

Free Radical Chemistry as the Underpinning for Advanced Oxidation Processes
in Sustainable Water Management

William J. Cooper
Professor and Director
Urban Water Research Center, and
Department of Civil and Environmental Engineering
University of California, Irvine
Irvine, CA 92697-2175

Stephen P. Mezyk
Department of Chemistry and Biochemistry
California State University at Long Beach
1250 Bellflower Blvd
Long Beach, CA, 90840, USA

James J. Kiddle
Department of Chemistry
Western Michigan University
3425 Wood Hall
Kalamazoo, MI 49008

Bruce J. Mincher
US Department of Energy
Idaho National Laboratory (MS 7113)
PO Box 1625
Idaho Falls, ID 83415-7113

Advanced Oxidation Processes (AOPs) are a group of technologies that have great potential to quantitatively destroy and/or detoxify trace amounts of organic pollutants in water. All AOPs are based on free-radical chemistry; specifically they generate radicals in the water being treated that then react with contaminants to destroy them. The defining chemistry of AOPs is that of the hydroxyl radical, $\cdot\text{OH}$, formed from the breaking of the H-OH water bond. However, other reactive species may also be formed depending upon the actual process. A summary of various AOPs, and the radicals they use in the destruction of contaminants in water, is given in Table 1. The chemistry of how these radicals destroy contaminants in water can be incredibly complex, however, this knowledge is required for the development of efficient engineering schemes to clean up contaminated waters, industrial effluents, and decontaminate drinking water. Clearly, it is not cost-effective to study every single contaminant chemical individually. Therefore we propose a more effective approach, which is to establish the radical-based destruction chemistry for selected chemicals within groups of contaminants, and then generalize this chemistry to the remainder of the group. A group of free radical based destruction technologies has emerged that are commonly referred to as advanced oxidation processes (AOPs). For example, processes that are being studied include ozone, ozone in combination with UV light or hydrogen peroxide.

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| Table 1. Summary of Advanced Oxidation Processes and the reactive species involved in contaminant chemical destruction. |
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| System | $\cdot\text{OH}$ | e_{aq}^- | $\cdot\text{H}$ |
|--|------------------|---------------------------------------|-----------------|
| O_3/UV or $\text{O}_3/\text{H}_2\text{O}_2$ | X | | |
| $\text{TiO}_2/\text{h}\nu$ | X | Conduction band electron ¹ | |
| $\text{ZnO}/\text{h}\nu$ | X | Conduction band electron ¹ | |
| Sonolysis | X | | X |
| $\text{H}_2\text{O}_2/\text{UV}$ | X | | |
| Pulsed UV | X | | |
| Fentons (or Photo-Fentons) | X | | |
| Electro-hydraulic Cavitation | X | | X |
| Supercritical water | X | | X |
| Electron-beam irradiation | X | X | X |
| ¹ These conduction-band electrons are typically scavenged by O_2 in solution to form O_2^- , which is less reducing than the solvated electron. | | | |

There are also process's that result in both oxidizing and reducing species that are under investigation, including heterogeneous catalysis, with TiO_2 the most widely catalysis, sonolysis, and the electron beam process. The increased emphasis in AOPs results from the recent shift in treatment philosophy to change from phase transfer, aeration stripping or activated carbon, to destruction technologies. A fundamental understanding of the chemistry of new environmental technologies is critical to the appropriate application of the processes to solve complex environmental problems. With the increased concern in sustainability of drinking water supplies we feel that the application of these processes will increase. As the importance of water reuse increases the application of advanced technologies will also likely increase. We have initiated a long-term program in developing a better understanding of free radical based processes. Two chemicals, methyl tert-butyl ether and trichloronitromethane are briefly reviewed below.

Kinetic Models. The goal of our research approach is to provide the necessary tools for environmental engineers to model advanced oxidation processes for the destruction of classes of contaminant chemicals in water. In addition, these models could be used for process optimization and economic evaluations. Kinetic models for AOPs can be divided into three discrete sections or series of equations that describe the:

- 1) **formation of the radicals**, such as hydroxyl radicals ($\cdot\text{OH}$),
- 2) radical-induced **destruction chemistry** of the contaminant of interest, and
- 3) **fluid dynamics** or reactor type to be studied.

The focus of our studies is the second step in the formulation of an overall kinetic model.

