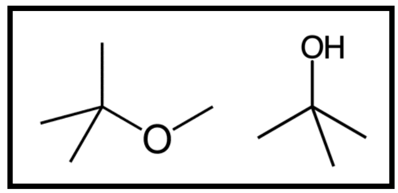
Methyl Tert-butyl Ether (MTBE) & Tert-butyl Alcohol (TBA) Interactions With Ozone

Methyl tert-butyl ether, more commonly known as MTBE, can be described using the chemical formula $(CH_3)_3COCH_3$. During the late seventies, this compound slowly replaced tetraethyl lead in gasoline as an effective fuel oxygenate and octane booster, allowing gasoline to undergo a cleaner, more complete combustion.[1] TBA, or tert-butyl alcohol, is a manufacturing by-product of MTBE and fuel oxygenate used in gasoline, although less popular than MTBE. TBA has also been identified as one of the major degradation products resulting from ozonation of MTBE in groundwater.[1]



These chemicals have become controversial in the United States due to their high occurrence in the environment. Leaking underground storage tanks (UST), gasoline surface spills, and other incidences have allowed MTBE to

Due to its high solubility, mobility and persistence in soil and groundwater environments, MTBE plumes migrate rapidly through soil and are capable of covering large areas.[1] Numerous remediation techniques including in-situ bioremediation, pump and treat, aremove MTBE nd air sparging have been used in order to and TBA from groundwater.[1] In-situ chemical oxidation using ozone and Advanced Oxidation Processes are also effective in the removal of these fuel oxygenates from soil and groundwater.

The high oxidation potential of ozone (2.1V) ensures that MTBE and any other fuel oxygenates that react with it will be thoroughly degraded. Similarly, the unselective, highly reactive hydroxyl radical produced from Advanced Oxidation Processes is also very effective in breaking down MTBE and TBA. Since the oxidation potential of the OH radical is even greater than that of molecular ozone, the rate of degradation of the target molecules is accelerated when Advanced Oxidation Processes are applied.

The oxidation reactions and products of MTBE using molecular ozone and hydroxyl radical have both been thoroughly studied. A study conducted by Mitani, et al. investigated the kinetics and products of reactions of MTBE with molecular ozone and ozone/hydrogen peroxide in water.

Tert-butyl formate (TBF), tert-butyl alcohol (TBA), methyl acetate, and acetone were identified as major products of MTBE oxidation with molecular ozone.[2] Formic acid and acetic acid were also

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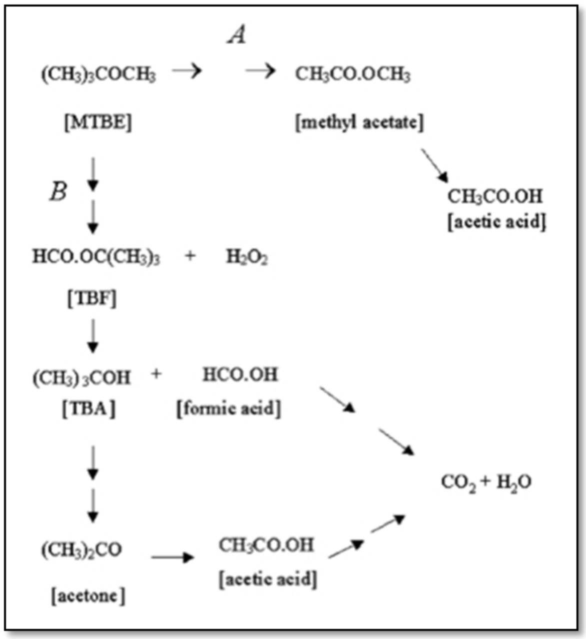

Figure 2.

Figure 2 demonstrates the observed reaction pathway devised by Mitani. Pathway A results in the production of methyl acetate from attack on the tert-butyl group of MTBE.[2] The alternate pathway reveals the production of TBF as a major product. Reaction of TBF with hydrogen peroxide produces TBA, which is eventually broken down into environmentally friendly products such as CO_2 and H_2O.

