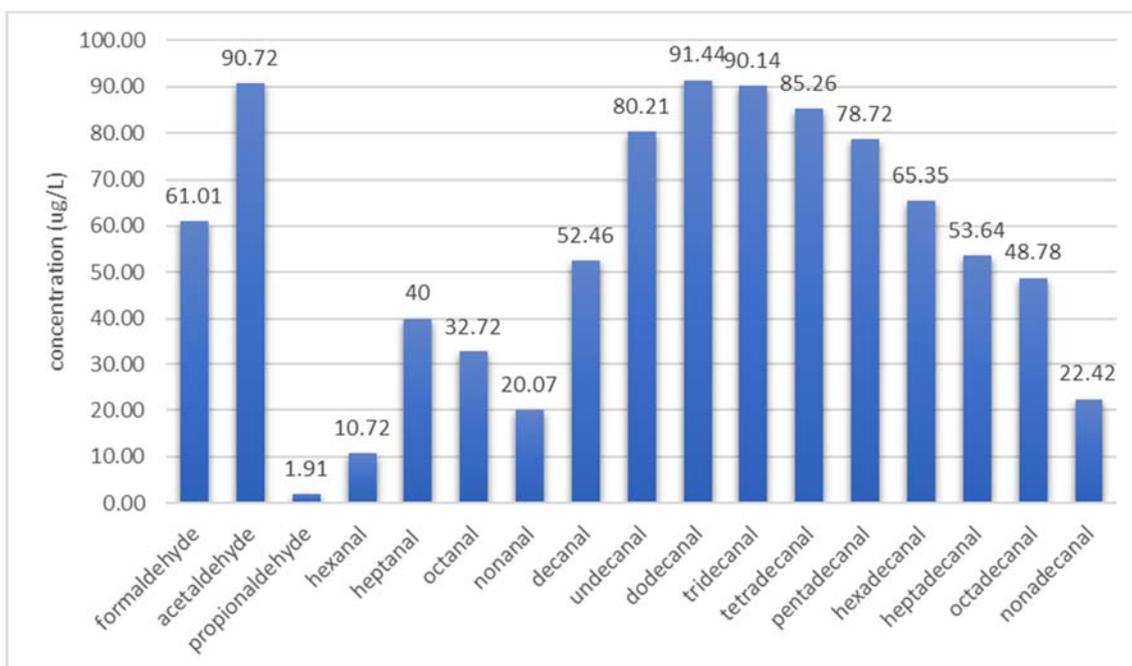

Figure 7: concentration of products due to ozonation of C-8 to C-20 alkenes in 1mg/L DOC solution of WTI crude oil

Looking at Figure 7 one can see that most of the aldehyde concentration is due to ozonation of higher molecular weight alkenes. Ozonolysis of alkenes follows second order kinetics where the reaction is of first order with each of the reactants. In other words, one mole of ozone reacts with one mole of alkene to produce one mole each of the product aldehyde. Therefore, looking at the product concentrations listed in Figure 7, 198.16 μg of ozone would be consumed by 1 L of WTI crude oil solution having DOC of 1 mg/L.

Mohan et al. studied the formation of low molecular weight aldehydes due to ozonation of a crude oil water mixture. Figure 8 below gives the measured concentrations of the aldehydes for different ozone/ water contact times. The ozone dose was maintained at 4 mg/L.
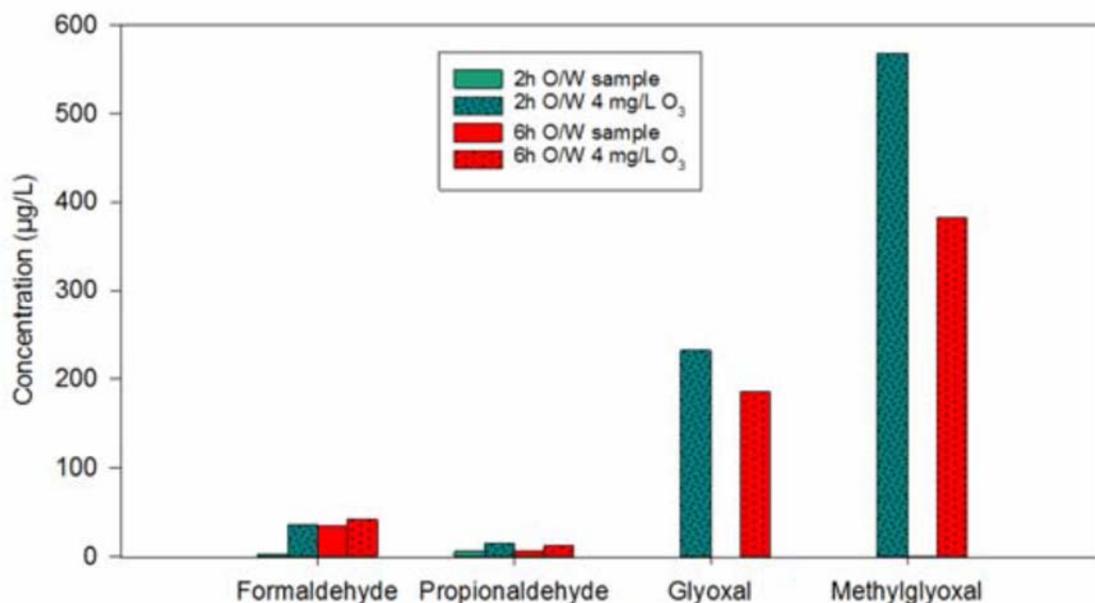