Methyl tert-butyl ether (MTBE). Methyl *tert*-butyl ether (MTBE), used almost exclusively as a gasoline additive, has emerged as one of the most common environmental contaminants. It is found in the troposphere and also in surface and ground water and snow. There have been numerous reports of its fate in both air and water, and it appears that it reacts primarily *via* free radical pathways. Because of its increasing presence in waters intended for drinking, there have been numerous studies investigating treatment processes for MTBE removal from waters. Of the treatment processes, free radical based destruction using hydroxyl radicals, i.e., Advanced

Oxidation Processes (AOPs) have been studied in some detail. Although several studies have proposed mechanisms for MTBE destruction, most of these appear to be incomplete and do not account for all of the reaction by-products. We have comprehensively reviewed the free radical-initiated reactions of MTBE and have proposed an overall mechanism that accounts for all of the reaction by-products that have been reported and have proposed the likely occurrence of others. This mechanism has been linearized in a form that will be used for developing a kinetic model that describes MTBE destruction, the formation and destruction of its reaction by-products and can be used in water treatment or remediation [1].

Initially reaction rate constants for the radical attack were re-evaluated [2] and it was shown that the major route of initial attack is via $\bullet\text{OH}$ -hydrogen abstraction (Figure 1). It is thought that the two peroxy radicals then combine to form three tetroxides which through intramolecular decomposition result in a number of primary reaction by-products (Table 2).

Table 2. Quantitative distribution of reaction by-products of MTBE and reaction by-products.

| Reference | Compound (initial concentration) | Process | Reaction by-products | Conversion (percent of parent) |
|-----------|----------------------------------|-----------------------------------|------------------------------------|--------------------------------|
| [4] | MTBE | $\text{O}_3/\text{H}_2\text{O}_2$ | TBF | 42 |
| | | | TBA | 13 |
| | | | MMP | 19 |
| | | | acetone | 18 |
| | | | methyl acetate | 8 |
| | TBF | | hydroxy- <i>iso</i> -butyraldehyde | 62 |
| | | | acetone | 38 |
| | TBA | | Hydroxy- <i>iso</i> -butyraldehyde | 60 |
| | | | acetone | 40 |
| [5] | MTBE (0.92 μM) | UV/ H_2O_2 | TBF | 22 |
| | | | TBA | 11 |
| | | | MMP | 11 |
| | | | acetone | 38 |
| | | | methyl acetate | 8 |
| | | | formaldehyde | 18 |

Using iterative steps, published literature and suggesting reaction mechanisms for those reactions not as yet published we have proposed an overall mechanism for the destruction of MTBE that accounts for all of the known reaction by-products. This has resulted in a model that is over 250 equations and has as yet not been tested. However, it is a beginning and our research efforts are to complete this overall study. One motivating factor is that as degradation occurs compounds are formed that are the same for many other compounds.

