

# Kinetics and products of reactions of MTBE with ozone and ozone/hydrogen peroxide in water

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## Abstract

Methyl-*t*-butyl-ether (MTBE) has become a prevalent groundwater pollutant due to its high volume use as a nationwide gasoline additive. Given its physicochemical properties, it requires new treatment approaches. Both aqueous O<sub>3</sub> and a combination of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, which gives •OH, can remove MTBE from water, making use of O<sub>3</sub> a viable technology for remediation of groundwater from fuel contaminated sites. Rate constants and temperature dependencies for reactions of MTBE with O<sub>3</sub> or with •OH at pH 7.2, in a range of 21–45°C (294–318 K) were measured. The second-order rate constant for reaction of MTBE with O<sub>3</sub> is  $1.4 \times 10^{18} \exp(-95.4/RT)$  (M<sup>-1</sup> s<sup>-1</sup>), and for reaction of MTBE with •OH produced by the combination of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> is  $8.0 \times 10^9 \exp(-4.6/RT)$  (M<sup>-1</sup> s<sup>-1</sup>), with the activation energy (kJ mol<sup>-1</sup>) in both cases. At 25°C, this corresponds to a rate constant of 27 M<sup>-1</sup> s<sup>-1</sup> for ozone alone, and  $1.2 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> for O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>. The concentration of •OH was determined using benzene trapping. Products of reactions of O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> with MTBE, including *t*-butyl-formate (TBF), *t*-butyl alcohol (TBA), methyl acetate, and acetone, were determined after oxidant depletion. A reaction pathway for mineralization of MTBE was also explored. Under continuously stirred flow reactor (CSTR) conditions, addition of H<sub>2</sub>O<sub>2</sub> markedly increases the rate and degree of degradation of MTBE by O<sub>3</sub>. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** MTBE; Ozone; Reaction pathway; Hydroxyl radical; Kinetics; Byproducts; TBA; TBF

## 1. Introduction

Methyl-*t*-butyl-ether (MTBE) has been used as a gasoline oxygenate in the US for over two decades. It eliminates the need for leaded gasoline and is the most common fuel oxy-

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### Nomenclature

$C_{Bf}$	concentration of benzene in outlet ( $\text{mol l}^{-1}$ )
$C_{Bo}$	concentration of benzene in inlet ( $\text{mol l}^{-1}$ )
$C_{mf}$	concentration of MTBE in outlet ( $\text{mol l}^{-1}$ )
$C_{mo}$	concentration of MTBE in inlet ( $\text{mol l}^{-1}$ )
$C_{OH}$	concentration of $\bullet\text{OH}$ ( $\text{mol l}^{-1}$ )
$C_{O_3}$	outlet concentration of $\text{O}_3$ ( $\text{mol l}^{-1}$ )
$k_1$	rate constant for reaction of MTBE with $\text{O}_3$ ( $\text{M}^{-1} \text{s}^{-1}$ )
$k_2$	rate constant for reaction of MTBE with $\bullet\text{OH}$ ( $\text{M}^{-1} \text{s}^{-1}$ )
$k_3$	rate constant for reaction of benzene and $\bullet\text{OH}$ ( $\text{M}^{-1} \text{s}^{-1}$ )
$R_B$	global rate of disappearance of benzene ( $\text{M s}^{-1}$ )
$R_m$	global rate of disappearance of MTBE ( $\text{M s}^{-1}$ )
$v_f$	volumetric flow rate of outlet stream ( $\text{ml s}^{-1}$ )
$v_o$	volumetric flow rate of inlet stream ( $\text{ml s}^{-1}$ )
$V_r$	volume of reactor (l)

genate used to reduce air pollution and increase octane ratings [1]. MTBE may comprise up to 15% by volume of gasoline, and it became the second highest volume chemical produced in the US in 1997 [2]. The high volume use as well as the chemical characteristics of this gasoline additive have resulted in contaminated water supplies around the world where MTBE is used as a gasoline additive.

MTBE is very water soluble, making its movement in the environment almost as fast as groundwater, with practically no retardation due to sorption on soil particles. Once released, MTBE is quite persistent due to its molecular structure, i.e. the presence of the *t*-butyl group, which inhibits environmental degradation under normal conditions and strongly inhibits natural biodegradation [3,4]. This results in widespread contamination when MTBE escapes into the environment. A major concern arises from leaking underground fuel tanks that contaminate groundwater at much higher concentrations than surface sources. Contamination of lakes and rivers by two-stroke gasoline engines is also a problem [5]. MTBE uncontained in the environment inevitably results in groundwater pollution, and it was the second most frequently detected chemical in samples of shallow ambient groundwater from the US Geological Survey's National Water Quality Assessment Program [6].

Although, recent progress in in situ treatment has been reported, there are many circumstances where aboveground treatment is required [7]. Some methods simply separate MTBE from water, such as air stripping or GAC adsorption, while others involve oxidation to harmless products [8]. Although, separation techniques may be less expensive than oxidation, they require an additional step for the treatment or disposal of the pollutant.

Ozonation has been shown to be a viable option in the treatment of waste and drinking water. With the development of large scale ozone ( $\text{O}_3$ ) generators and lower operating costs, there has been increasing interest in using  $\text{O}_3$  to remove compounds that are difficult or too expensive to remove by other methods. In some cases,  $\text{O}_3$  treatment alone adequately degrades contaminants to meet water quality standards [9].

