

# Reactivity and By-Products of Methyl Tertiary Butyl Ether Resulting from Water Treatment Processes

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## Abstract

MTBE has been detected as a contaminant in drinking water sources in California and throughout the Continental United States. Oxidizing agents used in water treatment processes like chlorine species, ultraviolet light (UV) and UV/H<sub>2</sub>O<sub>2</sub> have the potential to degrade MTBE, potentially forming by-products that may pose health concerns. A study was conducted to investigate the impact and significance of water chlorination and UV disinfection processes on water containing MTBE. The study also investigated the use of UV/H<sub>2</sub>O<sub>2</sub> as treatment strategy to degrade MTBE, the kinetics of the treatment and the by products that were formed.

MTBE containing water samples buffered to pH 4 or 7 were treated with sodium hypochlorite in batch completely mixed systems in a darkroom. The reactivity of aqueous solutions of peroxide and MTBE was assayed in a closed batch system. UV and UV/peroxide studies were conducted in a recirculating batch reactor with a low pressure mercury lamp. Dark and UV-only tests were conducted to separate the effects of MTBE loss to system components and photolytic processes. Hydrogen peroxide/UV tests were conducted at initial concentrations of 4:1, 7:1 and 15:1 on a moles H<sub>2</sub>O<sub>2</sub>:MTBE basis. Benzene was added in some experiments to measure the hydroxyl radical concentration. The concentration of MTBE, H<sub>2</sub>O<sub>2</sub>, benzene and byproducts were measured over a 120 minute period using a purge-and-trap GCMS method. Hydrogen peroxide actinometry was used to measure the incident UV intensity in the reactor.

No measurable degradation of MTBE occurred when water was chlorinated with sodium hypochlorite over a 24-hour period. No conclusive evidence of degradation of MTBE by exposure to UV light emitted from a low-pressure mercury lamp was found. UV/H<sub>2</sub>O<sub>2</sub> treatment resulted in 99.9% removal of MTBE in water with the major by-product identified as tert-butyl formate. The second order rate constant for the degradation of MTBE from the hydroxyl radical during the UV/Peroxide treatment process was found to be  $4.82 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  with a standard deviation of  $1.28 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ . The mean second order rate constant for the reaction of tert butyl formate with the hydroxyl radical was found to be  $1.19 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  with a standard deviation of  $4.47 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ . The yield for the formation of tert butyl

formate from the reaction of MTBE and the hydroxyl radical was calculated to be 0.27 with a standard deviation of 0.0378.

## **Introduction**

Disinfection processes like chlorination and ultraviolet irradiation are necessary to destroy disease-causing microorganisms in drinking water supplies. These processes also have the potential to oxidize or breakdown various constituents found in water sources. Hypochlorous acid (HOCl) which is involved in the chlorination process has the potential to oxidize various contaminants present in the water to form new compounds known as disinfection by-products. Among the contaminants found in water, chlorine has been found to degrade various herbicides like Isoproturan (Lopez et al., 1996) and pesticides like Aldicarb (Miles, 1991, Mason et al., 1990). Ultraviolet (UV) radiation has the potential to increase the energy in a molecule, causing it to break down to form new chemical compounds in a process known as photolysis.

Advanced oxidation processes (AOPs) are water treatment processes that have been developed in recent years specifically to break down contaminants in water supplies by generating the hydroxyl radical (Standard electrode potential, 2.80 Volts), a chemical oxidant that is twice as strong as chlorine (Standard electrode potential, 1.50 Volts). A common AOP used to generate the hydroxyl radical relies on the photolysis of hydrogen peroxide by ultraviolet light or UV/Peroxide treatment. UV/Peroxide treatment has been shown to degrade 99.9% of various contaminants found in water, including benzene (Sundstrom et al, 1987), trichloroethylene (Weir et al, 1993) and acetone (Stefan et al, 1996). Other methods used in advanced oxidation processes to generate the hydroxyl radical are a combination of ultraviolet light with titanium dioxide slurries, ozone, ozone/hydrogen peroxide, and Fenton's reagent (Venkatadri and Peters, 1993 and Clark and Knowles, 1982).

Since both traditional water disinfection processes and advanced oxidation processes may result in the formation of new chemical compounds that potentially may have a higher toxicity than the original contaminants present, it is important to identify what compounds are formed when these processes are used.

The primary objective of this study were to investigate the impact of the use of UV/Peroxide as a treatment strategy to degrade MTBE, to quantify the kinetics of the treatment process and to identify any by products formed. In addition, the impact and significance of UV and water chlorination on degradation of MTBE was studied.

## **Background Chlorination**

In reviewing the literature, no studies have been published which reflect the effect of chlorination on water containing MTBE. Ultraviolet light when applied at the 254 nm wavelength has been found to remove 10-30% of

MTBE from water in a batch reactor over a two-hour period (Wagler and Malley, 1993).

Chlorination of public water has been in practice since 1904 when continuous chlorination of domestic water supplies began in England (Sawyer et al., 1994). Today chlorine is required for almost all domestic water supplies to prevent the spread of waterborne diseases. It is also used for slime control in industrial water treatment and for control of filamentous bulking in wastewater treatment plants.

Chlorine is usually added in the form of chlorine gas immediately dissolved in water, sodium hypochlorite (NaOCl) or calcium hypochlorite (Ca(OCl)<sub>2</sub>). When chlorine is added to water, a weak acid, known as hypochlorous acid is formed. While it is still unclear exactly how the addition of chlorine and other oxidants to water deactivate microorganisms in water, it is known that hypochlorous acid (HOCl) is the active compound in the disinfection process (White, 1992). Hypochlorous acid has an equilibrium constant,  $K_a$  of  $10^{-7.5}$  with the hypochlorite ion, OCl<sup>-</sup>. Above a pH of 7.5, the hypochlorite ion, which has a much lower disinfecting capacity than hypochlorous acid, is predominant. For this reason, pH control is an important factor in the disinfection of water with chlorine.

When added to water, chlorine has been found to be reactive with a variety of compounds found in water including ammonia, total organic carbon, organic nitrogen, iron, and other inorganics.

#### **Ultraviolet Treatment**

When a molecule is exposed to radiation it may absorb, transmit or reflect the radiation. The absorbed radiation may promote an electron to a higher molecular orbital, increasing the energy of a molecule. This increase in energy may then eventually result in the return to its original energy state or may result in a photochemical reaction, breaking down the original molecule and forming new chemical compounds.

Ultraviolet disinfection relies on a photochemical reaction to sterilize potable water and wastewater by targeting the DNA molecule of a microorganism to deactivate it. Since it has been found that the ideal wavelength to effectively deactivate microorganisms is 260 nm, ultraviolet light has been traditionally applied to the water by means of a low-pressure mercury lamp which emits 98% of its energy in the 254 nm wavelength. The ultraviolet light causes a rearrangement of genetic information in the DNA molecule by means of a photochemical reaction, preventing it from being able to reproduce. This same mechanism that causes a photochemical reaction in a microorganism's DNA also has the potential to cause a photochemical reaction in other constituents found in water supply sources. Various contaminants have been found to degrade under exposure to a low-pressure mercury lamp, including trichloroethylene (Beltran et al, 1995) and benzene (Sundstrom et al, 1987).

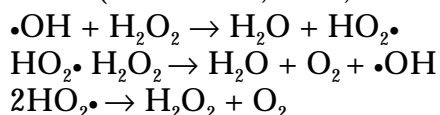
#### **Advanced Oxidation Processes and Ultraviolet/Hydrogen Peroxide Treatment**

Advanced oxidation processes (AOP) involve the generation of the hydroxyl radical ( $\Sigma\text{OH}$ ), in order to degrade a chemical to remove it from

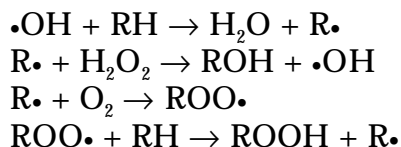
water (Brown et al., 1995). The hydroxyl radical may be generated by means of ultraviolet light, ozonation or ozone/ultraviolet treatment. An advantage to AOPs over activated carbon and air stripping is that, if effective, the contaminant is degraded into other compounds, removing the contaminant from the environment, not just from the aqueous phase. AOPs have proven to work well in dilute solutions and can achieve removal of 70-99% of organic contaminants in water. A major disadvantage to AOPs is that by-products formed may have a higher toxicity than the original contaminant and may differ depending on the characteristics of the water being treated.

Several studies have been conducted involving the degradation of MTBE in aqueous solution using advanced oxidation processes. The studies conducted involved ozone and ozone/hydrogen peroxide treatment in a combined MTBE and ethyl-tert butyl ether (ETBE) in dilute aqueous solution (Leitner et al, 1994), photocatalytic degradation of MTBE in TiO<sub>2</sub> slurries (Barreto et al, 1995), ultraviolet (UV)/hydrogen peroxide treatment (Wagler and Malley, 1993) and hydrogen peroxide in the presence of Fe(II) otherwise known as Fenton's Reagent (Novak and Yeh, 1995). The major by-products identified as a result of these studies are tert-butyl formate, acetone, tert-butyl alcohol and methanol and formaldehyde (Leitner et al, 1994, Novak and Yeh, 1995, Barreto et al, 1995, Wagler and Malley, 1993).