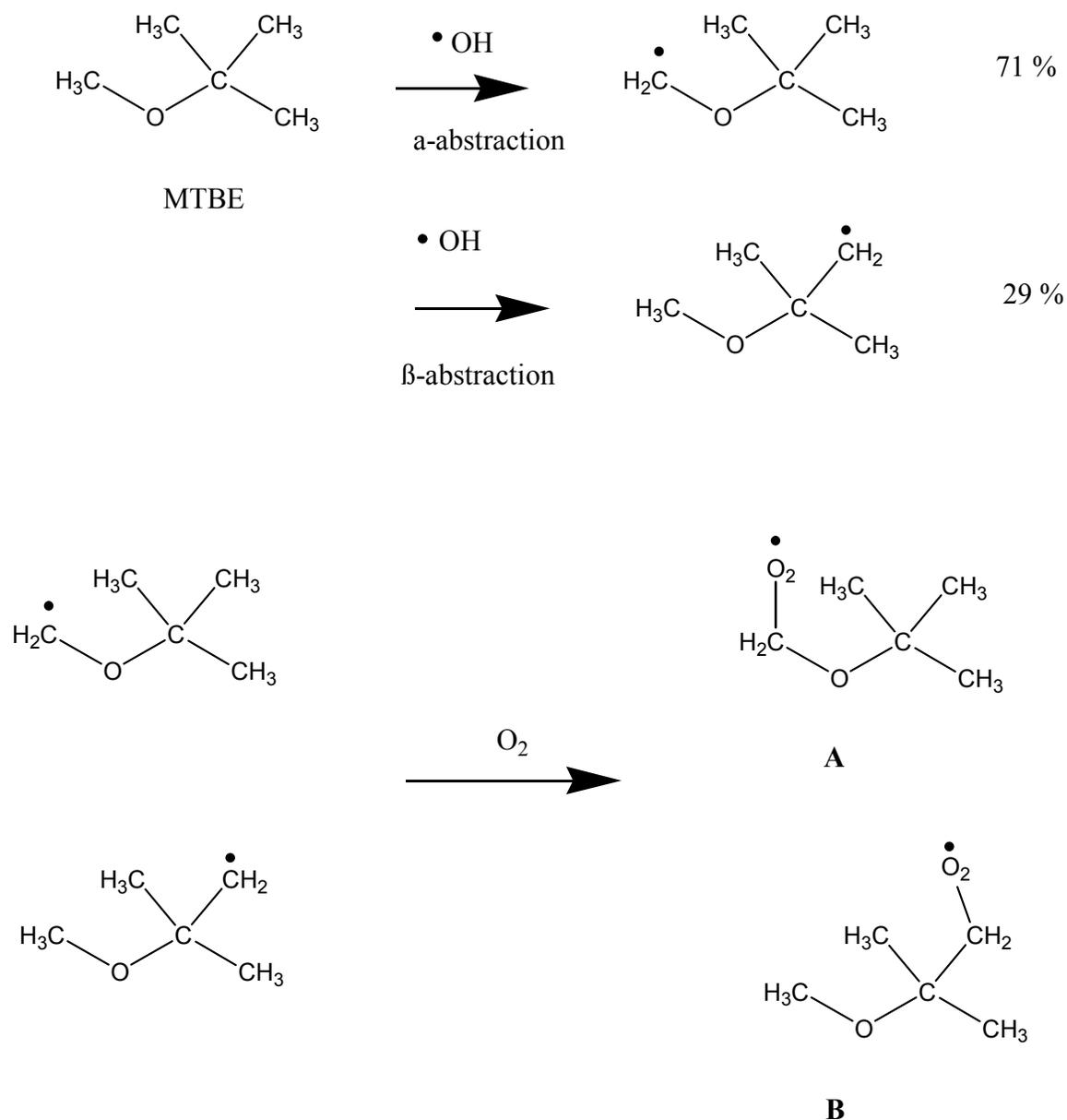


Figure 1. Initial reaction of $\bullet\text{OH}$ with MTBE and the branching ratio of that attack [3]. Subsequent reaction of the carbon-centered radicals results in the formation of two peroxy radicals (**A** and **B**).

Trichloronitromethane (chloropicrin). We have identified nitrogenous disinfection by-products (N-DBPs) as one major group of chemicals that are a high priority for potential treatment by AOPs. These DBPs are of great current interest and concern, based upon the recent work conducted by EPA and the Nationwide Occurrence Study. They are also receiving increased interest in water reuse programs (21st Annual Water Reuse Symposium, Hollywood, CA, Sept. 10-13, 2006). We have identified nitrogenous disinfection by-products (N-DBPs) as one major group of chemicals that are a high priority for potential treatment by AOPs. These DBPs are of great current interest and concern, based upon the recent work conducted by EPA and the Nationwide Occurrence Study [6-8]. They are also receiving increased interest in water reuse programs (21st Annual Water Reuse Symposium, Hollywood, CA, Sept. 10-13, 2006).

Initially, we evaluated the reaction rate constants for the nine halonitromethanes [9]. Then, chloropicrin solutions were prepared at a nominal concentration of 1 mM and irradiated to different doses to provide increasing energy and partial degradation (Table 3).

Table 3. Summary of experimental results for ^{60}Co irradiation of TCNM solutions (1.13 mM) in ultra-pure water at doses up to 8.54 kGy and kinetic model results.

| Dose (kGy) | Experimental | | | Kinetic Model | | |
|------------|-------------------|-----------------|-------------------|----------------|-----------------|-------------------|
| | TCNM (mM) | Cl \cdot (mM) | NO $_3\cdot$ (mM) | TCNM (mM) | Cl \cdot (mM) | NO $_3\cdot$ (mM) |
| 0 | 1.13 | 0.00 | 0.00 | 1.13 | 0.00 | 0.00 |
| 1.22 | 0.80 | 0.92 | 0.29 | 0.80 | 0.98 | 0.26 |
| 2.44 | 0.42 | 1.67 | 0.44 | 0.54 | 1.71 | 0.41 |
| 3.66 | 0.17 | 2.17 | 0.58 | 0.23 | 2.50 | 0.59 |
| 6.1 | NM ^a | 2.73 | 0.79 | - ^c | 3.13 | 0.95 |
| 8.54 | BMDL ^b | 3.13 | 0.89 | - ^c | 3.13 | 0.94 |

^a not measured
^b below method detection limit
^c modeled data is below detection limit

The details of the modeling approach are beyond the scope of this extended abstract; however, it can be seen that we were able to model the removal of the chloropicrin and the formation of the stable reaction by-products [10]. We have an ongoing study to determine some of the hypothesized reactions and their rates.

Summary. In summary it has been shown that radical processes are extremely complex even for the two chemicals that we have studied in detail. However, it is essential that these studies be conducted and expanded as it is through the detailed description of destruction mechanisms that it becomes possible to, using kinetic models, optimize treatment alternative, evaluate the cost effectiveness of processes and possibly provide some insight into the potential of adverse health effects of the compounds.

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