O<sub>3</sub> may either react directly with organic compounds, or decompose generating more reactive species, such as the hydroxyl radical (•OH), which control subsequent oxidation reactions [10]. •OH is one of the most important oxidants due to its high reactivity and unselectivity towards organic compounds. The addition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to O<sub>3</sub> in water generates •OH, thereby increasing the oxidative capabilities of the system. Appendix A presents O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> chemistry that is applicable to this study. The rate of decomposition of O<sub>3</sub> in water,  $R_{O_3}$  (mol l<sup>-1</sup> min<sup>-1</sup>) can be calculated using the rate equation derived by Sotelo et al. [20]:

$$R_{O_3} = 3.26 \times 10^5 \exp\left(\frac{-4964}{T}\right) [O_3] + 5.69 \times 10^{18} \exp\left(\frac{-10130}{T}\right) [OH^-]^{0.5} [O_3]^{1.5} \quad (1)$$

There are several recent studies of MTBE oxidation using ultrasonic irradiation in the presence of ozone, UV/H<sub>2</sub>O<sub>2</sub>, or simply ozone [11–13]. Optimally, O<sub>3</sub> oxidation should completely mineralize MTBE to CO<sub>2</sub> and H<sub>2</sub>O. Byproducts from incomplete oxidation of MTBE during ozonation are of great concern because they may be as toxic, or more, than MTBE. *t*-Butyl-formate (TBF) and *t*-butyl alcohol (TBA) are major initial products in many oxidative reactions of MTBE [4,8,13]. From recent toxicologic studies, TBF and TBA may pose greater health hazards than MTBE [14]. Therefore, it is important to identify the various products of reactions between MTBE and O<sub>3</sub> or O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, under conditions of incomplete oxidation.

This study focuses on the reaction of MTBE with O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> after oxidant depletion, as well as the kinetics of MTBE oxidation and the intermediate products formed from reaction, in order to better understand the oxidation process for treatment of MTBE contaminated water.

## 2. Experimental methods

### 2.1. Oxidation kinetics

To determine the order of the reaction between MTBE and ozone, a stirred, 2000 ml batch reactor was used at a constant temperature. MTBE or ozone was monitored at various times with the other reactant in large excess. The reaction rates, at various initial concentrations of either MTBE or ozone, were extrapolated to zero time to obtain the reaction order with respect to each reactant. Initial concentrations for MTBE ranged from 0.34 to 1.2 ppm (0.0035–0.014 mM), and initial ozone concentrations ranged from 6.0 to 12.1 ppm (0.13–0.25 mM). For both sets of experiments, ozone was bubbled into a buffered solution in the batch reactor until equilibrium conditions were attained, and then MTBE was quickly injected and stirred continuously. Five to eight sets of samples were taken in timed intervals of 10 s for MTBE and 30 s for ozone and analyzed immediately.

To determine the rate of reaction, kinetic studies were carried out by using a 1000 ml continuous flow stirred reactor (CFSR) system. Inlet streams of aqueous MTBE and O<sub>3</sub>

saturated water were pressure fed into the reactor. The O<sub>3</sub> stream used the pressure from the O<sub>3</sub> generator and the MTBE solution reservoir was pressurized with nitrogen, and flow rates of the inlet streams were controlled with calibrated rotometers. The flow rate was 0.3 ml s<sup>-1</sup> for each reactant solution. Experiments with added H<sub>2</sub>O<sub>2</sub> involved a reference reactant, benzene, in order to quantify •OH. When H<sub>2</sub>O<sub>2</sub> was added, flow rates were increased to 1.5 ml s<sup>-1</sup>. H<sub>2</sub>O<sub>2</sub> was added to the flask containing MTBE and benzene, where previous experiments showed that H<sub>2</sub>O<sub>2</sub> by itself does not react with MTBE or benzene at the concentrations and temperatures used for this study. Other studies indicate similar results [4,13]. The reactor was placed in a constant temperature bath for temperature control, with experiments performed in a range of 18–50°C. At steady state, inlet and outlet samples were withdrawn by using 20 ml syringes, and the samples were analyzed for the organic reactants and products and for O<sub>3</sub>. Samples were analyzed immediately after being withdrawn from the reactor, or within a 30 min time period where no change in concentration was observed. Inlet O<sub>3</sub> concentrations in aqueous solution ranged from 6.1 to 6.7 ppm (0.13–0.14 mM). MTBE concentrations ranged from 8.7 to 11.8 ppm (0.10–0.13 mM) and benzene concentrations were in the range from 7.5 to 11.1 ppm (0.10–0.14 mM). Reaction conditions were designed so that there was residual MTBE and benzene in the outlet.

## 2.2. Product formation

Product studies were conducted batchwise in 40 ml amber vials with known volumes and concentrations of organic substrates (MTBE, TBF, or TBA in water). A known amount of aqueous O<sub>3</sub>, and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> when applicable, was added to the vial and allowed to react until there were no further reaction. This was indicated by no change in the substrate or products concentrations over time. Concentrations of unreacted substrate and identifiable products were then measured in a gas chromatograph/mass spectrometer (GC/MS), as explained in more detail below. Initial O<sub>3</sub> concentrations in aqueous solution ranged from 4.8 to 6.0 ppm (0.10–0.11 mM). MTBE, TBF, TBA, and acetone concentrations initially ranged from 7.4 to 14.5 ppm (0.08–0.20 mM). In all batch reactions, O<sub>3</sub> was the limiting reactant with residual unreacted organic compounds. All reactions were at room temperature, 22–24°C.