UV/Peroxide treatment is an advanced oxidation process that uses ultraviolet radiation to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical (Clark and Knowles, 1982; Glaze, 1987). The hydroxyl radical can then be scavenged by an organic compound to oxidize the organic, recombine with other hydroxyl species to reform hydrogen peroxide or initiate a radical chain degradation of hydrogen peroxide in the series of reactions shown below (Glaze et al, 1987; Clarke and Knowles, 1982):



Hydroxyl radicals may attack organic molecules by abstracting a hydrogen atom from the molecule (Clark and Knowles, 1982). A common pathway for the degradation of organics by the hydroxyl radical can be found below (Carey, 1990):



While hydrogen peroxide is photoreactive over the 185nm-400nm wavelength range, short-wave ultraviolet energy (200-280 nm) results in the highest hydroxyl radical yields (Glaze et al., 1987, Clarke and Knowles, 1982). The molar absorptivity of hydrogen peroxide at 253.7 nm is 19.6 M<sup>-1</sup>cm<sup>-1</sup> (Baxendale and Wilson, 1957).

Factors that may affect the photolysis of hydrogen peroxide are suspended particles and other absorbing particles in the aqueous solution being treated (Glaze et al., 1987). Constituents in water which may affect the degradation of organic contaminants include carbonate, bicarbonate, humic substances, hydrogen phosphate and phosphate ions. Inorganic compounds present in water may also precipitate during UV treatment, coating lamp tubes and affecting the amount of UV light that is available for water treatment (Venkatodori and Peters, 1993).

## **Experimental**

### **Water Chlorination Experiments**

Water chlorination experiments were conducted in batch reactors (500 mL bottles) containing 500 mL of Nanopure water buffered to an initial pH of 4 and 7 and 340 mL (~ 500 mg/L) of MTBE (99.99% HPLC Grade, Fisher Scientific, Hampton, New Hampshire). Reactors were dosed with 80 mL of 4-6% sodium hypochlorite solution (Fisher Scientific), placed in a darkroom and monitored over a 24-hour period. Water was buffered using potassium hydrogen phthalate ( $\text{HOCOC}_6\text{H}_4\text{COOK}$ ) and hydrochloric acid (pH=4) or  $\text{NaH}_2\text{PO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  (pH=7). An identical reactor without sodium hypochlorite addition served as a control to check for volatile losses. In order to verify the presence of HOCl in the sodium hypochlorite solution, 1 gram of potassium iodide (KI) was added to 15 mL of the sodium hypochlorite solution. MTBE concentration was measured using a direct vapor headspace method.

### **Hydrogen Peroxide Experiments**

To determine if hydrogen peroxide alone has the potential to oxidize MTBE an experiment was conducted in a batch reactor (500 mL bottles) containing 500 mL of Nanopure water buffered with  $\text{NaH}_2\text{PO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  and adjusted to an initial pH of 7 with sodium hydroxide. 340 mL (~500 mg/L) of MTBE (Fisher Scientific, 99.99% HPLC GRADE) were added to each reactor. Reactors were dosed with 40mL of 31.5% hydrogen peroxide solution (Fisher Scientific), to create a molar ratio of hydrogen peroxide to MTBE of 15, and monitored over a 2-hour period. In order to verify the concentration of hydrogen peroxide in the solution used in this experiment, the absorbance of the hydrogen peroxide in the solution added to the reactor was measured on a UV spectrophotometer (Shimadizu, UV160U, Kyoto, Japan) at a wavelength of 240 nm. MTBE concentration was measured using a direct headspace injection technique described in the Analytical Methods section of this report.

### **UV and UV/Peroxide Experiments**

The UV and UV/Peroxide experiments were carried out in a flow through reactor using one low pressure mercury lamp, 2 cm in diameter and 26 cm long enclosed in a stainless steel reactor six centimeters in diameter and 27 cm long (Trojan, Advantage 2, Ontario, Canada). A schematic of the reactor can be found in Figure 1. In order to control the water temperature, the reservoir was placed in a water bath which was cooled by running water at

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a temperature of 22 °C through a coil of copper tubing placed in the water bath. The water temperature of the reservoir was found to be 25 ± 3 °C over the course of the experiment. The ultraviolet lamp was warmed up for 1 hour before each experiment to ensure optimal lamp performance. Nanopure water was buffered to a pH of 6.5 with NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O and Na<sub>2</sub>HPO<sub>4</sub>·7H<sub>2</sub>O and pumped through the reactor at a flow rate of approximately 2.8 L/min with a peristaltic pump (Cole Palmer, Vernon Hills, Illinois) into a 5 L capacity glass reservoir mixed with a magnetic stirrer. The water only came into contact with the reservoir, stainless steel reactor, and the tubing (Masterflex, silicone peroxide cured, Cole Palmer). Enough water was added to the system to minimize headspace in the reservoir and reduce volatile losses. Approximately 10 ppm of MTBE was added to the system followed by the addition of hydrogen peroxide concentrations that had a molar ratio with MTBE ranging from 4:1 - 15:1. In experiments conducted to monitor the kinetics of the reaction, approximately 500 ppb of benzene was added to the system to monitor hydroxyl radical formation by monitoring the disappearance of benzene.

Samples were taken at given time intervals and analyzed by purge and trap GC-MS to monitor MTBE and benzene degradation and formation of any by-products. Hydrogen peroxide concentration was monitored by a colorimetric method using a salt of titanium dioxide to react with the hydrogen peroxide to develop a yellow color. (Eisenburg, 1943).

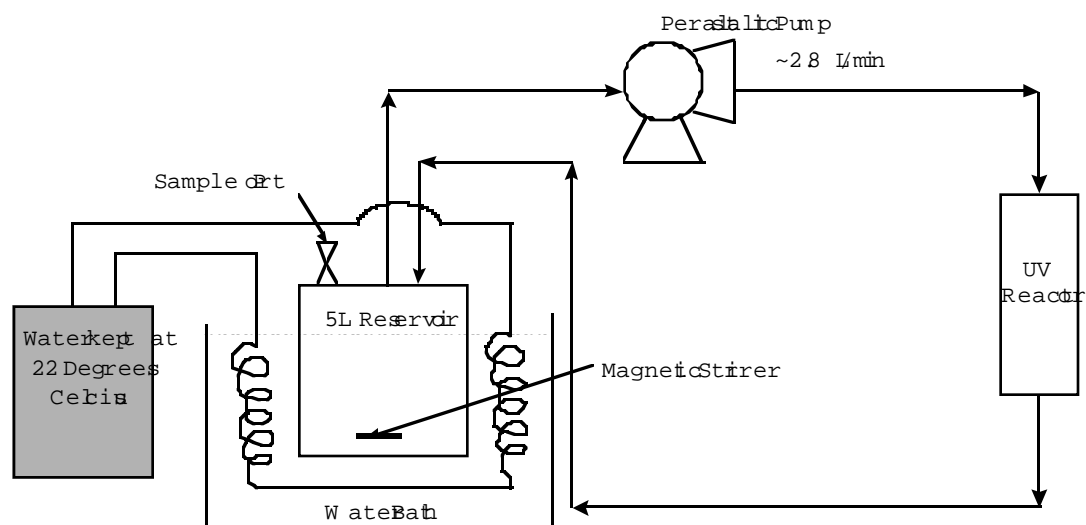


Figure 1: UV Reactor Schematic

## Analytical Methods

### Direct Headspace Injection Technique for Measurements of MTBE at High Concentrations

Rapid measurement of high MTBE concentrations (above 20 ppm) was accomplished with a direct headspace injection technique. In this technique, MTBE concentration was measured using direct vapor injections from the headspace of sample bottles using a gas chromatograph (Hewlett Packard 5810, Palo Alto, California) with a flame ionization detector and an integrator unit (Hewlett Packard 3396A). To determine the minimum equilibration time required for vapor-liquid equilibrium to be attained, a series of trials were conducted in which 20 mL crimp top bottles containing 5 mL of sample were shaken and allowed to stand for various time periods. A volume of 0.1 milliliter of gas was extracted with a gas tight syringe from the sample bottle and injected into the GC. The GC column was set at 55 °C for 2.5 minutes. Results were compared to those obtained for samples containing the same MTBE concentration prepared 1-2 hours ahead of time that had already come into equilibrium with the gas phase. After a series of trials, it was found that shaking the sample for 2 minutes and allowing it to stand for 30 seconds produced reproducible results for various known concentrations of MTBE in water.