Figure 8: Low molecular weight aldehydes for two different ozone/water contact times.

According to Figure 8, the samples exposed to 4 mg/L ozone for 2 hours showed increases in formaldehyde and propionaldehyde concentrations of 32.74 μg/L and 9.1 μg/L respectively. On comparing these numbers to the formaldehyde and propionaldehyde concentrations predicted for ozonation of 1 mg/L DOC aqueous solution of WTI crude as shown in Figure 7, it is apparent that while the two sets of numbers are not identical they are of the same order of magnitude. This would suggest that the model presented in this report is fairly accurate, and can provide a good starting point for future calculations.

Conclusion

The value of the second order rate constant of aqueous ozonolysis for 1-hexene was found to be fairly close to the values for ethene and propene. Therefore, the value of the rate constant must not change substantially with an increase in carbon chain length. Ozonation of crude oil contaminated water would lead to almost complete consumption of alkenes to form the product aldehydes due to fast reaction rates. This is borne out by Figure 4, which shows % removal for 1-hexene dissolved in water vs 'CT' for ozone. Figure 7 tells us that of all the aldehydes formed due to ozonation of water containing C-8 to C-20 alkenes, formaldehyde and acetaldehyde dominate, especially when looking at molar concentrations. This is because simple alkenes present in crude oil almost always have unsaturation at the '1' and '2' carbon positions, as evidenced by data reported by Mohan et al. Finally, the aldehydes listed in Figure 7 pose many chronic health risks, and any attempt to mitigate the effects of an oil spill in a water body should be informed with strategies to minimize their formation.
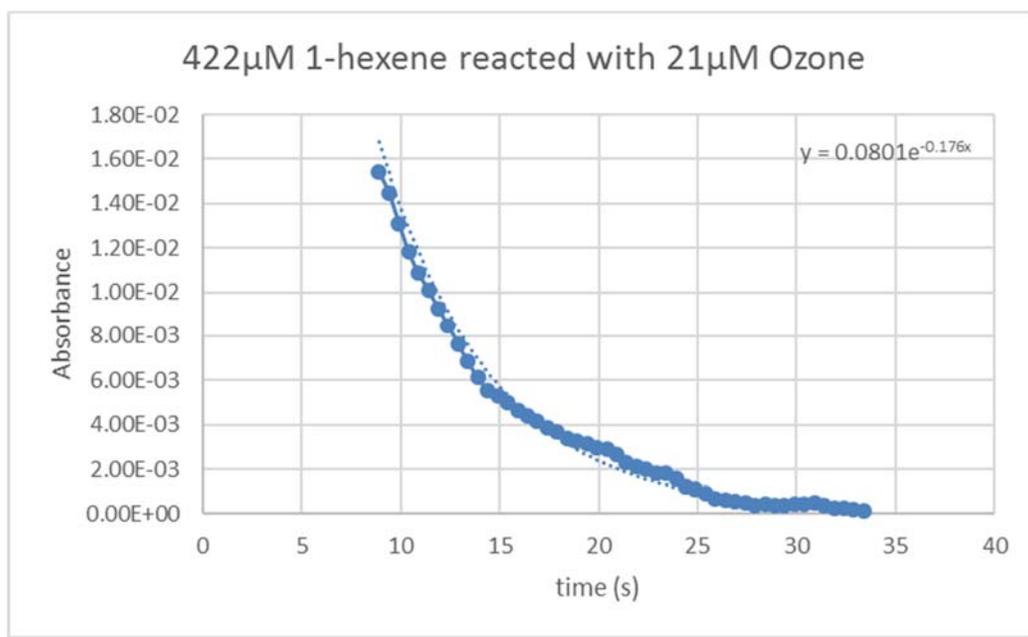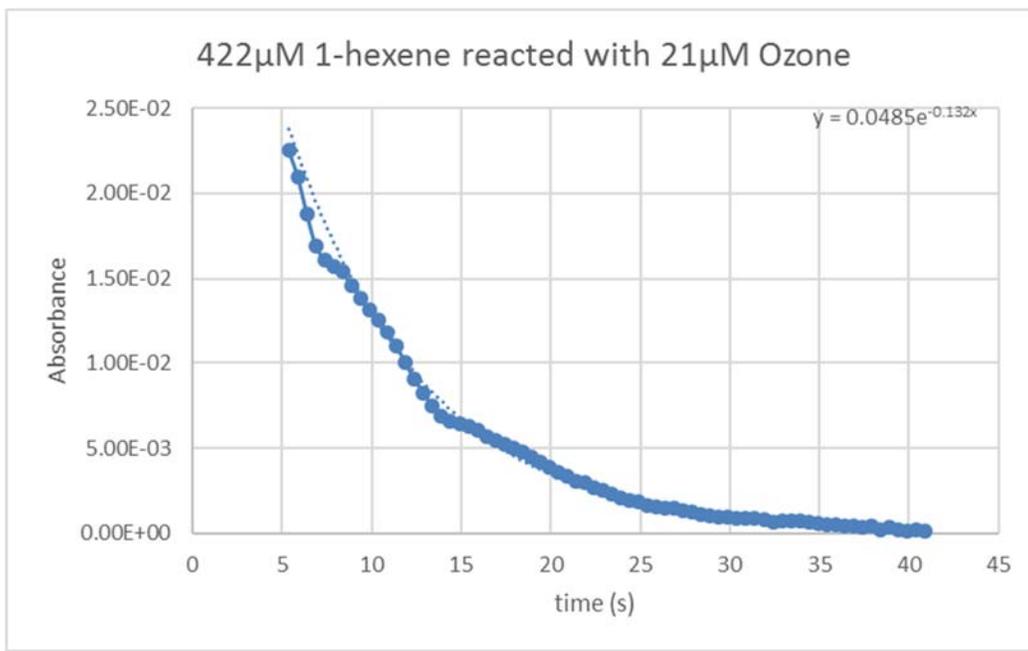
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7. APPENDIX
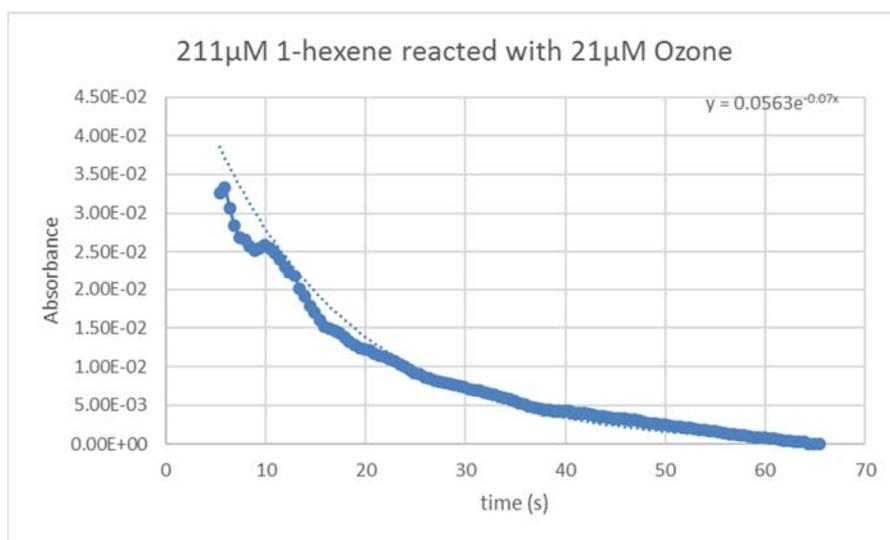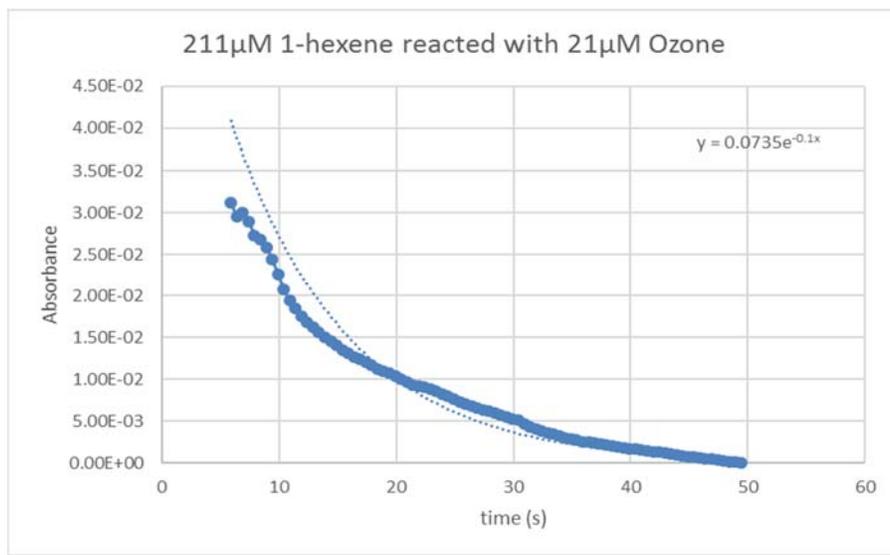
Figures A1 and A2 above represent the absorbance vs time plot for the spectrophotometric data when 211μM of 1-Hexene was reacted with 21μM of Ozone. The data was fitted to a first order decay curve, which was used to determine the pseudo-first order decay constant.