MTBE (Sigma–Aldrich), TBF (Aldrich), TBA (Aldrich), methyl acetate (Aldrich), acetone (Fisher), and benzene (Fisher) at purities >99% were used. H<sub>2</sub>O<sub>2</sub> (30%) (Fisher) was diluted as necessary. A mole ratio of approximately 0.5–0.6 of H<sub>2</sub>O<sub>2</sub> to O<sub>3</sub> was chosen on the basis of the stoichiometry of their reaction [15], but some kinetic experiments were repeated with a higher mole ratio of approximately 1. All aqueous solutions were prepared with Milli-Q water (Barnstead), buffered to pH 7.2, which is in the generally accepted range for wastewater treatment [16]. Potassium phosphate buffer (Fisher) at 30 mM was used for all solutions. The O<sub>3</sub> solutions were obtained by sparging the oxygen/O<sub>3</sub> gas mixture from a Welsbach O<sub>3</sub> Generator (Model T-408) into water. The indigo dye method [17] was used to measure the O<sub>3</sub> concentration, with absorbance of unreacted dye measured in a spectrophotometer (Spectronic Instruments).

A Hewlett-Packard 5890 gas chromatograph equipped with a Hewlett-Packard 5970 mass selective detector was used to qualitatively and quantitatively analyze reactants and products. A solid-phase microextraction (SPME) fiber was used to extract organic components from the aqueous reaction mixture and they were then thermally desorbed from the fiber in the

injection block of the GC, kept at 250°C [18]. A 65  $\mu\text{m}$  polydimethylsiloxane/divinylbenzene SPME fiber was used for most of the analyses and reproducibly and quantifiably extracted MTBE, benzene, TBF, TBA, acetone ( $\text{Me}_2\text{CO}$ ), and methyl acetate ( $\text{MeOAc}$ ). Concentrations for all organic compounds were based on calibration standards which were carried out at the same pH and temperature as the reaction conditions. Formic acid and acetic acid were detectable by using this fiber, but the extraction was not reproducible. The 100  $\mu\text{m}$  polydimethylsiloxane SPME fiber gave a higher extraction of MTBE, but did not extract the more soluble organic compounds and therefore was not generally used. For both fibers, an exposure time of 2 min with stirring and a desorption time of 1 min were used. The fiber was injected into a VOCOL (Supelco) capillary column (30 m  $\times$  0.25 mm  $\times$  1.5  $\mu\text{m}$ ) with a temperature ramp programmed to 100°C for 3 min and increased 20°C  $\text{min}^{-1}$  to 150°C. All analyses were made in duplicate with a reproducibility of  $\pm 10\%$ .

### 3. Results

#### 3.1. Kinetic studies

The initial rates of reaction of aqueous  $\text{O}_3$  and MTBE show that reactions are first order with respect to  $\text{O}_3$  and MTBE individually; i.e. second-order overall. Mechanistically, this is most likely due to the activating effect of  $\text{O}_3$  attack on methoxy hydrogen [19]. However, decomposition products of aqueous  $\text{O}_3$ , namely  $\bullet\text{OH}$ , may react with MTBE or intermediates, and in some cases may be the predominant oxidant during oxidation by  $\text{O}_3$ . The formation of  $\bullet\text{OH}$  involves reaction of  $\text{O}_3$  and the hydroxide ion (initiation).

The calculated rate of  $\text{O}_3$  decomposition by reaction with hydroxide ion ( $\text{OH}^-$ ), producing  $\bullet\text{OH}$  using Eq. (1), accounts for approximately 10% of the rate of disappearance of  $\text{O}_3$  in our system. This indicates that reaction of MTBE with  $\bullet\text{OH}$  is not negligible and must be included in the rate expression. Also, the disappearance of  $\text{O}_3$  is approximately three to four times faster than the disappearance of MTBE, indicating that  $\text{O}_3$  is reacting with other species such as  $\text{OH}^-$ , various oxygen radicals produced by  $\text{O}_3$  decomposition, and other products of MTBE oxidation. MTBE may also react with species other than  $\text{O}_3$  or  $\bullet\text{OH}$ , but we assume that these reactions are negligible.

Based on these considerations, the following kinetic rate expression in the stirred flow reactor is applicable:

$$R_m = k_1 C_{\text{O}_3} C_{\text{mf}} + k_2 C_{\text{OH}} C_{\text{mf}} \quad (2)$$

where  $R_m$  is global rate of disappearance of MTBE ( $\text{M s}^{-1}$ ),  $k_1$  the rate constant for reaction of MTBE with  $\text{O}_3$  ( $\text{M}^{-1} \text{s}^{-1}$ ),  $k_2$  the rate constant for reaction of MTBE with  $\bullet\text{OH}$  ( $\text{M}^{-1} \text{s}^{-1}$ ),  $C_m$  the concentration of MTBE ( $\text{mol l}^{-1}$ ),  $C_{\text{mf}}$  the outlet concentration of MTBE ( $\text{mol l}^{-1}$ ),  $C_{\text{O}_3}$  the outlet concentration of  $\text{O}_3$  ( $\text{mol l}^{-1}$ ),  $C_{\text{OH}}$  is the concentration of  $\bullet\text{OH}$  ( $\text{mol l}^{-1}$ ).  $R_m$  can also be related to the operating conditions, using a mass balance:

$$R_m = \frac{v_o C_{\text{mo}} - v_f C_{\text{mf}}}{V_r} \quad (3)$$

where  $C_{mo}$  is the concentration of MTBE in inlet ( $\text{mol l}^{-1}$ ),  $v_o$  the volumetric flow rate of inlet stream ( $\text{ml s}^{-1}$ ),  $v_f$  the volumetric flow rate of outlet stream ( $\text{ml s}^{-1}$ ),  $V_r$  is the volume of reactor (l).

The concentration of  $\bullet\text{OH}$ ,  $C_{OH}$ , is determined using a relationship developed by Elovitz et al. [21] which defines the ratio of exposures of  $\bullet\text{OH}$  and  $\text{O}_3$ ,  $\int [\bullet\text{OH}] dt / \int [\text{O}_3] dt$ . They measured the concentration of  $\bullet\text{OH}$  as a function of  $\text{O}_3$  concentration over time by using a probe (decarboxylation of *p*-chlorobenzoic acid), which rapidly and quantitatively traps  $\bullet\text{OH}$  and does not react with  $\text{O}_3$ . A calibration of this probe system has been made [10]. The study indicates that  $\bullet\text{OH}$  concentration does not change significantly with temperature or pH, although  $\text{O}_3$  concentration is a stronger function of these parameters.

The value of  $k_1$  can be determined from Eqs. (2) and (3) using measurable parameters:

$$k_1 = \frac{v_o C_{mo} - v_f C_{mf} - k_2 C_{OH} C_{mf}}{V_r C_{O_3} C_{mf}} \quad (4)$$

The value of  $k_2$  was obtained from experiments with  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , benzene and MTBE, described below. In these experiments,  $\bullet\text{OH}$  was generated by reaction of  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  and was trapped competitively by benzene and MTBE,  $k_2$  was found to be  $\sim 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

Fig. 1 presents the Arrhenius plot for ozonation of MTBE in the absence of  $\text{H}_2\text{O}_2$ . The apparent activation energy ( $E_a$ ) for ozonation of MTBE is  $95.4 \text{ kJ mol}^{-1}$ . The experimental data is presented in Table 1. The measured temperature dependence of  $k_1$  ( $\text{M}^{-1} \text{ s}^{-1}$ ) is

$$k_1 = 1.4 \times 10^{18} \exp \frac{-95.4}{RT} \quad (5)$$

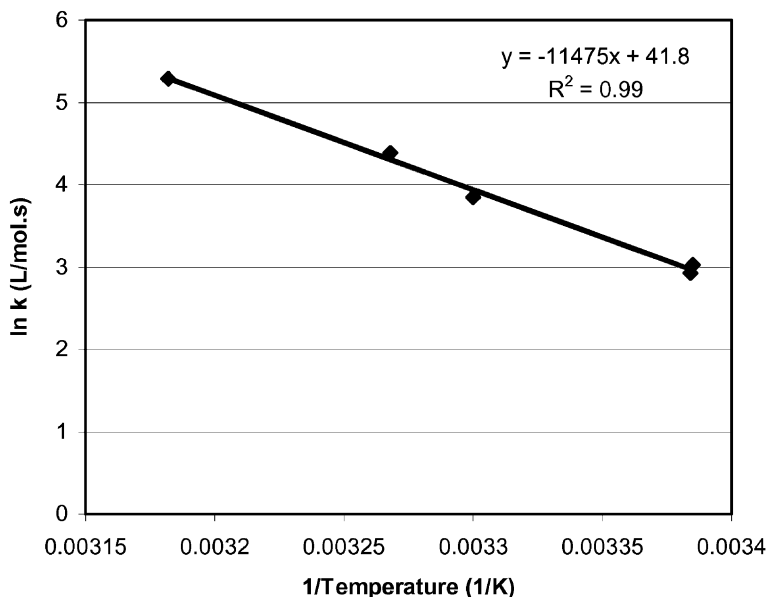


Fig. 1. Arrhenius plot for the reaction between MTBE and ozone.

Table 1

Experimental results for reaction of MTBE with O<sub>3</sub> in CFSR, with  $v_o = 0.3 \text{ ml s}^{-1}$ ,  $v_f = 0.6 \text{ ml s}^{-1}$ 

Temperature (°C)	$C_{mo} \times 10^{-5}$ (mol l <sup>-1</sup> )	$C_{mf} \times 10^{-6}$ (mol l <sup>-1</sup> )	$C_{O_3o} \times 10^{-4}$ (mol l <sup>-1</sup> )	$C_{O_3f} \times 10^{-5}$ (mol l <sup>-1</sup> )	$V_f$ (ml)	$C_{OH} \times 10^{-13}$ (mol l <sup>-1</sup> )	$R_m \times 10^9$ (M s <sup>-1</sup> )	$k_1$ (M <sup>-1</sup> s <sup>-1</sup> )
22.4	1.93	4.59	1.29	1.24	537	8.33	5.65	20.7
22.5	2.07	4.29	1.16	1.58	551	10.6	6.60	18.7
30.0	2.07	4.48	1.29	1.24	505	8.33	6.97	46.9
33.0	3.69	9.47	0.218	0.727	492	4.89	11.0	80.4
41.3	2.07	4.66	1.19	0.496	535	3.33	6.38	197.5