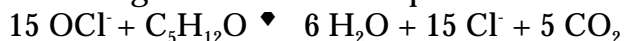
#### **GC-MS Purge and Trap Method**

Samples were taken at given time intervals and analyzed for MTBE, benzene and by-products using a purge and trap concentrator (Tekmar 3000, Cincinnati, Ohio) followed by a gas chromatograph (Varian Star 3400 CX) with 30 m column (J&W Scientific DB-5 MS, I.D. 0.25 mm, stationary phase, 0.5 mm, Folsom, California) and a mass spectrometer (Varian Saturn 4D). Water samples (5mL) were heated to 40° C for five minutes and purged with helium gas for 15 minutes. The analytes were trapped on a Tenax/Silica Gel/Charcoal trap (Tekmar) and desorbed for 4 minutes at 175° C . The GC oven temperature was maintained at 40°C for five minutes, was ramped to 200° C at a rate of 20° C/min, and was held at 200° C for 1.25 minutes. MTBE, benzene and potential by-products were quantified using external standards prepared for MTBE (99.9%, HPLC Grade, Fisher Scientific), benzene (99.9% ACS Certified, Fisher Scientific), tert butyl alcohol (99.4% Malinckrodt Chemical, Paris Kentucky) and tert butyl formate (99%, Aldrich, Milwaukee, WI).

## **Results and Discussion**

### **Water Chlorination Experiments**

Theoretically, chlorine has the potential to oxidize MTBE with the following stoichiometric equation:



A graph showing the MTBE concentration vs. time and a linear regression can be found in Figure 2. At a 95% confidence interval, the slopes of the “best fit” lines are statistically indistinguishable and differentiation between the pH 4, pH 7 and control reactors cannot be made (See Table 1). Based upon these results, no significant degradation of MTBE occurred over a 24-hour period in Nanopure water dosed with sodium hypochlorite solution.

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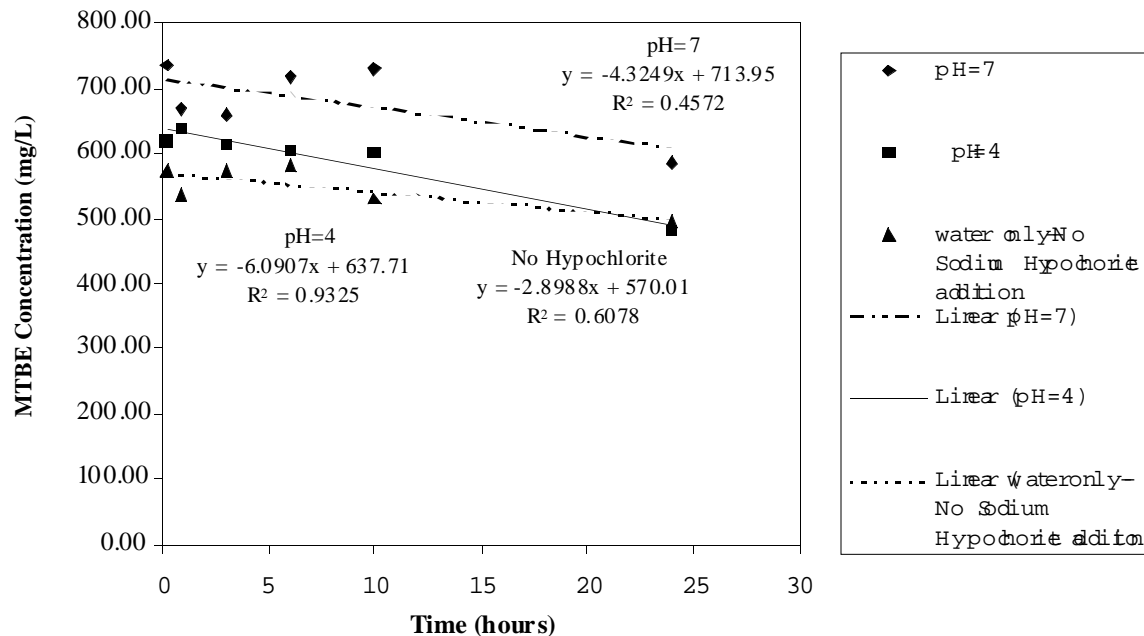


Figure 2: MTBE Concentration vs. Time

Table 1: Level of Confidence of Data in Figure 2

Reactor	Slope of Best Fit Line	Lower 95%	Upper 95%
pH=7	-4.32	-10.87	2.23
pH=4	-6.09	-9.184	-4.624
Control (No Sodium Hypochlorite)	-2.90	-6.132	0.328

### Preliminary Experiments

Prior to conducting the UV/Peroxide and UV experiments, two preliminary experiments were conducted to determine losses of MTBE to hydrogen peroxide and losses of MTBE, benzene and hydrogen peroxide to the experimental system.

### Hydrogen Peroxide Experiment

Like chlorine, hydrogen peroxide (Standard electrode potential 1.77 V) has the potential to oxidize MTBE. Figure 3 shows a graph monitoring MTBE concentration

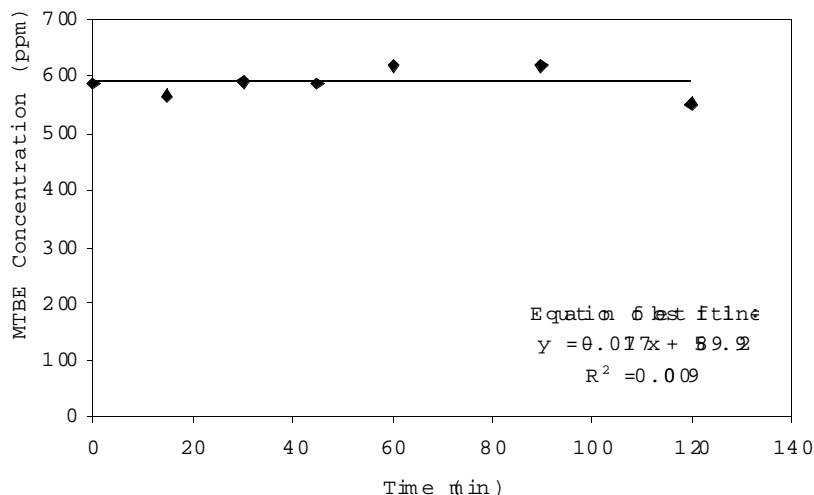


Figure 3: Removal of MTBE with time after exposure to hydrogen peroxide over a two hour period

with time when dosed with a 15:1 molar ratio of hydrogen peroxide to MTBE in a batch reactor. After a 2-hour period, no significant degradation of MTBE was observed.

#### Dark Reaction and Ultraviolet Light Experiment

In order to measure possible losses of MTBE, benzene and hydrogen peroxide to the UV reactor system shown in Figure 1, a dark reaction experiment was conducted. In this experiment, water containing approximately 10 ppm of MTBE, 500 ppb of benzene and enough hydrogen peroxide to create a 15:1 molar ratio with MTBE was pumped through the ultraviolet reactor with the ultraviolet lamp off. The next set of experiments was conducted to determine the effect of a low pressure mercury lamp emitting light primarily at the 254 nm wavelength on MTBE in the absence of hydrogen peroxide. Figure 4 compares the percent removal of MTBE from the UV experiment with that of the dark reaction experiment. The slope of the best-fit lines for the dark reaction and UV experiment at a 95% confidence interval is  $-0.054 \pm .182$  and  $-0.134 \pm 0.0497$

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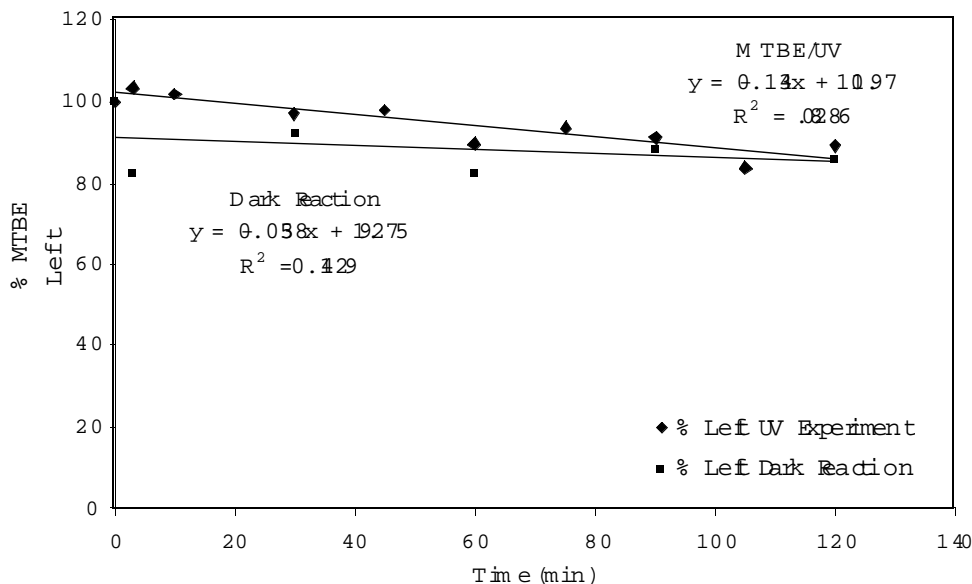


Figure 4 Percent Removal of MTBE for Ultraviolet and Dark Reaction Experiments

respectively. Based upon the results obtained in the dark reaction experiment, no conclusive measurable losses can be attributed to degradation by UV light in an aqueous solution.

MTBE has been shown to be non-reactive under exposure to UV light emitted at the 254 nm wavelength (Schuchmann and Sonntag, 1973). Wagler and Malley (1994) reported a 10-30% removal of MTBE in an aqueous solution when exposed to a low-pressure mercury lamp, however, it is unclear if the results of this experiment took into account volatile losses.

