ANL/CHM/CP-100502

2000 ACS Spring Meeting, Environmental Chemistry Division Proceedings

RADIATION CHEMISTRY OF ALTERNATIVE FUEL OXYGENATES-SUBSTITUTED ETHERS

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Abstract

The electron beam process, an advanced oxidation and reduction technology, is based in the field of radiation chemistry. Fundamental to the development of treatment processes is an understanding of the underlying chemistry. We have previously evaluated the bimolecular rate constants for the reactions of methyl *tert*-butyl ether (MTBE) and with this study have extended our studies to include ethyl *tert*-butyl ether (ETBE), di-isopropyl ether (DIPE) and *tert*-amyl methyl ether (TAME) with the hydroxyl radical, hydrogen atom and solvated electron using pulse radiolysis. For all of the oxygenates the reaction with the hydroxyl radical appears to be of primary interest in the destruction of the compounds in water. The rates with the solvated electron are limiting values as the rates appear to be relatively low. The hydrogen atom rate constants are relatively low, coupled with the low yield in radiolysis, we concluded that these are of little significance in the destruction of the alternative fuel oxygenates (and MTBE).

Introduction

The electron beam process, an advanced oxidation (and reduction) technology (AOT), is based in the field of radiation chemistry. It appears that it may be an economically viable alternative for the destruction of MTBE and alternative fuel oxygenates in aqueous solutions. One part of our research program it to continue to develop a better understanding of this process as an alternative to other AOT's, particularly in the area of fuel oxygenate compounds.

The electron beam process can be thought of as a continuous injection of electrons into a flowing stream of water. In distilled water the initial chemistry can be described by the following:

$$H_2O \text{ -/\backslash/\backslash/\backslash-> } \mathbf{2.7}\ OH,\ \mathbf{0.6}\ H,\ \mathbf{2.6}\ e_{aq}^-,\ \mathbf{0.45}\ H_2,\ \mathbf{0.7}\ H_2O_2,\ \mathbf{2.6}\ H_{aq}^+ \qquad (1)$$

The numbers in bold are G values and represent the number formed for each 100 eV absorbed dose.

Fundamental to developing this treatment process is an understanding of the basic radiation chemistry. We use an approach that involves first determining bimolecular reaction rate constants between the reactive intermediates in equation 1 and the compound(s) of interest. Secondly, we try to develop a detailed understanding of the reaction mechanism that describes the radiolytic decomposition of the compound in aqueous solution. After the rates and mechanism are known then we can use the kinetic model that we have been working on for several years to predict the removal of the compound. Lastly, we conduct large scale studies of the compound(s) at the Electron Beam Research Facility in Miami, FL. From these studies we can estimate treatment costs of the process.

DISCLAIMER

An important issue in understanding any destruction technology for various environmental applications is the formation and destruction of reaction intermediates. To obtain this information we use an understanding of the reaction mechanism developed under controlled conditions. Within this mechanism the myriad of possible reaction by-products or reaction intermediates are determined and then can be analyzed for in larger scale studies and field trials.

We have previously reported bimolecular rate constants and a tentative mechanism for the destruction of methyl *tert*-butyl ether (MTBE). In this study we re-evaluated the hydrogen atom rate with MTBE and extend our study to other alternative oxygenates. Thus, we have evaluated the bimolecular rate constants for the reactions of ethyl *tert*-butyl ether (ETBE), di-isopropyl ether (DIPE) and *tert*-amyl methyl ether (TAME) with the hydroxyl radical, hydrogen atom and solvated electron using pulse radiolysis.

Methods

The pulse radiolysis facility at the DOE Notre Dame Radiation Laboratory was utilized for the determination of the ·OH and e_{-aq} reaction rates. The H· Rates were determined at the DOE Argonne National Laboratory. Details of these systems are published elsewhere (1).

Results and Discussion

Table 1 summarizes the data (bolded) that we have obtained for the bimolecular rate constants of the four oxygenates that we studied. For comparison where data exist they are included in the table with references.

TABLE 1. Bimolecular Reaction Rate Constants ($M^{-1}\ s^{-1}$) of MTBE and the Alternative Fuel Oxygenates ETBE, DIPE and TAME.

Compound	·OH	e_{-aq}	H·
MTBE	1.6×10^9 (2) 2.1×10^9 (3)	1.75×10^7(3)	**$3.49 \pm 0.06 \times 10^6$** $<8.0 \times 10^6$ (3)
ETBE	**$1.81 \pm 0.03 \times 10^9$** 2.7×10^9(4)	8.45×10^7 (?)	**$7.04 \pm 0.11 \times 10^6$**
DIPE	**$2.49 \pm 0.04 \times 10^9$**	**6.7×10^6**	**$6.70 \pm 0.09 \times 10^7$**
TAME	**$2.37 \pm 0.04 \times 10^9$**	**4.0×10^6**	**$3.09 \pm 0.06 \times 10^6$**

For all of the oxygenates the reaction with the hydroxyl radical appears to be of primary interest in the destruction of the compounds in water. The rates with the solvated electron are limiting values as the rates appear to be relatively low. The rate for the ETBE with the solvated electron is probably incorrect and reflects an impurity in the compound as received.

In a companion paper we discuss initial mechanistic considerations for the destruction of the fuel oxygenates by AOP's (5).

Acknowledgments

Partial support for this research was provided by the National Science Foundation, BES 97-29965. The pulse radiolysis experiments were conducted at Notre Dame Radiation Laboratory which is supported by the US DOE Office of Basic Energy Sciences, and the work at Argonne National Laboratory was supported by the US Office of Basic Energy Sciences, Division of Chemical Sciences, US-DOE under contract number W-31-109-ENG-38. This work has not been reviewed by AECL and no official endorsement should be inferred.

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