

学校编码: 10384
学 号: 22620101151404

密级

厦 门 大 学

硕 士 学 位 论 文

**天然光敏剂对蒽和苯并[a]蒽光解动力学的
影响研究**

**Effect of Photosensitizers in Atmospheric Aerosol on
Photodegradation of Anthracene and Benzo[a]anthracene**

杨冰玉

指导教师姓名: 吴水平 副教授

专 业 名 称: 环 境 科 学

论文提交日期: 2013 年 5 月

论文答辩时间: 2013 年 6 月

2013年6月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为()课题(组)的研究成果,获得()课题(组)经费或实验室的资助,在()实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称,未有此项声明内容的,可以不作特别声明。)

声明人(签名):

年 月 日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

1. 经厦门大学保密委员会审查核定的保密学位论文，于
年 月 日解密，解密后适用上述授权。

2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年 月 日

目 录

摘要.....	V
ABSTRACT	VII
第 1 章 绪 论	1
1.1 背景及目的.....	1
1.2 研究进展.....	3
1.2.1 蒽、苯并[a]蒽和光敏剂的物理化学性质.....	3
1.2.2 光化学反应原理.....	4
1.2.3 蒽和苯并[a]蒽的光降解研究进展.....	4
1.2.4 多环芳烃的光解路径研究.....	8
1.2.5 光敏剂对多环芳烃光解的影响机制.....	11
1.3 研究内容及技术路线.....	12
第 2 章 实验部分	15
2.1 实验材料、装置、分析及数据处理.....	15
2.1.1 实验材料.....	15
2.1.2 实验装置及操作步骤.....	16
2.1.3 分析方法的建立.....	18
2.2 数据处理.....	21
第 3 章 3 种光敏剂对蒽和苯并[a]蒽的光降解影响	22
3.1 不同溶剂体系中蒽和苯并[a]蒽的直接光解动力学.....	22
3.2 不同溶剂体系光敏剂对蒽和苯并[a]蒽光解的影响.....	27
3.2.1 4-甲基邻苯二酚对蒽和苯并[a]蒽的光降解影响.....	27
3.2.2 愈创木酚对蒽和苯并[a]蒽的光降解影响.....	33
3.2.3 紫丁香醇对蒽和苯并[a]蒽的光降解影响.....	39
3.3 不同光敏剂之间的差异性比较.....	45

3.3.1 正己烷相中光敏剂对蒽和苯并[a]蒽的光降解影响差异比较	45
3.3.2 甲醇相中光敏剂对蒽和苯并[a]蒽的光降解影响差异比较	46
3.3.3 水相中光敏剂对蒽和苯并[a]蒽的光降解的影响差异比较	48
3.4 小结	55
第 4 章 结论和展望	56
参考文献	59
附录	67
致谢	68

Contents

Abstract in Chinese	V
Abstract	VIII
Chapter 1 Introduction	1
1.1 Research backgrounds and purposes	1
1.2 Overview	3
1.2.1 Physicochemical properties of anthracene, benzo[a]anthracene and photosensitizers	3
1.2.2 Principle of photochemical reaction	4
1.2.3 Progress of study on photodegradation of anthracene and benzo[a]anthracene	4
1.2.4 Proposed pathways of PAHs photodegradation.....	8
1.2.5 Effect of photosensitizers on photodegradation of PAHs	11
1.3 Contents and research route	12
Chapter 2 Materials, methods and data analysis	15
2.1 Materials, equipment and methods	15
2.1.1 Materials	15
2.1.2 Equipment and pretreatment	16
2.1.3 Methods.....	18
2.2 Data analysis	21
CHAPTER 3 Effect of photosensitizers on photodegradation of anthracene and benzo[a]anthracene	22
3.1 Direct photodegradation of anthracene and benzo[a]anthracene in different solvents	22
3.2 Effect of photosensitizers on photodegradation of anthracene and	

benzo[a]anthracene in different solvents	27
3.2.1 Effect of 4-methycatechol on photodegradation of anthracene and benzo[a]anthracene in different solvents	27
3.2.2 Effect of guaiacol on photodegradation of anthracene and benzo[a]anthracene in different solvents	33
3.2.3 Effect of 2,6-dimethoxyphenol on photodegradation of anthracene and benzo[a]anthracene in different solvents.....	39
3.3 Comparison of anthracene and benzo[a]anthracene decay with different photosensitizers	45
3.3.1 Comparison of anthracene and benzo[a]anthracene decay with different photosensitizer in hexane solution	45
3.3.2 Comparison of anthracene and benzo[a]anthracene decay with different photosensitizer in methanol solution.....	46
3.3.3 Comparison of anthracene and benzo[a]anthracene decay with different photosensitizer in pure water.....	48
3.4 Conclusions	55
Chapter 4 Conclusions and prospections	56
References	59
Appendix	67
Acknowledgements	68