### UV/Peroxide Experiments

The last set of experiments was conducted to determine if the addition of hydrogen peroxide used in combination with a low pressure mercury lamp would be able to degrade MTBE and to identify any purgable by-products that may form from the process. In the first experiment, a 15:1 molar ratio of hydrogen peroxide to MTBE in the presence of benzene with a concentration 20 times less than MTBE to determine hydroxyl radical concentration was employed. It was found that 99.9% removal of MTBE may be achieved after 75 minutes, agreeing with results obtained by Walger and Malley (1994). By verifying GC retention times and comparing the mass spectrum obtained from the GC-MS unit with that of the mass spectrum of tert butyl formate (TBF), it has been concluded that TBF is the major degradation by-product with the formation of TBF immediately after the start of the treatment process. Figures 5 and 6 compare the mass spectra of TBF from the National Institute of Standards and Technology (NIST) database and the compound with the same retention time as TBF. It is important to note that other by-products may have been formed that are not purgable or are too volatile, to appear in the analytical results. Tert butyl alcohol was reproducibly detectable

at concentrations of approximately 158 ppb and did not appear above this level in any of the samples.

The results of the by-product identification generally agree with the results of other AOP studies for the removal of MTBE from aqueous solution. Wagler and Malley (1994) used UV/Peroxide as a treatment strategy and appeared to identify TBF as the major degradation by-product (although there is a conflict between the name and diagram of the identified byproduct). Barretto et al. used photocatalytic degradation with  $\text{TiO}_2$  as a treatment strategy and identified tert butyl formate as the primary degradation by-product and tert butyl alcohol and acetone as secondary by-products. Yeh and Novak used Fenton's reagent as a means of generating the hydroxyl radical and identified tert butyl alcohol and acetone as the two major by-products formed.

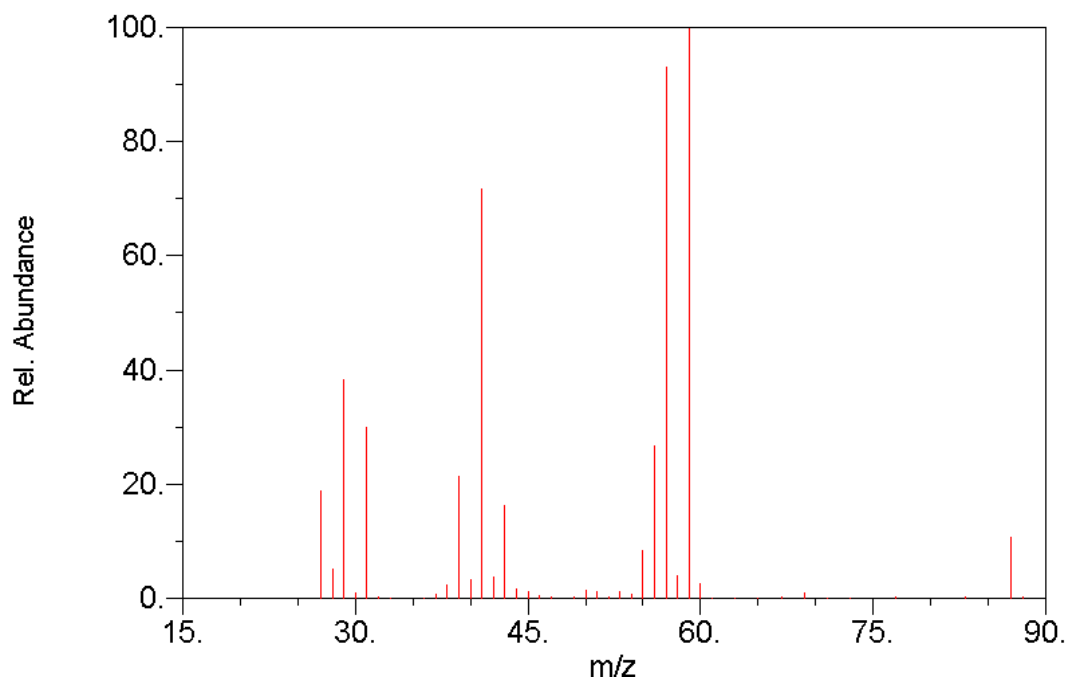


Figure 5: Mass spectrum of tert-butyl formate from NIST database

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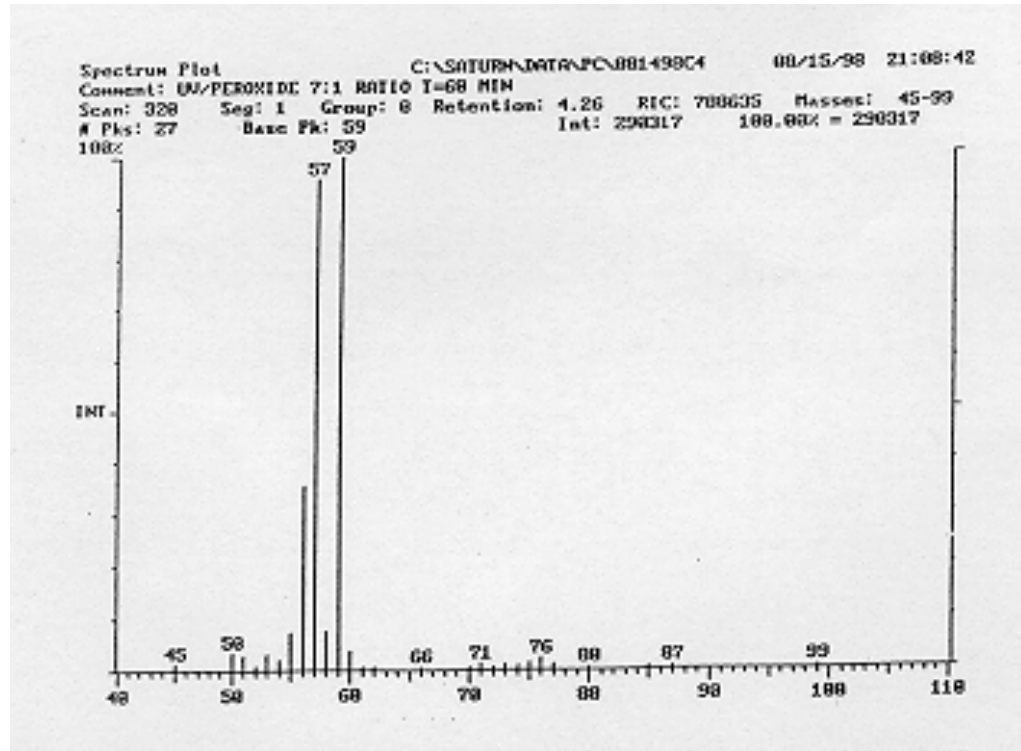


Figure 6: Mass spectrum of compound eluted at the same retention time as tert-butyl formate

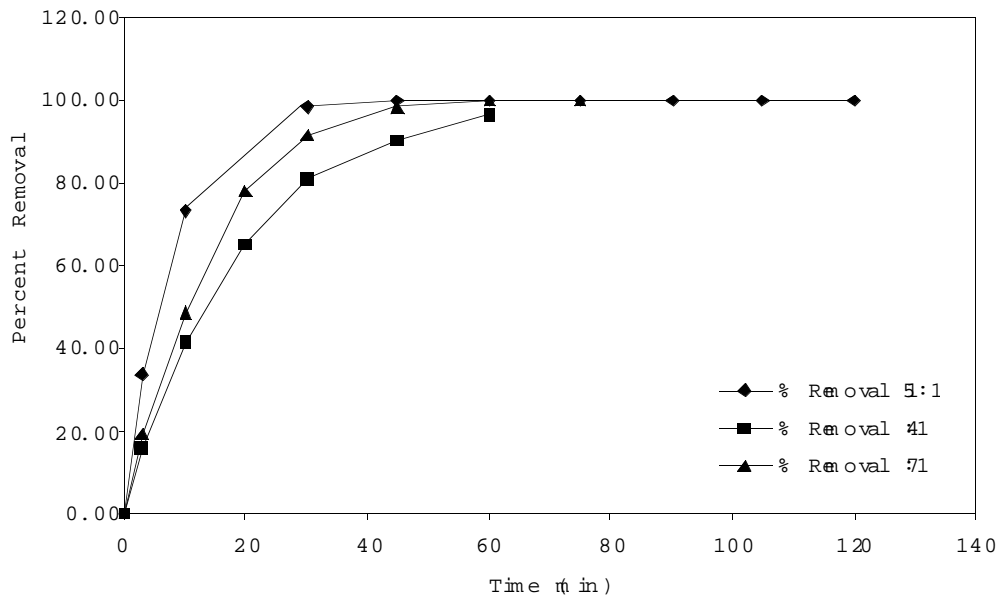


Figure 7: Percent Removal of MTBE With Time

Since the concentration of hydrogen peroxide may affect the rate of degradation of MTBE, two more experiments were conducted with hydrogen peroxide to MTBE molar ratios of 7:1 and 4:1. Figure 7 shows percent MTBE removal with time. Figures 11-13 shows the disappearance of MTBE and

appearance of TBF with time for each of the hydrogen peroxide to MTBE ratios. These figures include the modeling results described below. It was found that at a lower H<sub>2</sub>O<sub>2</sub>/MTBE ratio, MTBE removal and TBF formation became slower. In addition, a separate experiment with a 4-to-1 hydrogen peroxide to MTBE molar ratio was conducted in the absence of benzene to determine if the benzene present at a concentration of 500 ppb had any significant impact on the kinetics of MTBE degradation. The presence of benzene appeared to cause no significant impact on MTBE degradation kinetics.