$\text{H}_2\text{O}_2$  is a powerful co-reactant, which promotes the formation of  $\bullet\text{OH}$ . The highest concentrations of  $\bullet\text{OH}$  are obtained with approximately equimolar  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  [22]. When  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  are introduced to the reactor, they are assumed to form  $\bullet\text{OH}$  rapidly, which is a much faster oxidizing agent than  $\text{O}_3$  [23–25]. Thus, for the purposes of these experiments,  $\bullet\text{OH}$  was assumed to be the predominant oxidant.  $C_{\text{OH}}$  was estimated by measuring the rate of disappearance of benzene, using a previously measured value for the second-order rate constant,  $k_3$ , of  $7.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [26]. Other studies have used this approach [13,27].

Following the approach used for Eqs. (2) and (3), the global rate of disappearance of benzene,  $R_{\text{B}}$  ( $\text{M s}^{-1}$ ), neglecting direct oxidation from  $\text{O}_3$ , is

$$R_{\text{B}} = k_3 C_{\text{Bf}} C_{\text{OH}} = \frac{v_o C_{\text{Bo}} - v_f C_{\text{Bf}}}{V_r} \quad (6)$$

where  $C_{\text{Bo}}$  is the concentration of benzene in inlet ( $\text{mol l}^{-1}$ ), and  $C_{\text{Bf}}$  is the concentration of benzene in outlet ( $\text{mol l}^{-1}$ ). So that  $C_{\text{OH}}$  can be estimated as follows:

$$C_{\text{OH}} = \frac{v_o C_{\text{Bo}} - v_f C_{\text{Bf}}}{V_r C_{\text{Bf}} k_3} \quad (7)$$

Typical values of  $C_{\text{OH}}$  measured in these experiments are presented in Table 2. Given the reactivity of  $\bullet\text{OH}$ , it has a very small activation energy and thus a weak temperature dependence. After determining  $C_{\text{OH}}$ ,  $k_2$  ( $\text{M}^{-1} \text{ s}^{-1}$ ) and the activation energy for MTBE oxidation by  $\bullet\text{OH}$  is estimated using

$$k_2 = \frac{v_o C_{\text{mo}} - v_f V_{\text{mf}}}{V_r C_{\text{OH}} C_{\text{mf}}} \quad (8)$$

The results of these experiments are presented graphically in Fig. 2. The activation energy ( $E_a$ ) for the reaction between MTBE and  $\bullet\text{OH}$  in the CFSR was calculated as  $4.6 \text{ kJ mol}^{-1}$ . The temperature dependence is

$$k_2 = 8.0 \times 10^9 \exp\left(\frac{-4.6}{RT}\right) \quad (9)$$

The global rate of disappearance of MTBE increases by a factor of 5 after addition of  $\text{H}_2\text{O}_2$  at  $30^\circ\text{C}$ , i.e.  $k_2 C_{\text{mf}} C_{\text{OH}} / k_1 C_{\text{mf}} C_{\text{O}_3\text{f}} = 5.2$ . At lower temperatures, this ratio increases. Thus, the addition of  $\text{H}_2\text{O}_2$  can greatly reduce the consumption of  $\text{O}_3$ .

### 3.2. Product formation during oxidation of MTBE

The major organic products identified in the reaction of MTBE and  $\text{O}_3$  by our analytical method were TBF, TBA, acetone, and methyl acetate. More water soluble compounds, such as formic acid and acetic acid, were seen at certain reaction times but not quantified due to poor adsorption onto the SPME fiber. Aldehydes may also have been present in very low concentrations but were not detected or quantified due to limitations in the analysis and since they are readily oxidized. Therefore, we used a combination of literature and our experimental data to elucidate a pathway for oxidation of MTBE. Ratios of products to reactants from reaction of MTBE and  $\text{O}_3$  or  $\text{O}_3/\text{H}_2\text{O}_2$  after oxidant depletion in the



Table 2  
 Experimental results for reaction of MTBE with O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> in CFSR, with  $v_o = 1.5 \text{ ml s}^{-1}$ ,  $v_f = 3.0 \text{ ml s}^{-1}$

Temperature (°C)	$C_{mo} \times 10^{-4}$ (mol l <sup>-1</sup> )	$C_{mf} \times 10^{-5}$ (mol l <sup>-1</sup> )	$C_{Bo} \times 10^{-4}$ (mol l <sup>-1</sup> )	$C_{Bf} \times 10^{-5}$ (mol l <sup>-1</sup> )	Residence time (s)	$R_B \times 10^{-7}$ (M s <sup>-1</sup> )	$C_{OH} \times 10^{-13}$ (mol l <sup>-1</sup> )	$R_m \times 10^{-8}$ (M s <sup>-1</sup> )	$k_2 \times 10^9$ (M <sup>-1</sup> s <sup>-1</sup> )
21.0	0.987	4.07	0.967	2.04	177	1.58	10.2	4.87	1.17
21.8	1.01	4.33	1.11	2.72	160	1.78	8.61	4.43	1.19
30.5	1.34	5.69	1.11	2.62	182	1.6	8.06	5.43	1.18
30.5	1.33	5.66	1.19	2.88	158	1.94	8.87	6.27	1.25
39.9	1.08	4.48	1.13	2.54	182	1.71	8.85	5.18	1.31
40.0	1.15	4.81	1.31	3.06	184	1.88	8.09	5.06	1.30
45.0	1.02	4.19	1.42	3.18	184	2.13	8.79	4.99	1.36
45.1	1.09	4.45	1.17	2.56	181	1.81	9.29	5.63	1.36