摘要

多环芳烃 (Polycyclic Aromatic Hydrocarbons, 简称 PAHs) 是一类半挥发性有毒有机物, 一旦排放进入大气, 就会在气相和颗粒相之间进行分配, 其中高分子量 PAHs 主要以颗粒相形式存在, 低分子量 PAHs 则主要以气相形式存在。吸附于气溶胶上的 PAHs 在大气迁移过程中, 可由干湿沉降和光降解从大气中清除, 其中 PAHs 的光降解速率受 PAHs 本身的性质及颗粒基质组成所影响。气溶胶颗粒中存在的光敏剂如 4-甲基邻苯二酚、愈创木酚 (又称 2-甲氧基酚)、紫丁香醇 (又称 2, 6-二甲氧基苯酚) 可在一定程度上改变 PAHs 的光解速率, 进而影响 PAHs 的大气停留时间和迁移距离。

本研究以蒽 (Anthracene, 简称 Ant) 和苯并[a]蒽 (Benzo[a]anthracene, 简称 BaA) 两个受光解影响显著的化合物为代表, 研究在正己烷相、甲醇相和水相体系中上述 3 种光敏剂对 Ant 和 BaA 光降解速率的影响, 获得如下结果:

1. 在紫外辐射条件下, Ant 和 BaA 均发生直接光降解, 且均是在水相中光解速率最大, 其次是甲醇相, 在正己烷相中光解速率最小。

2. 光敏剂本身在紫外辐射的条件下, 也具有光降解性。

3. 当溶剂体系为甲醇时, 同一浓度的光敏剂, 其浓度越高, 越促进 Ant 和 BaA 的光解; 当溶剂体系为正己烷时, 4-甲基邻苯二酚和愈创木酚促进 Ant 和 BaA 的光解, 紫丁香醇抑制 Ant 和 BaA 的光解; 当溶剂体系为水相时, 同一浓度的光敏剂, 其浓度越低, 反而越促进 Ant 和 BaA 的光解。

4. 当同一光敏剂浓度一定时, Ant 和 BaA 的光解速率在正己烷相、甲醇相和水相体系中差异性明显, 不同溶剂中 Ant 和 BaA 的光解速率大小顺序是水相 > 甲醇相 > 正己烷相。

5. 相同溶剂中, 不同光敏剂对 Ant 和 BaA 的光降解速率影响也是呈现差异性。在正己烷相中, 愈创木酚对 Ant 的光解促进作用最大, 4-甲基邻苯二酚和紫丁香醇促进作用相当; 光敏剂对提高 BaA 的光降解速率影响大小顺序是愈创木酚 > 4-甲基邻苯二酚 > 紫丁香醇。甲醇相中 3 种光敏剂对提高 Ant 的光降解速率影响大小顺序是 4-甲基邻苯二酚 > 愈创木酚 > 紫丁香醇; 光敏剂对提高

BaA 的光降解速率影响大小顺序是 4-甲基邻苯二酚 > 紫丁香醇 > 愈创木酚。在水相中, 3 种光敏剂对提高 Ant 的光降解速率影响大小顺序是愈创木酚 > 4-甲基邻苯二酚>紫丁香醇; 光敏剂对提高 BaA 的光降解速率影响大小顺序是愈创木酚 > 4-甲基邻苯二酚≈紫丁香醇。

6. 根据本实验室的模拟研究, 推测在气溶胶由非极性变为极性老化过程(包含吸附的水分)中, Ant 和 BaA 的光解速率逐渐提高。在不考虑外界来源输入的前提下, 当气溶胶老化到最终阶段时, Ant 和 BaA 的光解速率最大。