### **Kinetics of MTBE Degradation and tert-butyl formate Formation**

Pseudo first order decay constants for MTBE and benzene can be found from the slopes obtained from the slopes of the linear portions of the natural logarithm of species concentration versus time (Figures 8-10). Table 2 shows the values of the pseudo first order decay constants and the associated 95% confidence intervals.

Table 2: Pseudo First Order Rate Constants for MTBE and Benzene at the 95% Confidence Interval for Various Hydrogen Peroxide to MTBE Molar Ratio

Hydrogen Peroxide to MTBE Molar Ratio	Pseudo First Rate Constant, 95% Confidence Interval			
	MTBE (min <sup>-1</sup> )		Benzene (min <sup>-1</sup> )	
15:1	0.1309	± 0.0026	0.2575	± 0.080
7:1	0.096	± 0.0058	0.2965	± 0.259
4:1	0.0545	± 0.0032	0.0978	± 0.029

Using the known second order rate constant for the formation of phenol from benzene and the hydroxyl radical of 7.8 X 10<sup>9</sup> L/mol s (Buxton et al., 1988) and the quantum yield value of 0.75 (Arakaki and Faust, 1998) a hydroxyl radical concentration can be calculated from the pseudo first order decay constant obtained for benzene using equation 1:

$$[\text{OH} \cdot] = \frac{k'_{\text{benzene}} \phi}{k_{\text{benzene}}} \quad (1)$$

Where,  $k'_{\text{benzene}}$  = Pseudo first order decay constant for benzene (L mol<sup>-1</sup>s<sup>-1</sup>)  
 $k_{\text{benzene}}$  = Second order reaction constant for the formation of phenol from benzene (s<sup>-1</sup>)  
 $\phi$  = Quantum yield for the formation of phenol from benzene

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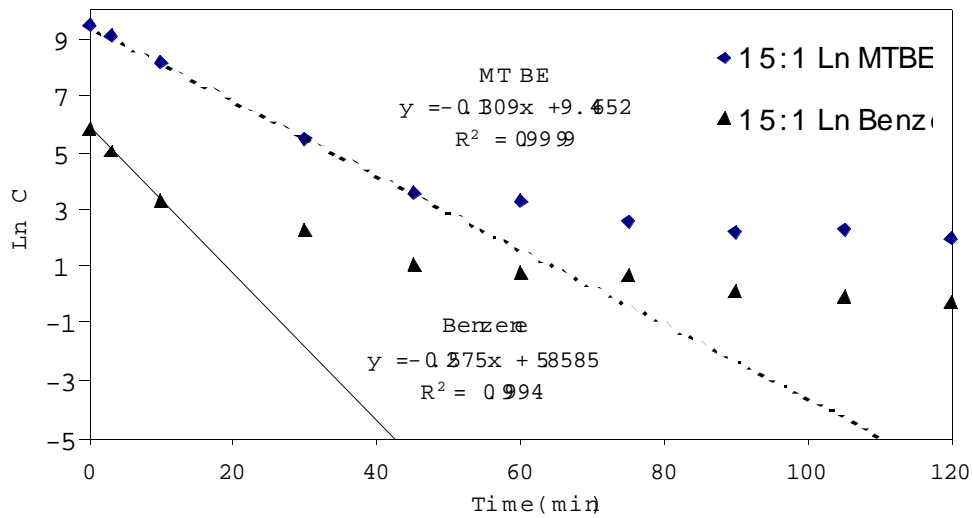


Figure 8: First Order Plot of MTBE and Benzene Concentration for 15:1 Peroxide:MTBE Ratio

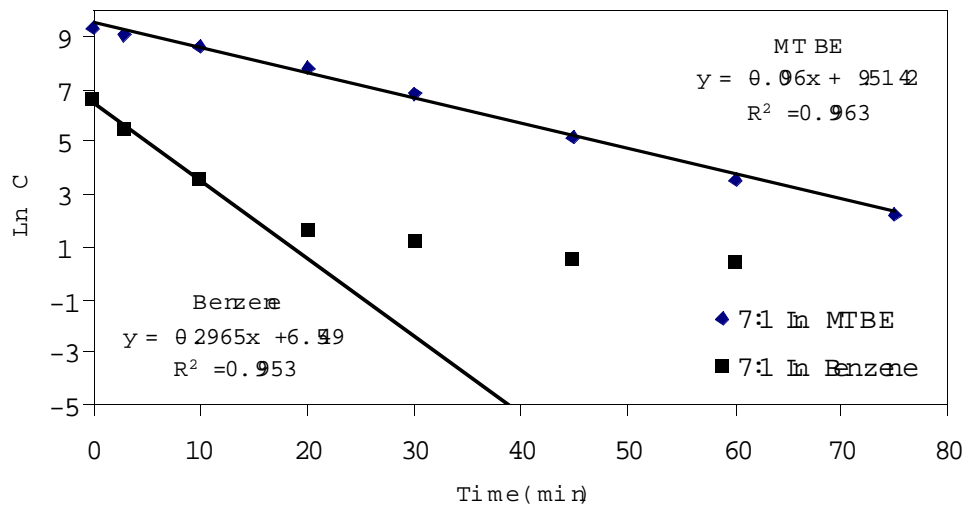


Figure 9: First Order Plot of MTBE and Benzene Concentration for 7:1 Peroxide:MTBE Ratio

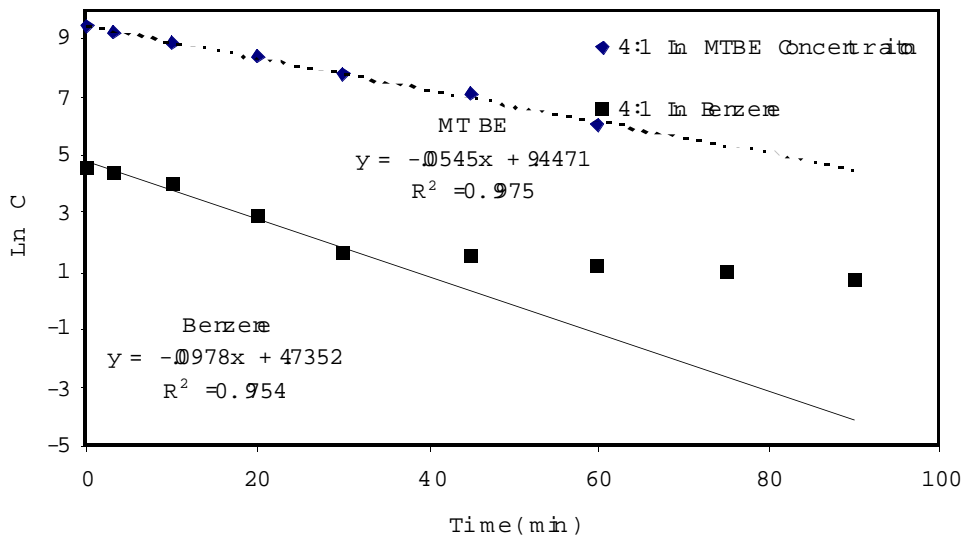


Figure D: First Order Plot of MTBE and Benzene Concentrations for 4:1 Peroxide:MTBE Ratio

Using the hydroxyl radical concentration and the pseudo first order decay constant obtained for MTBE, a second order constant for the reaction between the hydroxyl radical and MTBE can be obtained using equation 2:

$$k_{\text{MTBE}} = \frac{k'_{\text{MTBE}}}{[\cdot\text{OH}]} \quad (2)$$

Where,  $k_{\text{MTBE}}$  = Second order reaction rate constant for the MTBE and the hydroxyl radical ( $\text{L mol}^{-1} \text{s}^{-1}$ )

$k'_{\text{MTBE}}$  = Pseudo first order decay constant for MTBE ( $\text{s}^{-1}$ )

Table 3 shows the second order reaction constants obtained for MTBE and the hydroxyl radical concentration using various hydrogen peroxide ratios. It was found that the second order rate constant for MTBE degradation is  $4.82 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  with a standard deviation of  $1.28 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ . This value is in the range of the second order rate constant of  $1.6 \times 10^9$  obtained by Elbenberger (1980) for the MTBE reaction with the hydroxyl radical in aqueous solution.