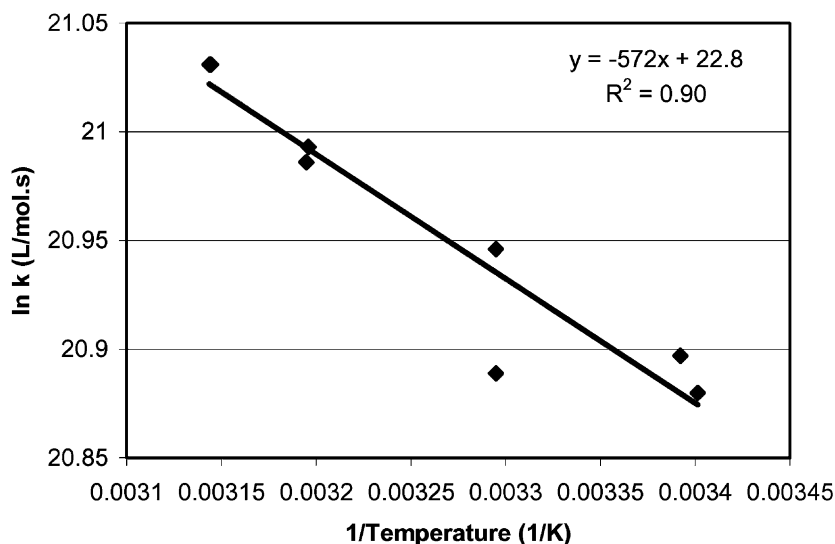


Fig. 2. Arrhenius plot for the reaction between MTBE and the hydroxyl radical, generated by ozone and hydrogen peroxide.

batch reactor are presented in Table 3. The system of MTBE and  $O_3/H_2O_2$  resulted in similar products, but in different proportions. As can be seen in Table 3, the amount of organic products decreased upon addition of  $H_2O_2$  to the system, indicating more complete oxidation.

Formic acid was initially found in the batch reactor when  $O_3$  was used alone, but it was undetectable after oxidant depletion. For the  $O_3/H_2O_2$  system, formic acid was never detected at any stage of the reaction, probably because of its rapid reaction with  $\bullet OH$  which gives  $\bullet COO^-$ . This radical then reacts with oxygen or other oxidants to ultimately form  $CO_2$  [28,29].

Based on identification of intermediates, products and studies of rates, we postulate a main pathway for mineralization of MTBE, TBF, and TBA. Fig. 3 shows the proposed reaction

Table 3  
Mole ratios of products to reactants from experiments in a batch reactor at pH 7.2 and  $\sim 23^\circ C$

Initial reactant	Products	Product/reactant with $O_3$ (mole ratio)	Product/reactant with $O_3/H_2O_2$ (mole ratio)	Decrease with $O_3/H_2O_2$ (%)
MTBE	TBF	0.50	0.34	32
	TBA	0.14	0.10	29
	Acetone	0.20	0.12	40
	Methyl acetate	0.13	0.10	23
TBF	TBA	0.24	0.15	38
	Acetone	0.34	0.24	29
TBA	Acetone	0.28	0.20	29

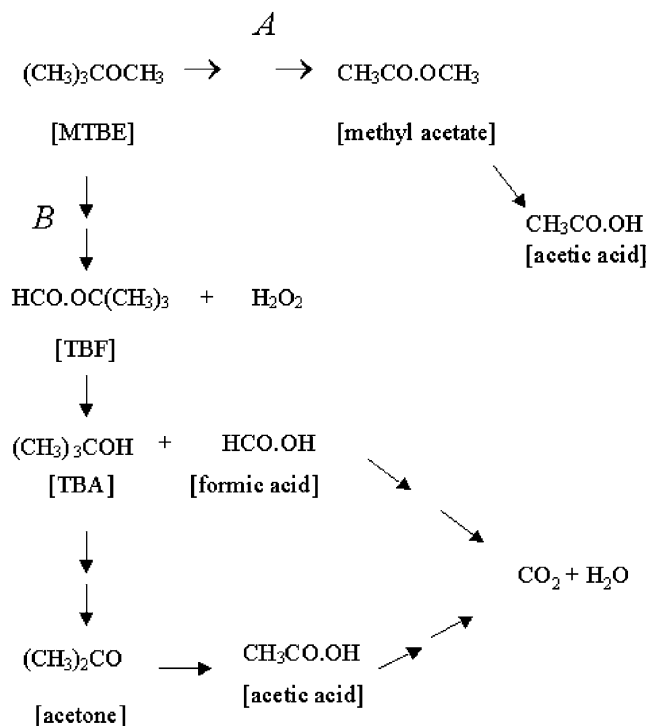


Fig. 3. Suggested pathway for reaction of MTBE with ozone reaction: Pathway A shows attack on the *t*-butyl group to form methyl acetate. The major reaction is at the  $\beta$ -hydrogen of MTBE to form TBF, pathway B [18].