A similar study by Acero, et al. investigating MTBE oxidation by conventional ozone and ozone/hydrogen peroxide under drinking water conditions proposed an oxidation pathway similar to that proposed by Mitani. Major degradation products identified in this study include TBA, TBF, 2-methoxy-2-methyl propionaldehyde (MMP), acetone, methyl acetate, hydroxyisobutyraldehyde (HiBA), and formaldehyde.[3]

Figure 3 describes the pathways of MTBE oxidation as observed by Acero. Note that the major reaction products proposed by Mitani (TBF, TBA, and acetone) are also observed in the Acero paper.

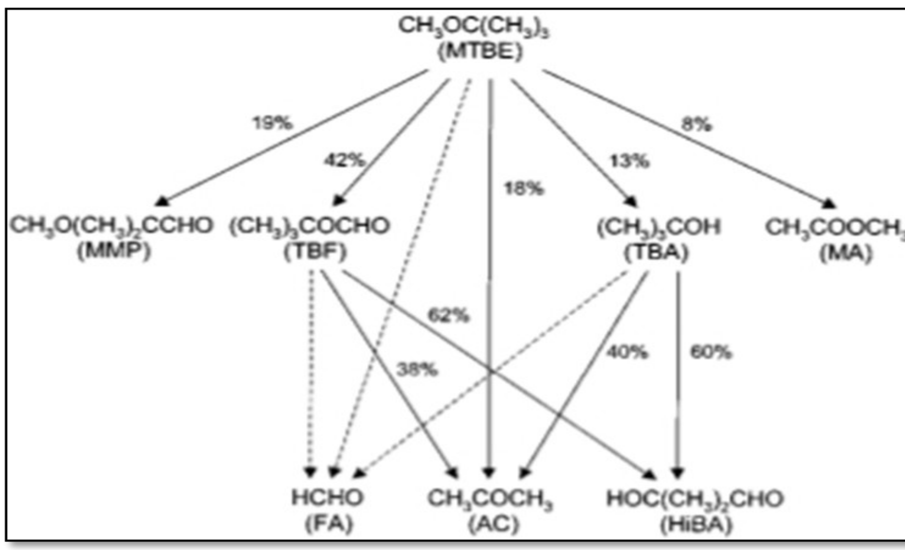

Figure 3.

Ozonation pathways of TBF and TBA were also examined. Degradation of TBF and TBA followed similar pathways to complete oxidation as MTBE, however, acetone was identified as the sole remaining organic product after the oxidant was completely consumed.[2] These reactions are also illustrated in the figure to the right.

In-situ molecular ozone and Advanced Oxidation Processes have proven effective in complete degradation of MTBE and TBA. However, it is important to note that the high mobility of these contaminants of concern (COCs) in soil and groundwater must be taken into consideration when evaluating remediation techniques.

Due to the accelerated rate of oxidation associated with AOPs, it is recommended that this technique be used in order to increase concentrations of the highly reactive hydroxyl radical in treatment areas. High OH radical concentrations ensure that MTBE/TBA will be rapidly oxidized, and will terminate plume movement throughout the environment.

We at Piper Environmental Group, Inc. have had extensive experience with in-situ and ex-situ ozone and Advanced Oxidation Processes, and can easily tailor our systems in order to ensure complete remediation of the desired contaminants.

References:

[1] ITRC (Interstate Technology & Regulatory Council). 2005. Overview of Groundwater Remediation Technologies for MTBE and TBA. MTBE-1. Washington, D.C.: Interstate Technology & Regulatory Council, MTBE and Other Fuel Oxygenates Team. Available on the Internet at http://www.itrcweb.org.

[2] Mitani, M. M., Keller, A. A., Bunton, C. A., Rinker, R. G., & Sandall, O. C. (2002). Kinetics and products of reactions of MTBE with ozone and ozone/hydrogen peroxide in water. *Journal of Hazardous Materials*, *B89*, 197-212.

[3] Acero, J. L., Haderlein, S. B., Schmidt, T. C., Suter, M. J.-F., & von Gunten, U. (2001). MTBE Oxidation by Conventional Ozonation and the Combination Ozone/Hydrogen Peroxide: Efficiency of the Processes and Bromate Formation. *Environ. Sci. Technol.*, (35), 4252-4259.

Company Profile

Piper Environmental Group, Inc. offers ozone technology, equipment, and services for a wide-range of environmental applications. The company designs, manufactures, and integrates ozone systems and related equipment for short and long-term projects, offering equipment for rent or purchase. Services include project design assistance, oxidation pilot studies, contract service, equipment repair, consulting. Our area of expertise is large remediation projects.

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