Table 3: Calculated Second Order Rate Constants for MTBE Degradation In UV/Peroxide Experiments

Hydrogen Peroxide to MTBE Molar Ratio	Second Order Rate Constant ( $\text{L/mol s}$ )	Calculated $[\cdot\text{OH}]_0$ (mol/L)
15:1	$5.29 \times 10^9$	$4.12 \times 10^{-13}$
7:1	$3.37 \times 10^9$	$4.75 \times 10^{-13}$
4:1	$5.79 \times 10^9$	$1.57 \times 10^{-13}$

Using the second order decay constants for MTBE and benzene, a model was constructed to produce a yield coefficient and second order rate constant for the formation of tert butyl formate. The model was also designed to predict MTBE degradation and benzene degradation with time. MTBE degradation can be described using equation 3:

$$[\text{MTBE}]_{t+Dt} = [\text{MTBE}]_t - k_{\text{MTBE}} [\text{OH}][\text{MTBE}]_t Dt \quad (3)$$

Where,  $[\text{MTBE}]_{t+Dt}$  = MTBE concentration at time t+Dt, (mol/L)

$[\text{MTBE}]_t$  = MTBE concentration at time t, (mol/L)

$k_{\text{MTBE}}$  = Second order rate constant for MTBE (L/mol s)

$[\text{OH}]$  = Hydroxyl radical concentration calculated from equation 1 (mol/L)

Dt = time increment, seconds

Benzene degradation can be described by equation 4:

$$[\text{Benz}]_{t+Dt} = [\text{Benz}]_t - k_{\text{Benz}} [\text{OH}] [\text{Benz}]_t Dt \quad (4)$$

Where,  $[\text{Benz}]_{t+Dt}$  = Benzene concentration at time t+Dt, (mol/L)

$[\text{Benz}]_t$  = Benzene concentration at time t, (mol/L)

$k_{\text{Benz}}$  = Second order rate constant for benzene (L/mol s)

Tert butyl formate formation can be described by equation 5:

$$[\text{TBF}]_{t+Dt} = [\text{TBF}]_t + Y_{\text{TBF}} k_{\text{MTBE}} [\text{MTBE}]_t [\text{OH}] Dt - k_{\text{TBF}} [\text{TBF}]_t [\text{OH}] Dt \quad (5)$$

Where,  $[\text{TBF}]_{t+Dt}$  = tert butyl formate concentration at time t+Dt, (mol/L)

$[\text{TBF}]_t$  = tert butyl formate concentration at time t, (mol/L)

$Y_{\text{TBF}}$  = Yield coefficient for the formation of tert butyl formate from MTBE

$k_{\text{TBF}}$  = Second order reaction rate for tert butyl formate (L/mol s)

$[\text{MTBE}]_t$  = MTBE concentration at time t obtained from equation 3, (mol/L)

In order to determine the appropriate  $Y_{\text{TBF}}$  and  $k_{\text{TBF}}$  coefficients for each experiment, values for  $Y_{\text{TBF}}$  in .01 increments were matched with values for  $k_{\text{TBF}}$  in  $1 \times 10^8$  increments to determine the combination of  $Y_{\text{TBF}}$  and  $k_{\text{TBF}}$  which minimize the sum of the squared deviations between the data and the model. Table 4 shows the  $Y_{\text{TBF}}$  and  $k_{\text{TBF}}$  coefficients that best fit the data and the respective  $R^2$  values for each hydrogen peroxide to MTBE ratio. Figures 11-13 compare the model fits to the experimental data for different hydrogen peroxide to MTBE ratios. The mean yield for TBF from MTBE was calculated to be 0.27 with a standard deviation of 0.0378. The mean second order rate constant for the formation of TBF was  $1.19 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  with a standard deviation of  $4.47 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ .

### **Lamp Intensity**

The intensity of the lamp used in this experiment was measured by hydrogen peroxide actinometry as described by Nicole et al. (1990). According to Nicole, the incident photonic flux can be calculated from equation 6:

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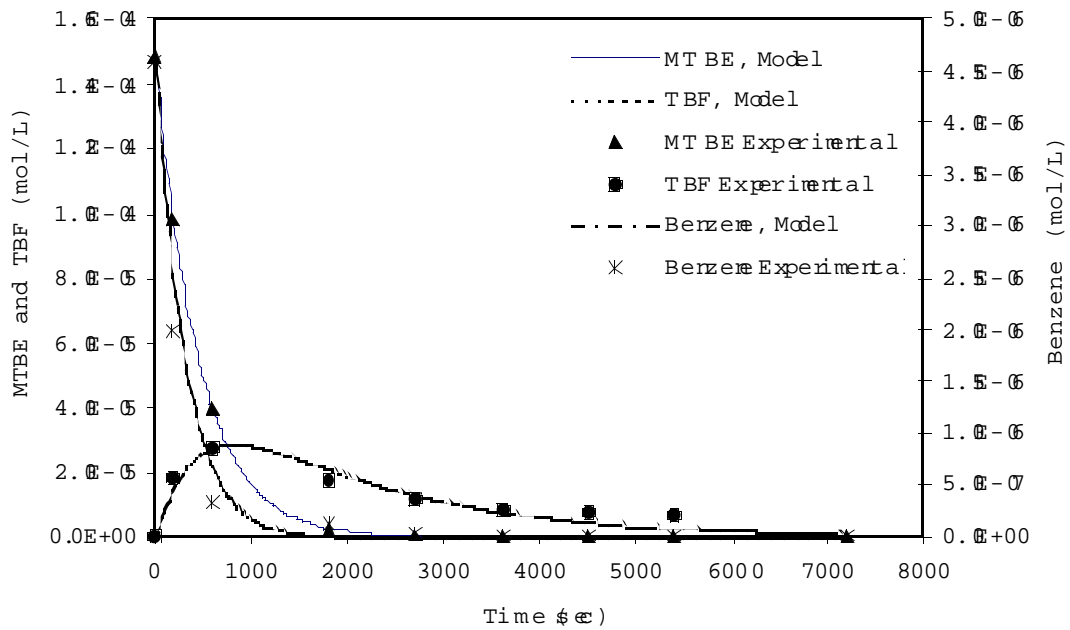


Figure 1: Comparison of Kinetic Model and Experimental Data for MTBE, TBF and Benzene, 15:1 hydrogen peroxide to MTBE ratio

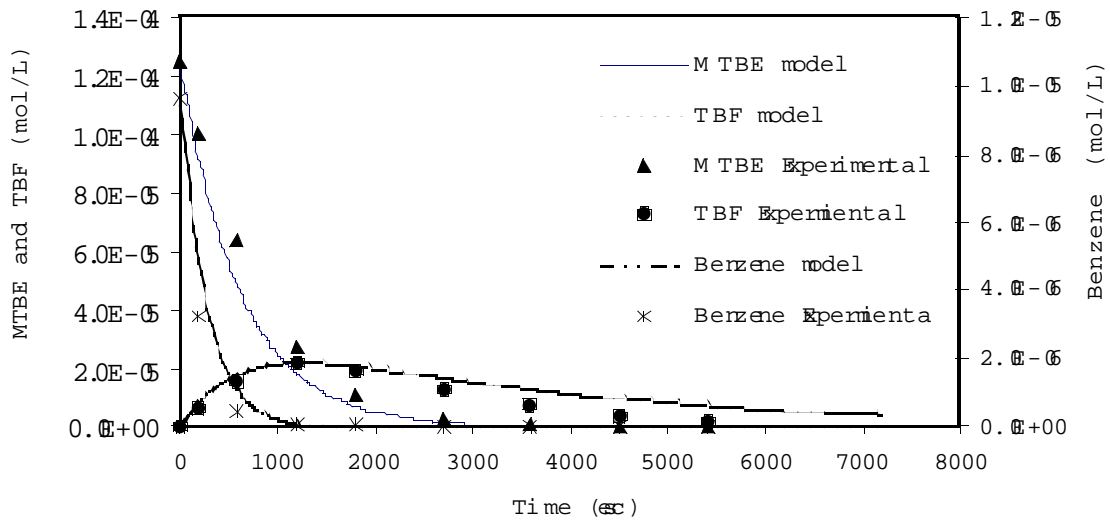


Figure 2: Comparison of Kinetic Model and Experimental Data for MTBE, TBF and Benzene, 7:1 hydrogen peroxide to MTBE Ratio

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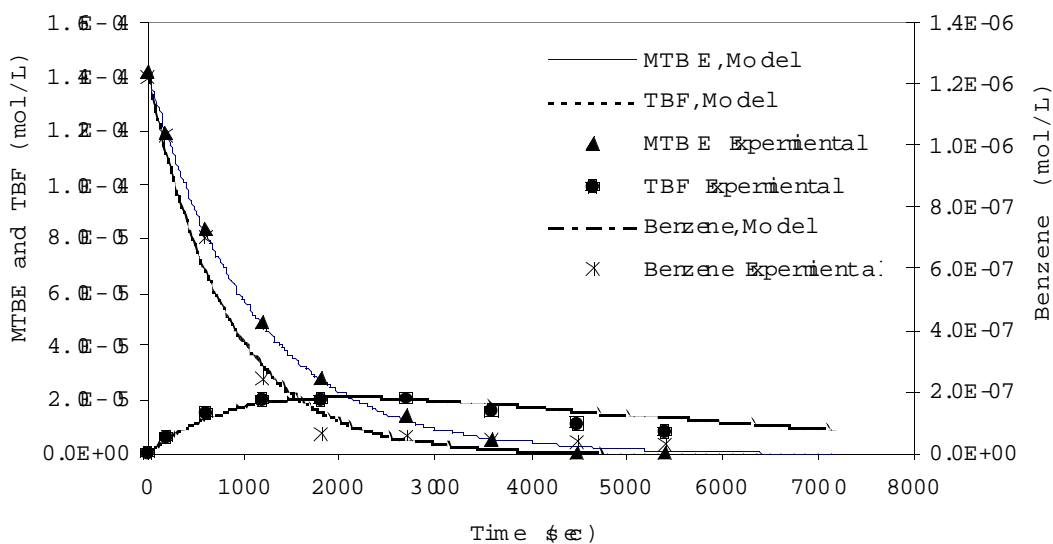