pathway of MTBE with  $\text{O}_3$  based on our experimental results and literature. The main initial product of the reaction of  $\text{O}_3$  with MTBE is TBF. TBF can be generated by insertion of  $\text{O}_3$  at the  $\alpha$ -hydrogen to form a hydrotrioxide intermediate, as shown for ozonation of other ethers [19]. Subsequently, reactions may follow either of two pathways after  $\text{O}_3$  insertion. TBF and  $\text{H}_2\text{O}_2$  may be formed from the trioxide intermediate. The other possibility is formation of a TBF radical, which ultimately forms TBF, again producing  $\text{H}_2\text{O}_2$  by (1) simple electron transfer or (2) reaction with MTBE itself and propagating a chain reaction.

$\text{O}_3$  could attack a  $\beta$ -hydrogen of MTBE, but the tertiary methyl group sterically disfavors the reaction. Another indication of  $\text{O}_3$  insertion at the  $\alpha$ -hydrogen is the dominant formation of TBF as the initial product. If  $\text{O}_3$  did preferentially attack a  $\beta$ -hydrogen, TBF would not be the main product.

However, formation of methyl acetate in MTBE oxidation indicates that there may be attack on the *t*-butyl group of MTBE by  $\text{O}_3$  or an oxidant from  $\text{O}_3$  decomposition. Esters are formed from ketones in the Baeyer–Villiger reaction with hydroperoxides or peroxy acids, but we excluded this reaction by performing control experiments with acetone and  $\text{O}_3$  and  $\text{O}_3/\text{H}_2\text{O}_2$ , since only unreacted acetone was identified after oxidant depletion. In separate experiments, reactions of TBF and TBA with  $\text{O}_3$  and  $\text{O}_3/\text{H}_2\text{O}_2$  did not generate methyl acetate. Therefore, methyl acetate is not derived directly from acetone, TBF or TBA,

but indirectly from MTBE, by attack on the *t*-butyl group. Other studies have also detected methyl acetate as a by-product in the reaction of O<sub>3</sub> and MTBE [11].

As mentioned previously, TBF is hydrolyzed in aqueous media to TBA and formic acid in the absence of oxidants. Acids and bases catalyze this reaction, where a larger deviation from neutral pH causes an increase in the rate of hydrolysis, especially at higher pH. Recent work by Church et al. have estimated the half-life of TBF at pH 7 to be 5 days [30].

Since TBA is a radical scavenger, it is not surprising that it is not the major product of reaction of MTBE with O<sub>3</sub>. Once TBA is formed, its oxidation can generate acetone [31]. The reaction of TBA with •OH and/or other radicals can form •OHCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub> and oxygen may react with the TBA radical to form •OOCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>OH [31]. Both these radicals should decompose giving acetone and •CH<sub>2</sub>OH (hydroxymethyl radical), which is ultimately oxidized to CO<sub>2</sub>.

Acetic acid is a product of TBA oxidation by O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, but it is undetectable after oxidant depletion. Control studies indicate that the acetic acid detected in our reactions is derived by oxidation of TBA at the *t*-butyl group. In a control experiment of acetone oxidation by O<sub>3</sub> or O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, acetic acid was not seen as a product with the concentrations of reactants used in this work. In addition, the formation of methyl acetate from MTBE could involve oxidation of two methyl groups from the *t*-butyl group and replacement by oxygen, in a multistep process [19], and the corresponding oxidation of the *t*-butyl group of TBA should generate acetic acid.

### 3.3. Product formation during oxidation of TBF or TBA

In these experiments, TBA or TBF were reacted with O<sub>3</sub> or O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>. Degradation of TBF or TBA followed similar pathways to complete oxidation as MTBE, through intermediates identified in initial and final stages of ozonation. In the reaction of TBF with O<sub>3</sub> or O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, TBA and acetone were the identified organic products. In the reaction of TBA with O<sub>3</sub> or O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, acetone was the only detectable organic product after oxidant depletion. Table 3 presents the mole ratios of reactants and products after oxidant depletion and also confirms that the amount of organic products always decreased for the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system. Based on identifiable products at different stages of oxidation of TBF and TBA, we conclude that TBF and TBA follow the reactions shown in Fig. 3.

## 4. Conclusion

The major products of environmental concern in the oxidation of MTBE by O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> are TBF and TBA. Because oxidants were limiting reactants under our batch conditions, there were significant residual organic products, especially when O<sub>3</sub> is used alone. Addition of H<sub>2</sub>O<sub>2</sub> reduced the organic products, and increased mineralization of MTBE.

The yield of TBF in the stirred flow reactor, with a mean residence time of ~850 s, was consistently ~25% of the initial MTBE, in moles. This indicates that the TBF produced reacts with O<sub>3</sub>, which explains why the transformation of O<sub>3</sub> is greater than that of MTBE. As temperature increased from 22 to 41 °C in the CFSR, the rate of disappearance of MTBE increased by 11% with O<sub>3</sub> alone. It would be necessary to increase the residence time,

the temperature, or the concentration of  $O_3$  in order to increase the complete oxidation of MTBE to  $CO_2$ .