422μM 1-hexene reacted with 21μM Ozone

$y = 0.0485e^{-0.132x}$

422μM 1-hexene reacted with 21μM Ozone

$y = 0.0801e^{-0.176x}$

Figures A3 and A4 above represent the absorbance vs time plot for the spectrophotometric data when 422μM of 1-Hexene was reacted with 21μM of Ozone. The data was fitted to a first order decay curve, which was used to determine the pseudo-first order decay constant.
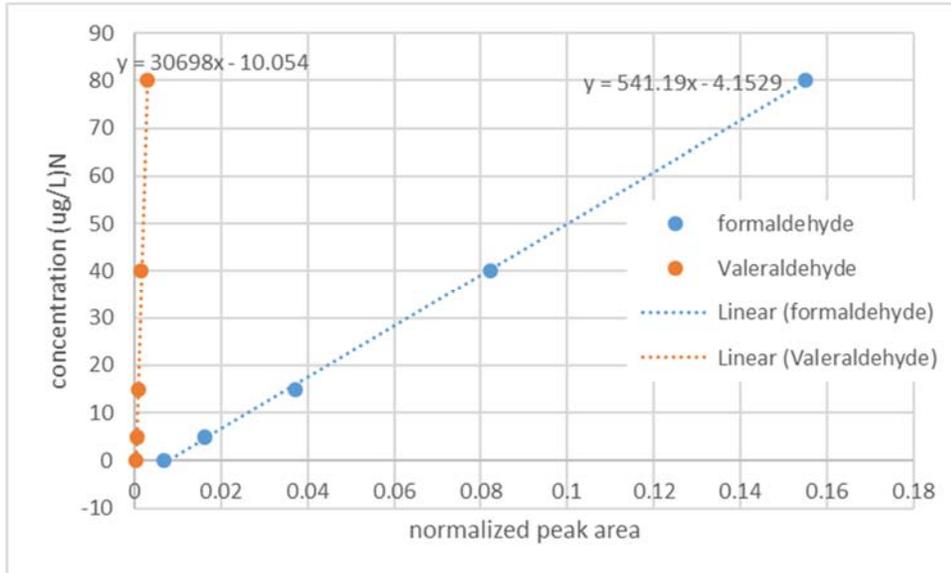
Figures B1 above represents an example of the calibration curves used to calculate formaldehyde and valeraldehyde concentrations in samples.