Figure B: Comparison of Kinetic Model and Experimental Data for MTBE, TBF and Benzene, 4:1 hydrogen peroxide to MTBE Ratio

Table 4: Second order rate constant for the reaction of tert butyl formate with the hydroxyl radical and yield coefficient for tert butyl formate obtained from model for various peroxide to MTBE Ratios

Peroxide to MTBE ratio	Second order rate constant (L mol <sup>-1</sup> s <sup>-1</sup> )	Yield	R <sup>2</sup> value for fit of model with data
15:1	1.4 × 10 <sup>9</sup>	0.31	0.89825
7:1	6.8 × 10 <sup>8</sup>	0.25	0.97429
4:1	1.5 × 10 <sup>9</sup>	0.24	0.99323

$$P_o = \frac{kV}{2.3\epsilon \phi I} \quad (6)$$

Where,  $k$  = Pseudo first order reaction constant for hydrogen peroxide degradation (s<sup>-1</sup>)

$\epsilon$  = Molar extinction coefficient at wavelength  $\lambda$  (at 254 nm,  $\epsilon = 19.6 \text{ M}^{-1} \text{ cm}^{-1}$ , Baxendale and Wilson, 1957)

$l$  = Optical path length (2 cm)

$f$  = Quantum yield of photolysis of compound C at wavelength  $\lambda=254$  nm (Quantum yield for hydrogen peroxide, 1.0, Baxendale and Wilson, 1957).

$P_o$  = Incident photonic flux, (Einstein s<sup>-1</sup>)

$r$  = Reflection coefficient (1.75 for stainless steel, Nicole et. al, 1990)

$V$  = Total reactor volume (6.45 L).

Figure 14 shows the pseudo first order plots of the hydrogen peroxide degradation. Using the pseudo first order decay constants, the mean intensity of the light emitted from the lamp was found to be  $5.31 \times 10^{-6}$  Einstein/s with a standard deviation of  $1.12 \times 10^{-6}$  Einstein/s.

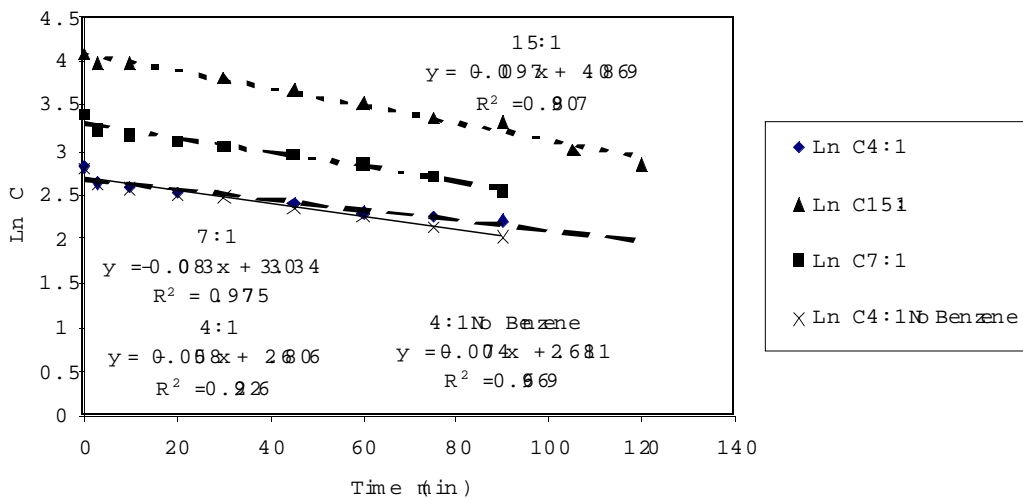


Figure 14 FirstOrder Plot of Hydrogen Peroxide Concentration

## Opportunities for Further Research

The experiments conducted for the UV and UV/Peroxide treatment involved using a low-pressure mercury lamp as the primary UV source. Low-pressure mercury lamps emit light primarily at the 253.7 nm wavelength. Medium-pressure ultraviolet lamps have become more developed in recent years and emit light at a wider range of wavelengths, both at wavelengths above and below 253.7 nm. The absorptivity of hydrogen peroxide at 220 nm is about five times the absorptivity at 254 nm (Carey, 1990). Using a medium pressure lamp may increase the efficiency of the UV/Peroxide process and may potentially be able to photolyse MTBE in dilute aqueous solutions. Further study of UV/Peroxide treatment with various medium pressure ultraviolet light may be conducted to further improve the efficiency of the UV/Peroxide treatment process in degrading MTBE.

The presence of suspended solids, humic substances and bicarbonate in the background water being tested may affect the concentration of the hydroxyl radical formed from the treatment process. Further experimental studies may be conducted to determine how the presence of one or more of these components may affect the outcome of the study conducted here.

Little is presently known about the toxicity of tert butyl formate in water. Further investigation into the toxicity of tert butyl formate may be

conducted to determine if UV/Peroxide treatment for the removal of MTBE is a feasible water treatment alternative.

## **Conclusions**

1. Chlorination of water samples with sodium hypochlorite at pH 4 or pH 7 caused no measurable loss of MTBE over a 24-hour period.
2. Ultraviolet disinfection using a low-pressure mercury lamp emitting light primarily at the 254 nm wavelength caused no conclusive measurable degradation of MTBE.
3. UV/Peroxide water treatment has the potential to remove 99.9% of MTBE in water containing an initial concentration of 10 ppm.
4. The major by-product identified from the degradation of MTBE resulting from UV/Peroxide treatment is tert-butyl formate.
5. The second order rate constant for the degradation of MTBE from the hydroxyl radical during the UV/Peroxide treatment process was found to be  $4.82 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  with a standard deviation of  $1.28 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ .
6. The yield for the formation of tert-butyl formate from the reaction of MTBE and the hydroxyl radical from MTBE was calculated to be 0.27 with a standard deviation of 0.0378.
7. The mean second order rate constant for the reaction of tert-butyl formate with the hydroxyl radical during the UV/Peroxide treatment process was found to be  $1.19 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  with a standard deviation of  $4.47 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ .

## **References**

Arakaki, Takemitsu and Faust, Bruce. "Sources, sinks, and mechanisms of hydroxyl radical (OH) photoproduction and consumption in authentic acidic continental cloud waters from Whiteface Mountain, New York: The role of the Fe(r) (r = I,II) photochemical cycle." Journal of Geophysical Research. Volume 103, No. D3, pp3487-3504, 1998.

Baxendale, J.H. and Wilson, J.A. "The Photolysis of Hydrogen Peroxide at High Light Intensities." Trans. Faraday Society. Vol. 53: 344-356.

Barreto, Reynolds D, Kimberly A Gray and Krista Anders. "Photocatalytic Degradation of Methyl tert-Butyl Ether in TiO<sub>2</sub> Slurries: A Proposed Reaction Scheme." Water Research. Vol. 29, No. 5, pp1243-1248, 1995.

Beltran, F. J., M. Gonzales, F.J. Riveris, and N. Jaramillo. "Application of Photochemical Reactor Models to UV Irradiation of Trichloroethylene in Water." Chemosphere. Vol 31, No. 3, pp 2873-2885, 1995.

*Reactivity & By-Products of MTBE Resulting from Water Treatment Processes*

Book, Steven, A. "MTBE in California Drinking Water." Proceedings from MTBE: A Workshop to Explore Needs for Drinking Water Treatment and Research, Sacramento, California, 30 Sept-1 Oct. 1997.

Brown, Anthony, J.S. Deviring, M.K. Davis, T.E. Browne and R.A.Rogreguez. "A Review of Potential Technologies for the Treatment of Methyl tertiary Butyl Ether (MTBE) in Drinking Water" Proceedings from MTBE: A Workshop to Explore Needs for Drinking Water Treatment and Research, Sacramento, California, 30 Sept-1 Oct. 1997.

Buxton George, V., Greenstock, Clive L., W. Phillip Helman and Alberta B. Ross. "Critical Review of Rate Constants for Reactions with Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals (OH/O) in Aqueous Solutions." Journal Physical Chemical Reference Data. Vol. 17 No. 2, 1988.

California Department of Health Services. "Drinking Water Standards for MTBE." 24 July 1998.  
<http://www.dhs.cahwnet.gov/ps/ddwem/chemicals/mtbe/mtbestand.htm>

California Environmental Protection Agency. "MTBE methyl tertiary butyl ether: A Briefing Paper". 30 March 1998 update.