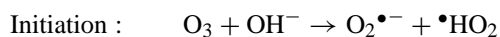
For the  $O_3/H_2O_2$  system, the global rate of disappearance of MTBE was increased by a factor of approximately 5, relative to  $O_3$  only, which is more significant at lower temperatures. A temperature increase from 21 to 45°C increases the rate of disappearance of MTBE by 14% in the CFSR using the combination of oxidants. Our results show that  $H_2O_2$  improves the oxidative process by generating reactive and unselective radicals and its use in the degradation of pollutants is desirable in view of its efficacy.

## Acknowledgements

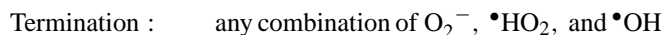
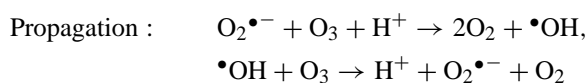
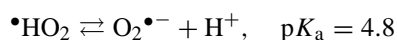
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## Appendix A

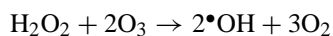
The rate of decomposition of aqueous  $O_3$  increases rapidly with increasing pH, due to the initiation reaction of  $O_3$  with  $OH^-$  as first proposed by Weiss [34]. Although, many features of these reactions remain uncertain, pulse radiolysis showed that reactions of the transient  $\bullet OH$ ,  $\bullet HO_2$ , and  $O_2^{\bullet -}$  radicals with  $O_3$  play a key role in decomposing  $O_3$  via chain reactions [32]. This work also showed that  $\bullet OH$  is the dominant intermediate in accelerating decomposition of  $O_3$ . The dominant reactions in water at pH 7 to give the overall stoichiometry of  $2O_3 \rightarrow 3O_2$  are:



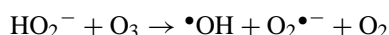
where



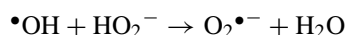
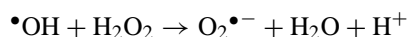
Some of the transient decomposition products of  $O_3$ , such as  $\bullet OH$ , are more potent oxidants than  $O_3$  itself [20,33–35]. We therefore assume that these decomposition products of  $O_3$ , as well as products of its decomposition with  $H_2O_2$ , significantly contribute to oxidations of organic compounds. The free radicals are short-lived, but react rapidly and nonspecifically with organic compounds generally with diffusion-controlled rates as indicated by a very low activation energy. For this reason, it is difficult to elucidate all the reactions for oxidation of organic substrates leading to mineralization.  $H_2O_2$  reacts with  $O_3$  to form  $\bullet OH$  with the following stoichiometry:



The hydroperoxide ion ( $\text{HO}_2^-$ ), the conjugate base of  $\text{H}_2\text{O}_2$ ,  $\text{p}K_a \sim 11$ , is the primary initiator of  $\text{O}_3$  decomposition in the  $\text{O}_3/\text{H}_2\text{O}_2$  system.  $\text{H}_2\text{O}_2$  reacts slowly with  $\text{O}_3$ , whereas  $\text{HO}_2^-$  reacts rapidly to give  $\bullet\text{OH}$  [22]. This reaction, which produces the superoxide ion,  $\text{O}_2^{\bullet-}$ , and  $\bullet\text{OH}$ , is much faster than reaction of  $\text{O}_3$  with  $\text{OH}^-$ . There is little  $\text{HO}_2^-$  at neutral pH, but it is sufficiently reactive to rapidly decompose  $\text{O}_3$  in these conditions:



Once  $\bullet\text{OH}$  is formed, it can react with  $\text{H}_2\text{O}_2$  or the hydroperoxide ion to yield  $\text{O}_2^{\bullet-}$ . Reactions are given below:



Reaction of  $\bullet\text{OH}$  with  $\text{H}_2\text{O}_2$  is slower than that with the hydroperoxide ion to form  $\text{O}_2^{\bullet-}$  by several orders of magnitude [34]. In both these reactions,  $\text{O}_2^{\bullet-}$  is the predominant product. It can be concluded that adding  $\text{H}_2\text{O}_2$  to  $\text{O}_3$ , not only is the  $\bullet\text{OH}$  concentration increased, but that of  $\text{O}_2^{\bullet-}$  is also increased and  $\text{H}_2\text{O}_2$  reacts with  $\text{O}_3$  to form both  $\bullet\text{OH}$  and  $\text{O}_2^{\bullet-}$ .

The O–H bond energy is higher than that of C–H. Therefore, hydroxyl and other radicals unselectively abstract hydrogen from a C–H bond of organic compounds.

$\bullet\text{OH}$  rapidly and indiscriminately abstracts hydrogen atoms from organic compounds generating alkyl radicals which may be involved in chain reactions. It is therefore difficult to distinguish between direct ozonation and hydrogen abstraction by  $\bullet\text{OH}$ , because both can generate similar products with final mineralization. For example,  $\text{O}_3$  reacts directly with ethers and the reaction can convert MTBE into TBF, but  $\bullet\text{OH}$  can abstract a hydrogen atom from either  $\text{OCH}_3$  and/or  $\text{CCH}_3$  groups. It is probable that products derived from MTBE without the intermediacy of TBF or TBA are generated by reaction of  $\bullet\text{OH}$  with  $\text{CH}_3$  of the tertiary butyl group.

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