OF1) Two-Phase Chemical Oxidation of Pyrene

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) can be formed from both natural and anthropogenic sources. While both sources are contributors of environmentally hazardous compounds, anthropogenic sources are considerably more damaging to the environment. We are exposed every day to an environmental containing a myriad of potentially harmful substances, both natural and anthropogenic (Lee 1981). PAHs are generally formed during incomplete combustion or pyrolysis of organic matter containing carbon and hydrogen. PAH-contaminated sites are associated with processing, combustion, and/or disposal of fossil fuels (Wilson and Jones, 1993).

In order to reduce the risk of high PAHs levels in drinking water, several methods of water treatment is practiced, such as chlorination and ozonation. Although chlorination may reduce PAH levels, the formation of chlorinated PAH derivatives is likely (Oyler et al., 1982). However a series of chlorinations of some PAHs were accomplished and the chlorinated PAHs were tested for mutagenicity. Ozone is another strong disinfectant that has being widely used as an alternative to chlorine. Due to its high oxidant capacity and electrophilic character, ozone is the most appropriate oxidant to degrade PAHs (Beltrain et al., 1995).

This study examines the breakdown of pyrene by ozone first in hexane, followed by further degradation of the intermediates by ozone in the aqueous phase. The purpose of this research is to identify the byproducts and intermediates of pyrene formed during ozonation, and demonstrates the biodegradability of these compounds.

2. Materials and Methods

Ozonation with the hexane solution was done with a batch reactor. The experiments were carried out in 125 ml Erlenmeyer flasks with a magnetic stir bar controlled by a magnetic stirrer. A high-voltage discharge ozonator (Model T-816 polymetrics Corp.) was used to produce ozone from air. The air was supplied to the ozone generator continuously at a flow rate of 2 L/min. The air/ozone mixture was introduced through a glass sparger. A total of 0.1 g of pyrene was dissolved in 50 ml of hexane. The ambient temperature was at 21 °C.
Ozonation experiments with the aqueous phase were also done with a batch reactor. The experiments were carried out in a 300 ml beaker with a magnetic stir bar controlled by a magnetic stirrer. A variable speed pump controlled by a pH meter and controller was used to deliver a 0.1 M NaOH for pH adjustment. To introduce the air/ozone mixture a glass sparger was used. The volume of test solution was 300 ml. The ambient temperature was at 21 °C. All experimental conditions were identical for all procedures. The products contained in both phases were identified by GC/MS.

3. Results and Discussion

After 2, 3, and 10-minute periods’ ozonation in 2000 mg/L hexane pyrene solutions, the yellowish solids were precipitated. So as to identify the byproducts and intermediates of pyrene, the yellowish solids and hexane solvent were separated with 2, 3, and 10-minute periods’ ozonation in 2000 mg/L hexane pyrene solutions. After the yellowish solids were separated by using by using a centrifuge, and the solids were analyzed by a pyrolysis gas chromatography. The solids consist of 66% of Carbon, 4% of Hydrogen, and 27% of Oxygen. The solids were dissolved in 50 ml of methanol in order to inject GC/MS directly. 2, 3, and 10-minute periods’ ozonation hexane solutions were injected in GC/MS. Six samples were collected and identified for intermediates and byproducts of pyrene via GC/MS.

The bonds between fused angular rings, as 4,5- and 9,10- bonds show double-bond character and are more reactive than other bonds. The preferential attack of O₃ on 4,5- and 9,10- bonds of the pyrene molecule could be given an account of in terms of less delocalization energy that makes the site first activated reactive site for oxidation most reactive (Bailey, 1982). At the initial stage of this reaction, pyrene molecule reacted with ozone to form an aldehyde and/or dialdehyde. 4,5-Phenanthenedialdehyde was both in the hexane phase and the yellowish solids. In 4,5-Phenanthenedialdehyde molecular ion peaks, a parent peak is m/z 234. According to the loss of aldehydes group (CHO-), other fragments have m/z 205 and m/z 176. A phenanthrene fragment was corresponded to m/z 176. In 5-Methoxy phenanthrene-4-carbaldehyde molecular ion peaks, a parent peak is m/z 236. According to the loss of methyl ether group(CH₃O-) and aldehydes group (CHO-), other fragments have m/z 205 and m/z 176.

In the hexane phase, two types of ozonation products were formed that ozone reacted with hexane and pyrene. Six compounds which were 3-Pentanol, 3-methyl; 3 Hexanone; 2 Hexanone; Cyclopentanol; 1-Methyl, 3 Hexanol and 2 Hexanol were found in the hexane-type products. Major product of ozonation of hexane was 3-Hexanol. As the concentration of ozone increased, the concentration of hexane-type products also increased. When ozone reacted with pyrene in hexane phase, three phenanthrene-types
which were 5 Phenanthrenealdehyde; 4,5 Phenanthrene and Phenanthro [4,5-c] furan-1,3-dione, and one biphenyl-type that was 2,2',6' Biphenyltrialdehyde was formed. Ring opening of pyrene molecule occurred at the 4,5-bonds by ozone. By attacking 4,5-bond of pyrene under ozone, dialdehyde was formed at the 4,5 position. Upon further ozonation, the dialdehyde group could close ring with ketone group, and phenanthrene-type products became biphenyl-type product by second ring cleavage at the 9,10 position (Yao et al 1998). Major compound in the hexane phase was 4,5 Phenanthrene.

In the yellow solids, four compounds which were 5-Methoxy phenanthrene-4-carbaldehyde; 4,5 Phenanthrene; 2,2',6,6'Biphenyltetraldehyde and 9,10-Dihydroxypyrene-4,5-dione were identified.

Since structures of these compounds are more polar than structures of compounds in hexane phase, these compounds were precipitated in hexane phase. Major compounds in the yellowish solids were 4,5 Phenanthrene and 2,2',6,6'Biphenyltetraldehyde.

4. Conclusions

Selectivity solvent is the most important requirement for an efficient ozonation when the ozone reacts with polycyclic aromatic hydrocarbons. This research showed there was an advantage of a higher solubility of PAH and ozone concentration in hexane in comparison to water. Dissolving and ozonation pyrene in hexane first made higher ozone solubility, that is, lower ozone generation requirements. By using the advantage of the higher ozone solubility, the insoluble a recalcitrant pyrene as HMW PAHs could be easily attacked by biological process. Chemical and biological treatments of the by-products, intermediates, and pyrene were susceptibility to rapidly degradation by each process. The design of integrated chemical and biological systems are the more effective and efficient than an individual system. Since ozone reaction with pyrene produced a ring-cleavage and hydroxylated byproducts and intermediates such as aldehydes and carboxyl acid that became more soluble in water. This makes a further ozonation and could be subsequently biodegraded in the aqueous solution. The ozonated products that were dissolved in hexane phases and precipitated in hexane solution were identified by GC/MS. Reozonated by-products and intermediates of pyrene in aqueous solution also rendered them all nontoxic.

References