California Environmental Protection Air Resources Board. "Fact Sheet 3: Comparison of Federal and California Reformulated Gasoline." March 1996.

California Environmental Protection Air Resources Board. "Fact Sheet: Reduced Benzene Levels Since Introduction of Cleaner Burning Gasoline." 18 July 1996.

California Environmental Protection Air Resources Board. "Questions and Answers about Cleaner Burning Gasoline." March 1996.

Carey, J.H. "An Introduction to Advance Oxidation Processes (AOP) for Destruction of Organics in Wastewater." A Symposium on Advanced Oxidation Process for of Contaminated Water and Air, Proceedings. Toronto, Canada. 4 June 1990- 5 June 1990.

CH2M Hill Engineers. "Proceedings from the MTBE Workshop to Explore Needs for Drinking Water Treatment Research." Hyatt Regency Hotel, Sacramento, California. 30 Sept. 1997-1 Oct. 1997.

Clarke, N. and Knowles, G. "High Purity Water using H<sub>2</sub>O<sub>2</sub> and UV Radiation." Effluent and Water Treatment Journal. September 1982: 335-341.

*Reactivity & By-Products of MTBE Resulting from Water Treatment Processes*

Cooney, Catherine. "California Struggles with Presence of MTBE in Public Drinking Water Wells." Environmental Science and Technology. Vol. 31:269A. 1997.

Delzer, Gregory C. John S. Zogorski, Thomas J. Lopes and Robin L. Bosshart. "Occurrence of the gasoline Oxygenate MTBE and BTEX Compounds in Urban Stormwater in the United States, 1991-95." Water Resources Investigation Report 96-4145. 1996.

Eibenberger, J. "Pulse Radiolytic Investigations Concerning the Formation of Oxidation of Organic Radical in Aqueous Solution." PhD Thesis. Vienna University, Austria, 1980.

Eisenburg, George M. "Colorimetric Determination of Hydrogen Peroxide." Industrial and Engineering Chemistry, Analytical Edition. Vol. 15. pp 327-328: 1943.

Glaze, William, Joon-Wan Kang and Douglas Chapin. "The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide, and Ultraviolet Radiation." Ozone Science and Engineering. Vol 19: 335-352. 1987.

Halman, Martin M. Photodegradation of Water Pollutants. CRC Press, 1995, pp 1-2, 253.

Horspool, William and Diego Armesto. Organic Photochemistry: A Comprehensive Treatment. Prentice Hall: 1992.

Leclair, Vincent. "MTBE Water Contamination Issues Raises Health Concerns, Research Questions." Environmental Science and Technology. Vol. 31, No. 4: 176-177, 1997.

Leitner, N Karpel Vel et al. "Oxidation of Methyl tert Butyl Ether (MTBE) and Ethyl tert-Butyl Ether (ETBE) by Ozone and Combined Ozone/Hydrogen Peroxide." Ozone Science and Engineering. Vol. 16: 41-54, 1994.

Lopez, A. G. Maweolo, R. Foldenyl, and R. Passino. "Disinfection By Product Formation During Hypochlorination of Isoproturon Contaminated Groundwater." Water Science Technology. Vol. 34, No 7-8: 351-358, 1996.

Malcom Pirnie. "Technical Memorandum: Estimates of Annual Costs to Remove MTBE from Water for Potable Water Uses." Oxygenated Fuels Association, 1997.

*Reactivity & By-Products of MTBE Resulting from Water Treatment Processes*

Mason, Yael, Ehud Choshen and Chaim Rav-Acha. "Carbamate Insecticides: Removal From Water by Chlorination and Ozonation." Water Research. Vol. 24, No. 1: 11-21, 1990.

Miles, Carl, J. "Degradation of Aldicarb, Aldicarb Sulfoxide and Aldicarb Sulfane in Chlorinated Water." Environmental Science Technology. Vol. 25: 1774-1779, 1991.

Mosteller, D.C. K.F. Rearden, A.W. Bourquin, B.Desilets, D. Dumount, R. Hines, and S. Kilkenny. "Biotreatment of MTBE Contaminated Groundwater". (Abstract). American Chemical Society Preprints of Papers. April 13-17, 1997. Vol. 37 No. 1.

Nicole, I., J. De Laat, M. Dore, J.P. Duguet, C Bonnel. "Use of U.V. Radiation in Water Treatment: Measurement of Photonic Flux by Hydrogen Peroxide Actinometry." Water Research. Vol. 24, No. 2 pp. 157-158, 1990.

NIST Chemical Database. <http://webbook.nist.gov>

Novak, John T and Yeh, Carol K. "The Effect of Hydrogen Peroxide on the Degradation of Methyl and Ethyl tert-Butyl Ether in Soils." Water Environment Research. Vol. 67, No. 5: 828-834, 1995.

Oxygenated Fuels Association. Benefits of a National Oxygenated Fuels Policy. April 1993.

Owen, E.D. "Principles of Photochemical Reactions in Aqueous Solution." Organic Compounds in Aquatic Environments. Dekker Publishers, 1979.

Sawyer, Clair N. Perry L. McCarty and Gene F. Parkin. Chemistry for Environmental Engineers, 4<sup>th</sup> Edition. McGraw-Hill, 1994. Pp. 494-496.

Schuchmann H. P. and Sonntag C.V. "The UV Photolysis (185 nm) of Liquid t-Butyl Methyl Ether" Tetrahedron. Vol. 29: 1811-1818, 1973.

Squillace, Paul J., James F. Pankow, Nic E. Korte and John S. Zogorski "Environmental Behavior and Fate of Methyl tert-Butyl Ether (MTBE)." USGS Fact Sheet FS-203-96, 1996.

Squillace, Paul J., James F. Pankow, Nic E. Korte and John S. Zogorski "Review of Environmental Behavior and Fate of Methyl tert Butyl Ether." Environmental Toxicology and Chemistry. Vol. 16, No.9 p 1836-1844.

Stern and Kneiss, J.J. "Methyl Tertiary-butyl Ether (MTBE) Use As An Oxygenate in Fuels." Journal of Applied Toxicology.: 17 (S1-S2) 1997.

*Reactivity & By-Products of MTBE Resulting from Water Treatment Processes*

Sundstrom, D.W., B.A. Wier and H.E. Klei. "Destruction of Benzene by Ultraviolet light-Catalyzed Oxidation with Hydrogen Peroxide." Hazardous Waste and Hazardous Materials. Vol. 14, No. 2, 1987.

Stefan, Mihaela, I. Aitken R. Hoy and James R. Bolton. "Kinetics and Mechanism of the Degradation and Mineralization of Acetone in Dilute Aqueous Solution Sensitized by the UV Photolysis of Hydrogen Peroxide". Environmental Science and Technology. Vol. 30, No. 7, 1996.

Truong K.N. and Parmele, Charles. "Cost Effective Treatment Technologies for Reducing the Concentrations of Methyl tertiary Butyl Ether and Methanol in Groundwater". In Calabrese E.J. and Kostecki, P.T., eds. Hydrocarbon Contaminated Soils in Groundwater, Vol. 2. Lewis Publishers, Chelsea Michigan: pp. 461-486.

United States Environmental Protection Agency Office of Water. Provisional Health and Consumer Acceptability Advisory for Methyl tertiary Butyl Ether (MTBE). Nov. 1997.

United States Environmental Protection Agency, Office of Underground Storage Tanks. "State By State MTBE Map." 27 April 1998. <http://www.epa.gov/OUST/mtbe/mtbemap4sld001.htm>

Venkatadri, Rajagopalan and Peters, Robert W. "Chemical Oxidation Technologies: UV Light/Hydrogen Peroxide, Fenton's Reagent, Titanium Dioxide Assisted Photocatalysis." Hazardous Waste and Hazardous Materials. Vol. 10, No. 2:107-149, 1993.

Wagler, Jennifer and Malley, James P. "The Removal of Methyl tertiary butyl Ether from a Model Groundwater using UV/Peroxide Oxidation." Journal NEWWA. September 1994.

Weir, Barbara A. and Sundstrum, Donald W. "Destruction of Trichloroethylene by UV. Light Catalyzed Oxidation with Hydrogen Peroxide." Chemosphere. Vol. 27, No. 7 p 1279-1291, 1993.

White, Geo C. Handbook of Chlorination an Alternative Disinfectants. 3<sup>rd</sup> Edition. Van Nostrand Reinhold. New York, 1992.

Wilson, Richard D. Testimony of Richard D. Wilson, Acting Assistant Administrator, Office of Air and Radiation, U.S. Environmental Protection Agency, Before the Subcommittee on Health and Environment Committee on Commerce, U.S. House of Representatives., 22 April 1998.

*Reactivity & By-Products of MTBE Resulting from Water Treatment Processes*

Zogroski, John S. et al. Final Report: Fuel Oxygenates and Water Quality: Current Understanding of Sources, Occurrence in Natural Waters, Environmental Behavior, Fate and Significance. Prepared for the Interagency Oxygenated Fuel Assessment. October 1996.