关键词: 光敏剂; 气溶胶老化; 蒽; 苯并[a]蒽; 光降解

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are identified to be one of the major toxic air pollutants in urban. When PAHs enter into aerosol, it will be distributed between gas phase and particles phase. PAHs mainly exist in the particle phase with high molecular weight, while exist in the gas phase with low molecular weight. When PAHs are absorbed in aerosol, they will be cleared from the atmosphere by dry/wet deposition and photodegradation in atmospheric migration. The photochemical behavior of PAHs can be influenced by organic matter and properties of PAHs. There are large amounts of photosensitizers in wood smoke particles, such as 4-methylcatechol, guaiacol and 2,6-dimethoxyphenol, they can change the photodegradation dynamics of anthracene and benzo[a]anthracene under stimulated sunshine, which both effect residence time and migration distance of PAHs in air.

This study choose anthracene (Ant) and benzo[a]anthracene (BaA) as representative PAHs, to better understand the effect of aerosol polarity and concentrations of photosensitizers to photodegradation dynamics of anthracene and benzo[a]anthracene when the aerosol is aging. The results are as follows:

1. Photodegradation experiments of anthracene and benzo[a]anthracene show that they could photodegrade under stimulated sunlight. The photolysis rates of anthracene and benzo[a]anthracene in methanol, hexane and water decrease as this order: water > methanol > hexane. Much faster decay of anthracene and benzo[a]anthracene are observed in water.

2. Photosensitizers can also photolysis under stimulated sunlight.

3. Photodegradation experiments of effect of photosensitizers to anthracene and benzo[a]anthracene in different solvents show that faster decay of anthracene and benzo[a]anthracene in methanol composed of high concentration of photosensitizers. The photodegradation rates of anthracene and benzo[a]anthracene are increased in hexane composed of 4-methylcatechol and guaiacol, while photodegradation rates are decreased in hexane composed of 2,6-dimethoxyphenol. The photodegradation

rates of anthracene and benzo[a]anthracene are decreased in water composed of photosensitizers, the lower concentration of photosensitizers, the faster decay of anthracene and benzo[a]anthracene.

4. Photodegradation experiments of effect of solvents to anthracene and benzo[a]anthracene in different photosensitizers show that the photolysis rates of anthracene and benzo[a]anthracene as this order: pure water > methanol > hexane.

5. When the solvent is same, the effect of photosensitizers to the photodegradation of anthracene and benzo[a]anthracene are also different. The photolysis rates of anthracene in methanol decrease as this order: 4-methylcatechol > guaiacol > 2, 6-dimethoxyphenol. The photolysis rates of benzo[a]anthracene in methanol decrease as this order: 4-methylcatechol > 2, 6-dimethoxyphenol > guaiacol. The effect of guaiacol to the photodegradation of anthracene in hexane is larger than 4-methylcatechol and 2, 6-dimethoxyphenol. The effect of 4-methylcatechol and 2, 6-dimethoxyphenol to the photodegradation of anthracene is almost same. The photolysis rates of benzo[a]anthracene in hexane decrease as this order: guaiacol > 4-methylcatechol > 2, 6-dimethoxyphenol. The photolysis rates of anthracene in pure water decrease as this order: guaiacol > 4-methylcatechol > 2, 6-dimethoxyphenol. The photolysis rates of benzo[a]anthracene in hexane decrease as this order: guaiacol > 4-methylcatechol \approx 2, 6-dimethoxyphenol.

6. According to the results of this study, we can indicate that when the aerosol is aging, polarity of aerosol become stronger and aerosol contains much of water in the end, the photolysis rates of anthracene and benzo[a]anthracene increase, and photolysis quickly when the ratio of water is increasing.

The photodegradation products of anthracene and benzo[a]anthracene with photosensitizer under stimulated sunshine are also preliminary discussed in this study. The main photodegradation products of anthracene and benzo[a]anthracene contain benzy alcohol, 2-methyl-phenol, 3-methyl-phenol, 2-benzyltoluene, 4-methyl-phenol, 2-methoxy-phenol, 3, 3'-dimethylbiphenyl, mequinol and so on. Different products are produced in different solvents with different photosensitizers.

Key words: Photosensitizers; Aerosol aging; Anthracene; Benzo[a]anthracene;
Photolysis

Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.

廈門大學博碩士論文摘要庫